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FOREWORD

The impact power generation has on human health and the environment is becoming an ever increasing concern in the decision-making process when considering the energy options and power systems required by a country in order to sustain its economic growth and development. The continuing dependence on conventional fossil fuels and the deterioration of air quality have spurred the need for clean and efficient power systems resulting from the development of new technologies.

Hydrogen is a strong emerging candidate with a significant role as a clean, environmentally benign and safe-to-handle major energy carrier of the future. Its enhanced utilization in distributed power generation as well as in propulsion systems for mobile applications, such as automotive transportation, will help to significantly mitigate the strong negative effects on the environment particularly prominent in the large population centers of the world.

It is also nuclear power that will be of utmost importance in the energy supply of many countries over the next few decades. Nearly 500 nuclear power plants are currently being operated or are under construction around the world. The development of new, innovative reactor concepts utilizing passive safety features for process heat and electricity generation applications are considered by many to play a substantial role in the world's energy future in helping to reduce greenhouse gas emissions.

This report was developed under a contract with the International Atomic Energy Agency (IAEA). It documents past activities as well as those currently in progress by many Member States in the development of hydrogen as an energy carrier and its corresponding production through the use of nuclear power. It provides an introduction to nuclear technology as a means of producing hydrogen or other upgraded fuels and to the energy carrier hydrogen and its main fields of application. Emphasis is placed on high-temperature reactor technology which can achieve the simultaneous generation of electricity and the production of high-temperature process heat. This report was compiled and edited by Karl Verfondern, Forschungszentrum Jülich (FZJ), Jülich, Germany, and was reviewed by the experts named at the end of the report.

The IAEA officers responsible for this publication were L. Brey and G. Woite of the Division of Nuclear Power.

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Chapter 1

INTRODUCTION

1.1. WORLD ENERGY SITUATION

In 1996, the world's consumption of primary energy amounted to 8380 million TOE[1], which was 3 % more compared with the previous year. Most of the energy, 90 %, originated from fossil fuels (coal: 27 %, oil: 39.5 %, gas: 23.5 %) and the remainder from nuclear power (7.4 %) and renewable energies (hydro: 2.6 %) [8]. About 30 % of the primary energy consumed is used for electricity production. Currently hydro and nuclear are the only significant non-fossil contributors to electricity production with hydro representing about 20 % and nuclear about 17 % of global electricity. Other renewables have been able to penetrate only limited niche markets [5].

As described in a study by the European Commission, global energy supply is expected to increase by 1.6 % per year. Renewable energies are gaining mainstream acceptance with a 2.0 % increase per year, nuclear not more than 0.5 % per year. Natural gas is currently the fastest growing energy source with an annual increase of 2.7 %. The energy intensity of many products has fallen, but energy consumption is increasing: consumers have developed new needs, developing countries want to achieve higher economic and social levels. The energy trade is growing rapidly [7].

The future energy supply mix will depend on the magnitude of demand growth, changing objectives and social priorities, and the technologies to meet them [5]. The International Energy Agency (IEA) in Paris does not expect a significant change in the world's energy mix, because long time periods are required to develop new or improved energy technologies before they can be commercially deployed. What it does expect is a strong demand for more energy (1.6 %/yr) due to population increase and rapid economic growth in some regions of the world. The US Electric Power Research Institute (EPRI) does not anticipate primary fuel resources to be an economic constraint in the next century although their absolute and comparative cost might shift with time. A balanced and stable program without pursuing extreme policies has the best prospects of achieving lowest long-term social cost, therefore it recommends facing the future with an array of options and flexible strategies [5].

1.2. GLOBAL ENVIRONMENTAL IMPACT

Most of the world's fuel supply is some sort of hydrogen combined with carbon, hydrocarbons. Burning hydrocarbons means liberating carbon oxide gases with undesirable side effects: CO is toxic to life, CO_2 is currently labeled as one of the primary causes of the greenhouse effect. The other aspect of hydrocarbons is their limited supply on earth.

Although the problem of global warming has been recognized, there is still a discrepancy between the global trend of CO_2 emission and the global target of CO_2 reduction. The agreement of 154 countries at the Rio earth summit in 1992 was to pursue

---

[1] 1 TOE (= ton oil equivalent) = 1 428 TCE (= ton coal equivalent) = 41,868 MJ

"sustainable development" by reducing the emission of greenhouse gases to the 1990 level by the year 2000. Figures from 1996 revealed a new record high with CO_2 emissions increased by 2.8 % compared with 1995. According to a prediction by the PROGNOS AG in 1991, compared with 1989 global CO_2 emissions will be increased by 67 to 170 % in 2040. Even if the industrial countries were successful in achieving a CO_2 reduction of 80 %, total emissions would still increase by 30 to 100 % due to the enormous energy demand of the developing countries [4]. For the OECD, there is a predicted 13 % increase of CO_2 emission between 1990 and 2010 versus the declared goal of a 15 % decrease in the respective period [6]. CO_2 contributes 40 % to the anthropogenic greenhouse effect [1] with a long lifetime of up to 100 years in the atmosphere. More than half of the CO_2 emissions come from energy production. Traffic contributes a great deal to the environmental impact by using fossil fuels at low efficiency.

A recent analysis by EPRI expects that even with a favorable scenario, total carbon combustion will rise from the 5.5 gigatons of 1986 to at least 8.6 gigatons in 2060 despite the introduction of renewables and a relaunch of nuclear development [5]. In contrast, a reorientation has occurred in some sectors, in particular, in the automotive industry where low emissions of nitrogen oxides and hydrocarbons are mandatory.

The United Nations Convention on Climate Change has prompted initiatives by various countries to identify and implement methods for curbing the rise in greenhouse gas emissions. Studies by the International Panel on Climate Change (IPCC) have shown that a stabilization of the atmospheric CO_2 would be achieved in the second half of the next century, if CO_2 emissions are reduced by 60 % within the next few decades. In the short term, the desired reductions are likely to be achieved through energy savings combined with the deployment of more advanced, more efficient supply and utilization technologies. However, it is generally recognized that the longer-term targets will require substantial increases in the deployment of new and improved technologies.

Three conferences of parties to the **United Nations Framework Convention on Climate Change** have been held so far to discuss the global warming issue. The summit in Toronto in 1988 resulted in the promise of a 20 % CO_2 reduction by 2005; the reality today is a 16 % increase compared with the 1988 level. During the conference in Rio de Janeiro in 1992, it was decided to go back to the 1990 level by 2000; so far there has been an increase of 8 % in the OECD countries. At the third world summit in December 1997 in Kyoto, Japan, the 167 participating countries came to an agreement which, if finally accepted[2], will for the first time be an obligatory agreement according to international law. It includes the commitment by the 38 industrialized countries to reduce their overall emissions of the gases, which contribute to the global warming potential, by 5.2 % compared with 1990 and 1995[3] by the years 2008/2012, respectively. Emission change ranges between -8 % (EC) and +10 % (!) (Iceland) for the single countries. No goal has been specified for the developing countries. The introduction of new economic instruments such as the possiblities of trading emission permits and of taking so-called "phantom" emissions into

---

[2] The draft protocol has legal effect 90 days after it has been ratified by 55 % of the parties of the convention, among them industrial nations with more than 55 % of all CO_2 emissions [2].
By midth of May 1998, 35 countries have signed the protocol including industrialized countries (among them Japan and Germany) with in total 39 % of the worldwide CO_2 emissions.

[3] The 1990 level is the baseline for the greenhouse gases CO_2, CH_4, N_2O. The 1995 level is the baseline for the greenhouse gases sulfur hexafluoride (SF_6), perfluorocarbons (PFCs), hydrofluorocarbons (HFCs).

account meaning that the creation of CO_2 sinks (e.g., reforestation) could be balanced with emissions, was a matter of controversy and needs further elaboration.

1.3. WHY NUCLEAR POWER?

Limited fossil energy resources and pending environmental issues are likely to increase the significance of non-fossil energy forms – hydro, nuclear, solar, wind, geothermal, tidal – in the long run. Despite its low growth at present, nuclear power is foreseen by the World Energy Council as gaining importance in the future representing, besides renewables, a serious option for decoupling the existing energy demand from CO_2 emissions.

Usually the sites of high energy potentials are not identical with the sites of energy consumption. This situation offers the following options:

- on-site generation of energy-intensive products
- generation of electricity and transport via grid
- transformation of electricity into chemical energy carriers, e.g., hydrogen, methanol
- direct generation of hydrogen and transport via pipeline.

Nuclear power is considered by many to be the most promising CO_2-free energy technology with long-term fuel supply security. According to a statement by IAEA, in 1996 the nuclear power installed worldwide saved an additional impact on the atmosphere of 2.3 billion tons of CO_2 per year corresponding to 8 % of additional release [3]. Principally used as base load power plants, nuclear off-peak electricity could be applied for hydrogen production.

The operation of nuclear power plants in the "Combined Heat and Power" (CHP) mode, i.e., cogeneration of electricity plus heat including the production of process heat is a means of significantly raising energy conversion efficiencies. Furthermore the refinement of fossil fuels, e.g., coal, by nuclear power contributes to the fundamental objectives of energy policy: (i) energy security, (ii) saving of resources, (iii) protection of the environment. Cost is a major concern, but nuclear power seems to be competitive in the long term.

1.4. WHY HYDROGEN?

Hydrogen, the most abundant element in the universe, is – as a fuel – clean, powerful, renewable, and environmentally benign. It can be burnt to water vapor at a very low level of pollution releasing its chemical energy as heat. It can be stored directly or transported for later usage. Most of the hydrogen is bound in chemical compounds, i.e., it must be extracted prior to its use by means of a primary energy resource. The introduction of hydrogen as a significant contributor to meet the world's energy demand in the future requires an infrastructure, economy, and last but not least, safety.

An important driving force for development work on hydrogen has always been developing a further secondary energy carrier, in addition to electricity, for the non-electric market. Economic solutions for generation, storage, transport, distribution, and application may help to introduce a new energy concept with hydrogen playing an essential role as a secondary energy carrier.

The fact is that billions of cubic meters of hydrogen are produced every year, but unfortunately mostly converted from fossil fuels and only to a small extend used for energy purposes. In a future low-emission energy economy, the hydrogen energy carrier could play a pertinent role using its advantages compared with other alternatives. With the energy carrier hydrogen, all the subtasks of an energy transmission can be performed in a safe and appropriate way. A major drawback of hydrogen is its hazard potential if inadvertantly released and mixed with the ambient air to form a flammable gas mixture. Therefore it is necessary to assess its risks to society.

1.5. OVERVIEW

The report covers all main issues concerning hydrogen and its potential connection to nuclear power. It presents for either area goals achieved so far and ongoing research activities. Also secondary areas are described including processes with hydrogen as an intermediate step.

The first part comprising three chapters deals with nuclear power as the primary energy source for producing electricity and process heat / steam which could be utilized for hydrogen production. Chapter 2 treats the design of nuclear power plants for process heat application and the components required. Safety considerations described in chapter 3 concentrate on the aspects that are peculiar to nuclear process heat plants. International activities on using nuclear power to be utilized in process heat applications, for example for hydrogen production in the past, present, and future are listed in chapter 4.

The second part of the report focuses on key technologies as the basic elements of an economy with hydrogen as an energy carrier. Chapter 5 (plus appendix A) describes the production methods for hydrogen including those which are still at an early research stage. Chapter 6 (and appendices B and C) contains the description of methods and components for the storage, transportation, and distribution of hydrogen. In chapter 7, both major and minor areas of applications of hydrogen as a feedstock for (petro)chemical processes and, in particular, as a fuel are presented. The safety aspects which have to be considered in a hydrogen energy economy including some examples of a safety and risk assessment are given in chapter 8. This part on hydrogen is terminated by giving a – most probably incomplete – list of international activities for promoting the use of hydrogen including a more detailed description of some examples of an autonomous hydrogen energy system or subsystem, some in operation, others still at the design stage.

The report ends with a rough description of a future large-scale hydrogen energy economy, in which nuclear power may play a significant role, and the efforts needed to reach this goal.

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Chapter 2

NUCLEAR POWER AND ITS POTENTIAL FOR HYDROGEN GENERATION

The world's primary energy consumption amounts to well over 300,000 peta Joule and more than two thirds of it are used in the transportation sector or converted to hot water, steam and space heat. Unlike fossil energy carriers, nuclear power is almost exclusively used for electricity production. Only a few nuclear power plants are being used for heat applications. If nuclear power is to utilize its full potential of substituting the energy carrier oil, it needs to be introduced into the heat market for heating (< 100 °C) or low-temperature process heat ($\approx$ 200 °C). This could easily be provided in combination with electricity production by light-water reactors (LWR). It implies, however, near-customer sites for the plants or even on-site installation. Even more favorable would be Combined Heat and Power (CHP) from a high-temperature gas-cooled reactor (HTGR), in particular, the one-cycle gas turbine variant because of its higher temperature output and its higher efficiency [4]. Clearly nuclear heat production could play a major and important role in the non-electric sector. Numerous studies on small and medium-sized reactors have shown their option for heat application to be technically and economically viable [15].

With respect to a large-scale hydrogen production, nuclear power can play a significant role if used as a provider of electricity in the electrolysis process or as a provider of high-temperature heat in fossil fuel conversion. An introductory option would be the use of cheap surplus electricity. Production of hydrogen as a bulk energy carrier is by a factor of about 2 too expensive compared with the today's commercial business of natural gas and oil, however, the trend to include external effects into the energy cost may help to achieve economic attractiveness [2].

A look at the use of different reactor types demonstrates the dominant role of the LWR line in commercial electricity production. From 428 nuclear power plants operating worldwide in 1996 to produce 363 GW(e) or 17 % of the international electricity supply – plus 62 units under construction to produce 55 more GW(e) – 342 plants are LWRs, 249 PWRs and 93 BWRs, for a total of 311 GW(e) [27]. And the trend to larger power units was observed. Not more than 5 GW(th) of global nuclear power are presently employed to supply hot water and steam, mostly in Canada, China, Kazakhstan, Russia, and Ukraine [25].

Nuclear growth depends on the future public perception of the comparative benefits, cost, and risks of alternatives. Based on the comparative evaluation of tangible risks to public health, safety, and environment, nuclear power appears to be a better choice than coal [39].

2.1. SIGNIFICANCE OF PROCESS HEAT FOR THE INDUSTRY

The structure of energy demand in the industries for the generation of certain process heat temperature levels is shown in Figs. 2-1 and 2-2 for the examples of Germany and Japan, respectively [5, 17]. In principle, there is a great demand in the low temperature

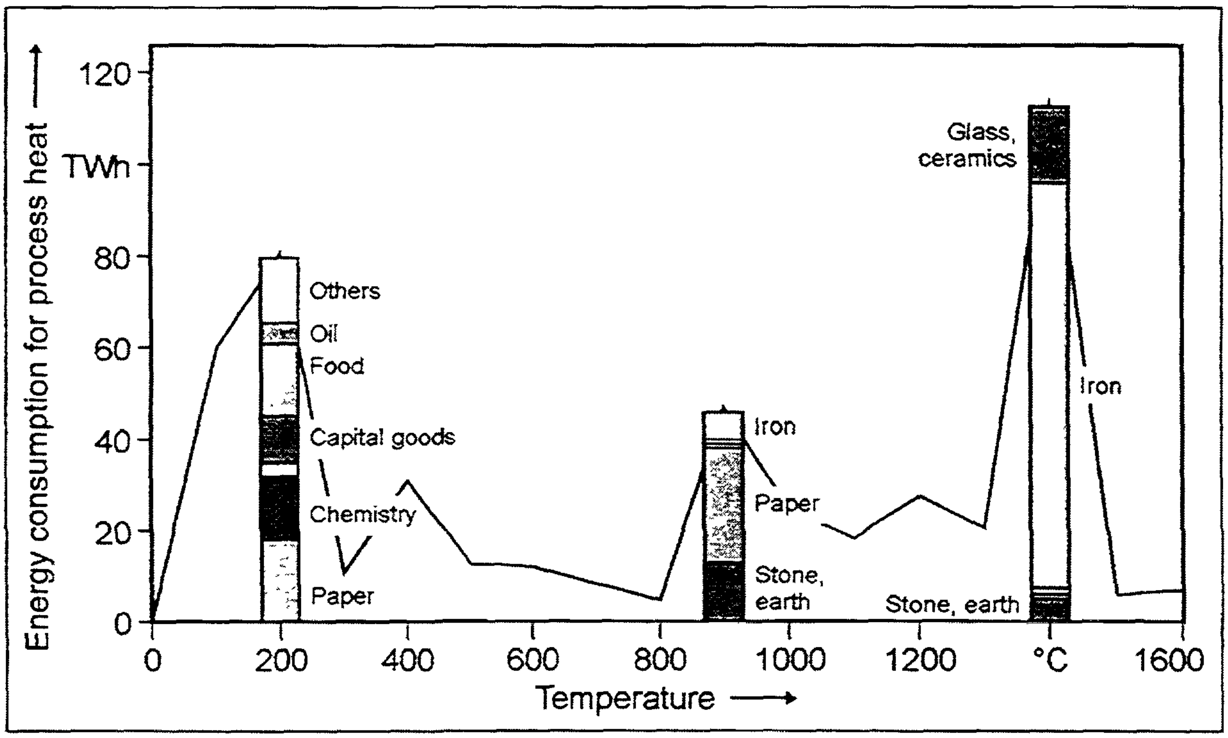

Fig. 2-1: Process heat spectrum in the industries as a function of process temperature in Germany as of 1996, from [5]

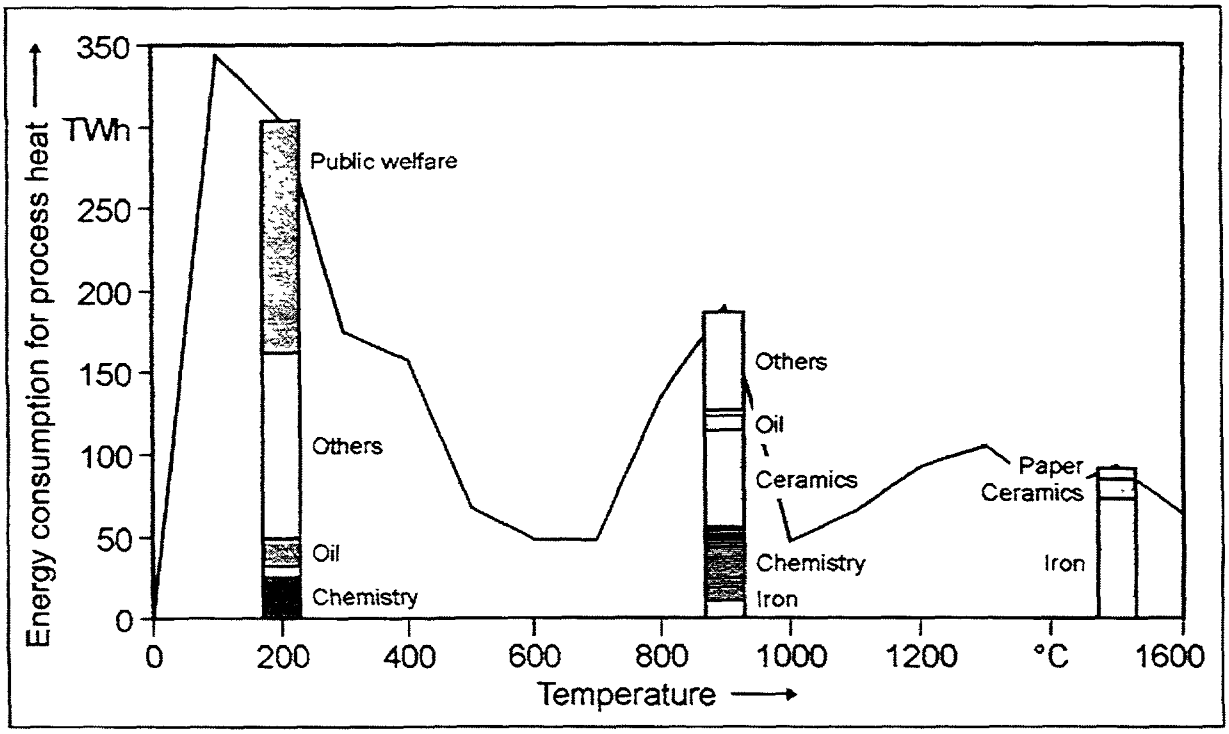

Fig. 2-2: Process heat spectrum in the industries as a function of process temperature in Japan as of 1983, from [17]

Table 2-1: Steam vessels in selected industrial branches in Germany as of 1987, from [19]

Branch	No. of steam power plants	Accumulated plant power [t/h]	No. of plant sites
Paper, pulp	278	9.3	131
Chemical	438	29.1	105
Iron	157	8.9	36
Road Vehicle Construction	117	6.9	21
Sugar	137	5.3	43
Petrochemical	120	7.6	30
Others	323	8.2	139
Σ	1570	75.3	505

range of 100 - 300 °C to be used in petrochemical and refinery processes or the paper and textile industries. Other distinct peak demands are given in the high temperature range at about 900 °C in the chemical and non-ferrous industries and at about 1500 °C in the iron and steel producing, and glass and ceramics industries. Power plants operated in the CHP mode generally provide heat below the 500 °C level [5].

For the introduction of nuclear process heat into the energy market, the estimation of present and future industrial demand for process steam needs to be made first as well as establishing how nuclear power fits into the energy needs profile [19]. Inevitable fluctuations in industrial process heat/steam demand have to be expected. Also the consumer circle for secondary energy is limited for industrial plants compared with public power plants, thus smaller units would be preferable. On the other hand, nuclear units are economically operated only at a certain minimum capacity. Units of 500 MW(th) are thought in [7] to allow economic use of the nuclear option. A more recent study from 1990 [19] takes plants of 2 * 100 MW(th) as a minimum into consideration increasing the industrial potential of nuclear plants. Table 2-1 summarizes the number of process steam plants, sites, and steam production capacity in Germany valid for the year 1987 [19].

Temperature requirements range from low level (e.g., hot water, district heating, desalination) to a high level of up to 1000 °C (e.g., petrochemical industry, water splitting). Applications at temperatures beyond 1000 °C can be served by nuclear power only in connection with secondary energy carriers such as electricity, hydrogen, or synthesis gas. From all industrial branches, the chemical industry is the most pertinent in terms of process steam representing in Germany about 50 - 70 % of the total potential [19]. Depending on the nuclear steam generation system, steam can be generated at different levels of pressure and temperature according to the needs of the process industries. Process steam must be produced on-site, since its long-distance transportation is not practicable. An estimated fraction of 30 % of installed steam capacity in the chemical industries could be based

Table 2-2: Steam parameters for different nuclear steam-generating systems, from [10]

Nuclear system	Steam parameters		
	Pressure [MPa]	Temperature [°C]	Mass flow [t/h]
SIEMENS PWR	6.5	280	7400
B&W PWR	6.9	312	7280
SIEMENS PHWR	5.6	271	3440
Candu - PHWR	4.7	260	1090
Phenix LMFBR	16.3	510	2100
SIEMENS BWR	5.5	270	1185
THTR-300	18.1	530	918
Fort St. Vrain HTGR	17.3	541	1044

Table 2-3: Survey of Japanese industries suitable for electricity / steam cogeneration, from [42]

Industry	Temperature range [°C]	Ratio of steam consumption [%]	Ratio of independent power generation [%]
Chemical	300 - 600	18.6	18.6
Paper - Pulp	300 - 600	34.3	49.2
Ceramic - Pottery	800 - 900	5.0	12.6
Iron & Steel	> 1000	2.1	16.4
Nonferrous Metal	-	0.7	16.8

Table 2-4: Typical heat application plant models for selected industries, from [42]

Industry	Production scale	Steam conditions		Steam consumption [t/h]	Power consumption [MW(e)]
		Temperature [°C]	Pressure [MPa]		
Petrochemical	400,000 t/yr ethylene	250 198 152	4 1.5 0.5	20 170 205	60
Paper - Pulp	750,000 t/yr newspaper	188 134	1.2 0.3	10 235	204
Oil refinery	210,000 bbl/d	530 320 190	12 2.1 0.3	22 225 40	55

on nuclear whereas the major fraction will remain to be produced in conventional power plants [7].

In the field of enhanced oil recovery, high steam pressures are required as could be provided by gas-cooled reactors; water-cooled reactors would need an additional steam compression step [25]. Characteristic parameters are given in Table 2-2 for various designs. For the example of the Japanese industries, process steam temperature range and energy consumption structure are presented in Tables 2-3 and 2-4.

2.2. NUCLEAR POWER PLANTS

In order to optimally exploit a heat source for power generation, the Carnot cycle process should work at the largest possible temperature difference. In **HTGR**s and in fossil-fueled conventional plants, steam temperatures are in the range of 530 °C. Using the above systems in the combined heat power (CHP) mode, steam and electricity production in an HTGR or an conventional plant can be accomplished consecutively by routing the steam first through a turbine and then to the steam application system (Fig. 2-3).

In contrast, the steam temperature in an **LWR** is no higher than 320 °C due to the low coolant outlet temperature allowing steam production at a lower quality level in a typically parallel arrangement of steam and electricity production (Fig. 2-4). The electricity output for various process steam outputs at a constant total thermal power of the plant is shown in Fig. 2-5. Smaller electricity output results in a higher waste heat loss, which on the other hand is decreasing with increasing steam output. The electricity produced out of one ton of steam varies between 120 - 270 kWh depending on process steam output for an HTGR, and between 40 - 184 kWh for an LWR [7].

For the liquid metal fast breeder reactor (**LMFBR**), the upper temperature limit of the steam produced is approximately 500 °C (505 °C in the Russia BN-600 reactor, 495 °C in the German SNR-300 concept or 483 °C in the Japanese Monju reactor) prior to entry into the turbine. LMFBRs have not been considered so far for delivering process heat.

In principle, all reactors are able to provide process steam and long-distance heat to bridge a distance between the locations of heat production and heat demand. Even if LWRs are not able to provide heat at a temperature level sometimes required by the industry, their temperature level could be raised by some additional conventional heating. However, only the HTGR is capable of opening the market for direct high-temperature process heat applications (Fig. 2-6) [19].

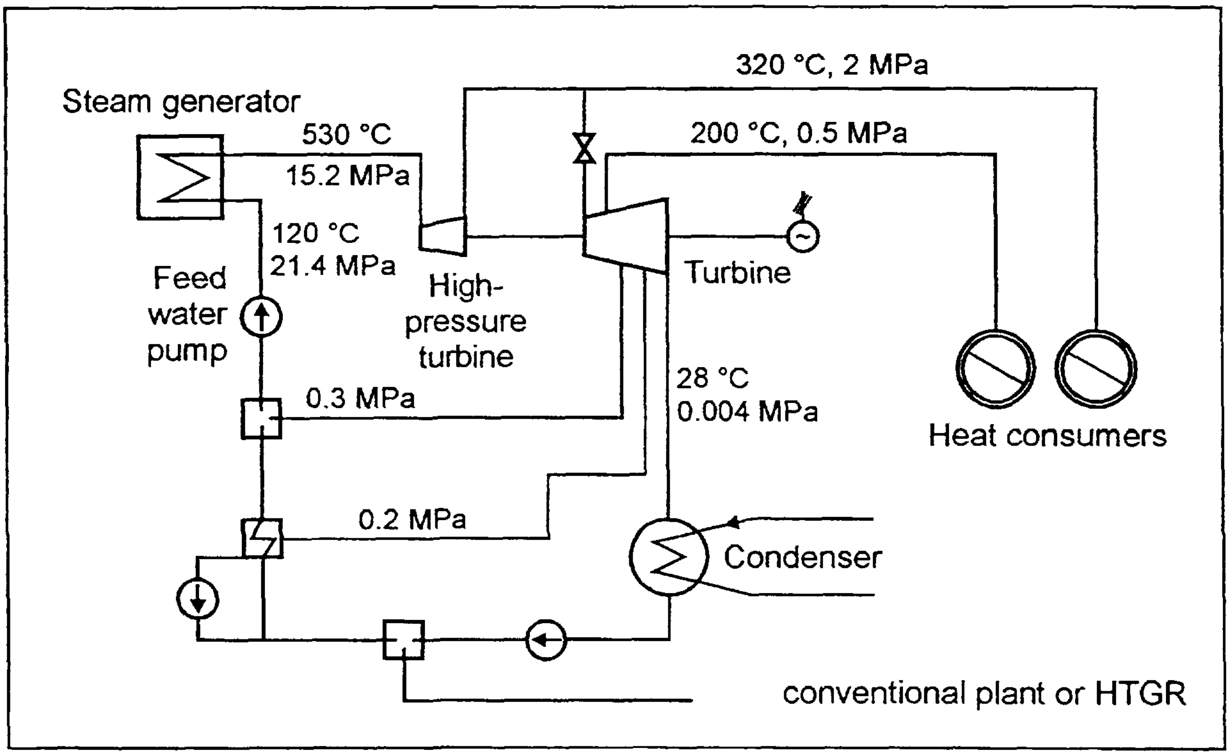

Fig. 2-3: Secondary circuit of industrial power plant with HTGR, from [7]

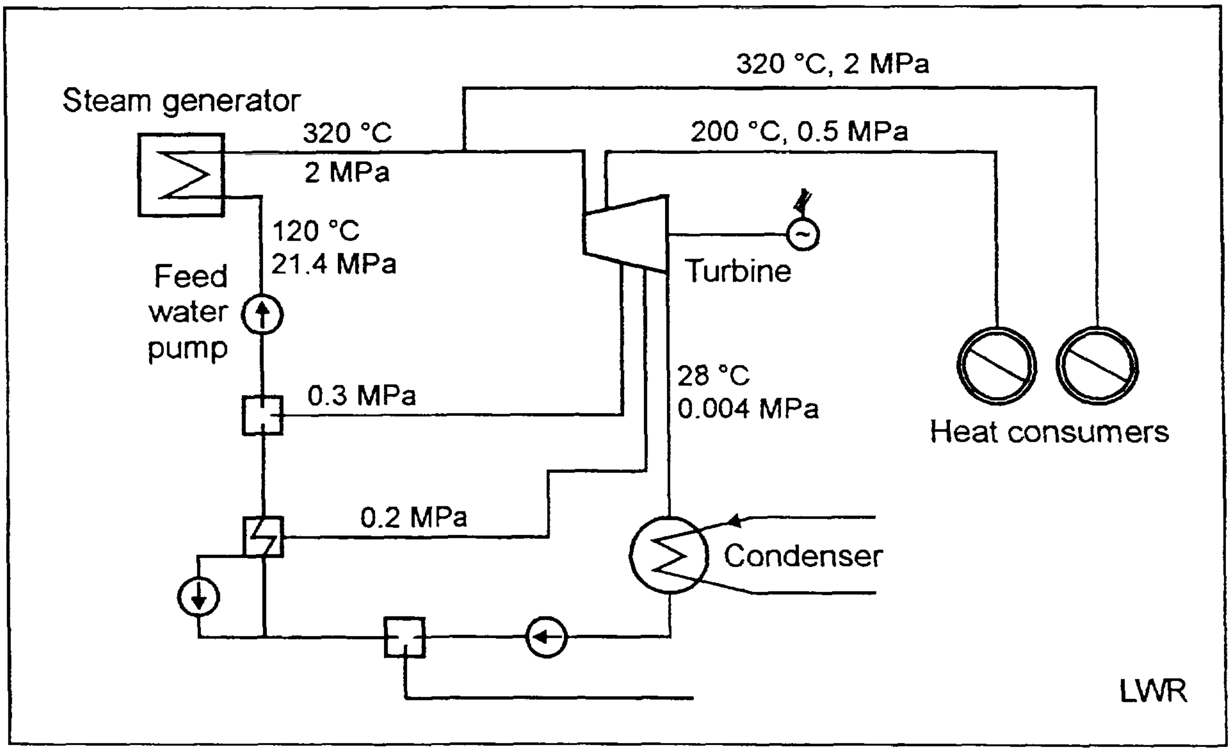

Fig. 2-4: Secondary circuit of industrial power plant with LWR, from [7]

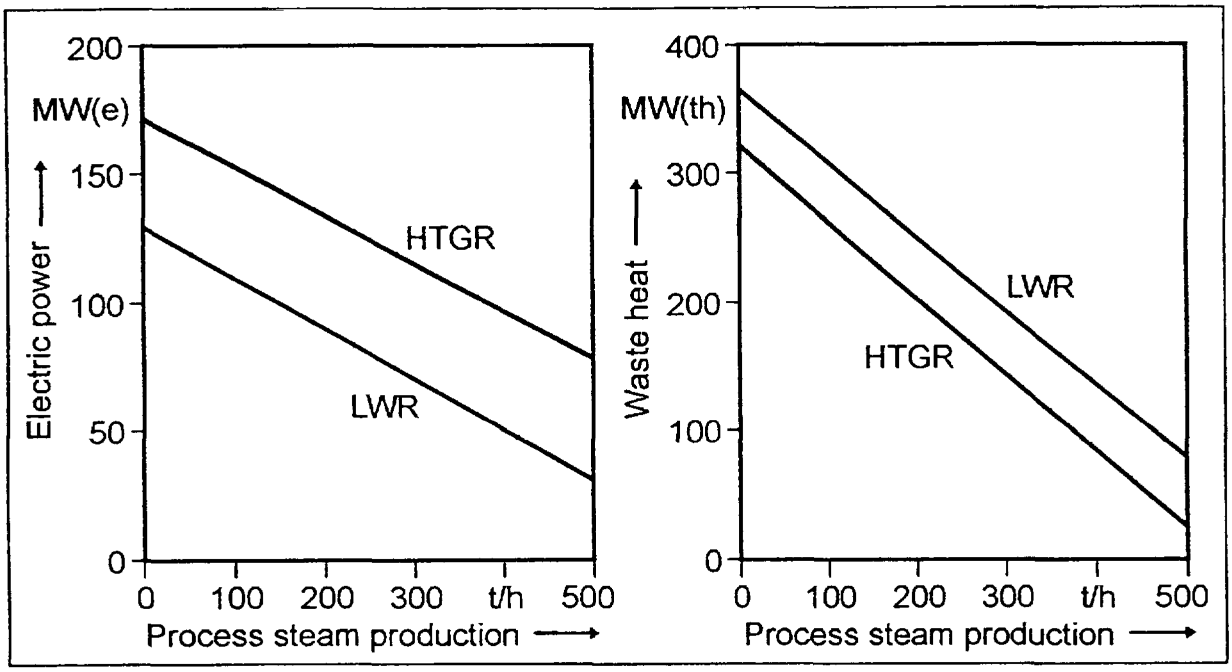

Fig. 2-5: Electric power output and waste heat as a function of steam output, from [7]

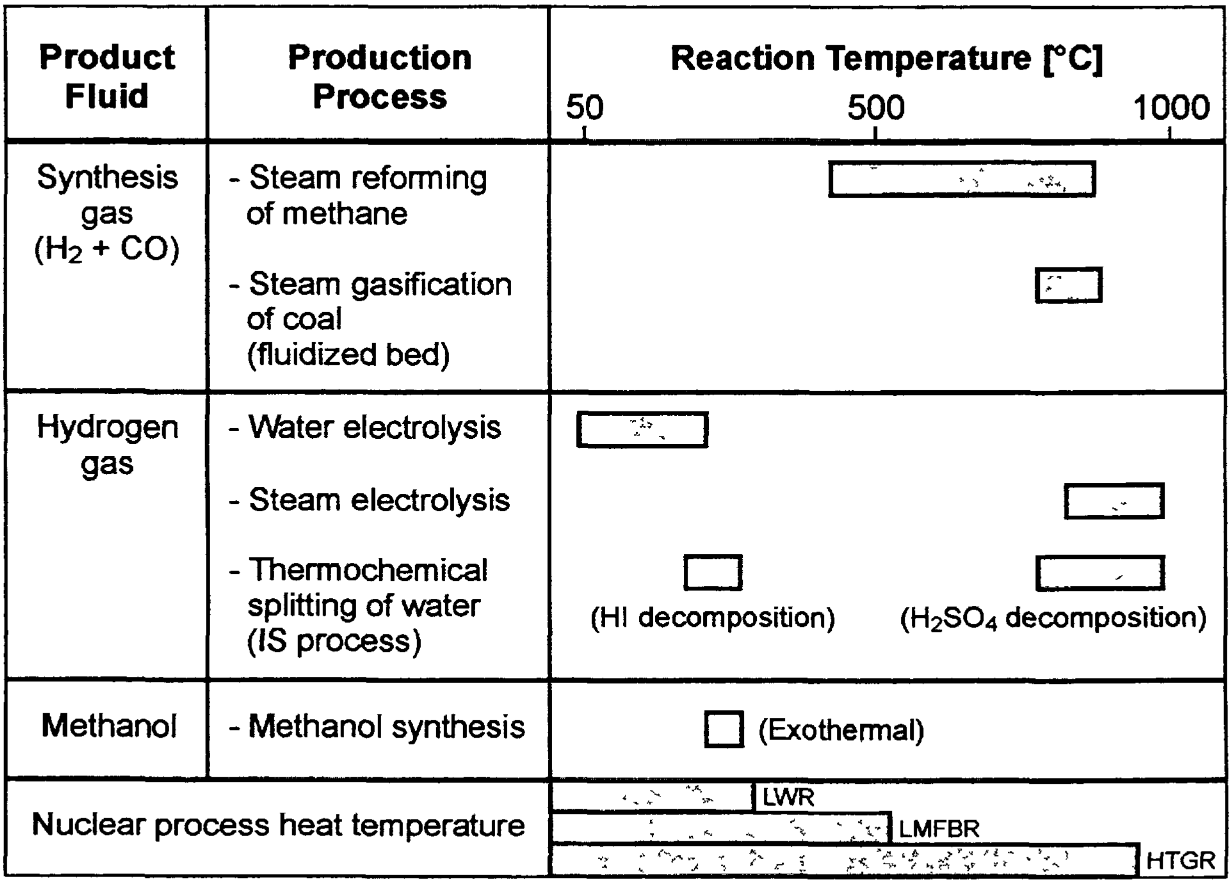

Fig. 2-6: Reaction temperature ranges for various industrial production processes dependent on type of nuclear reactor, from [11]

2.2.1. Light-Water Reactor

With regard to the heat market, a light-water reactor (LWR) of the size of the German Biblis A reactor (1200 MW(e)) has the potential to provide 10,000 GJ/h low-temperature heat in the CHP mode. Since hot water and process steam cannot be transported directly over long distances, nuclear power can be economically used only in areas with large heat consumption density like chemical industrial complexes, or in long-distance heating systems [4]. With respect to the latter, some of the candidate systems are operated at lower temperatures and could be used in connection with an LWR, if the catalyst conversion processes can be properly controlled [14].

The fact that steam generation by LWRs is limited to lower temperature steam (≈ 280 °C) makes the introduction of LWRs into the heat market conceivable for the chemical industry where large amounts of process steam are required as a heat carrier or as a medium used for synthesis gas and hydrogen generation.

The procedure of using electricity in the electrolysis of water to produce hydrogen is not competitive with the methods of extracting the hydrogen from fossil raw materials. The overall efficiency then is no higher than approx. 35 %. Electrolysis is applied when cheap electricity is available or high-purity hydrogen is desired [4].

2.2.2. High-Temperature Gas-Cooled Reactor

The high-temperature gas-cooled reactor represents one type of the next generation of nuclear reactors for safe and reliable operation as well as for efficient and economic generation of energy. Present HTGR designs are based on about four decades of R&D including operating experience with six prototype reactors [37].

2.2.2.1. Features of HTGR-Based Chemical Processing

The concept of the high-temperature gas-cooled reactor has important features such as

- production of electricity,
- production of high-temperature heat up to 1000 °C,
- production of high-temperature steam of about 530 °C,
- realization of fundamental safety features, and
- potential for economic attractiveness.

In reference to the CHP mode, the industrial power plant with HTGR could be named "CHHP", because it provides three energetical connection points: high-temperature heat, low-temperature heat, and electricity. With respect to electricity production, the achievement of a 40 - 43 % efficiency is possible when using steam turbines. Gas turbines reach efficiencies up to 48 %. A combination of both could even reach the 50 % level. Cogeneration applications are estimated to allow efficiencies in the range of 80 - 90 % [24].

Physical requirements for process heat HTGRs are

- gas outlet temperature of 950 -1100 °C,
  which allows for sufficient reaction velocity of chemical process;

- gas inlet temperature of 350 - 500 °C,
  which is necessary in order to use recuperation heat of product gas;
- lower system pressure,
  which raises the efficiency of the chemical processes;
- separation of the nuclear system from the chemical system,
  which reduces the risk of radioactivity release after an accidental chemical explosion;
- separate components for high-temperature and low-temperature heat consumption, which allow for different constructions and materials;
- arrangement of primary and secondary circuit in a non-integrated design because of better accessibility.

Steam applications include the generation of electricity in the steam cycle, the production of process heat in cogeneration with electricity, and the production of district heat. Steam on a higher temperature level offers the chance to open up new markets for process steam applications in the chemical and petrochemical industries or for enhanced oil recovery. The ratio of electricity to steam production can be adopted over a wide range according to the needs of the consumer. In **heat applications**, heat is delivered from the helium coolant with an outlet temperature at the high end of 750 - 950 °C, for the conversion of solid and liquid fossil fuels into "clean" gaseous and liquid fuels synthesis gas, hydrogen, methanol. Chemical **energy transmission** systems could be most effectively utilized when integrated with a parallel electric transmission system, taking the high-end temperature range for driving the heat pipe and the low-end for generating electricity.

Chemical industrial plants could be optimized in terms of product spectrum and product volume such that the total energy output of an HTGR, whether as heat or steam or electricity, could be utilized on-site [7].

A direct-cycle reactor system strongly depends on the **HTGR fuel quality**. The available high quality TRISO (SiC) fuel[4] has not been rigorously tested under gas turbine conditions, but appears satisfactory under moderate conditions, i.e., reactor outlet temperature of 850 °C and time-averaged fuel temperature under operating conditions of < 1200 °C. Options to improve fission product retention capability are to enlarge the thickness of the SiC layer or to replace the SiC coating layer by a ZrC coating layer. TRISO (ZrC) fuel, however, will require a long and expending development program. ZrC coatings are under study in Japan and the USA. The effect of a thicker SiC layer has been investigated within the German HHT project [16, 31].

2.2.2.2. Chemical Processes for Hydrogen Production

A widely applied method for the production of hydrogen is the decomposition and gasification of fossil fuels. Reaction temperatures are typically in the range > 500 °C, which could be ideally provided by an HTGR. The non-fossil generation of heat for the endothermal reforming reaction represents a means of reduction of CO_2 emissions. In relation to the same amount of CO_2 produced, the reforming of natural gas with an external heat source increases the hydrogen output by 40 - 50 %, in case of coal gasification even by

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[4] A TRISO coated fuel particle consists of a 0.5 mm diameter UO_2 kernel surrounded by subsequent layers of buffer, inner pyrocarbon, silicon carbide (SiC), and outer pyrocarbon. The 35 μm thick SiC layer provides an efficient barrier to all safety relevant radionuclides.

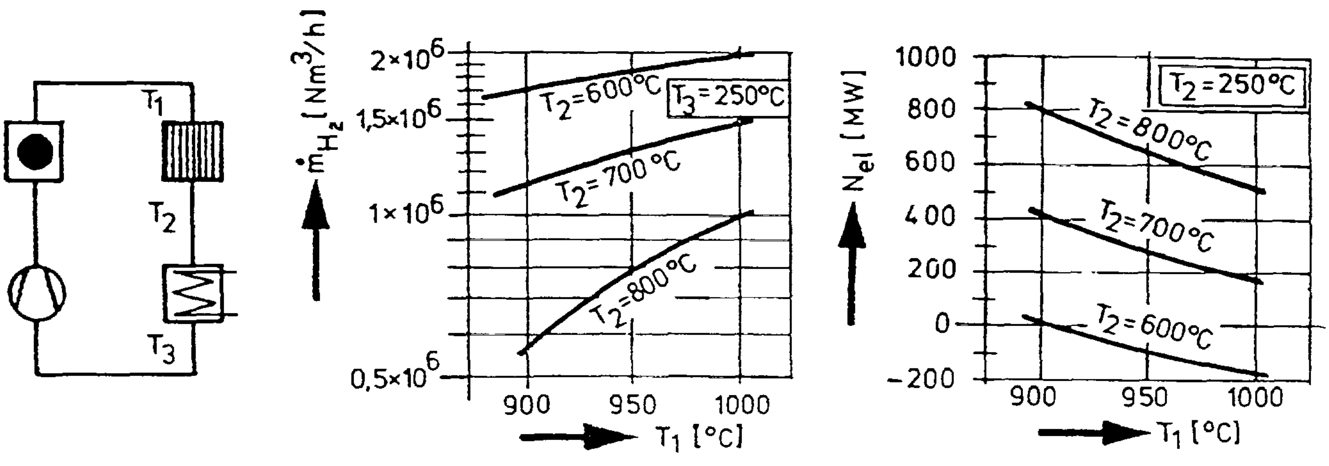

Fig. 2-7: Dependence of hydrogen and electricity production on helium temperature at steam generator inlet (T_2) with T_1: reactor outlet temperature (950 °C), and T_3: reactor intlet temperature (250 °C), from [23]

Table 2-5: Influence of process heat temperature split-up in a 3000 MW(th) nuclear process heat plant with six loops, from [23]

Temperature split-up [°C]	**950...800...250**	**950...700...250**	**950...600...250**
Steam reformer			
Power for process heat [MW(th)]	640	1070	1500
ΔT [°C]	235	180	137
Heat flux density [kJ/(m^2 s K)]	76	64	52
Required heat transfer area [m^2]	8,468	16,731	28,667
Power density [MW/m^3]	1.4	1.2	1.0
Diameter [m]	3.2	4.4	5.8
Steam generator			
Power for electricity [MW(th)]	2360	1930	1500
ΔT [°C]	148	112	70
Heat flux density [kJ/(m^2 s K)]	174	128	81
Required heat transfer area [m^2]	13,531	15,089	18,429
Power density [MW/m^3]	6.6	4.9	3.1
Diameter [m]	3.5	3.5	3.5

Table 2-6: Mass balance for hydrogen production, from [23]

	Inlet mass flow rate [kg/h]	Outlet mass flow rate [kg/h]	Mass converted [kg/h]	From scrubber [kg/h]	From low-temp. separation [kg/h]	Methane recycled [kg/h]	H_2 produced in methanation step [kg/h]
H_2	406	108,474	122,446	624	121,416	406	114,744
CH_4	384,528	135,968	135,968	704	30,528	104,736	48,320
CO	11,620	238,588	42,980	224	31,136	11,620	-
CO_2	-	326,876	634,260	634,260	-	-	-
H_2O	1,297,782	884,430	758,682	-	-	-	(20,016)
Σ	1,694,336	1,694,336	1,694,336	635,812	183,080	116,762	163,064 (183,080)

66 % compared with the conventional processes [35]. Cogenerated electricity is applicable in H_2 production methods based on the decomposition of steam in the high-temperature electrolysis or in thermochemical cycles. The chemical processes of hydrogen generation are described in further detail in chapter 5 and appendix A, respectively.

2.2.2.2.1. Reforming Process

The HTGR allows a splitting of the nuclear reactor heat for methane reforming and for steam generation. According to the selected design, the shares of synthesis gas and electricity production are variable over a wide range adjusted by the steam generator inlet temperature, T_2. The dependence is shown in Fig. 2-7.

For the industrial processes of ammonia synthesis, hydrocracking, hydrogenation, a suitable heat split-up would be made at a T_2 value in the range of 625 - 670 °C. In the direct iron ore reduction process, a steam generator inlet temperature, T_2, of 810 - 830 °C would be chosen. It is obvious that the heat split-up has a significant influence on the designs of both steam reformer and steam generator [23]. Some exemplary data are given in Table 2-5 for different T_2 values. A mass balance for hydrogen production based on the medium T_2 value (= 700 °C) is given in Table 2-6.

Unlike conventional fossil-fueled reformer tubes, the helium-heated reforming plant connected to an HTGR has to meet the much more stringent requirements of a "nuclear" component in terms of construction, quality assurance, and scheduled re-testing. The reforming tube placed in the primary circuit has the function of forming a radioactivity barrier between the primary helium and the process gas. Another major difference is the manner of heat input, which is convective transport with the helium in the nuclear version.

Synthesis gas is the starting material for numerous chemical products and it can be processed to hydrogen if desired. It is the intermediate step in the synthesis of methanol to serve as a motor fuel.

2.2.2.2.2. Steam-Coal Gasification

Since heat input for the coal gasification process is a significant cost factor, nuclear process heat provided by an HTGR was considered as a substitute for conventional firing. From the perspective of Germany, the most economic hydrogen may be produced from imported cheap coal in a steam coal gasification process using HTGR heat [2]. Another important advantage of nuclear coal gasification is its environmental effect since no coal is fired to provide the reaction heat. Only smaller amounts of pollutants such as SO_2, CO_2, dust are emitted into the atmosphere. The main problem, however, is the need to transfer the nuclear heat via two heat exchangers to the coal gasification process.

Fig. 2-8 presents a flow chart of the **steam-coal gasification** process with the numerical example based on a 3000 MW(th) HTGR. High-temperature heat of 950 °C is passed to a secondary helium circuit via a He/He heat exchanger where it enters with a 900 °C temperature a steam gasifier. Hot steam is routed into a coal bed where the coal is gasified in two steps to give synthesis gas. As a result of the carbon-steam reaction, the helium is cooled to approx. 810 °C. If desired, a subsequent methanation process could be added to provide synthetic natural gas (SNG) [9]. Compared with a conventionally fired coal gasification plant, the nuclear-driven process could increase the output by up to about 60 %, because no coal is spent on direct combustion [4]. As an example, with 680 MW(th) power from an HTGR plus 3470 t of hard coal, the yield is 2690 Nm^3 of SNG [18].

For methanol synthesis, the purified coal gas is compressed to 7.5 MPa. The power of 680 MW(th) from an HTGR plus 2680 t of hard coal result in 2390 t of methanol [18].

A combined system of coal, steel, and nuclear energy has been discussed for the production of methanol and raw iron comprising the steps:

(i) partial (50 %) steam gasification of hard coal by means of HTGR process heat,
(ii) Klöckner-steel-gas process for iron ore reduction by means of fine coke,
(iii) methanol synthesis from the product gases.

The combination of all three steps appears economically attractive. A balance assessment assumes an input of 1.4 million t/yr of hard coal and 500 MW(th) delivered from two HTGR units to result in the production of 1.23 million t/yr of methanol and 0.8 million t/yr of raw iron [1].

2.2.2.2.3. Hydro-Gasification

For the **hydro-gasification** process (Fig. 2-9), an intermediate circuit is deemed unnecessary. An alternative to the above described coal gasification process was pursued by the German Rheinische Braunkohlenwerke AG, Cologne: the nuclear hydriding coal gasification. Nuclear power is here introduced in a steam reformer for methane splitting. From the resulting synthesis gas, hydrogen is taken to be the input for the exothermal gasification reaction.

Coupling hydro-gasification of lignite with a methanol synthesis process is possible after cooling and purification of the coal gas and mixing it with the reformer gas. The crude methanol yielded is then separated from the residual gas mixture by condensation. For the

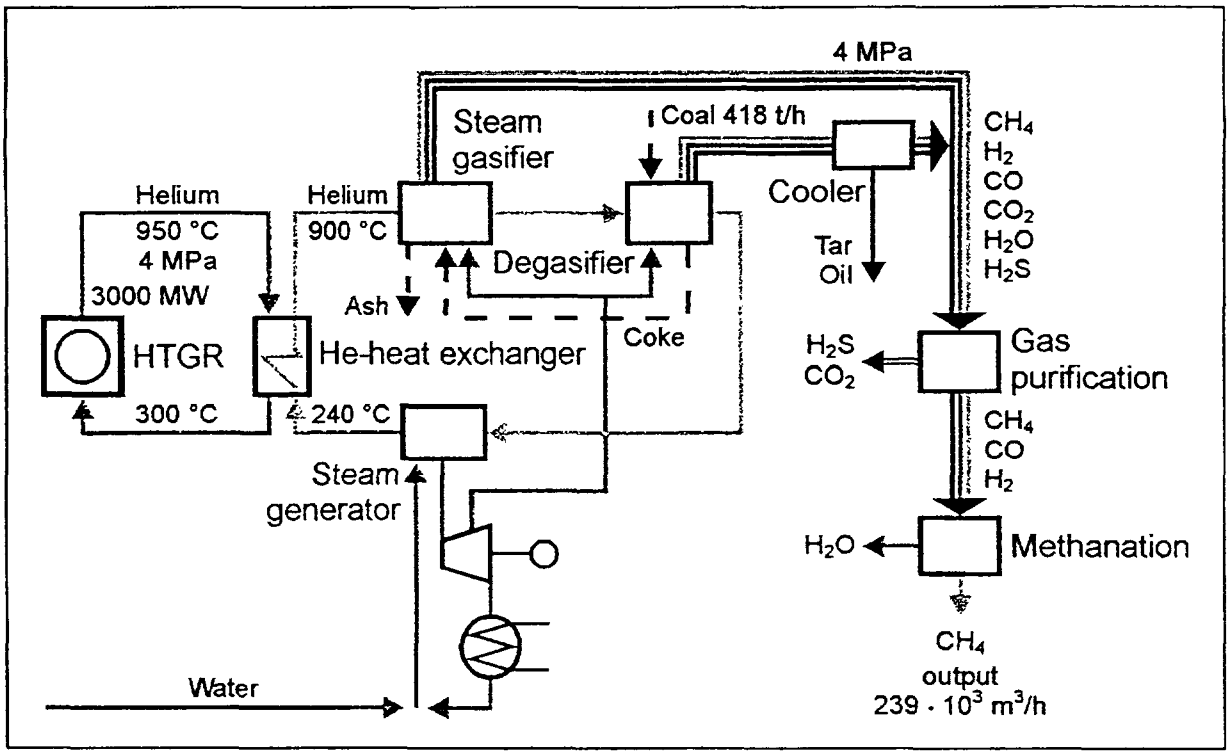

Fig. 2-8: Flow chart of the process of steam gasification of coal (hard coal), from [9]

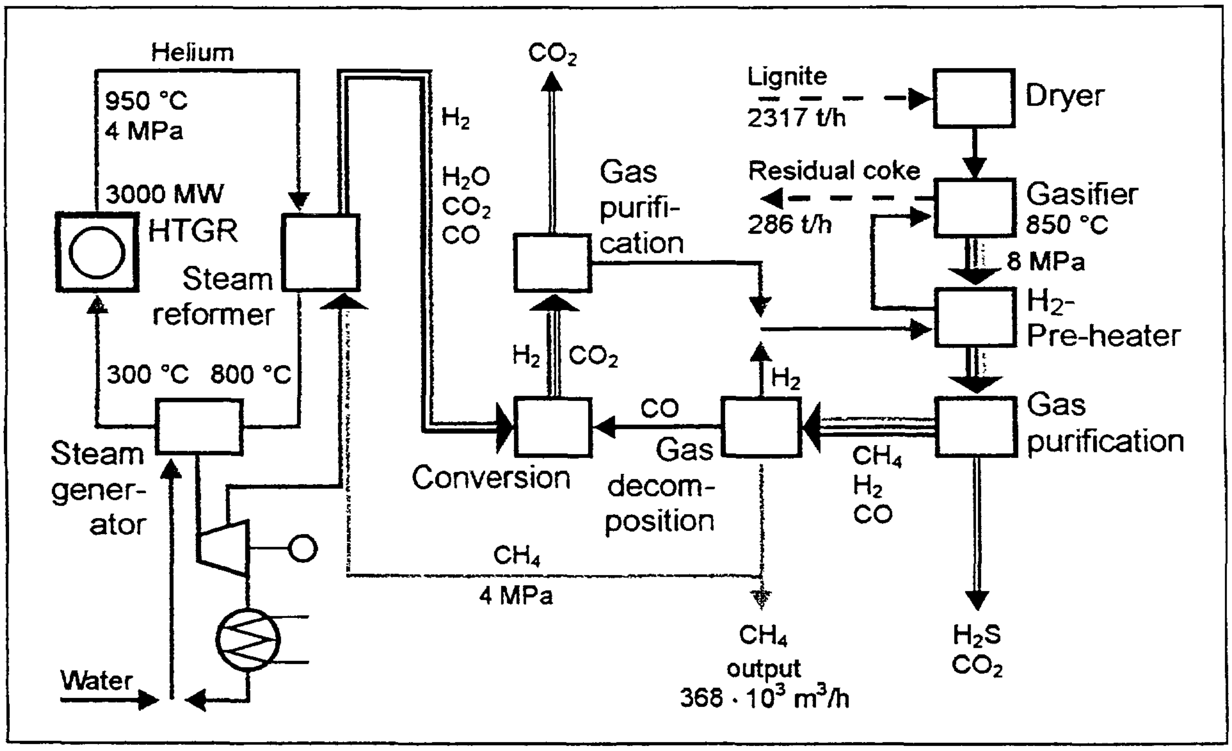

Fig. 2-9: Flow chart of the process of hydro-gasification of coal (lignite), from [9]

example of 680 MW(th) power from an HTGR, the input of 2650 t of lignite would allow a production of 2530 t of methanol [18]. If synthetic natural gas production is desired, the coal gas passes a purification and a cryogenic gas separation step to obtain H_2, CO, and CH_4 fractions. Some of the CH_4 is used for H_2 production in the steam reformer to serve as a feed gas in the gasifier. The remaining methane is the product [18].

The process of hydrogen or methanol production by using a raw iron producing blast furnace, also for stack gas utilization, can be realized with a process heat HTGR, shown in [34] for a 250 MW(th) unit (see section 4.3.2.8.).

A concept for the “non-integrated” employment of an HTGR in the iron and steel industry has been proposed in [28] as described in section 7.1.3. The nuclear reactor is sited at a location favorable for the reduction gas generation from which the gas is delivered via a pipeline to the iron and steel industrial sites. A 3000 MW(th) nuclear power plant (HTGR) was chosen where 2167 MW(th) are taken for naphta splitting and an operation time of 8000 h/yr assumed would be able to provide $6.75*10^9$ Nm^3/yr of hydrogen [28]. An HTGR is favorable, if an H_2 - CO mixture as a reduction medium is used.

2.2.2.2.4. Biomass Conversion

A process for the conversion of biomass into methanol by means of an HTGR has been proposed [3]. Wood, represented by the chemical formula $C_6H_{8.64}O_{3.7}$, is gasified by superheated steam. Electrolytic hydrogen is added to the product gas and then converted to methanol or methane. Both heat and electricity are provided by an HTGR. The partial processes of steam gasification, water splitting and methanol / methane synthesis are summarized in the overall reaction [3]:

$$C_6H_{8.63}O_{3.7} + 2\ H_2O + 5.66\ H_2O \quad \rightarrow \quad 6\ CH_3OH + 2.68\ O_2$$

$$C_6H_{8.63}O_{3.7} + 2\ H_2O + 5.66\ H_2O \quad \rightarrow \quad 6\ CH_4 + 5.68\ O_2$$

Additional requirements to an energy system as to be environmentally benign and application friendly, the energy carrier of choice would be liquid methanol rather than gaseous methane due to lower losses and easy and economically competitive storage and transportation.

2.2.2.2.5. Water Splitting

The high-temperature heat from HTGRs could be used to convert heat energy directly into chemical energy in the form of the (lower) heat of combustion of hydrogen. There are three processes of water splitting appropriate for process heat utilization from an HTGR:

- high-temperature electrolysis,
- thermochemical cycle,
- thermochemical-electric hybrid cycle.

There is a great economic potential of nuclear thermochemical cycles, i.e., the H_2 production by means of water and nuclear heat compared with electrolytic H_2 from nuclear electricity. The HTGR is typically considered the high temperature heat source of

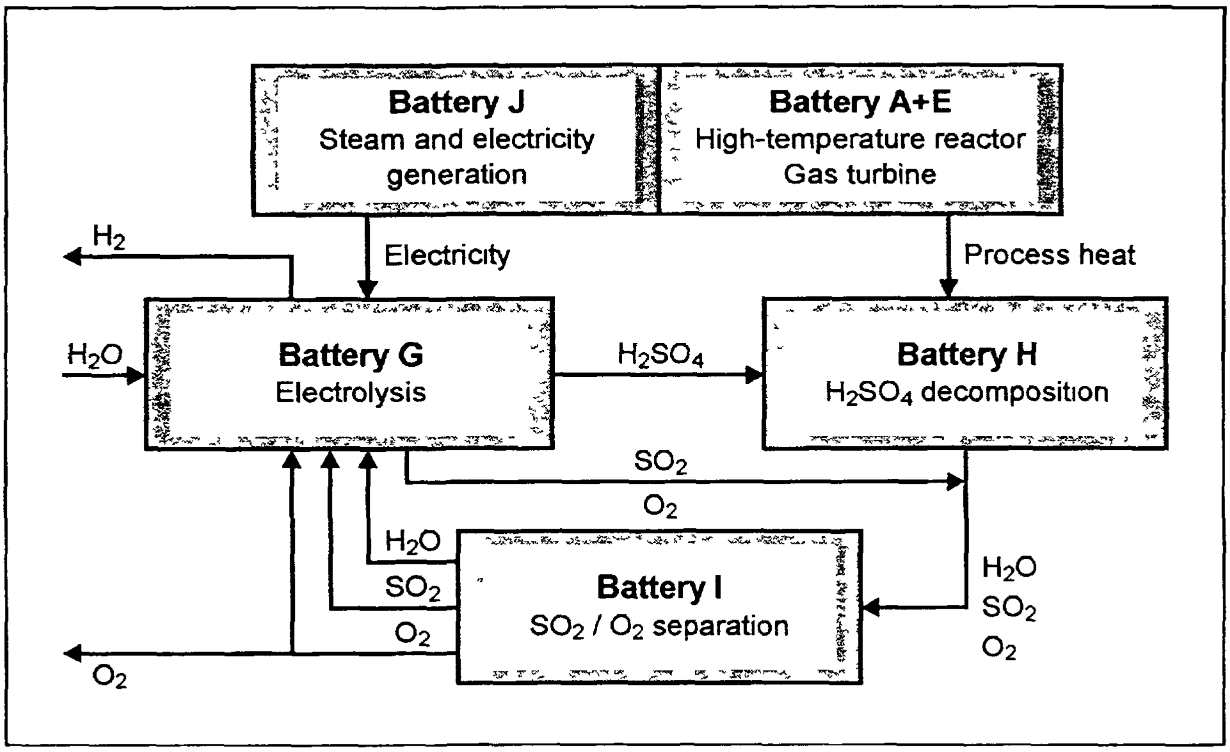

Fig. 2-10: Diagram of the Westinghouse sulfuric acid hybrid cycle, from [20]

choice, although other heat sources are, of course, also possible. Most of the promising thermochemical cycles are based on sulfuric acid processes [20] (see section 5.2.2. and appendix A).

In the Westinghouse sulfuric acid hybrid cycle shown in Fig. 2-10 (see also appendix A.3.2.), HTGR heat will be used for the H_2SO_4 decomposition step. Both high-temperature and electric steps have been experimentally investigated at the Research Center Jülich. The above hybrid cycle has undergone a detailed balance and cost analysis already in a plant design based on nuclear power [8].

Materials corrosion problems arise by the fact that the system pressure of 4 MPa on the primary side of the HTGR needs to be also on the secondary side of the process gas.

2.3. COMPONENTS

2.3.1. Nuclear Steam Reformer

Reformer tube heating with a high-temperature nuclear reactor is performed with helium, typically at 950 °C, as the heat source. The aim of reaching a heat flux density similar to that of the conventional method can be achieved by employing a helium-heated counterflow heat exchanger (see Fig. 2-11). Helium under pressure shows excellent heat transfer properties. Furthermore, precautions must be taken to minimize the effects of asymmetry or hot gas streaks in the helium flow as well as a non-uniform process gas flow. The materials of a helium-heated steam reformer should be selected such that the

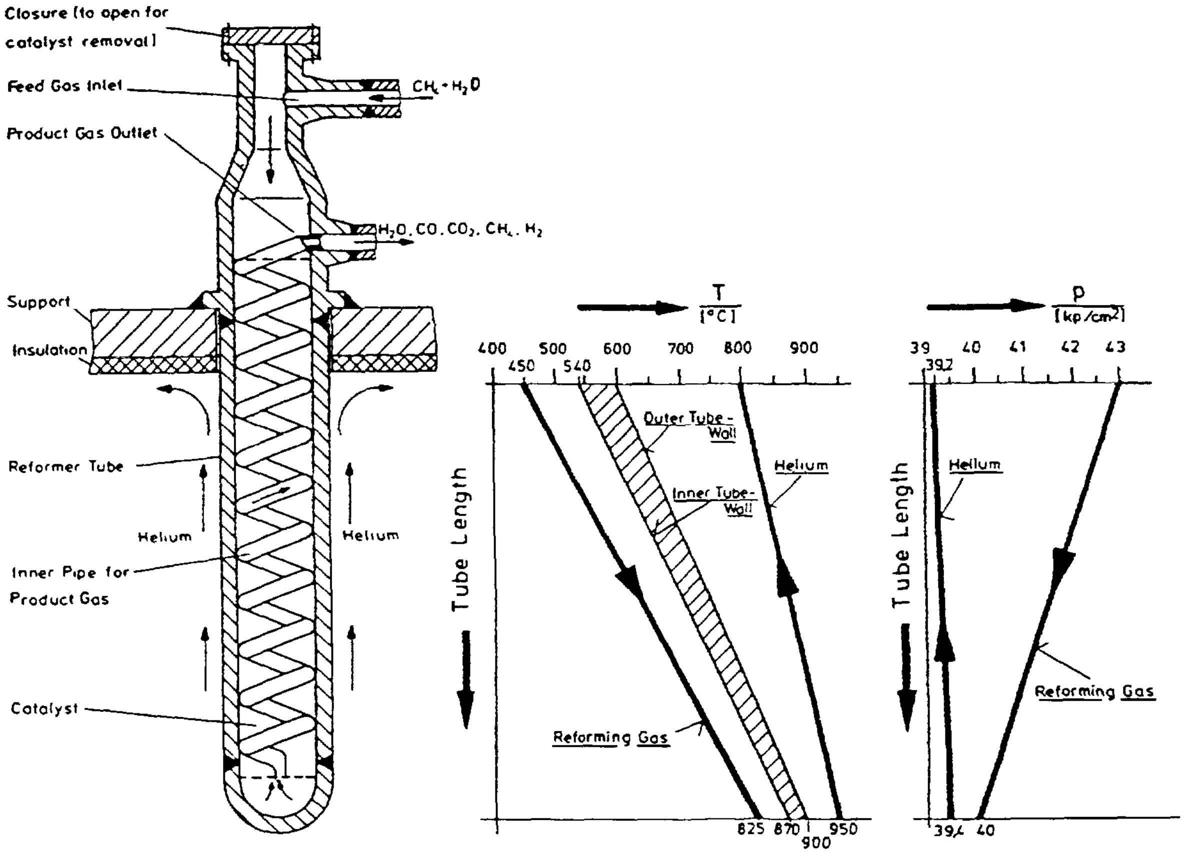

Fig. 2-11: Principle of a reformer tube for nuclear applications, from [23]

operation is made with a maximum tube wall temperature of 900 °C; for further increase, research on improved materials outside the range of currently known and tested materials is needed. A comparison of conventional reformer data with those of a helium heated reformer is given in Table 2-7 [23].

Experience in construction and operation was gained with the EVA-I and EVA-II facilities at the Research Center Jülich (see section 4.3.2. and appendix B.1.). The replacement of the catalyst is difficult because of the presence of the internal return pipe ("pigtail"). Using a vacuum cleaner was found to be inefficient. A new hydraulic system developed at Jülich reduced the replacement time down to a few minutes [38].

The reference design of the German 60 MW **PNP steam reformer** consists of approx. 200 single reforming tubes composed to a bundle. Helium at 950 °C enters the reformer pressure vessel through a short horizontal hot gas duct. With an outlet temperature of 720 °C, the helium is then routed through a short coaxial duct into the steam generator pressure vessel. After exiting the steam generator at a temperature of 300 °C, the helium flows back to the steam reformer and through the outer wall to keep it on cold gas temperature before it is led back to the reactor.

On the secondary side, a steam-methane gas mixture with a ratio of 4:1 enters the reformer at a temperature of 330 °C and is distributed to all reforming tubes. The feed

Table 2-7: Comparison of the data of a conventional with those of a helium-heated reformer, from [36, 23]

Parameter	Conventional Plant	Nuclear Plant
Tube length [m]	8 - 12	10 - 12
Inner diameter [mm]	100 - 150	$\approx$ 100
Wall thickness [mm]	15 - 20	$\approx$ 15
Product gas return pipe	outside reformer tube	inside reformer tube
Reforming pressure [MPa]	0.1 - 2.5	4
Reforming temperature [°C]	800 - 850	800 - 850
Pressure on heating side [MPa]	0.1	4
Heat transfer	Radiation	Convection
Tube density [tubes/m^2]	< 1	45
Maximum heating temperature [°C]	1400 - 1500	950
Maximum tube wall temperature [°C]	900 - 950	900
Maximum pressure difference across tube wall [MPa]	0 - 2.5	0.1 (hot part) 0.4 (cold part)
Maximum temperature difference across tube wall [°C]		30
Ratio H_2O : CH_4	2:1 - 5:1	2:1 - 5:1
Mean heat flux [kW/m^2]	80	70 - 80
Heat flux ratio max. over min.	10:1	1.5:1
Product gas flow rate [(Nm^3 H_2+CO)/(m^2 s)]	14	14
Goal of service lifetime [h]	100,000	100,000

gas is heated up by recuperators to 560 °C before it enters the catalyst section reaching a final temperature of 810 °C while reformed at the same time. The hot product gas is then cooled in the recuperators and leaves the reformer at a temperature of 480 °C [33].

To overcome the perceived disadvantages of a nuclear steam reformer with its comparatively low heat transfer and its high system pressure, improvements of the Japanese design of the **HTTR nuclear reformer** have been proposed (Fig. 2-12):

(i) increase heat input to process gas by applying a bayonet type of reforming tube,
(ii) increase heat transfer rate by using combined promoters of orifice baffles and cylindrical thermal radiation pipes, and
(iii) increase conversion rate by optimizing chemical composition of feed gas.

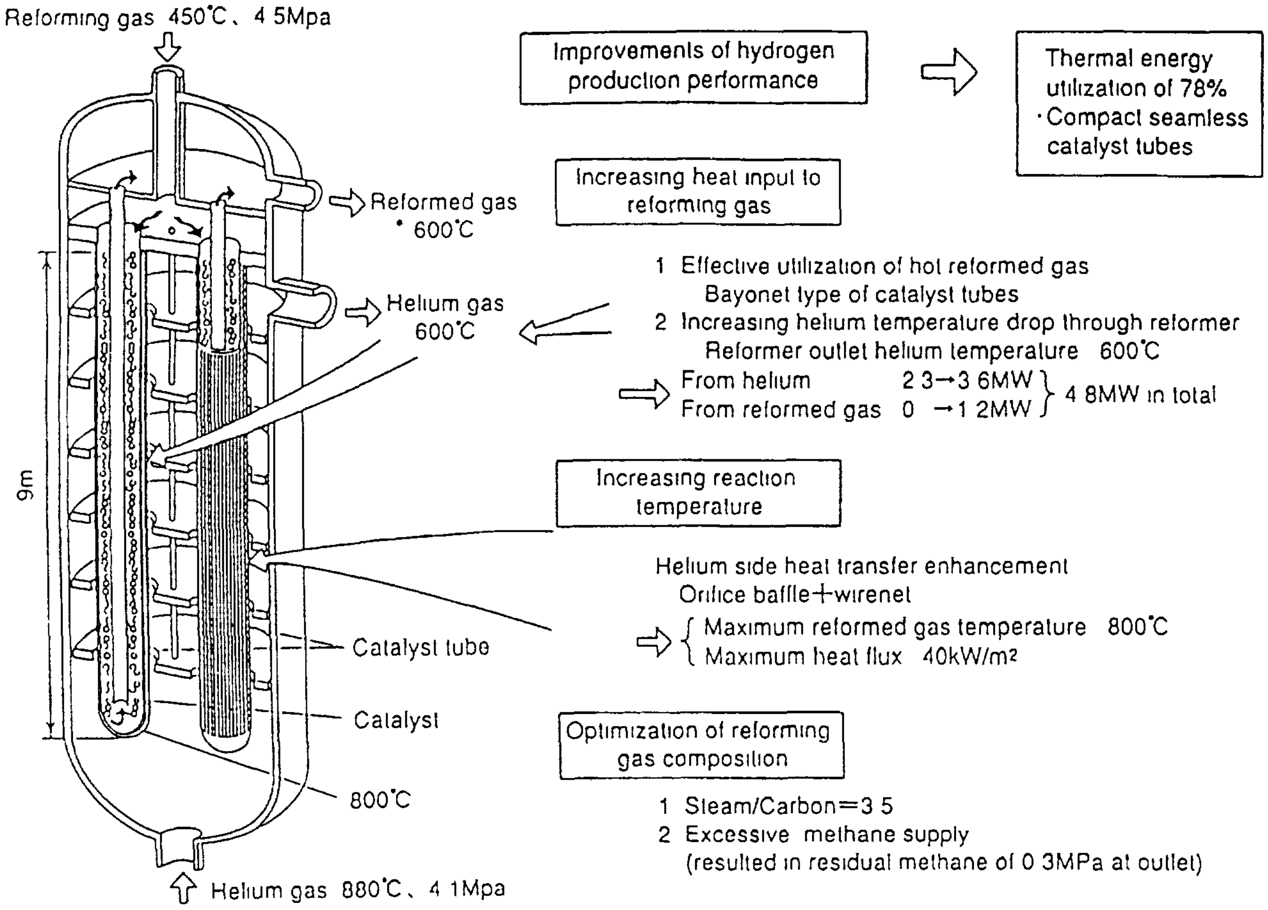

Fig. 2-12: Improvement of performance of Japanese helium-heated steam reformer, from [30]

With these improvements, it is estimated to achieve an H_2 production rate of approx. 3800 Nm^3/h for a 10 MW heat input [12, 30].

The installation of a steam generator as a downstream cooler of the endothermal reforming reactor was analyzed to provide stable controllability of the thermodynamic behavior in the system and to be universally applicable [13].

2.3.2. Helium-Helium Intermediate Heat Exchanger

An **intermediate heat exchanger (IHX)** circuit serves as an interface component to connect the nuclear with the chemical system. It thus

- minimizes contamination of the process heat exchanger and allows it to be placed outside the reactor containment,
- prevents water and process gas ingress into the nuclear core in case of a tube rupture, and
- reduces hydrogen permeation from the process gas into the primary helium as well as tritium permeation in the reverse direction.

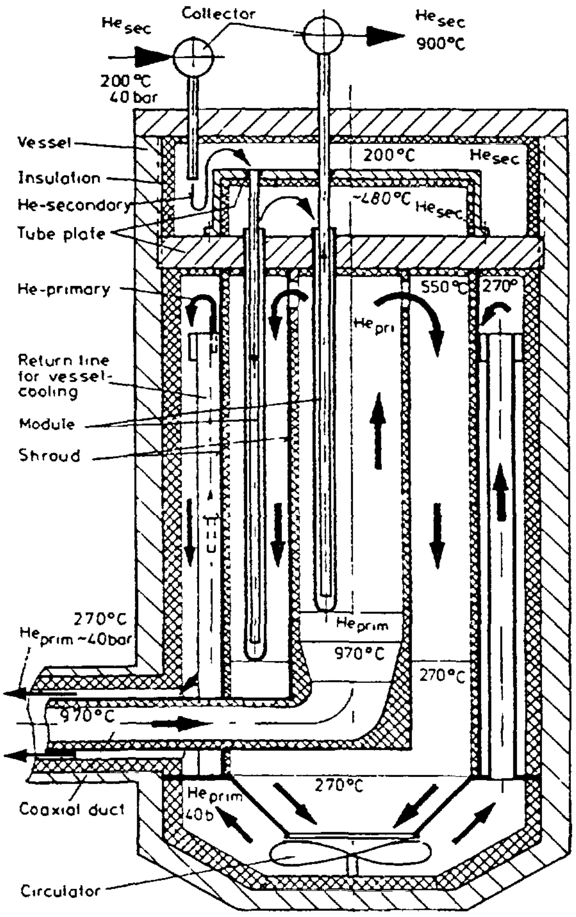

Fig. 2-13: Principle gas flow in a helium-to-helium intermediate heat exchanger, from [22]

Table 2-8: Comparison between IHX design data of test modules operated in the KVK loop and the PNP component [29]

	U-tube countercurrent compact IHX design				**Helical type IHX design**			
	PNP		**KVK**		**PNP**		**KVK**	
	Prim.	**Secon.**	**Prim.**	**Secon.**	**Prim.**	**Secon.**	**Prim.**	**Secon.**
Power [MW]	125		10		125		10	
Flow rate [kg/s]	36.9	35.6	3.0	2.9	36.9	35.6	2.95	2.85
Temperature in [°C]	950	220	950	220	950	220	950	220
Temperature out [°C]	293	900	293	900	293	900	293	900
No. of tubes	1900		180		1444		117	
Tube length [m]	32.7		32.7		17.5		17.5	

The IHX is a new type of component in terms of its specific nuclear requirements and its thermal load. The aim is a service life of 140,000 h at a system pressure of 4 MPa and temperatures up to 950 °C [29].

Drawbacks of an IHX are its technical problems due to the higher temperature, plus 50 - 70 K, compared with the reformer, its additional electricity demand, 50 MW(e) in a 3000 MW(th) PNP HTGR, which reduces the overall efficiency and last but not least, the fact that it presents an additional component which may fail.

The most economic medium for the IHX is helium. However, others such as CO_2, N_2, steam, Ne, or Ar could be used also. The design of an IHX is shown in Fig. 2-13. It is composed of two separate heat exchanging systems for high-end and low-end heat, here with a heat split-up at 550 °C [22].

For the **German PNP project** (see section 4.3.2.2.), two concepts of a He - He intermediate heat exchanger for a heat rating of 125 - 170 MW have been selected: (i) the helical heat exchanger elaborated by Sulzer/Steinmüller, and (ii) the U-tube compact heat exchanger elaborated by Balcke-Dürr. For both, a 10 MW test plant has been operated in the KVK loop (see section 4.3.2.6.). Design data of the test modules, as shown in Table 2-8, corresponded to the future nuclear component data with the exception of the helium flow rate. The test program included fatigue tests (temperature cycles) and creep buckling tests (cooling in the presence of strong pressure gradients) for the as-manufactured and the fatigued components, as well as steady-state operation at 40 - 100 % load and non steady-state tests, e.g., startup / shutdown operation [29].

The helium-to-helium intermediate heat exchanger (IHX) designed and fabricated for the **HTTR in Japan** (see section 4.5.2.2.) is a vertical helical coil counterflow type heat exchanger with 10 MW thermal power. As a primary circuit component, it has to meet the requirements on structural integrity as a class 1 component during its service life. The tube bundle consists of 96 heat transfer tubes which have an effective height of 4.87 m, an outer diameter of 31.8 mm and a wall thickness of 3.5 mm. The tubes are fabricated from the Ni-base superalloy Hastelloy XR. Radiation plates between the tubes are to increase heat transfer and restrain flow-induced vibrations. Operating conditions are a temperature of 950 °C and a pressure of 4.1 MPa on the primary side and 905 °C and 4.2 MPa, respectively, on the secondary side. The construction of the IHX was successfully finished in 1994 and installed in the HTTR reactor building in 1995 [21].

2.3.3. Hot Gas Duct

The **hot gas duct** is represented by coaxial pipes between core and reformer. The inner hot gas pipe is insulated on the inside and cooled by counterflow on the outside. Since the steam generator has to be on the alert in case of a decay heat removal action, the pipe system has to be safely constructed. In particular, fast pressure transients which could be destructive should be avoided by means of flow limitation.

For the 3000 MW(th) PNP plant, the inner diameter is 1.3 m, the insulation thickness is 100 mm (Fig. 2-14). The mass flow rate is 205 kg/s at a speed of 51 m/s. The

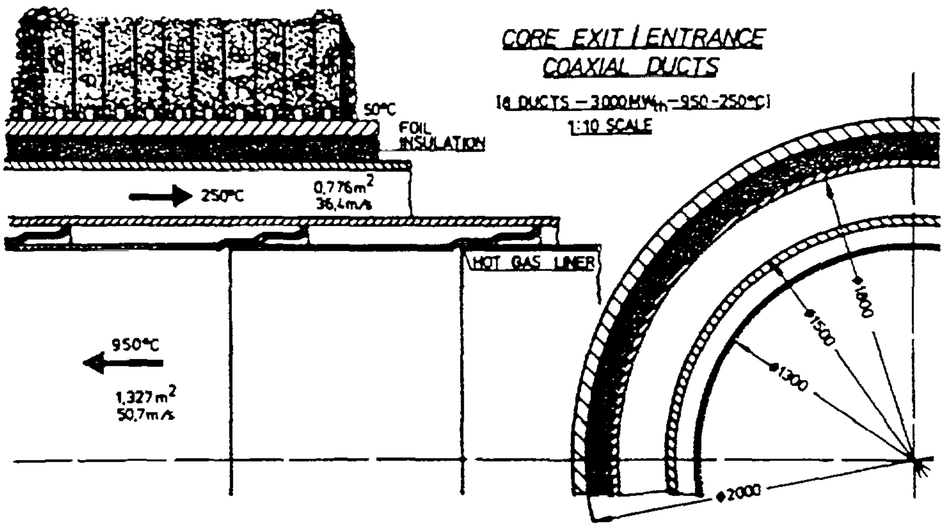

Fig. 2-14: Schematic of a hot gas duct between the reactor core and the steam reformer, from [36]

depressurization rate is limited to 0.1 MPa/s. The component is designed to be removable as long as no reliable data on its lifetime are available [36].

Experimental work has been conducted at the Research Center Jülich starting in 1971 to verify thermal efficiency, mechanical performance, applicability of materials and coatings for the hot gas duct insulation. Facilities used were the ARGUS loop (max. temperature 1000 °C, max. pressure 1 MPa), a high pressure wind tunnel (max. temperature 400 °C, max. pressure 4 MPa), and the high temperature helium test rig, HHV, (max. temperature 850 °C, max. pressure 5.1 MPa). Also a full-scale test facility, ADI, (max. temperature 950 °C, max. pressure 8 MPa) was operated by HRB for endurance tests as well as the KVK loop by INTERATOM. Feasibility was demonstrated for the insulation design applied in the THTR-300, which is composed of 18 layers, each consisting of a 10 mesh gauze sandwiched between two stainless steel sheets [6].

Protective coatings for the hot gas duct tested were a NiCrAlY basis layer followed by a Y_2O_3 stabilized ZrO_2 layer. Other components which need to be especially designed are the isolation valves. Two different kinds have been investigated, axial-type and ball-type valves. Further tests before application are still necessary [41].

2.4. MATERIALS FOR NUCLEAR POWER PLANT AND PROCESS COMPONENTS

2.4.1. Materials Testing at the Research Center Jülich

A comprehensive testing program for metallic materials was initiated at the Research Center Jülich within the PNP and HHT projects in a joint effort with industrial partners [32]. It is of utmost importance for design and valuation of component behavior during operation, since temperature limits covered by the existing regulations are exceeded by the PNP and HHT design limits. Significant components are those with the highest operational temperatures (> 750 °C), those with a pressure load, and those which represent the boundary of the primary circuit. Considering a 40 years plant lifetime and in between one replacement of a critical component, the effective operation time should be in the order of 100,000 hours.

Priority tasks have been the selection of high temperature, high strength alloys and testing of candidate commercial alloys. The material characteristics investigated included creep behavior, fatigue properties, structural stability, and corrosion resistance [32].

The characterization program for high-temperature alloys included the alloy types:

- INCOLOY 800H
  representing Fe-Ni-Cr alloys used for nuclear steam generators,
- HASTELLOY X and NIMONIC 86
  representing Ni-Cr-Mo alloys developed for gas turbines,
- INCONEL 617
  representing Ni-Cr-Co-Mo alloys for gas turbines,
- NIMONIC 80A,
- ALLOY 713LC
  as turbine blade material,
- TZM
  on Mo basis with very high creep rupture strengths, however, becomes brittle at lower temperatures.

Creep rupture strength experiments have been conducted in the ZEMAK I - IV laboratory facilities in Jülich. Fig. 2-15 shows some measurement results. Also fatigue tests with periodic stress - strain impact have been made to simulate load changes.

Corrosion effects on the metallic surfaces changing the mechanical properties of the materials have been investigated. Different kinds of impurities in the hot helium have been observed to cause different corrosion phenomena resulting from the interaction of carbon dissolved in the alloy with the surface oxide [32].

When exposed to **neutron irradiation**, heat resistant austenitic alloys tend to embrittle above 500 °C caused by (n,α) transmutations. The effect can be measured by tensile and creep testing. Special thermo-mechanical treatment of the alloys was found to successfully improve their ductibility [32].

In the qualification program for metallic high-temperature materials, lifetimes of steam reformer and He-He heat exchanger materials have been approved to reach the required 100,000 h. Materials tested in the high temperature range of the KVK facility were the types 1.4876 ($\leq$ 800 °C) and 2.4663 ($\leq$ 1000 °C). Experience gained on the interaction between metallic and ceramic materials and the helium coolant confirmed the operating specifications. Furthermore, CFC materials for the hot gas duct are in development. Still the experience from the PNP and HHT projects has disclosed that the technical solution, in particular, of materials problems require further research in longer-term projects. It was the reason that the plan to operate the THTR-300 as a process heat plant was no longer pursued at that time and rather postponed this plan to be used in a future 900 MW(e) HTGR.

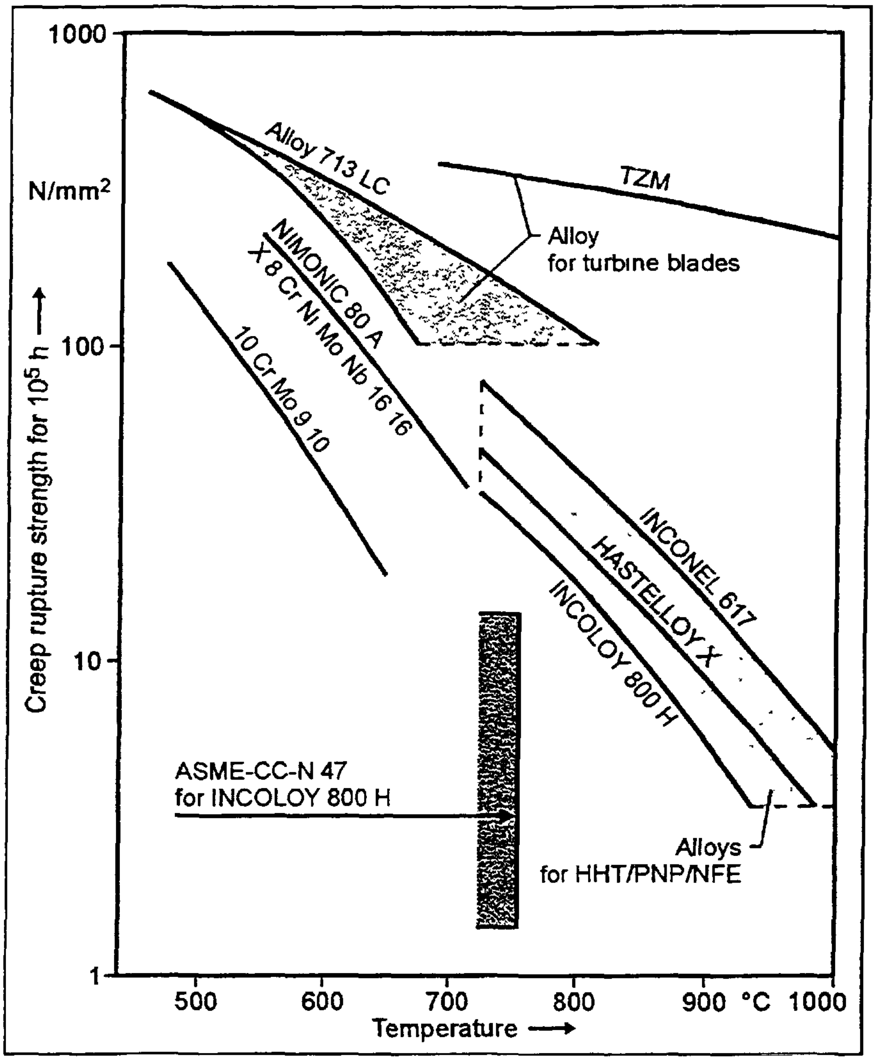

Fig. 2-15: Creep rupture strength experiments for different alloys under consideration for HTGRs [32]

2.4.2. Materials Testing at JAERI

The material chosen for the IHX and the steam reformer of the Japanese HTTR is HASTELLOY XR. Corrosion tests and long-term creep tests in helium atmosphere in the temperature range 800 - 1000 °C have been conducted reaching 50,000 hours. No significant degradation in creep properties was observed even after carburization. Creep rupture was found to be caused by nucleation, growth, and link-up of grain boundary cavities [26].

Satisfactory behavior of Hastelloy XR material has been found with respect to weldability, tensile and creep properties through optical microscopy and corresponding tests in air at room temperature and at high temperatures up to 950 °C, respectively [40].

Also the investigation of the potential use of SiC ceramics for heat exchanger and vessels, high-temperature properties and oxidation behavior has been started, e.g., on a

SiC-coated vessel with potential use for thermal chemical reactions for hydrogen processes. Other tests conducted at JAERI examine the corrosion exposure in boiling sulfuric acid. Mechanical bending tests are planned at the Research Center Jülich.

Further work will be focusing on lifetime prediction methods for gas turbine materials (superalloys) and experiments on fracture mechanics in superalloys as well as finite element calculations of multiaxial loaded tubes and validation of multiaxial tests (tension, torsion, internal pressure).

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Chapter 3

SAFETY CONSIDERATIONS CONCERNING NUCLEAR POWER PLANTS ASSOCIATED WITH PROCESS HEAT AND/OR HYDROGEN PRODUCTION

3.1. SAFETY DESIGN CONCEPT SPECIFIC TO NUCLEAR HEAT UTILIZATION SYSTEMS

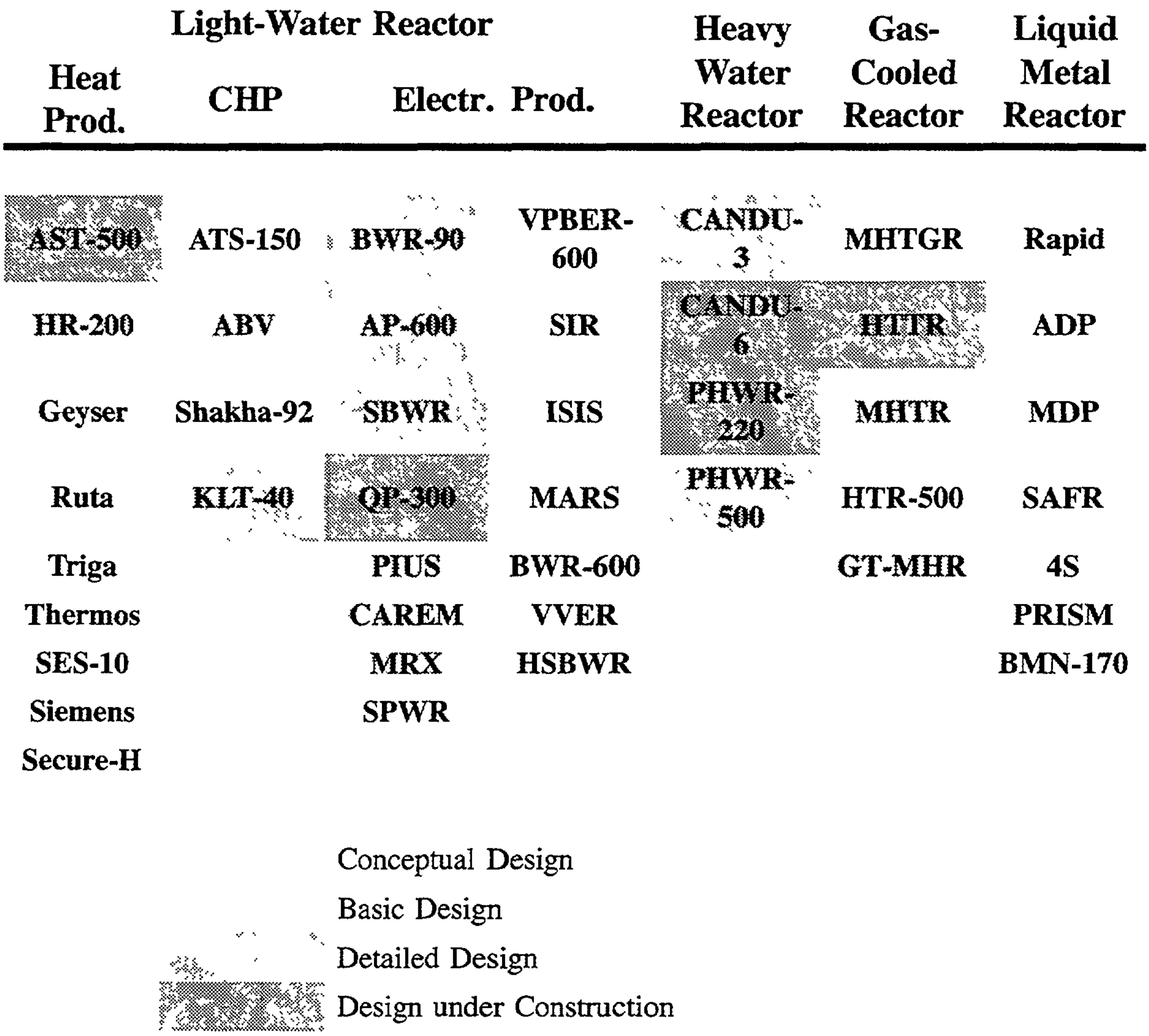
Present nuclear power plants must be designed and operated to current safety objectives and principles in order to achieve a high level of safety. Nuclear power has a small environmental impact when operating as designed, but faces serious public concerns about the risk of off-design accidental releases. This has stimulated the current engineering concentration on reducing the probability of such accidents.

After the severe accidents at the Three-Mile-Island and Chernobyl nuclear power stations, new designs with improved safety concepts have been proposed focusing on reducing the probability and consequences of severe accidents, on an improved containment system, and on more intensive consideration of passive safety characteristics. Different categories of passive systems have been defined by the International Atomic Energy Agency in the course of these discussions which appear to be beneficial [17], although no method has been finally agreed upon which type of system is more appropriate in certain cases. The criteria for a decision include maintenance, redundancy, diversity, quantification of reliability or human interaction. The key proposal is that also severe accidents beyond the design basis will be systematically considered during the design process for future reactors. Further research and development is required to assure the effectiveness and reliability of passive safety systems [15].

In many countries of the world, a large number of different R&D and design projects have been initiated to serve for a wide range of applications. Advanced light-water reactors (ALWR), also called evolutionary reactors, are to obey the overall design philosophy of being simple and rugged with high design margin, based on proven technology. The ALWR safety policy features an integrated design approach to safety based on defense-in-depth philosophy. This strategy includes the three levels of accident resistance, core damage prevention, and accident mitigation. Fig. 3-1 lists most of the projects of small and medium sized reactors and the current status of development as reported in [18]. Pros and cons as seen at DOE [52] are presented in Fig. 3-2.

A much more far-reaching demand for the introduction of **innovative nuclear power plants** in the future is made on a design such that fission product release is made impossible or, at least, restricted to the plant itself [27]. This means that emergency planning would no longer be necessary or in more detail:

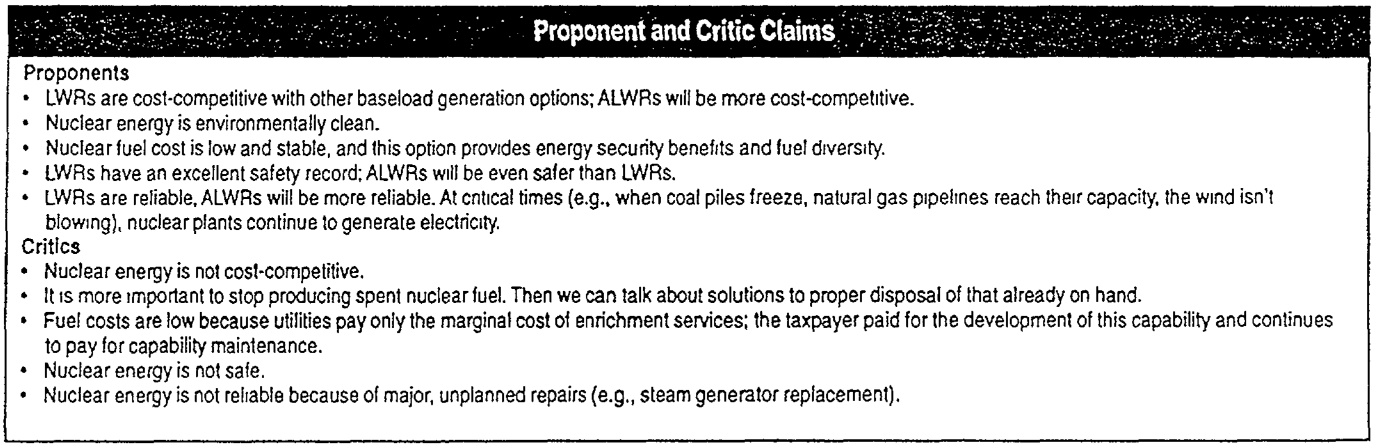
- no immediate fatalities outside the plant,
- no evacuation of population,
- no contamination outside the plant.



Light-Water Reactor				Heavy Water Reactor	Gas-Cooled Reactor	Liquid Metal Reactor
Heat Prod.	CHP	Electr. Prod.				
AST-500	ATS-150	BWR-90	VPBER-600	CANDU-3	MHTGR	Rapid
HR-200	ABV	AP-600	SIR	CANDU-6	HTTR	ADP
Geyser	Shakha-92	SBWR	ISIS	PHWR-220	MHTR	MDP
Ruta	KLT-40	QP-300	MARS	PHWR-500	HTR-500	SAFR
Triga		PIUS	BWR-600		GT-MHR	4S
Thermos		CAREM	VVER			PRISM
SES-10		MRX	HSBWR			BMN-170
Siemens		SPWR				
Secure-H						

Conceptual Design
Basic Design
Detailed Design
Design under Construction

Fig. 3-1: Small and medium reactor development lines in the world, from [18]



Proponent and Critic Claims

Proponents
- LWRs are cost-competitive with other baseload generation options; ALWRs will be more cost-competitive.
- Nuclear energy is environmentally clean.
- Nuclear fuel cost is low and stable, and this option provides energy security benefits and fuel diversity.
- LWRs have an excellent safety record; ALWRs will be even safer than LWRs.
- LWRs are reliable, ALWRs will be more reliable. At critical times (e.g., when coal piles freeze, natural gas pipelines reach their capacity, the wind isn't blowing), nuclear plants continue to generate electricity.

Critics
- Nuclear energy is not cost-competitive.
- It is more important to stop producing spent nuclear fuel. Then we can talk about solutions to proper disposal of that already on hand.
- Fuel costs are low because utilities pay only the marginal cost of enrichment services; the taxpayer paid for the development of this capability and continues to pay for capability maintenance.
- Nuclear energy is not safe.
- Nuclear energy is not reliable because of major, unplanned repairs (e.g., steam generator replacement).

Fig. 3-2: Pros and cons of an advanced light-water reactor (ALWR), from [52]

The demand for nuclear, thermal, chemical, and mechanical stability of a nuclear reactor needs to ensure the following safety requirements [27]:

- inherent limitation of nuclear power and of fuel temperature,
- passive decay heat removal,
- barrier fuel remains intact, integrity of core against corrosion attack,
- barrier reactor pressure vessel remains intact, integrity of core against mechanical failure,
- barrier containment remains intact,
- no interdependencies among barriers.

The safety philosophy for future nuclear plants will most probably include the protection against aircraft crash (penetration and induced vibrations) as well as chemical explosion waves such that a respective contribution to the risk is minimal.

3.2. SAFETY CONSIDERATIONS FOR A NUCLEAR PROCESS HEAT HTGR

3.2.1. Activity Enclosure

For safety reasons, the system design of an HTGR plant with process heat application has to assure the restriction of contamination with radionuclides to the primary circuit or its reduction to the least possible in the case of leakage or permeation. One possibility is to deploy an **intermediate loop** as an additional safety barrier to the system. In such an arrangement, all heat-consuming components are physically separated from the primary circuit by means of an intermediate heat exchanger. In the case of heat consuming components to be arranged in the primary circuit, they have to have themselves the quality of a safety barrier. In case of an accidental release of product gas, the gas mixture escaped into the reactor building and mixed with air, carries the hazardous potential of a local explosion.

Safety-related layout of the plant comprises double-walled pipes in product gas carrying ducts and deployment of isolation valves. Released process gases should be routed immediately into the atmosphere to avoid accumulation inside the reactor building.

The prevailing idea currently is to install the heat transferring components of a nuclear coal gasification plant – gas generator, steam superheater, steam generator – in a secondary circuit, whereas in a nuclear steam reforming plant, steam reformer and steam generator are thought to be safely operated within the primary circuit [46]. With respect to the operational conditions, a compromise has to be found between a high-pressure system with a positive effect on operational and accidental behavior and a low-pressure system in all circuits to minimize the load on the components. For the active reactor core, a two-zone fueling should be chosen to avoid radial temperature gradients to proceed to the heat exchanger [20].

The heat consuming components are, in general, not appropriate to serve as the decay heat removal system in case of a nuclear accident. Therefore, in the Japanese design of the HTTR, an **auxiliary cooling system** is planned to remove the decay heat via forced convection, as it was also the case in the former German PNP-500 process heat reactor design. In the most recent German AHTR-500 design, an adequate passive system is being planned based on natural convection and there is no demand for active safety systems.

Thermal loads upon the process heat exchanger do not allow rapid temperature change rates. Therefore in case of the demand for a decay heat removal system after a fast shutdown of the reactor, an auxiliary cooling system should be used rather than the main cooling system. In addition, much of the decay heat would be removed via the core surfaces to the liner cooling system [10].

In case of a pressure loss accident, the maximum escape rate of the primary coolant is restricted by flow restrictors. A depressurization will take at least two minutes so that destructive dynamic forces in the primary system can be excluded. All heat exchanging components incl. steam reformer are designed to keep their pressure, if there is a pressure loss in the primary system [10].

A safety feature, in particular for a nuclear power plant on an industrial site, is a compact arrangement which allows an underground construction. Such an arrangement as was proposed for the HTGR design PR 500 for process steam production would be safe against gas explosions and air craft crashes.

3.2.2. Primary Circuit Contamination

The deposition of fission products on primary circuit surfaces and, in particular, on the reformer tube walls causes difficulties during maintenance and catalyst refilling procedures, if the activity is intolerably high. Cesium and silver isotopes released during reactor operation are of major concern. Particularly silver diffuses easily out of the fuel elements at operating temperature conditions into the coolant and migrates easily into metal surfaces and is difficult to remove in decontamination operations [32].

In a gas turbine version of the HTTR, half of the radiation dose is estimated to originate from the silver isotope Ag-110m. Countermeasures could be either a fuel temperature reduction which would require a change of the core design, or the use of advanced fuel with the most efficient barrier against fission product release, the SiC coating layer, to be substituted by a ZrC layer. The higher retentivity of ZrC against Ag release, however, needs further confirmation [40].

3.2.2.1. Plateout Research Program

The circulating and plateout activities in the primary coolant circuit are potential sources of release into the environment in the event of primary coolant leaks or as a result of the venting of primary coolant in response to overpressuring the primary circuit, e.g., in response to significant water ingress. The fraction of the circulating activity lost during such events is essentially the same as the fraction of the primary coolant that is released, although the radionuclide release can be mitigated by pumpdown through the helium purification system, if the leak rate is sufficiently slow.

Numerous experimental and theoretical efforts have been made to examine the plateout distribution of fission products in the primary circuit both under normal operating and accident conditions. Different **in-pile and out-of-pile deposition loops** were operated in Germany, Japan, France, the UK, and the USA to study systematically the ad-/desorption behavior of fission product on metallic surfaces as a function of temperature and gas flow. The obtained experimental data as well as the measurements from the gas-cooled reactors AVR, THTR-300, Peach Bottom, Fort St. Vrain were taken to derive plateout parameters such as desorption energy or penetration coefficient to be used in corresponding calculation models. The most important computer codes which were tested and more or less successfully validated, are SPATRA (Germany), PLAIN (Japan), and PADLOC, TRAFIC (USA) [19].

Within the HHT program, the AVR reactor has been used to conduct several experiments for investigation of atomic or molecular radionuclides in the coolant flow as well as transport and deposition with graphitic or metallic dust. Cold gas filter tests and dust experiments were used to measure dust size and concentration as well as vapor-phase and dust-borne metallic fission product activities in the coolant under normal operating conditions. The in-pile experiments VAMPYR-I and VAMPYR-II starting in 1972 were hot gas sampling tubes to determine diffusion profiles of deposited fission products on various materials. The helium loop facility LAMINAR in Germany was operated in the turbulent flow range with Cs-134 or I-131 to examine their deposition behavior under varying temperature conditions and with desorption periods. Material samples were later inserted in steamoff/washoff experiments. In the out-of-pile circuit SMOC, cesium transport and deposition under the turbulent flow conditions of a depressurization accident were investigated by varying in a wide range of gas/wall temperatures and mass flow rates.

In Japan, the Oarai Gas Loop No. 1, OGL-1, installed in the JMTR, was used for cesium and iodine plateout distribution measurements basically under the normal operating conditions of the HTTR. Within a joint German/French effort, another plateout experimental series was conducted in the in-pile loop SAPHIR in the French PEGASE reactor. Also extensive plateout distribution data were obtained in the UK by examining components removed from the Dragon HTGR

The US CPL-2 test program was a series of four in-pile loop tests in the French PEGASE reactor using a small fraction of bare UO_2 kernels as the fission product source. Plateout data from heat exchanger tube consisting of various types of steels were gathered under somewhat complex temperature and flow field conditions. Out-of-pile loop data were obtained in five GA deposition loop tests to study plateout under conditions similar to sections of an HTGR steam generator or gas turbine. The COMEDIE loop in the French SILOE MTR composed of an in-pile and an out-of-pile section was capable of providing integral test data under realistic accident conditions. The plateout section simulated different metallic components in the primary circuit of an HTGR.

3.2.2.2. Corrosion

Furthermore impurities in the helium coolant, mainly the air constituents, can cause corrosion effects on the outside reformer tube walls which eventually change its properties. Measurements of impurity contents in Dragon and AVR revealed a large scattering of the data. Experimental results obtained within the Dragon project indicate a strong corrosion of aluminum and titanium, i.e., the formation of Cr-, Mn-, Si-, and Ti-oxide layers, and an increased corrosion rate in moist helium compared with a dry atmosphere [26].

3.2.3. Hydrogen and Tritium Behavior

Under conditions of nuclear process heat plant operation, **hydrogen** and **tritium** exhibit high mobility at 950 °C causing permeation through the walls of the heat-exchanging components. Tritium produced in the primary circuit could permeate into the product gas in the secondary circuit and eventually create a radiation problem to the consumer. In the opposite direction, hydrogen from the secondary circuit could diffuse into the primary circuit to cause corrosion of the fuel elements and of the graphite liner in the core with the formation of methane (which finally could decompose again and deposit carbon in the heat exchangers). Parameters which influence permeation are, besides temperature and partial pressure, wall material and thickness as well as surface size and roughness. An upper limit for the tritium contents in the product gas set by regulations as low as 10 pCi/g, turned out to be a key problem for the PNP project [47]. In the meantime, the limit has been raised to 135 pCi/g restricted to refined products of nuclear heat processes from fossil fuels in domestic applications.

The tritium production in a process heat HTGR is estimated to originate mostly from activation of Li-6 which is contained in the graphite, and with smaller fractions from fission and from He-3 activation. The release of tritium into the coolant is based on conservative assumptions, e.g., 10 % of the fission product tritium from defective coated particles. Estimated tritium production and release rates for a 170 MW(th) HTR-MODUL plant are given listed in Table 3-1 [8].

Table 3-1: Tritium production and release rates as estimated for a 170 MW(th) process heat HTR-MODUL, from [8]

Tritium source from	**Tritium production [10^3 Bq/s] ([%])**		**Tritium release into coolant [10^3 Bq/s] ([%])**	
	Initial phase	**Equilibrium**	**Initial phase**	**Equilibrium**
Fission	898 (14)	1245 (51)	89 (4)	126 (12)
Li-6	4721 (76)	846 (34)	1413 (66)	529 (52)
He-3	628 (10)	367 (15)	628 (30)	367 (36)

Possibilities of reducing the permeation streams are the formation of oxide layers (*in-situ* or pre-coated) or, as active measures, an improved design of the gas purification system or even the construction of an intermediate circuit between the primary and secondary circuit to serve as a sink for both hydrogen and tritium.

- **Oxide layers**
  Oxide layers on the heat exchanging material surfaces were found to be capable of significantly decreasing the tritium transport. Experimental investigations of the permeation process in high-temperature alloys were initiated at the Research Center Jülich [49]. Test facilities were "AUWARM", which allowed long-term (1000 - 3000 h) examination of hydrogen permeation in 16 tube specimens at a time with temperatures up to 1000 °C and pressures up to 3.2 MPa, "TRIPERM" operated with an argon-tritium mixture on the primary side for one tube specimen,

and “HD-PERM”, “SE-PERM”, “DEUPERM” for short- and medium-term analyses and pre-selection of materials at low pressures.

Results have shown that *in-situ* oxidic layers show a large inhibition of permeation in the medium and high-temperature range > 650 °C. The uncertainty is comparatively large in the lower temperature range. Also measurements from existing HTGRs (AVR, Peach Bottom) revealed significant uncertainties, meaning that data are not necessarily transferable to new plants [47].

- **Gas Purification System**

  An effective and powerful gas purification system could be designed by integrating additional components for hydrogen and tritium gettering from the coolant gas. Hydride formers such as Ti, Zr, and Ce or a cerium mixed metal were deemed appropriate. A respective experiment was planned at the AVR reactor to test a Cer mixed metal gas purification system with a throughput of 8 Nm^3/h [8].

- **Intermediate Circuit**

  An additional boundary between primary and secondary circuit would be provided by an intermediate circuit purified by a sweep gas flow. Adding oxygen or steam to the sweep gas, a fraction of the tritium will be bound as tritiated water HTO and no longer be available for permeation plus it would form a protective oxide layer. An inhibition effect was also found if hydrogen was injected (factor of 2 - 3). This effect, however, needs further understanding [47].

  An intermediate circuit was experimentally tested in a facility whose heart was a double tube consisting of Incoloy 800H. The inner tube simulated the secondary circuit carrying the product gas. The gap between inner and outer tube represented the intermediate circuit. The tubes were closed at both ends. Gas inlet/outlet was given by small pipes into the system. The whole construction was put underneath a quartz glas recipient which simulated the primary circuit. Argon was used as a sweep gas. Hydrogen concentrations in the different circuits were measured by means of gas chromatography, while the tritium concentration in the primary circuit was measured in ionization chambers. The facility was used to check how partial pressures of hydrogen and tritium in all circuits were affected by the design of the intermediate circuit, and to derive permeation constants and activation energies [5].

3.2.4. Disturbance During Steam Reformer Operation

In the hydrogen production system designed for the HTTR, an approximate 4 MW power share is consumed for the reforming reaction while 6 MW are utilized downstream for steam production in a steam generator. Analytical studies have been conducted at JAERI with the transient thermohydraulics computer code IRIS to investigate the steam generator as a passive heat sink in case of a failure of the heat removal system of the reformer to ensure its coolability [44]. JAERI has developed a computer model to analyze the transient behavior of the nuclear reformer system. It is able to treat the chemical reforming reactions under the influence of gas (methane, feedwater) flow disturbances connected to the transient thermohydraulics by using the **THYDE-HTGR code** to account for the reactor side [11].

Tests with the EVA-II plant in Jülich have shown that its normal operation is possible even if up to 30 % of the reforming tubes were blocked, meaning that isolation of single tubes would not disturb the operation, thus increasing the plant flexibility [45].

Advanced steam generators with a large steam drum (high reliability, passive cooling capability) can mitigate steam reformer disturbances. The German once-through type of steam generator is designed to be integrated inside the reactor pressure vessel. It has been tested in the EVA-II test facility.

Alternative design of a steam reformer contains a spherical type catalyst which itself moves downwards while the process gas flows upwards through the catalyst. This method increases the efficiency (smaller residual methane contents). Drawback is a catalyst damage due to the movement.

3.2.5. Rupture of Helium Line in Gasifier

The accidental potential of a coal gasification plant with a temperature of 950 °C which has combustible gases in the secondary and/or tertiary loop must be classified as being higher than that of a conventional nuclear plant. In PNP concepts, an isolation valve is considered to limit the amount of explosive gas mixture in the containment.

The system pressure in the gasifier is designed to be 2.1 MPa, meaning that in case of a ruptured helium line which is normally at 2 MPa, no radioactivity could escape from the primary circuit, but product gas and steam as well as coal particles could enter the primary helium circuit. Leakage will be detected by moisture sensors, helium lines shut off from the process gas circuit. The principal consequences of steam entrainment in a steam-producing HTGR are equivalent to those of a water ingress accident into the core. Coal dust in the primary circuit provides an additional carrier medium for radioactivity which could be released into the confinement during a depressurization accident. The escape of a coal dust - product gas - steam mixture into the confinement would result in a wet dust which makes an ignition unlikely [25].

3.2.6. Rupture of Process Gas Feedline

3.2.6.1. Release into the Containment

Any process heat plant design implies piping through the containment to connect the reactor vessel with the chemical plant. The fracture of a pipe could result in the accumulation of a flammable gas mixture in the containment. Precautions must be taken to minimize the risk of a fire or gas explosion such as avoidance of explosive gas ingress, proper detection devices, inerting, sufficient safety distances, appropriate layout of secondary coolant boundary, explosion-proofed wall, plant isolation valve. For the PNP-500, the use of two concentric pipes for the process gas carrying lines were recommended. Alternatives are concrete channels around the gas lines or inerting of the containment [10].

As part of the PNP safety program, Interatom has studied the **process gas ingress** into the containment for the scenario of a depressurization plus process gas pipe rupture. Various containment volumes as well as times for the process gas pipes have been examined showing that the equilibrium pressure will be in the range of 0.16 - 0.24 MPa at temperatures

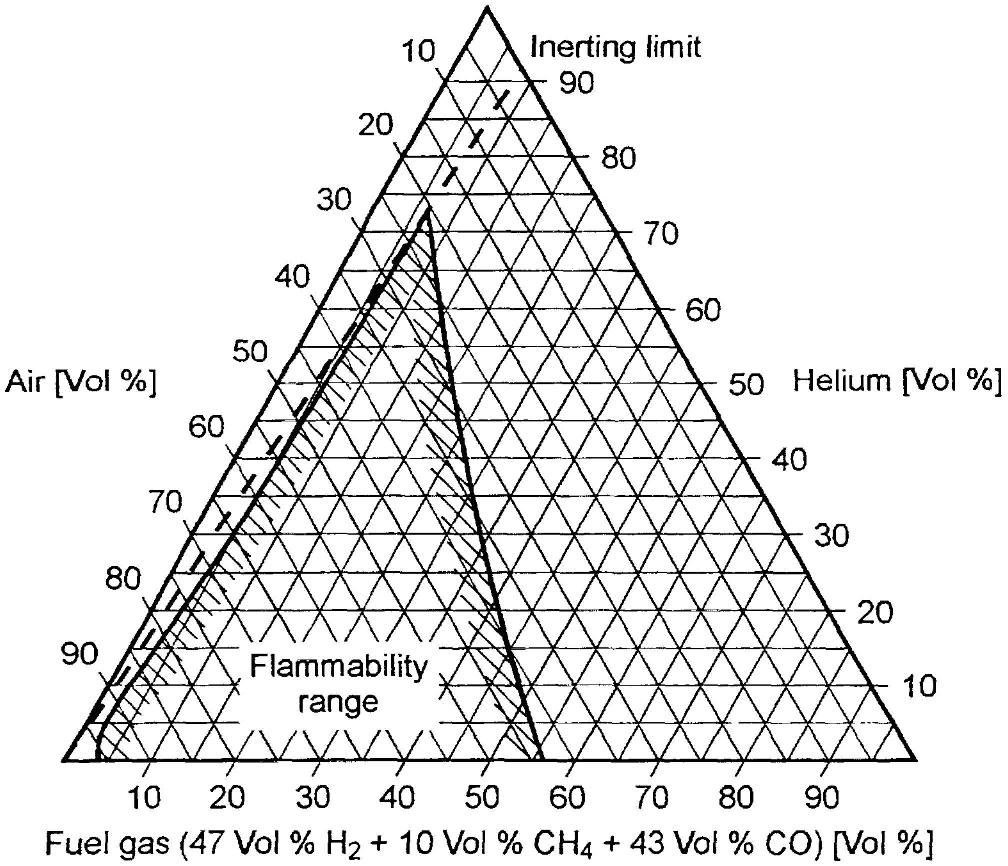


Fig. 3-3: Estimated flammability range of the three-gas mixture fuel gas-helium-air, from [13]

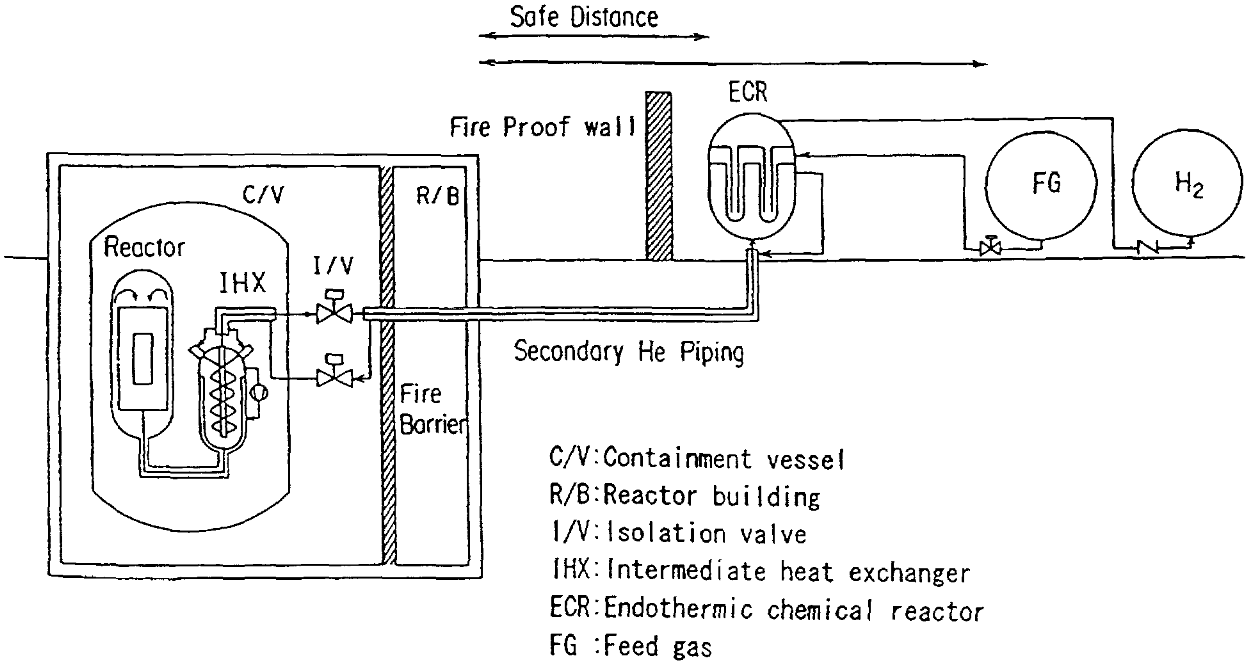


Fig. 3-4: Safety design concept in the Japanese HTTR against fire and explosion, from [33]

between 120 and 200 °C. Process gas mass released within an assumed time period of 20 s will be 1100 kg in the primary system winding up to 1700 kg of flammable gases, if all steam were transformed in the core to H_2 and CO. Composition of the gas will then be 47 % H_2, 43 % CO, and 10 % CH_4. The fraction that eventually enters the containment is no higher than 1.3 - 2.4 vol% which, however, does not preclude local flammable mixtures. For the above composition of the fuel gas and a temperature of 200 °C, the flammable range within the three-gas mixture fuel gas-helium-air has been estimated as shown in Fig. 3-3. For a fuel gas fraction of up to 2.4 vol%, no flammable mixture is expected, if a homogeneous mixture is assumed. Locally flammable mixtures, however, cannot be excluded during the mixing phase [13].

Under the assumption of a reformer tube rupture creating a leak size of 80 cm^2 with process gas to escape into the containment over 20 s before the stream is automatically cutoff, an estimated 3 % of the containment volume is occupied by the process gas. Furthermore, pessimistically assuming that a stoichiometric mixture is formed and explodes, results in an overpressure of 46 kPa within 3 s which is expected to cause no damage to the containment [10].

Safety assurance in the design of the HTTR steam reforming system against fire or explosion of flammable product gas mixtures is the task of the secondary helium piping system which is designed to limit gas ingress by means of a combination of containment vessel isolation valves and emergency shutoff valve in the process gas feed line [33].

3.2.6.2. Release into the Environment

According to a guideline on the protection of nuclear power plants against pressure waves from chemical reactions issued in Germany in 1974 (see section 3.5.1.), the plant has to be designed such that it withstands the static and dynamic load generated by the fast deflagration of a large gas cloud. Also minimum safety distances between plant and explosible gas mixture were fixed to be at least 100 m.

The release of product or feed gas into the environment and the formation of a **free flammable gas cloud** could result in heat radiation and blast wave impact from fire / explosion. For the German PNP design, it was proposed to ensure that the gas be routed through inerted channels away from the gasifier and flared at a safe spot. This measure, however, requires additional components in the confinement, e.g., to allow for a separation of the coal dust from the gas mixture and a cooling of the mixture [25].

The safety concept of the Japanese HTTR for process heat application in the case of fire and explosion (see Fig. 3-4) includes the appropriate blast wave resistance design of building structures, gas leak detection device, fire extinguishing system, emergency shutoff valve, safety distance which could be reduced by fireproof walls. Current JAERI design regulations do not allow overpressures beyond 10 kPa (Japanese standard is 12 MPa) and a wall-averaged temperature of the concrete structures beyond 175 °C [33]. Considering a natural gas vapor cloud explosion after the release of the total tank contents of 168 t (= 400 m^3) of LNG, the above upper limits translate into a safety distance of as much as 1900 m [12]. Presently, a more practicable figure of 470 m is in discussion for the HTTR.

An argument for a safety distance reduction could be the deployment of an underground, non-pressurized LNG storage tank and ventilation system [34].

3.3. SAFETY AND RISK ASSESSMENT FOR PROCESS HEAT HTGRS

The former Institute for Nuclear Safety Research (now: Institute for Safety Research and Reactor Technology) at the Research Center Jülich conducted in the past various studies on the safety and risk assessment for nuclear power plants or their designs. Among them were two dedicated to the German process heat HTGR concepts, AVR-II and the 170 MW(th) HTR-MODUL, whose results are presented in the following sections. A brief description of the general methodology applied is given in section 8.7.1.

3.3.1. AVR-II

In 1982, the Research Center Jülich presented the conceptual design of a 50 MW(th) nuclear process heat plant with a pebble-bed HTGR, named **AVR-II**, for which a safety-related study has been conducted [29]. Its characteristic features are a slim steel pressure vessel, no separate decay heat removal system, shutdown and control system via reflector rods, surface cooling system, and a simplified containment. The safety of the reactor is principally based on passive system features.

The cylindrical core of 4.1 m height and 2.5 m diameter is fueled in an OTTO loading scheme. The power density is 2.5 MW/m^3. The helium coolant inlet / outlet temperatures are 250 and 985 °C, respectively, at a system pressure of 4 MPa. The reformer consumes a thermal power of 20 MW. It consists of a bundle of 68 reforming tubes with a length of 15 m. Inlet / outlet temperatures of the primary helium are 950 and 680 °C, and of the product gas 825 and 550 °C, respectively. The steam generator consumes the residual 30 MW(th) with helium inlet / outlet temperatures of 670 and 250 °C with 80 % of the power providing process steam for the reformer.

Standardized protection actions include shutdown of the reactor, of the main cooling system (which is not required for keeping the reactor within safe limits) and of the reformer plant. The two (required) shutdown systems consist of in total 18 absorber rods which are moved in the side reflector. Diversity is given by the employment of different propulsion systems. In particular, the active cooling of the core by the main cooling system is not required because fuel temperatures remain within the safety limits. Only for reactor vessel protection purposes, the surface cooling system in the reactor is necessary which alone is able to account for heat removal.

Accident sequences investigated were decay heat removal without / with main cooling system. In the former case, both core and reformer are cutoff from the coolant circulation and a gradual temperature balance is obtained by heat conduction, radiation and small internal convection. The activation of the main cooling system delayed by 1 h encounters a merely changed temperature distribution allowing for a smooth and gentle restart.

Thermodynamic studies have shown that in case of a loss-of-forced-convection accident, the maximum fuel temperature is 1150 °C, if the reactor remains under pressure, and no higher than 1250 °C in a depressurized reactor. The predicted maximum temperature for the pressure vessel is ≈ 400 °C and for the containment wall ≈ 340 °C inside and ≈ 100 °C outside. All figures all uncritical. A temperature-induced release of fission products from the spherical fuel elements can thus be excluded. Besides, both reformer and steam generator surfaces provide an enormous adsorption potential for fission products which is utilized to a small extent only. The concrete walls enclosing the reactor vessel reach maximum temperatures of 300 °C within 10 days, but no damage to the reactor components is expected.

A depressurization accident with a subsequent **water ingress** was found to not represent an intolerable load upon the pressure-keeping containment in terms of peak pressure and pressure transient. Reactivity transients including false operation of absorber rods, water ingress, or a decrease of core inlet temperature were also analyzed to cause no serious damage to the heat exchanging components, unless both reactor shutdown and helium circulators fail at a time.

In a water ingress accident after pipe rupture, the maximum ingress rate is conservatively assumed to be 5 kg/s with a maximum amount of water of 200 kg in the primary system. The water causes graphite corrosion of not more than 1 % on the average keeping fission product release at a relatively low level. The rupture of a process gas line results in an escape rate of 5 kg/s process gas consisting of water (60 %), hydrogen (6 %) and CO_2, CO, CH_4. Maximum amounts to enter the primary circuit until the reformer is shut off, is 100 kg of water and 10 kg of hydrogen, low enough to be covered by the water ingress accident.

3.3.2. HTR-MODUL for Process Heat Application (170 MW(th))

A probabilistic safety analysis has been conducted at the Research Center Jülich for the process heat variant of the German modular HTGR with the purpose to identify differences compared with the electricity generating **HTR-MODUL** [55]. The process heat HTR-MODUL consists of a pebble bed core with 360,000 spherical fuel elements to produce a thermal power of 170 MW. Helium coolant gas inlet / outlet temperatures are 300 and 950 °C, respectively. The system pressure is 4 MPa. The connection to the secondary circuit is given by a He / He intermediate heat exchanger.

The safety concept considers two nuclear shutdown systems, a set of six reflector rods for reactor scram and power control and a "KLAK" system of small absorber balls for cold and long-term shutdown. Decay heat removal is made via the heat exchanger, an auxiliary cooling system, and the panel cooling system inside the concrete cavern, or, in case of a failure of these systems, passively by heat transfer via the surface of the reactor vessel.

The principal barriers against fission product release into the environment are the high quality TRISO fuel, the reactor pressure vessel, and the reactor building. The calculation of the fission product release during normal operation of the reactor (Fig. 3-5) which determines the contamination of the primary circuit and thus the source term in case of a depressurization or a water ingress accident has again identified silver to be the nuclide with the largest release fraction.

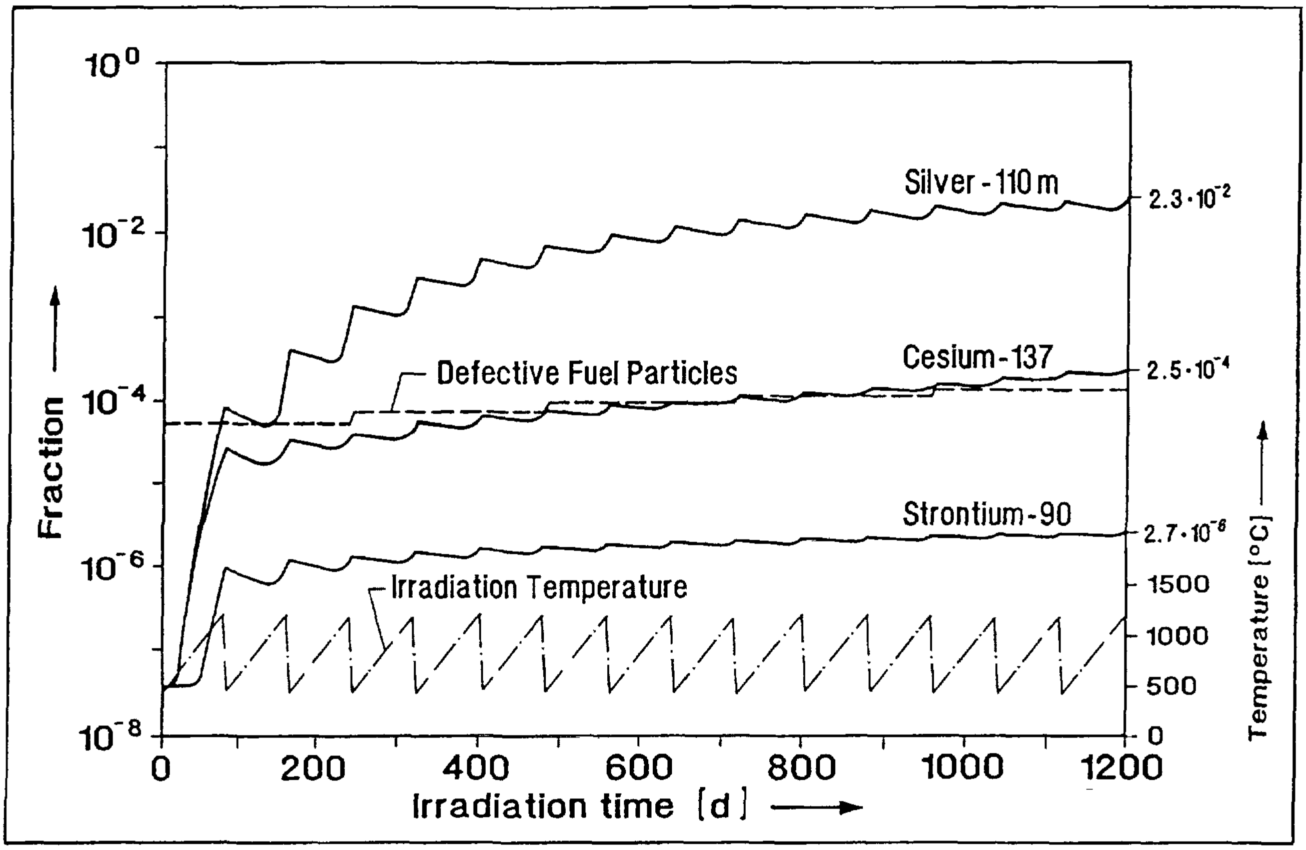


Fig. 3-5: Accumulated metallic fission product release fraction from a spherical fuel element in the 170 MW(th) process heat HTR-MODUL, from [55]

Events identified to initiate an accident with the release of radionuclides from the core are a small or large leak in the primary circuit, the loss of the main heat sink or the panel cooling system, and the loss of offsite power. Reactivity accidents have been excluded, because they were deemed insignificant in an HTR-MODUL in terms of fission product release. The event tree analyses have led to the classification of all accident sequences into four **release categories** with frequencies ranging between $1.8*10^{-5}$/yr and $5*10^{-8}$/yr. For those scenarios with the largest fission product release expected, deterministic studies applying conservative input data have been conducted. The severest case, a core heatup in the depressurized system, is predicted to result in a maximum core temperature of 1525 °C and a maximum core average of about 1000 °C. From the radiologically relevant nuclides under such temperature conditions, no cesium or strontium release from the core is expected due to a high sorptivity of the graphite in the core. Only silver escapes from the primary circuit in a considerable quantity. The release of iodine is determined by the fraction of free uranium in the core, which is a question of the fuel quality. Iodine-131 quantities released are predicted to be 111 GBq in a slow depressurization (small leak) and 46 GBq in a fast depressurization (large leak).

The higher fuel temperatures under normal operating conditions compared with the electricity generating variant result in a higher fission product contamination of the primary circuit outside the active core, a factor of 3 for iodine and a factor of 4 for cesium. In the case of a depressurization through a large leak, it is the dust-borne cesium and strontium dominating the activity release. Depressurization through a small leak makes coolant activities enlarged by desorbed plateout activity escape from the primary circuit; the values, however, are about two orders of magnitude lower.

3.4. HYDROGEN BEHAVIOR IN NUCLEAR POWER PLANT ACCIDENTS

The investigation of explosion hazards associated with the inadvertent existence of hydrogen in partially or fully confined spaces has been subjected to studies in different countries to assure the phenomena associated with hydrogen are understood with regard to reactor safety. Theoretical and experimental investigations have focused on the distribution of hydrogen-air-steam mixtures and its ignition and combustion. The physical phenomena and mitigation systems as well as the examples of experiments of the behavior of hydrogen in nuclear plant accidents are presented in the following sections because of the relevance to safety for hydrogen production systems. Further discussion on the combustion behavior of hydrogen and associated research activities for non-nuclear unconfined areas is presented in section 8.5.

3.4.1. Phenomena

Different categories apply to the hydrogen issue in nuclear reactor containments. During normal operation, small quantities of H_2 are generated by radiolysis of the coolant, 44 H_2 and 22 O_2 molecules per 10^4 eV of neutron radiation energy. Under accident conditions, significant amounts of hydrogen could be produced due to radiolysis and corrosion reactions.

The most important **hydrogen source** in a core meltdown accident is the in-vessel fuel element Zircaloy cladding/water reaction. The exothermal nature of the reaction enhances the H_2 production rate. Substantial hydrogen generation begins at temperatures > 1300 K. At a later stage, additional hydrogen could result at a much slower rate from radiolysis and aluminum oxidation in the containment. Flooding of an overheated core could terminate the core melt progression, but could also result in significant further H_2 generation and fission product release. For complete oxidation, H_2 generation was computed to range between 450 kg in smaller nuclear power plants and more than 900 kg in larger plants. However, there is still uncertainty in the precise quantification of hydrogen generation during a core meltdown event [36]; a rough rule of thumb is the generation of 1 kg of H_2 per MW(e) of the reactor core.

Under accident conditions, steam and hydrogen will be released simultaneously from the reactor vessel into the containment. Mixing with the containment atmosphere is by forced convection (pressure differences, jet flow, water spray system) or by natural convection (density differences). Slow mixing and steam condensation may result in locally high concentrations of hydrogen; rapid mixing could either prevent the formation of a flammable mixture by keeping the H_2 concentration low enough or result in an explosion that is global in nature provided large H_2 masses are quickly released. Containments with no recirculation fans to promote forced mixing are more vulnerable to locally high H_2 concentrations.

The most likely mode of H_2 combustion in a containment is **deflagration**. Elevated temperatures could lead to autoignition of the gas mixture, but there are also other ignition sources, so that a combustion, supposed the multicomponent gas mixture is in the flammability range, will be very likely, possibly as a diffusion flame near the release point after flash-back from the ignition point. Buoyancy plays a major role in the flame propagation: for upward propagation, 4 vol% H_2 are sufficient, whereas at least $\approx$ 9 vol% are required for a propagation in downward direction [2]. Intercell flow distribution and local steam condensation rates have a significant influence on the local gas fractions in each compartment. A rapid condensation, if possible, may convert an inert atmosphere into a detonatable mixture, which would threaten the containment integrity and the survival of safety equipment. Assuming a 75 % cladding/water reaction, the potential of DDT needs detailed investigations. It is decreased in the presence of diluents (steam, CO_2) and is increased by fan coolers, by obstacles in the flow path, or by spray systems which decrease the steam concentration.

The interaction between evolving pressure waves and internal structures is complex, because loads on the containment will be variable with position and time. Local deflagrations or detonations in complex geometries do currently not allow a prognosis and evaluation of the dynamic load on the containment structure [16].

A **radiological problem** arises with the hydrogen deflagration in a nuclear containment: In a severe core damage accident, extensive aerosol generation must be expected. One radiologically relevant compound released as an aerosol in significant amounts is CsI. Incompletely oxidized "metallic" aerosols such as those formed from iron (Fe) were found to increase the peak pressure by up to a factor of 3, because the Fe participates as a combustion fuel. Experimental studies have shown that 10 - 15 % of the CsI are decomposed during hydrogen combustion and liberate gaseous iodine which is less effectively retained in the containment filters and thus significantly affects the source term. Iodine release was observed to be independent of the steam contents in the containment atmosphere [42]. Current understanding, however, is still poor concerning the effects of hydrogen combustion on fission product behavior [16].

3.4.2. Hydrogen Mitigation Systems

In case of an accident in a nuclear containment where hydrogen is liberated and distributed within the building, a variety of methods can be employed for hydrogen mitigation [16]:

- **Mixing devices**, e.g. fans or helium injection, can prevent locally high H_2 concentrations as long as the H_2 release is small compared with the containment volume available, enhancing convective gas exchange with upper regions. Fan mixing could also serve as a heat removal system. A disadvantageous effect is the generation of turbulence in the containment atmosphere which reduces the combustion time and increases the severity of a possible explosion. Drawback of mixing devices is their dependence on availability of electric power.
- Although not directly dedicated to H_2 mitigation, **venting systems** can act so. It might be the more favorable system of choice, if in a severe accident, containment integrity has to be assured for long-term retention of radioactivity and rather allowing short-

term release. Venting removes reactants from the building, retards flame acceleration, and lowers peak pressures. Too small openings, e.g., in the top of ducts, however, could have the opposite effect due to turbulence generation. The ignition inside venting devices needs to be further investigated.

- The principal purpose of **inerting** is to limit the supply of oxygen. Strategies possible are a pre, post, or partial inerting of buildings. Pre-inerting is being widely applied in nuclear containments of BWRs as a consequence of the TMI accident. Partial inerting has the advantage of keeping at least a part of the building accessible by personnel. Media for inerting used or considered are N_2, CO_2, or Halon-1301.
- Catalytic, thermal, or flame **recombiners** allow an immediate and continuous H_2 removal. They are characterized by a high reliability and availability and no power supply is required. Catalytic recombiners also work in non-flammable, steam-inerted mixtures. Recombination systems can be located inside or outside the containment, normally some distance away from the possible hydrogen source.
- The **deliberate ignition** of lean (< 8 vol%) H_2-air mixtures in a containment is considered a possible method of partially consuming hydrogen. However, it always represents some challenge to building and equipment. It should be done as close as possible to the H_2 source location in order to provide relatively benign pressures and temperatures. Methods of ignition are by hot surface (in use), by spark, or in a catalytic system which does not require electric power. Igniters are simple, robust, and easy to install, but because of the difficulty of anticipating the consequences, deleterious effects under certain circumstances need to be investigated.
- Containment **spray systems** generate water droplets or fogs. Their prime purpose is to cool the equipment and the containment atmosphere when steam is released. Fogs exhibit a slightly inerting effect, thus reducing the burning rate, whereas larger droplets of water could even act as an obstacle field which can trigger a flame acceleration. The consideration of foam has been abandoned, because it could allow the formation of pockets enclosing high H_2 concentrations.

3.4.3. Accidental Hydrogen Explosions

During the accident in the **Three Mile Island** nuclear power plant in 1979, an estimated 150 - 600 kg of hydrogen ($\approx$ 400 kg as quoted in [36] with more than half presumed to be caused by reflooding of the melting core) were generated in the primary system, which were ignited at about 10 h into the accident resulting in a peak overpressure of 190 kPa, well below the 414 kPa design limit of the containment. The deflagration was presumed to have been initiated at a 7.3 - 7.9 vol% H_2 concentration [2, 16].

Also the **Chernobyl** accident resulted in a significant metal-water reaction with hydrogen generation, but no final conclusions could be made so far concerning the H_2 behavior and its contribution to the accident [16].

Hydrogen-oxygen offgas[5] explosions have occurred in some older **boiling water reactors** where no treatment of such gases was given. The explosions took place in various components from the condenser air injector downstream to the vent stack and

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[5] Offgases released into the primary coolant during normal operation consist of air leaked into the turbine condenser, activated gases, fission gases, and H_2 and O_2 from radiolytic decomposition of steam. A typical mixture could contain roughly a 6 - 8 % share of hydrogen.

partially caused radioactivity release into the plant. Among other ignition sources were mechanical sparks from closing valves or electrostatic discharges. Equipment damage, however, was minimal in most of the 25 cases reported [43]. Modern offgas treatment equipment tries to eliminate explosive mixtures as soon as possible by dilution with steam and passing them through a catalytic recombiner and activity filters before routing to the vent stack [53]. The offgas explosions are part of the incidents given under "Intentional operation" in Table 8-4 in section 8.6 on hydrogen accident statistics.

3.4.4. Containment Experiments

Hydrogen-air-steam combustion experiments have been conducted to simulate local detonations in confined structures and to validate the respective numerical detonation codes.

3.4.4.1. Experimental Activities in Germany

A hazardous potential was thought to exist in the **AVR** HTGR, Jülich, with a hydrogen-carbon monoxide-helium-air mixture, which could evolve in a water ingress accident scenario with an estimated 8 % H_2 + CO concentration resulting from the corrosive reaction between steam and hot fuel element graphite. Ignition experiments in a combustion chamber were conducted in 1971 to examine the lower combustibility limit in respective gas mixtures. The tests have shown that a mixture with 22 % H_2 + CO was not flammable at temperatures up to 120 °C [54].

In Germany, the Battelle Institute has employed the **Battelle model containment** (BMC) which is a 1/100 down-scaled model of a typical PWR containment. Between

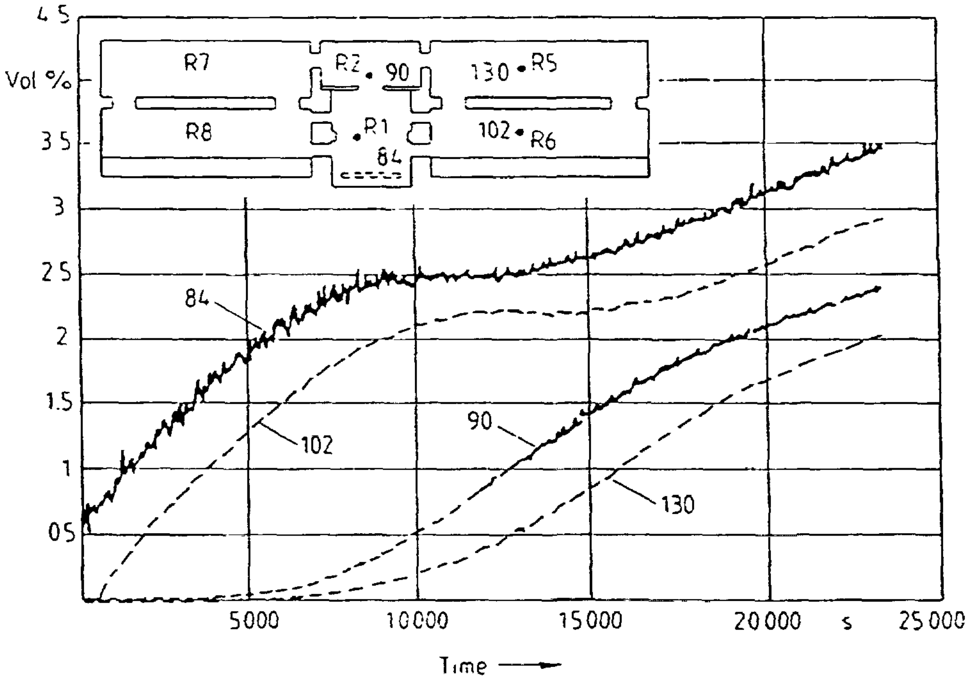

Fig. 3-6: Hydrogen concentration transients in a six-compartment structure of the Battelle model containment with inverse thermal stratification (the numbers are H_2 sensor positions as shown in the diagram at the top), from [28]

1977 and 1982, a six-compartment geometry with a total free volume of 640 m^3 was used to measure the concentration distribution of hydrogen released at rates of 0.2 and 1.0 Nm^3/h, respectively. Under isothermal conditions, a homogeneous distribution of the hydrogen was found. For the condition of an inverse thermal stratification (top: hot, bottom: cold), higher H_2 concentrations in the bottom compartment due to the larger density were measured until the concentration difference reached 2.2 vol% and a convective flow through all compartments eventually started (Fig. 3-6). In a combustion test series, hydrogen-air mixtures with 9 % H_2 were ignited in 2-, 3-, or 4-chamber structures [28]. Jet ignition was observed to create highly transient deflagrative combustion at H_2 concentrations around 10 %.

Another test series in the BMC was dedicated to deliberate ignition measures using a 5-compartment structure with 209 m^3 volume. Spark igniters caused deflagrative combustion at H_2 concentrations of 5.2 - 5.6 vol% and steam fractions up to around 50 vol%. Higher steam contents suppressed the deflagration. Catalytic recombiners require a starting threshold value which was 3.4 vol% H_2 for the device used, but are then able to remove hydrogen down to a remaining concentration of 0.3 - 0.4 vol% [22].

At the end of 1987, the investigation of hydrogen distribution on a real-size scale was started in the containment of the decommissioned German **Heißdampfreaktor (HDR)** (hot steam reactor) multi-compartment facility in Karlstein with dimensions of 60 m height, 20 m diameter and a free gas volume of 11,300 m^3. HDR consists of 72 subcompartments connected by about 300 flow paths with different and complicated geometry. A series of seven H_2 distribution experiments was conducted in 1989. In the test T31.5 considered as an international standard problem for benchmark calculations, 32 t of a water vapor mixture have been fed into one compartment within 60 s, another 2 t after 30 min and eventually 160 kg of a 15 % H_2 plus 85 % He light gas mixture after 36 min. Pressures, temperatures, and light gas concentrations were measured at various positions. The distribution tests have exhibited a stratification in terms of both temperature and H_2 concentration with higher values above the inlet location. There is only a slow exchange leading to equilibrium. Conclusions drawn from the distribution tests were positive in that significant amounts of energy were found to be withdrawn by the inner containment structures, but were also negative in that not anticipated distribution inhomogeneities were observed which do not allow a prognosis of the consequences of an H_2 explosion based on the assumption of a homogeneous mixture [23].

The HDR combustion tests were restricted to a two-chamber section with 530 m^3 volume filled with a mixture of H_2, steam, and air. Flow obstacles were removed on purpose to allow a comparison with earlier test series. In these tests, the influence of different ignition positions on the combustion has been investigated. A variety of pressure-time histories was observed depending on the location of ignition, of compartment geometry, and of initial H_2 concentration. Jet ignition of a H_2-25 vol% steam-air mixture resulted in the largest pressure loads peaking at 130 kPa for 10 vol% H_2 and 185 kPa for 12 vol% H_2 [24, 39]. Steam concentrations greater than 35 % strongly reduce the flame front propagation, whereas concentrations between 55 and 60 % completely suppress an ignition [23]. A problem in these tests was the undocumented hydrogen stratification prior to ignition.

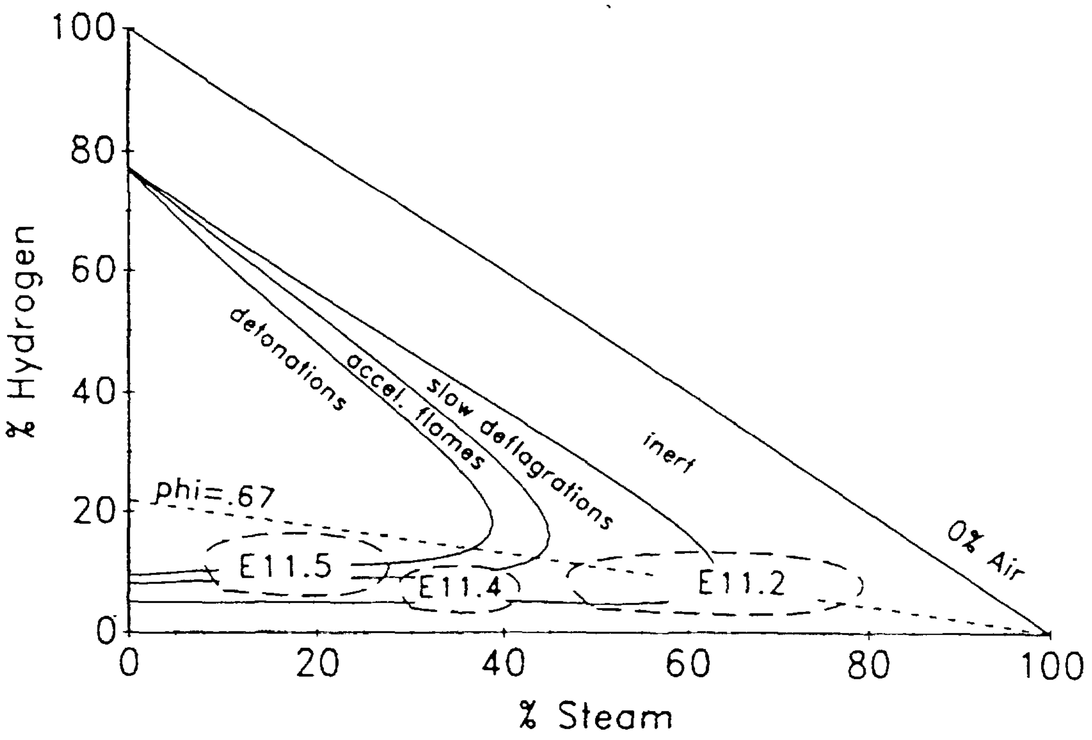

Fig. 3-7: Ternary diagram for hydrogen-steam-air mixtures at 100 °C deduced from the HDR experiments E11.2 simulating a small leak at a high location in the containment, E11.4 simulating a small leak at a low location, and E11.5 simulating a large leak at a low location, from [3]

Flammability data have been derived for various ternary mixtures including H_2, CO, air, H_2O, N_2, He, and CO_2 at different temperature levels. A general correlation for a ternary system between room and autoignition temperature is given in [36]. The ternary diagram in Fig. 3-7 shows the deflagration and detonation ranges on a large-reactor typical scale for H_2-steam-air mixtures depending on the mixture composition.

3.4.4.2. Experimental Activities in the USA

A part of the US Nuclear Regulatory Commission's (NRC) severe accident research program was dedicated to hydrogen issues in LWR containment designs under core meltdown conditions. The analysis included the in-vessel and ex-vessel hydrogen generation as well as its mixing and distribution in the containment.

The **Hanford Engineering Development Laboratories** (HEDL) have used a 20 m high, 7.6 m diameter and $\approx$ 300 m^3 volume annulus-shaped one-compartment test facility simulating the lower part of a PWR ice-condenser containment[6]. Hydrogen was replaced by helium released at 150 °C as a high-speed jet into the compartment which was at a 80 - 90°C temperature level. Maximum concentration differences of about 3 vol% during source release and up to 7.5 % only after switching off the source and subsequent local

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[6] A PWR ice-condenser containment has a smaller volume and a lower design pressure compared with others, because ice is used as a heat sink to condense the steam deliberated in an accident.

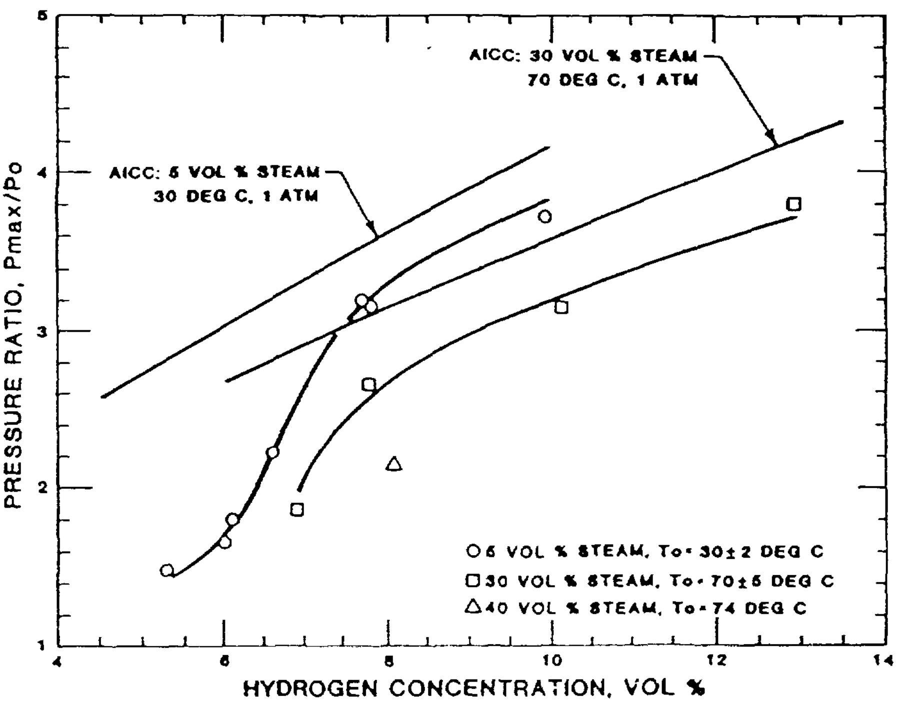

Fig. 3-8: Experimental and calculational pressure ratios during combustion tests with quiescent premixed H_2 mixtures in the NTS model containment, from [7]

condensation effects were observed [28]. The dominant mixing process was by the high velocity gas jet.

The EPRI experimental (and analytical) program comprised the study of H_2 combustion and control in a hydrogen-air-steam-water spray environment focusing on deliberate ignition methods. In several projects, investigations were done in test facilities of various scales ranging between 0.002 and 2100 m^3 of volume. Large-scale demonstration tests at the **Nevada Test Site** (NTS) have been conducted in a 2100 m^3 inner volume one-compartment spherical dewar representing a 1/4 scale model of a nuclear containment. Goals were the investigation of H_2 combustion in a premixed atmosphere or with a continuous injection flow, the study of equipment operability and thermal response, and the evaluation of the performance of mitigation methods. Results for the quiescent, premixed ignition tests with different H_2-air-steam mixtures are shown in Fig. 3-8 indicating a continuous increase in pressure ratio with increasing H_2 concentration. The combustion tends to be more incomplete towards lean mixtures. In the continuous injection tests, a stratified atmosphere was built up at low injection rates, whereas uniform concentrations were established immediately when water sprays were applied. Rapid mixing in the vessel was also achieved at high injection rates of 1 kg/min H_2 and 9.1 kg/min steam [7, 50, 51]. Combustion of lean mixtures (4 - 8 vol%) was generally observed to be incomplete as well as in the case of steam addition. Turbulence was found to drastically reduce time of combustion and increase the degree of completeness of combustion [36].

In cooperation and with funding by the Japanese NUPEC, the US NRC is investigating at the **Sandia National Laboratory** the containment building safety in a series of pressure tests with nitrogen up to the failure limit of a 1/10 scaled vessel of 5.8 m height. The failure occurred at a pressure of 4.66 MPa, the prediction was 4.50 MPa, the design basis value is 0.77 MPa. A second test containment will be a 1/4 scaled model with the final pressurization-to-failure test at the end of 1999 [31].

The Russian combustion tests in the large-scale channel **RUT** are described in more detail in section 8.5.2.2.

3.4.5. Containment Modeling

Many codes have been used to calculate the transport, convective mixing, and combustion of hydrogen in containments, some of which are shortly described in the following. Some more CFD computer codes are being briefly described in the sections 8.4.2. on atmospheric dispersion and 8.5.1. and 8.5.2. on combustion processes.

A multi-zone computer code **WAVCO** (Wasserstoff-Verteilung im Containment = Hydrogen Distribution in the Containment) has been developed by the Siemens company for predicting thermodynamics and hydrogen distribution during severe LWR accidents. The model solves an equation system consisting of separate mass and energy balances for both atmosphere (superheated or saturated steam and up to nine noncondensibles) and sump of each zone. Also mass balances for each component are used to determine the actual gas distribution. Validation was made against above mentioned hydrogen/helium distribution experiments of Battelle and HEDL with good agreement between calculated and measured data [38].

The Sandia code **HECTR** (Hydrogen Event: Containment Transient Response) is a lumped parameter[7] analysis code for modeling the containment atmosphere under accident conditions involving release, transport, and also combustion of hydrogen [37]. It can handle saturated and superheated conditions and it covers both short-term transients and long-term convection up to several hundred days.

The Sandia code **CONTAIN** is a lumped parameter code with mechanistical models for simulating the physical and chemical conditions in the nuclear containment to predict hydrogen and steam concentration distribution as well as the consumption of H_2 by respective combustion. Assuming a core meltdown accident and no vessel breach, i.e., no corrosion/concrete interaction, the code has predicted a thermally stratified containment atmosphere with relatively low temperatures in the central and lower regions which would permit steam condensation. Concerning H_2 deflagration, CONTAIN predicts respective burns, if sprays are used for steam removal [56].

The development of the computer code **RALOC** at the German GRS for the simulation of the distribution of hydrogen, air, and steam in a LWR containment after severe accidents has started in 1974. RALOC is based on a lumped parameter approach with a differential equation system which describes the composition of the containment atmosphere, temperature, and the transport phenomena of convection and diffusion. Validation

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[7] The lumped parameter or lumped volume technique uses control volumes connected by flow junctions. Gas exchange through the junctions is by convection and diffusion and is influenced by a certain flow resistance. In each zone, thermodynamic equilibrium and saturated steam-water conditions are assumed. The approach allows a modeling of gas distribution in highly complex multicompartmental structures. It does, however, not consider dynamic effects such as jets and local turbulence [16].

has been made against HDR distribution tests [21]. Due to continuous improvement, it is being considered now the most sophisticated lumped parameter code [16].

In cooperation with the Kurchatov Institute in Russia, the Research Center Karlsruhe (FZK) is developing the 3D computer code **COM3D** to simulate fast turbulent combustion in severe LWR accidents. A k-ϵ submodel is used to describe turbulence. The chemical kinetics submodel is adapted to hydrogen-air-steam mixtures. The reaction rate is calculated by using an eddy dissipation model which depends on the turbulent time scale and an empirical constant. The code validation was made against combustion experiments in the 12 m FZK tube and the Russian RUT facility (see section 8.5.2.). Agreement between calculational and measured results was optimal for the empirical constant being in a narrow range even for experiments with a different scale, geometry, and gas mixtures [4]. As a second step in the combustion modeling, a so-called PDF approach[8] is currently under development.

The k-ϵ model **BASSIM** (Battelle Strömungssimulator) of the German Battelle Ingenieurtechnik is a CFD model applicable to multi-dimensional transient compressible fluid flow problems considering heat and mass transport and chemical reactions in body-fitted grids. It has been employed to investigate flame development and pressure rise in hydrogen deflagration as measured in BMC and HDR tests. BASSIM could successfully reproduce the observed thermal stratification in the tests.

The computer code **GASFLOW** has been developed at the Los Alamos National Laboratory to simulate the distribution of a hydrogen-steam-air mixture in a multicompartment structure of a nuclear power plant containment, combustion processes after ignition, and the respective dynamic quasi steady state load due to H_2 combustion. Extensive model development at the Research Center Karlsruhe has brought the code into full containment applications. GASFLOW solves the Navier-Stokes equations in a 3D Eulerian grid and allows the description of processes on different time scales. The k-ϵ model is one option of turbulence modeling. A unique feature of the code is the simulation of countermeasures such as the activation of igniters and/or recombinators or the feeding of inerting gases. The code has been validated against numerous HDR and BMC experiments [39].

The general purpose computational fluid dynamics code **CFX** is a commercially available software of AEA Technology, Harwell, UK, to simulate a wide range of fluid flow and heat transfer processes based on the Navier-Stokes equations in complex 3D geometries. CFX comprises a selection of advanced turbulence models including the k-ϵ and Reynolds stress model plus a selection of numerical solution methods to accurately and efficiently describe subsonic or supersonic flows. The code is able to handle in body-fitted, multiblock grids any number of fluids and separate phases: liquids, solids, gases or chemical species. It includes a particle transport model according to the Lagrangian scheme as well as submodels for combustion, radiation, and chemical kinetics [1]. Combustion phenomena in confined areas including slow/fast deflagration, with weak or strong ignition, and transition to detonation, are currently been investigated within a CEC program on reactor safety using the CFX code. The R&D studies comprise the validation of state-of-the-art predictive

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[8] The employment of the "Probabilistic Density Function", PDF, is a statistical method for the determination of the mean combustion rate in a computational grid cell

methods for the description of combustion processes and mitigation measures (deliberate ignition) by a comparison with respective experimental work [9].

3.5. GAS EXPLOSION RESEARCH PROGRAMS

Gas explosion research programs have been initiated in various countries either one focusing on specific aspects of the offsite explosion and the consequences of flammable gas clouds, in particular, the impact of the pressure wave on the nuclear containment. Germany has started safety programs related to both light-water reactors and high-temperature gas-cooled reactors, the latter in connection with process heat applications. The USA have conducted an LNG investigation program to ensure the safety of LNG transportation and terminals. Both France and the European Community have conducted gas cloud explosion programs dedicated to light-water reactors. Norway has made special off-shore safety studies related to fire and explosion on off-shore drilling platforms.

3.5.1. The German LWR Program

Between 1979 and 1983, a research program on gas explosions has been conducted as a part of the program "Research on the Safety of Light-Water Reactors" funded by the German federal government [48]. The principal areas investigated were:

1. Conceivable mechanisms and configurations necessary for the evolution of detonation-like explosions,
2. Relationship between the characteristic features of incoming blast waves and the response of building structures,
3. Strength of blast waves assuming the detonation of a realistic gas cloud

with the overall goal to develop the methodology for a safety valuation of accidents with the explosion of transport gas nearby nuclear power stations.

A BMI[9] guideline from 1974, "Protection of Nuclear Power Plants Against Pressure Waves from Chemical Explosions by Design of the Nuclear Power Plant with Respect to Their Stability and Induced Waves as well as by Safety Distances", has defined a pressure-time function (Fig. 3-9) according to which a nuclear power plant has to be designed as a protection against extend explosions and a **safety distance** given by the general equation as introduced in section 8.5.4. with a k-factor of 8:

$$R = 8 * M^{1/3}$$

where R is the safety distance in m (minimum 100 m) and M the explosible mass in kg underlying the assumption of a homogeneously mixed, stoichiometric gas cloud of hemispherical shape and with ignition in its center. For multiply unsaturated hydrocarbons, M is the maximum mass released as well as for compressed gases, for pressurized liquid hydrocarbons, it is 50 % (or k = 6.3 m/kg$^{1/3}$) and for cryogenics or hydrocarbons under standard conditions, it is 10 % (or k = 3.7 m/kg$^{1/3}$).

For a nuclear coal gasification plant, the above safety distance relation is probably not practicable. Therefore it has to be guaranteed by respective studies, that the load upon the nuclear reactor building in case of an outdoors explosion is covered by the design limits.

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[9] BMI is the German Federal Ministry of the Interior

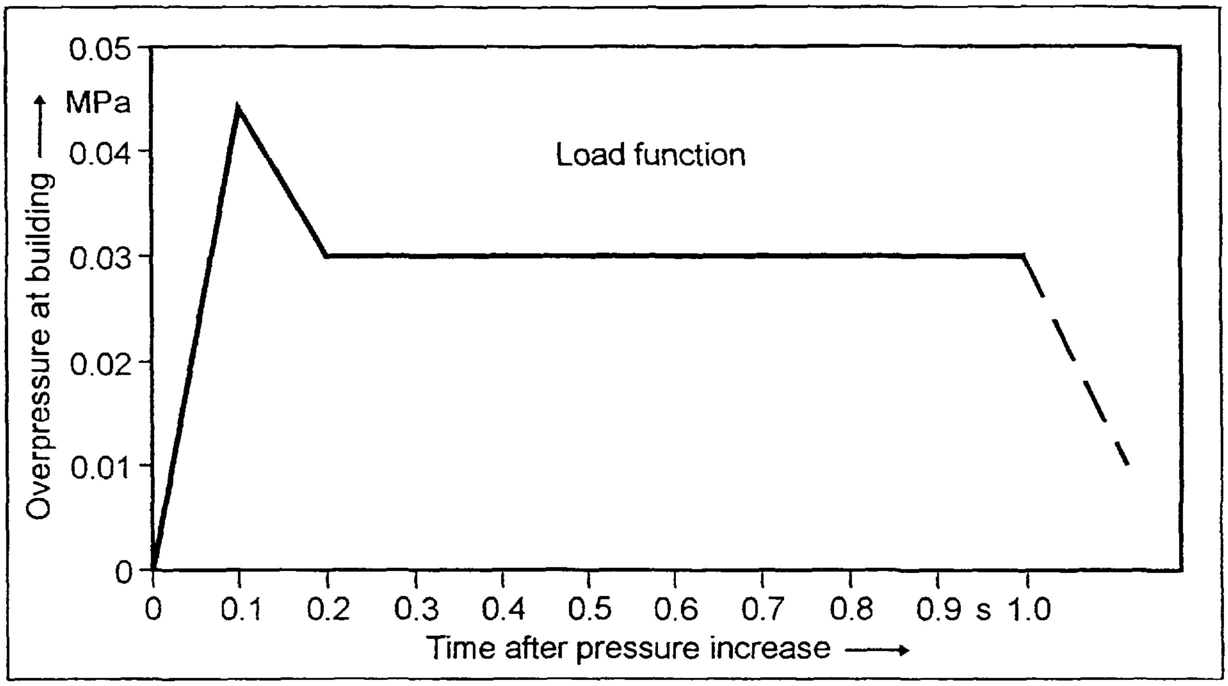

Fig. 3-9: Pressure-time function according to the BMI guideline from 1974, from [14]

The ratio of flame front velocity to speed of sound influencing flame acceleration in the gas cloud was theoretically shown to be at least 0.45 to cause a pressure wave which is still too weak to cause a detonation. The initiation of a detonation is only possible, if the ignition power density is high enough given by a explosive. Deflagrative ignition, e.g., flame, spark, hot surface, do not develop a detonation in an unconfined (real) gas cloud [35]. The required safety distance between an LH_2 (or LNG) tank and a nuclear reactor building according to the above definition would then be represented by curve #5 of Fig. 8-14 in section 8.5.4.

Results of the research program can be summarized as follows:

(a) The release of liquefied gases (no hydrogen) results in the formation of a flat (heavy) gas cloud. A reliable prediction of cloud size, gas concentrations, and flammable portion is not possible. There are indications that the BMI guideline provides conservative results.

(b) Only a strong ignition source has a significant influence on the flame spreading. The state of turbulence prior to and during the explosion is a decisive parameter for flame speed and overpressure. No fast deflagration with overpressures > 0.01 MPa are expected after explosions in open terrain; an exception may be the catastrophic failure of a pressure vessel.

Partial confinement and/or obstruction, e.g., a lane between buildings, is necessary to cause overpressures > 0.01 MPa with significant impact on building structures. The blast wave is weakened in obstruction-free areas, but presumably less pronounced the larger the scale.

(c) Prerequisite for DDT is the generation of very high flame speeds. A characteristic parameter is the detonation cell size with a higher reactivity of the fuel the smaller its cell size. The direct initiation of a detonation is only feasible with strong igniters and, thus, appears to be unlikely for accidents with mixed gas clouds.

(d) The blast wave of a deflagration may exhibit a steep pressure rise, multiple peaks or an underpressure phase creating a complex load function enhanced by reflection or pressure wave convergence.

(e) In comparison with a linear pressure slope, a stronger impact on containment and and components is expected for load functions characterized by multiple peaks or detonation or underpressure. The absolute impact, however, is in the range of elasticity and, thus, in accordance with the design.

Existing safety margins of modern nuclear containments guarantee a safe enclosure.

3.5.2. The German PNP Program

Delivery of process heat implies the coexistence of nuclear reactor and chemical plant, e.g., coal gasification, hydrogen production, ADAM-EVA transportation system. The main goals of the PNP gas explosion program were, in general, to improve understanding of the complex process of chemical explosions and its effect on the environment, and in particular, to demonstrate that a power station for nuclear coal gasification or process steam production is safely designed against explosions from outside, if the BMI guideline is applied. This is deemed true for explosions of transported hydrocarbons and minimum distance rules applied. However, some experimental studies on gas explosions under conditions typical for process gases inside the plant have revealed that under unfavorable circumstances, overpressures can exceed the respective maximum figures from the guideline. Experimental results were often complex and difficult to interpret. The experimental data base for the phase of flame acceleration is sufficient for a qualitative understanding of the phenomena and sound statements on flame speed and pressure within the frame of a safety analysis for an industrial complex. The transition to detonation itself, however, is strongly and decisively dependent on the turbulence structure which can only insufficiently be simulated in numerical models. It allows a derivation of specific DDT boundary conditions only in very concrete accident scenarios.

The PNP safety program [41] focused on the formation and explosion of clouds of the process gases H_2, CO, air and other representative combustible gases such as acetylene, ethylene, propane, methane, and the damage caused by the blast wave to simple structural elements (window pane, brick wall) after fast deflagration and detonation. Areas of investigations were

(i) flame front velocity in given scenarios and respective mechanisms of flame acceleration,

(ii) criteria for the transition to detonation, and

(iii) criteria for a passing on of a detonation.

Tasks within the study were dealing with deflagration damage analysis, mechanisms of combustion, regulations and limits comprising subtasks about

- identification of PNP specific accident scenarios which result in the release of flammable gas mixtures and assessment of corresponding gas masses to be expected,
- material-specific aspects such as burning velocity, flammability limits, flame spreading,

- the effects of a chemical explosion on building structures in relation to different degrees of partial confinement,
- evaluation and analysis of process gas cloud explosion accidents and experiments,
- derivation of the relation between a deflagrative pressure wave and characteristic destruction lines, upper limits of destruction, "design pressure wave",
- deduction of a load function by a damage analysis of the accident in Beek[10],
- experimental investigation of deflagrative combustion and its enhancement in the presence of initial turbulence in a channel with open top,
- Balloon explosion tests, and
- development of a computer code for the spherical spreading of a flame according to the piston model.

Experimental studies within the PNP gas cloud program were conducted and evaluated by the Fraunhofer Institute for Chemical Technology using flammable mixtures of hydrogen and other fuels with air in different shapes (sphere, hemisphere, tube), confined or unconfined. They are described in more detail in section 8.5.2. Experimental results from other test programs in the USA (explosion series in "FLAME") or Norway (jet ignition with transition to detonation in acetylene-air mixtures) were also taken into account. All tests were close to the go - no go boundary between deflagration and detonation.

An overall statement concerning the deflagration - detonation transition (DDT) was made within the frame of the PNP gas cloud program saying that the mechanisms and flame acceleration are qualitatively understood, however, they cannot be described on a quantitative basis, a statement that is, in principle, still valid today [6, 30, 41], although computational efforts are progressing tremendously.

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Chapter 4

ENERGY SITUATION AND ACTIVITIES ON NUCLEAR POWER WITH POTENTIAL USE FOR PROCESS HEAT AND HYDROGEN PRODUCTION IN SOME EXEMPLARY COUNTRIES

4.1. CANADA

Canada has an enormous potential of domestic natural energy resources, in particular natural gas and water. The electricity production in 1993 was approx. 610 TWh with 62 % from hydro power, 23 % from fossil fuels, and 15 % from nuclear power. Since 1969, Canada is a net energy exporting country. In most parts of the country, low-cost hydro-electricity is available and technologies are being developed to benefit from this privileged situation. Renewable energies (others than large-scale hydro) accounted for 6 % of the total Canadian primary energy demand in 1994. Canada is the world leader in long-distance electric power transmission. It is also ranking first with 18,000 kWh in the per capita electricity consumption. CO_2 emissions on a per capita basis are 16.1 t. The goal set at the Kyoto summit is a 6 % reduction relative to the 1990 level compared with a 9 % increase as was observed in the period 1990-95 [16].

On a per capita basis, the largest producer and consumer of hydrogen in the world is Canada producing more than 2 million t/yr. Primary sources for hydrogen are methane, hydrogen sulfide, and water. Hydrogen plays an important role in the Province of Alberta where 55 % of the production and 63 % of the consumption of all hydrogen in Canada takes place. Alberta's research activities are concentrating on hydrogen production, for example from the widely available H_2S.

4.2. CHINA

4.2.1. Energy Situation in China

Two decades of enormous economic growth in the People's Republic of China at a rate of 9.4 % per year (1978 - 1994) have led to a tremendous need for energy and electricity, and the demand for more is increasing at a rapid pace, in particular, in the industrially developing regions of East and South China [92, 91]. The power plant capacity reached about 200 GW at the end of 1994, out of which three quarters were provided by coal causing a serious transportation problem. The remainder is provided by hydro power and approx. 1 % by nuclear power. Today China has the third largest energy system in the world and is ranking 4th in the electricity production [91]. Still, at least 10 % of China's population has no access to electricity and, due to the large population, the electricity consumption per capita is no higher than 674 kWh/yr compared with, e.g., the world's average of 2200 or to Germany's of 6700 kWh/yr (data of 1992).

In terms of global anthropogenic CO_2 emission, China with 2373 Mt in 1990 is ranking 2nd in the world already, and no obligation of reduction has been put on the country during the Kyoto summit. It is expected to take the lead by 2010 with more than 5000 Mt/yr of emitted CO_2.

Chinese primary energy consumption is dominated by coal. Most part of the large domestic resources of coal are situated in North China currently hauled at a rate of 1.2 billion t/yr and utilized for electricity production and as a raw material in the chemical and steel industry. Transportation and distribution of the coal around the country causes an enormous logistic problem resulting in plans to erect large on-site coal power plants and rather transport the electricity. Coal burning is made with almost no preceding cleaning and produces 85 % of the total CO_2 emissions which undoubtedly turns into an international concern. Oil and natural gas is found mainly in the north and consumed as a raw material in the chemical industry and not for electricity production. Oil production will amount in 1997 to 160 million t, still China has turned into an oil importer after years as an oil exporter. Hydro power capacity was 44.7 GW in 1993 compared with 380 GW which are deemed to be economically available. At present, the largest hydro power plant is under construction at the Yangtse river with a capacity of 18.2 GW corresponding to about a tenth of China's present total electric power. In 1992 - 1994, the first nuclear power plants with a 300 MW(e) and 2 * 900 MW(e), respectively, have started commercial operation to provide a nuclear share of 1.3 % (beginning of 1997) in the electricity generation. Renewable energies are currently insignificant. Still, surprisingly China has become one of the world largest users of renewables (if including hydro), with firewood to be the largest resource, to be highly important for energy provision in rural and remote areas (wind, solar, geothermal, tidal) [3, 92]. A recently developed strategy, called the "China Sunlight Program", running up to 2010, is expected to further promote renewable energies [3], e.g., 1 GW by wind power.

The increasing demand for hydrogen in China is basically met by hydrocarbon steam reforming process. Presently there are 23 hydrogen production units in operation with a total capacity of 582,600 Nm^3/h [27].

In the future, China's power capacity development is estimated to reach 310 GW(e) in the year 2000 and 800 GW(e) in 2020. Because of the large distances between resources and sites of consumption, nuclear power is expected to gain more importance. The next two nuclear stations with 2 * 935 MW(e) and 2 * 575 MW(e), respectively, are planned to go into operation in 2001 and 2002. Nuclear power in the future is considered for various applications [79]:

- as baseload electricity where coal is short,
- for district heating in areas where most coal is consumed to serve as a clean energy source, or
- in the process heat industries (e.g., HTGR) to provide steam in the petrochemical industry and for coal gasification and liquefaction.

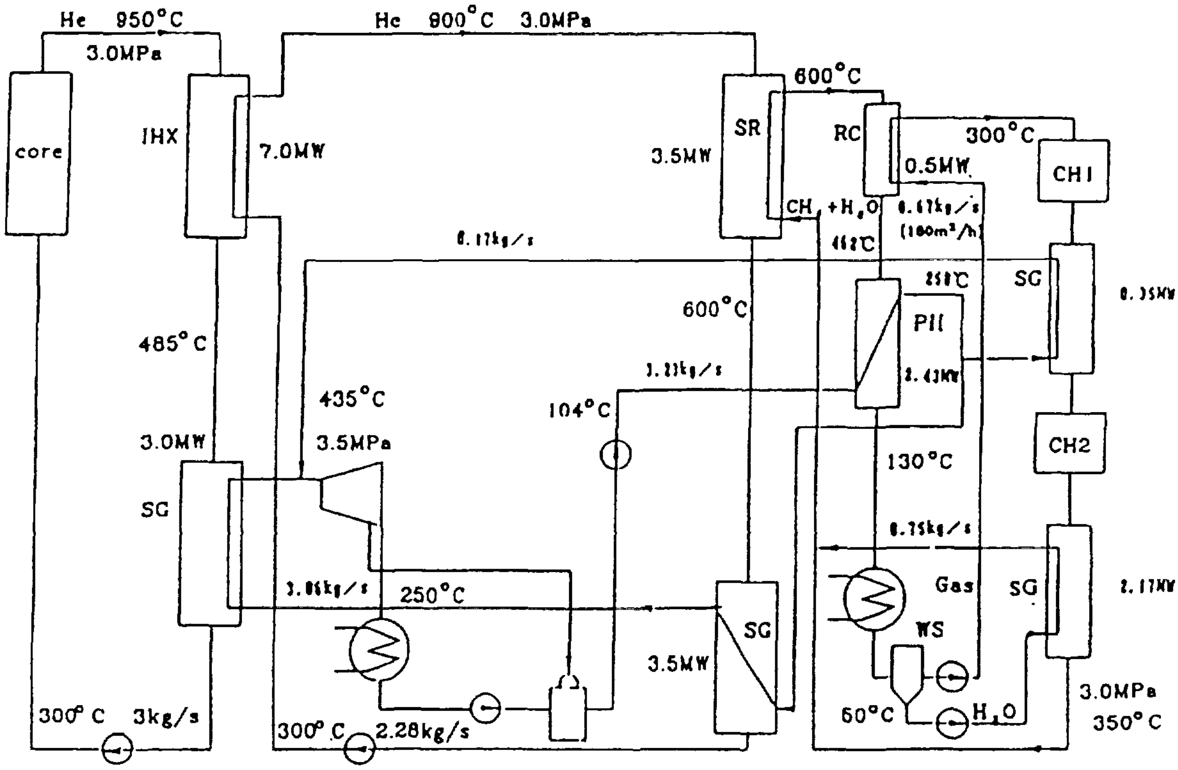
4.2.2. Experimental and Theoretical Activities in China

4.2.2.1. Nuclear Reactor Concepts

A 10 MW(th) HTGR test module, **HTR-10** [89], is under construction since 1995 by the Institute of Nuclear Energy Technology (INET) of Tsinghua University in Beijing. It is a pebble bed reactor with 27,000 spherical fuel elements and a coolant outlet temperature of 700 °C (later 950 °C). Its operation is expected to start end of 1999.

The HTR-10 is designed as a module for multipurpose research. In a first phase, the HTR-10 is planned to be operated in connection with a steam turbine which works in a cogeneration mode to provide electricity and heat. In a second phase, the coolant outlet temperature will be raised from 700 to 900 °C to be operated in a gas turbine cycle [79]. A long-term test program for nuclear process heat applications has been proposed in different phases [89]:

a. feasibility study
b. simulation experiments on a laboratory scale for coal gasification by means of hot helium to acquire technology, experience, and to optimize operational parameters
c. nuclear coal gasification test in a pilot facility where the HTR-10 is to be operated at 950 °C and to demonstrate IHX operation (see Fig. 4-1)



IHX: Intermediate Heat Exchanger, SG: Steam Generator, SR: Steam Reformer
WS: Water Seperator, CH: Methanization Device RC: Recuperator PH: Preheater

Fig. 4-1: HTR-10 circuit with process heat applications, from [89]

A 5 MW water-cooled **nuclear heating reactor** (NHR-5) is being operated by INET since 1985 for demonstrating nuclear heating (in winter), cooling (in summer) and desalination. A follow-up plant, NHR-200, with 200 MW has been designed; a respective construction permit has been released in 1997 [81].

R&D efforts on innovative nuclear power reactor designs were conducted in international cooperation. The Chinese design of an **AC-600** reactor which has been accepted by the International Atomic Energy Agency (IAEA) as a progressive concept is currently investigated by the Nuclear Power Institute of China [92].

4.2.2.2. Exploitation of Very Heavy Oil Fields

A concept was proposed exploiting **very heavy oil fields** in the north-east of China by the use of process steam from an HTGR [22]. This oil with an estimated total amount of 90 million tons is buried in a depth of 1500 - 1700 m. By means of injection of 370 - 390 °C steam, the very heavy oil resources are heated up for easier recovery. The consumption of steam is approx. 3 - 5 t per ton of oil delivered. The energy input is estimated to be 30 - 50 % of that contained in the produced oil. Estimated oil production rate is 1.5 - 2 million t/yr. Design data for the oil production by steam injection are for the steam-soak process a pressure of 16 MPa and a temperature of 370 °C, and for the steam-drive process a pressure of 10 MPa and a temperature of 350 °C.

Two pebble bed HTGR designs for 1000 MW(th) (5 units of HTR-OTTO-200 or 3 units of HTR-MEDUL-334) were shown to be able to provide steam with the required parameters to open up the very heavy oil resources [22].

A 4 x 200 MW(th) modular HTGR plant has been proposed to meet increased demand for process steam and electricity in the Chinese petroleum industry. Coal conversion processes by means of HTGR are projected to mitigate future shortage of oil supply [80].

4.3. FEDERAL REPUBLIC OF GERMANY

4.3.1. Energy Situation in Germany

Primary energy consumption in Germany totaled 340 million TOE in 1995[11] with significant contributions from oil (40.3 %), gas (20.0 %), hard coal (14.5 %), lignite (12.2 %), nuclear (10.1 %) and hydro (1.7 %), corresponding to an energy consumption per capita of 4.169 TOE. The consumption of primary energy has been stagnant since the 1980s due to energy saving and industrial restructuring and is expected to remain on this level until 2010, while gross internal production as well as electricity consumption have still been growing. Growth of the latter, however, was observed to be getting slower [84]. The share of renewable energies will increase from 2 % in 1989 to 3.5 % in 2010 with hydro as the most significant contribution [77]. The total installed electric power is presently 122 GW. The electricity generation in 1997 was $450*10^9$ kWh with 52 % provided by coal, 35.5 % by nuclear, 6.4 % by natural gas, 5.1 % by hydro and renewables, and 1 % by oil. The

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[11] Figures from 1996 are a total primary energy consumption of 350 million TOE with contributions from oil (39.5 %), gas (21.6 %), hard coal (13.9 %), lignite (11.5 %), and nuclear (12.0 %).

current opinion is that beyond the 20 units presently operated, no additional nuclear power plant will be constructed due to lack of consensus among the major political parties.

The industrial energy market in Germany has moved from coal and oil to more natural gas and electricity. Also the specific energy consumption in the industrial production has decreased from 1500 to about 850 kWh/1000 DM Gross Value Added (GVA) between 1970 and 1994. However, the energy demand structure did merely change. A fraction of 65 % of the industrially used energy is consumed in the process heat production [15].

The CO_2 emission in 1995 was 894 million t/yr of CO_2 which is by 12 % less than the 1990 level, however, with an increase of 2 % in 1996 compared with the year before. Traffic causes 17 % of the total CO_2 emissions and more than 50 % of the total NOX emissions with 85 % of all traffic emissions originating from road traffic (figures from 1987) [32] and a further increase is predicted. The need for CO_2 reducing technologies as demanded on the Toronto conference in 1988[12] is in contrast to the realization of the inner European market with the consequence of a strong competition on the energy sector that might turn out unfavorable for the renewables [77]. According to the 1997 earth summit in Kyoto, the European Community (which is treated as a whole "bubble") is obliged to reduce greenhouse gas emissions by 8 % (observed in 1990-95 for the EC: –2 %) with Germany – still sticking to its ambitious goal – taking over a 25 % portion within the bubble.

In 1994, the Enquete Commission "Protection of the Earth Atmosphere" has recommended to achieve an energy mix in Germany by the year 2050 with a 25 % share only from fossil fuels and another 25 % share from renewable energies and 50 % from nuclear power or imported energy.

Hydrogen production in Germany in 1988 was $19.1*10^9$ Nm^3 [70] with the main sources crude oil (46 %), followed by coal (30 %) and natural gas (19 %). Hydrogen consumption is by 33 % non-energetic, by 19 % in the petrochemical industry, and by 48 % direct energetic as a fuel gas (coke gas) [65]. As much as $8*10^9$ Nm^3 hydrogen per year are estimated to be generated in chemical processes as an undesired byproduct and mostly flared without any energy gain. As a large-scale energy carrier, hydrogen in Germany is presumed to be not competitive until 2010, even under a given demand of a 30 % CO_2 reduction. Only in a prognosis for the year 2040 assuming the need for a 60 % CO_2 reduction, the establishment of a hydrogen energy economy will be competitive, even necessary [77][13].

4.3.2. Experimental and Theoretical Activities in Germany

4.3.2.1. Reactor Designs for Process Heat Applications

In Germany, the potential of reducing CO_2 output through different hydrogen substitutions is not very high because of the specific energy demand structure. Due to its

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[12] In Toronto, the recommendation given was to reduce worldwide CO_2 emission by 20 % until 2005 and by at least 50 % until 2050.

[13] In this study, the assumption on CO_2 emission is a parameter in an optimization system to determine the structure of energy carriers to be utilized and the technology options to be selected. This optimization system determines the economic potential of hydrogen in Germany. Fundamental prerequisite is the assumption that hydrogen be produced by electrolysis from solar or hydro power. Concerning the origin of the hydrogen, several strategies were examined: (i) "diversification", allowing limited solar electricity and LH_2 imports, (ii) "EC autarchy", limiting H_2 import to < 1800 PJ and only from EC countries, and (iii) "electricity", including domestic photovoltaics and no limitation of solar electricity import.

high production cost, only hydro power or off-peak nuclear power are considered to be an economically comparable alternative primary energy source for hydrogen production. A breakthrough for the non-fossil hydrogen economy is not expected until the year 2020 [40].

At present, nuclear power in Germany does merely contribute to the heat market. So far it is just one plant, PWR Stade, to deliver 40 MW(th) to an industrial company in the vicinity of the plant. Saturated steam of 190 °C at a pressure of 1.05 MPa is provided at a rate of 60 t/h for condensation of a saline solution. Total delivery since 1983 winded up to 5.4 million tons of steam equivalent to 690 GWh by the end of 1996.

In a project of the German chemical company **BASF**, the installation of a nuclear power plant for cogeneration of electricity and process steam was planned. It was designed in two units for the generation of 1200 MW electricity and 3000 t/h of steam. Technical problems, e.g. storage of steam, and safety issues in connection with the central location within the chemical complex have finally stopped this project.

A concept of an evolutionary reactor is pursued with the joint French / German "European Pressurized Water Reactor", **EPR**, a 1525 MW(e) plant with evolutionary steam generating system and innovative double-walled containment [20]. A three years basic design phase as a prerequisite for the beginning of the licensing procedure was finished in 1997. The characteristic feature is a core catcher to restrict a possible core melt to the power plant itself. The joint effort by Germany and France, however, finds in both countries a situation where no further base load is required. The EPR, confirmed as a future standard in France, is projected to substitute decommissioned nuclear plants.

The 46 MW(th) **AVR** reactor in Jülich as a first-of-its-kind pebble bed HTGR has been operated for 21 years with a high percentage of availability demonstrating that nuclear power can be converted into high-temperature heat. For more than 10 years, the reactor was operated with an average outlet temperature of 950 °C. The operation allowed successful testing of a large number of high quality HTGR fuel elements [88].

A design for the reconstruction of the AVR into a process heat plant, **AVR-II**, has confirmed the technical feasibility. The installation of a segmental baffle type reformer was planned characterized by the existence of openings between baffles and reforming tubes to allow for a partition of the helium coolant into horizontal and vertical flows to reduce radial temperature gradients.

The prototype pebble bed reactor **THTR-300** [50] has demonstrated the expected large-scale applicability of HTGR technology [10] and the relatively low level of radioactivity in the HTGR plant. The measured generator power of 303 MW(e) translates into an efficiency of 39.7 %. The early shutdown after 423 efpd was not related to the reactor concept neither to any safety concerns, but primarily associated with technical and economic problems.

The present German HTGR reference design is the **HTR-MODUL** containing a large number of safety features with the possibility of process heat applications [76]. A two-vessel side-by-side design was selected for safety reasons and for better accessibility in terms of maintenance and inspection. The active core consists of 360,000 fuel balls in a 9.43 m tall and 3 m diameter cylindrical pebble bed to produce 200 MW(th) power in the electricity-generating version and 170 MW(th), respectively, in the process heat version. The results of a safety study for the latter are described in further detail in section 3.3.2. An application for a site-independent advanced concept license for a two-module facility was filed in 1987, but later stopped due to loss of interest by the potential user. A respective TÜV audit was practically completed and positive.

The **HTR-100** with 258 MW(th) was designed as a reactor for special applications including process steam generation with possible cogeneration of electricity. It applies the AVR principle of an upstream coolant flow with the steam generator arranged above the top reflector. Gas outlet temperature is 740 °C. As a twin plant in the cogeneration mode, it can provide 170 - 500 t of process steam per hour (1.6 MPa, 270 °C) plus a gross electricity output of 175 - 100 MW [66].

An industrial power plant with HTGR, **Ruhr 100**, was proposed for upgrading of hard coal. It was designed to produce synthetic natural gas by means of a Lurgi pressurized gasifier with the option of cogenerating methanol and, by applying the Mobil oil process, gaseous hydrocarbon fuels.

The "gas-plus-steam-turbine-cycle" concept for an HTGR, **HTR-GST**, with 200 MW(th) has been considered to maximize thermal efficiency. Assuming a gas turbine inlet temperature of 1050 °C, the calculated net efficiency is 54.5 % [12].

The **AHTR 500** is a further development of the HTR-MODUL design with 500 MW(th). The helium coolant is heated up from 330 to 950 °C. The system pressure is 2 MPa. The new feature of this reactor design is a central graphite column to provide an additional heat sink. It contains a passive decay heat removal system on the basis of natural convection which runs also during normal operation. No intermediate circuit is foreseen for the connection with a coal gasification system [41].

The concept of a **900 MW(e) HTR** (thermal power 2250 MW) has been developed to operate in an indirect cycle for electricity generation with the extraction of process steam to be used for coal gasification employing an improved Lurgi process. The plant is to provide 110 kg/s of process steam at 400 °C and 10 MPa.

4.3.2.2. "Prototype Plant Nuclear Process Heat" (PNP) Project

The **"Prototype Plant Nuclear Process Heat" (PNP)** project was founded in 1972 (and terminated in 1992) with the goals of

- developing HTGRs for high gas outlet temperatures of 950 °C as a source of process heat for coal gasification,
- developing and testing components for heat transfer to the process plant,
- developing and testing processes and experimental facilities for steam-coal gasification and hydro-gasification.

A first concept for high-temperature gas-cooled reactor for process steam production was proposed in [68]. The **PR-500** was designed for 500 MW(th) to produce 523 t/h of steam at 265 °C and 2 MPa plus a net electricity of 55 MW(e). The helium coolant was heated up from 265 to 865 °C. Three loops either one with heat exchanger and blower were arranged around the pebble bed reactor outside the prestressed concrete pressure vessel.

The **PNP-3000** reactor plant was designed for the generation of process heat for a steam reformer (1071 MW) and of electricity with 540 °C / 19.5 MPa turbine steam (1929 MW). The helium coolant is heated up from 250 to 950 °C at a primary system pressure of 4 MPa. Nuclear power density is 5 MW/m^3. Four (or more) loops are connected to the reactor either one with circulator, steam generator plus two steam reformers. Eight steam reforming furnaces are to be operated at 825 °C with a methane conversion of about 65 % [69].

Technical feasibility of a nuclear process heat reactor for the refinement of coal has been established, main components developed, and its basic licensing capability confirmed. The economic competitiveness compared with non-nuclear alternatives could be achieveable by using improvement potential, however, nowadays looking at low oil prizes realistically not existing. Studies on the technical feasibility and economic competitiveness of the processes for nuclear coal refinement were completed in 1987 [11].

4.3.2.3. Nuclear Long-Distance Energy Transportation

The steam reforming process was experimentally investigated in the **"Nuclear Long-Distance Energy" (NFE)** project. Two different bundles of steam reformer tubes were tested: (i) the "orifice baffle" design by Lurgi, and (ii) the "counter current concentric" design by Steinmüller. Convective helium heating was verified for both designs [28]. The reaction rate for bundle (ii) was found to be dependent on pressure and fictive velocity in the empty tube, but independent of temperature indicating a heat-controlled reaction. Postoperation inspections confirmed the integrity of all reformer tubes.

The complete EVA-II / ADAM-II system was operated for a total time of 10,150 hours including steady state conditions at both full and partial load, transient procedures, and also special test situations such as tube blockage [28] (see also section B.1.).

The nuclear variant of using CH_3OH as an energy carrier taking the HTGR as a primary source for the required process heat is schematically shown in Fig. 4-2. A congenial system is the methanol-carbon monoxide system.

4.3.2.4. EVA-II Pilot Plant

Within the PNP project, a **test reformer tube bundle, EVA-II**, with a power of 5 MW has been investigated to prove design and engineering and to demonstrate its feasibility as being used in nuclear process heat applications such as hydro-gasification of coal or long-distance energy transportation (see Fig. 4-3). EVA-II was successfully operated over 5800 h within the "Nuclear Long-Distance Transportation" project NFE in connection with the methanation plant ADAM-II (see also section B.1.) and then modified to account for PNP steam reforming conditions.

The nuclear heat source was again simulated by an electric heater. The new EVA-II reformer constructed by the Steinmüller company has used the concentric tube design. It

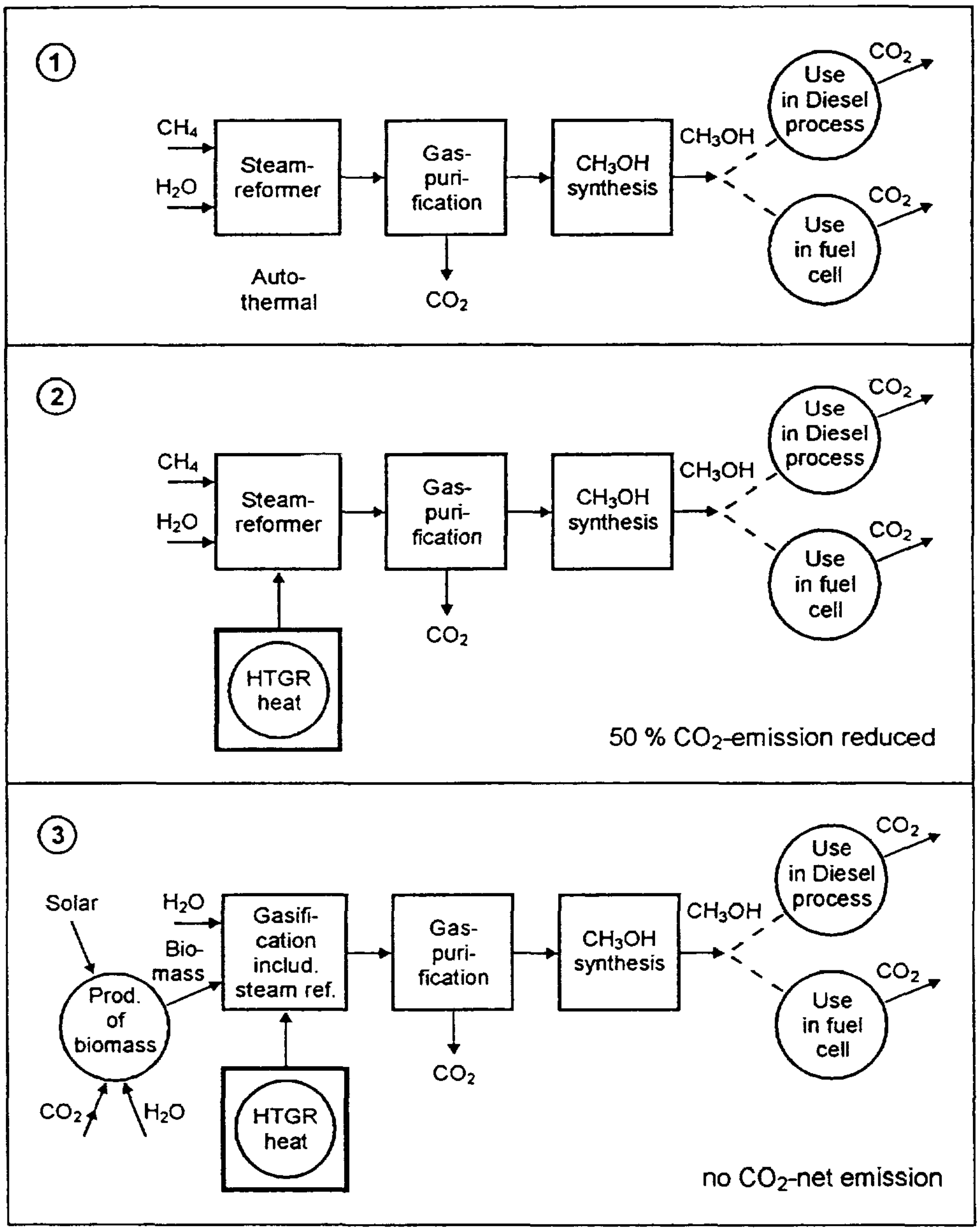

Fig. 4-2: Methanol as an energy carrier with different CO_2 emissions, from [Research Center Jülich, ISR]

consisted of a bundle of 18 reforming tubes. All other features remained essentially the same. The test program was conducted in two series with the operating conditions as given in Table 4-1.

In December 1986, the facility was shut down and a postexamination program was started. The tests have confirmed the expected thermodynamic and chemical processing behavior and also the predictive character of respective calculation models. After a total of 5200 h operation time, the reforming tubes were optically still in excellent shape. The procedures of catalyst changing need further improvement [53].

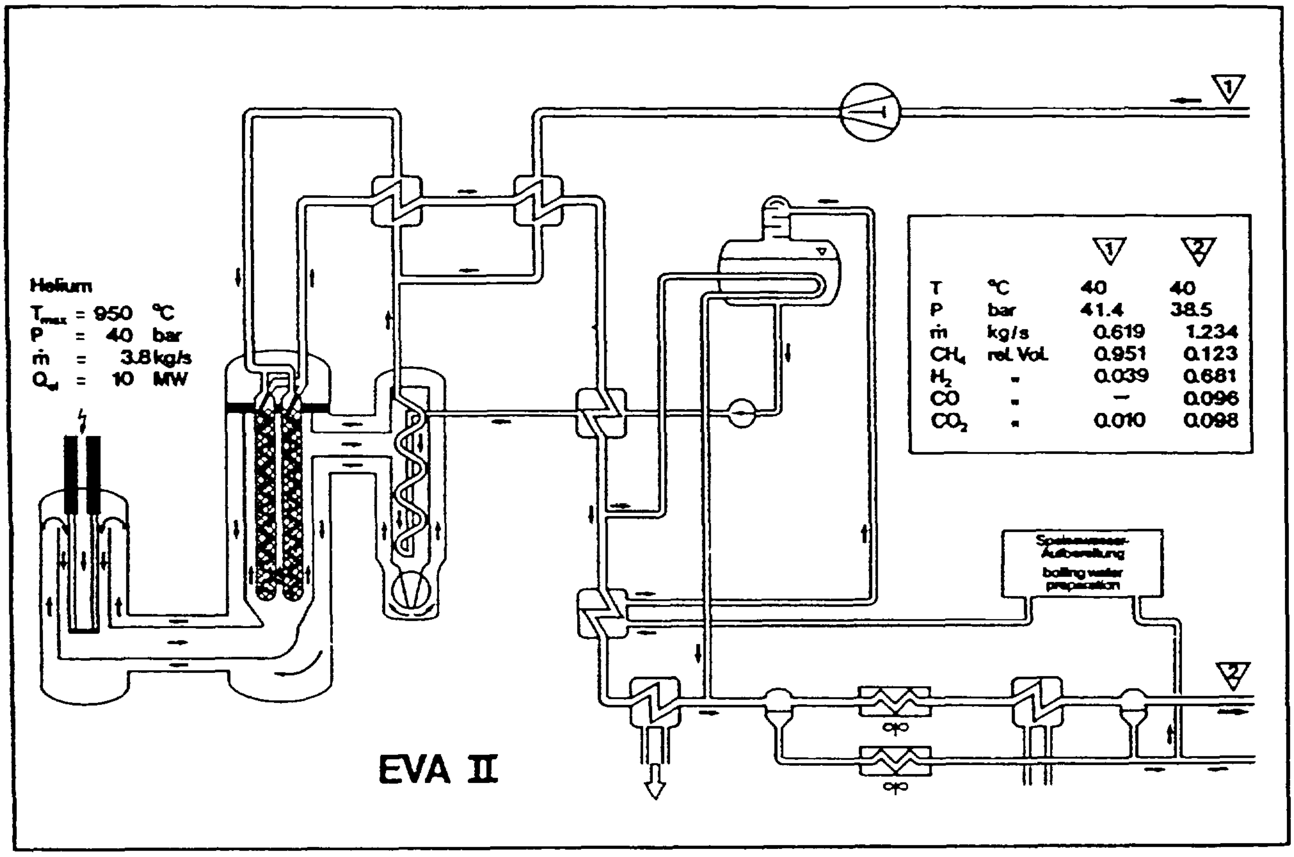

Fig. 4-3: Simplified flow chart of test facility EVA-II, from [53]

Table 4-1: Operating conditions in EVA-II test program, from [53]

	Series A	Series B
Helium mass flow [kg/s]	2.574	3.850
Feed gas mass flow [kg/s]	1.908	2.776
Helium inlet temperature [°C]	950	950
Feed gas inlet temperature [°C]	700	700
Feed gas temperature at catalyst entry [°C]	572	548
Product gas temperature at catalyst exit [°C]	810	791
Product gas outlet temperature [°C]	457	458
Thermal power [MW]	3.4	5.0

4.3.2.5. "High-Temperature Reactor with Helium Turbine of Large Power" (HHT) Project

Another subject of research parallel to PNP was the project of a closed-cycle "**High-Temperature Reactor with Helium Turbine of Large Power (HHT)**" initiated in 1968, started in 1972, and terminated in 1981 [83]. Main goals in this project, of course, were to achieve a higher efficiency and to reduce the number of components. But it was also considered to present a broad variety of utilizations, in particular, in the lower process temperature range. The heart of the HHT concept was a 2700 MW(th) high-temperature reactor to which three parallel loops were connected, either one containing a 350 MW(e) helium gas turbine, a recuperator, and a cooler. The helium coolant was heated up from 460 to 868 °C. All components were arranged in a prestressed concrete pressure vessel. Maintenance capability of turbine and hot gas ducts mainly depend on Cs-137 contamination which increases steadily during its long lifetime and produces a high γ-dose via its daughter nuclide Ba-137m [83].

Research activities in connection with HHT were

- a materials research program starting at BBC and at the Research Center Jülich to investigate the lifetime of the turbine, hot gas duct, and insulation materials in a helium atmosphere,
- the development and testing of the hot gas duct and insulation in the project ARGAS at the Research Center Jülich, and
- the investigation of fission product deposition behavior in the primary helium circuit (VAMPYR, SAPHIR).

The R&D program included two experimental setups both demonstrating helium as a closed-loop Brayton cycle working fluid [44]:

(i) a 50 MW cogeneration power plant for electricity and district heating, **EVO**, in Oberhausen, FRG, by employing a helium turbine. Operation time was 24,000 h with 11,500 h at 750 °C temperature,

(ii) the "High-Hemperature Helium Test Plant", **HHV**, at the Research Center Jülich for the development of helium turbomachinery and components. Helium is routed through the test section at a rate of 200 kg/s with a maximum temperature of 1000 °C. Operation was 1100 h with 325 h at a greater than 850 °C temperature.

4.3.2.6. Component Experimental Loop (KVK)

The 10 MW Component Experimental Loop (KVK) ("**Komponenten-Versuchs-Kreislauf**") was a high-temperature helium circuit operated by Siemens/Interatom in Bergisch Gladbach. It consisted of a primary and a secondary helium loop and a water steam system. Its flexible design, however, also allowed for a single loop operation. Various components were tested under the operating conditions of coal gasification.

Two concepts of a He - He intermediate heat exchanger for a heat rating of 125 - 170 MW have been selected. For both, a 10 MW test plant has been operated in the KVK loop verifying the operation of reformers with convective helium. A 10 MW decay heat removal system cooler, hot gas ducts including insulation and liner, hot gas valves, and a steam generator were other components of the KVK loop. Furthermore, a helium purification system was operated in a bypass of the main system. Starting in 1982, the KVK facility was operated for 18,400 h with approx. 7000 h above 900 °C [28]. Hot gas duct with internal insulation was operated at temperatures up to 950 °C. The KVK experimental loop has demonstrated reliability and availability even of newly developed components.

4.3.2.7. Coal Gasification

From 1976 to 1984 within the frame of the PNP project, the former German company Bergbau-Forschung, now: Deutsche Montan Technologie (DMT), has established and successfully tested catalytic and non-catalytic **steam-coal gasification** in a 1.2 MW semi-technical scale experimental facility, WKV, developed for hard coal, in the city of Essen. Heat was provided by helium electrically heated up to 950 °C via a steam generator. The plant was in hot operation for approx. 23,000 h with more than 13,000 h under gasification conditions. The maximum capacity was 230 kg/h of coal. The total amount of hard coal gasified was 1600 t [38].

The **hydro-gasification** process as an alternative to the above described steam-coal gasification process was pursued by the German Rheinische Braunkohlenwerke AG, Cologne. Its principle was successfully verified in a semi-technical test facility, HKV, in Wesseling, which operated for about 27,000 h with more than 12,000 h under gasification conditions from 1976 to 1982. The throughput was 320 kg/h of lignite corresponding to a power of 1.5 MW. The total amount of coal gasified was 1800 t. The largest non-stop operation was 748 h. Carbon gasification rates up to 82 % were achieved with methane contents in the dry raw gas up to 48 % [62]. Since 1983 until 1985, a followup pilot plant was operated with a throughput of 9.6 t/h of lignite corresponding to a power of 50 MW and an SNG production of about 8000 Nm^3/h. The temperature was between 850 and 950 °C, pressure was between 6 and 12 MPa. The inside diameter of the gasifier was 1 m. The translation into a large-scale gasification plant is still in the design phase. Focus is laid upon the non-catalytic gasification.

Higher coolant outlet temperatures allow for a smaller reaction volume and a higher coal throughput, respectively. The intermediate heat exchanger is required because of the difficulties expected when handling coal and ash within the reactor containment. Furthermore coal gasifiers have a shorter lifetime than steam reformers which means that the former should be outside the nuclear plant for shutoff and repair purposes [69].

4.3.2.8. Hydrogen / Methanol from Raw Iron Furnace

In Fig. 4-4, a schematic of an iron ore reduction plant is shown using hydrogen generated by a nuclear reforming process. The hydrogen is heated up to 900 °C and then routed into the blast furnace to act as a reduction gas [45].

A proposal was made in [56] to deploy a stack gas processing plant for either

- the generation of hydrogen
  in a homogeneous water gas reaction and removal of N_2 and residual CO by converting all CO with steam, or for
- the generation of methanol
  by applying the proper ratios of H_2, CO and CO_2 as well as removal of N_2. The H_2 to CO ratio is in the range of 2.4 - 4.5, the CO_2 fraction is 5 % for optimal synthesis at the expense of a reduced iron production.

A balance of such a plant with the combined production of raw iron and methanol / hydrogen is summarized in Table 4-2. Compared with the reference case 1 using a rich ore

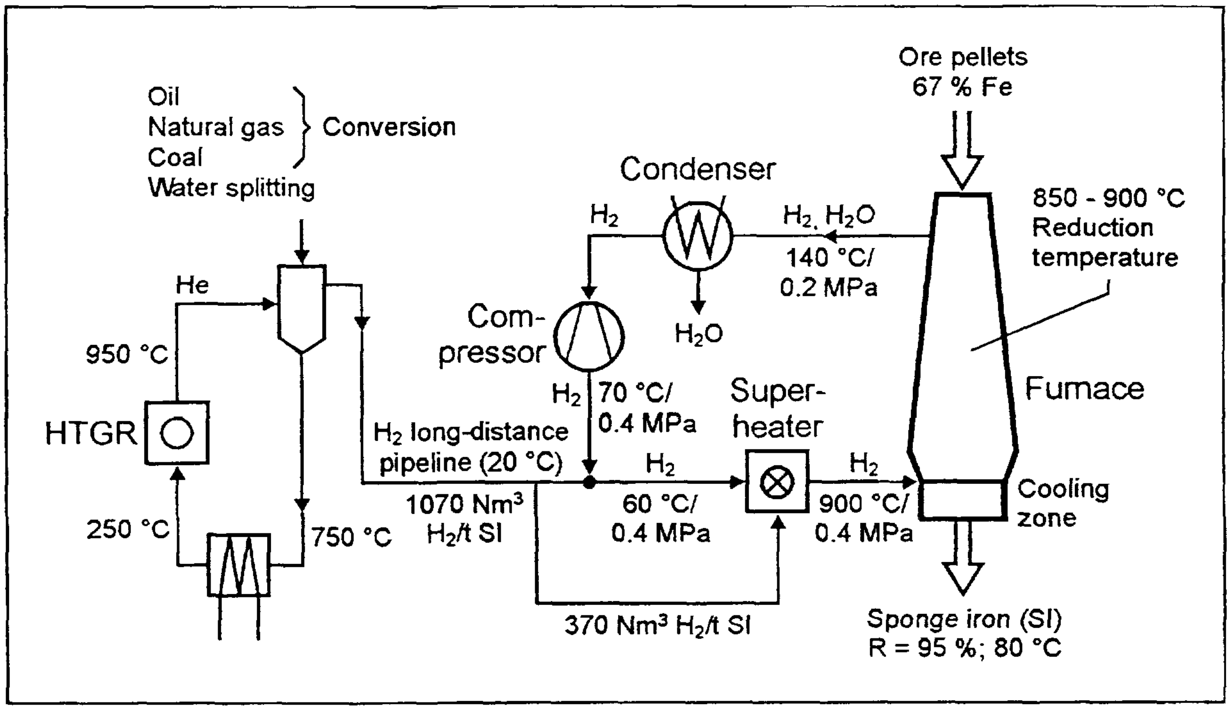

Fig. 4-4: Direct iron ore reduction plant, from [45]

Table 4-2: Balance of direct iron ore reduction plant, from [56]

	Hydrogen			**Methanol**
	Case 1 (rich ore)	**Case 2 (lean ore)**	**Case 3 (O_2/H_2O wind)**	**Case 3 (O_2/H_2O wind)**
HTGR [MW(th)]	250	250	250	250
Coke [t/h]	70	74	72	72
Stack gas [mol%]				
CO	37	40	65	65
CO_2	12	12	8	8
H_2O	6	7	16	16
H_2	2	3	10	10
N_2	43	38	1	1
Hydrogen of 99.9 mol% [Nm^3/h]	71,160	81,030	104,980	-
Methanol [t/h]	-	-	-	59
Raw iron [t/h]	81	87	73	73
Net electricity output [MW(e)]	28	23	34	5
Thermal efficiency [%]	49.0	50.8	57.6	55.6

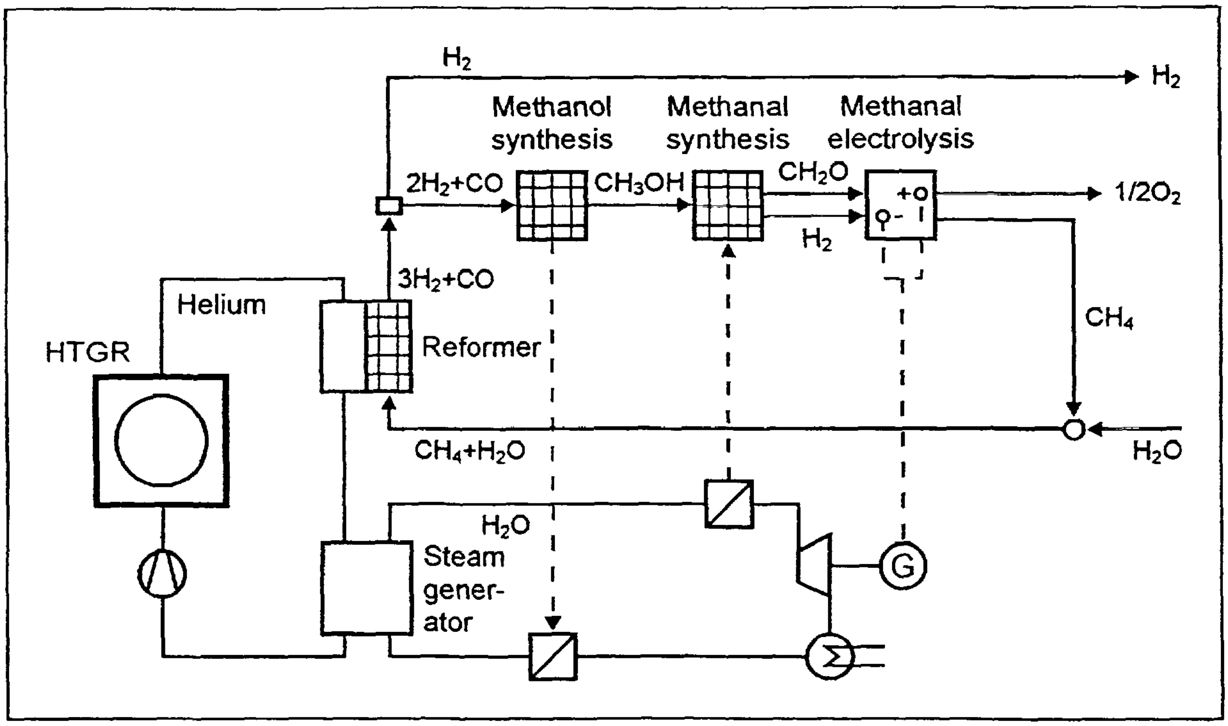

Fig. 4-5: Schematic of a nuclear plant design for the "methane-methanol-methanal" process with the main material streams, from [9]

and an oxygen/steam enriched furnace wind, case 2 treats an alternative for lean ore which demands more energy for the reduction step. In case 3, a pure oxygen/steam furnace wind is used which has the advantage of an almost nitrogen-free stack gas whose treatment is easier and less expensive. The process energy required is considered here to be provided by a 250 MW(th) HTGR. The thermal efficiency for the methanol production could even be increased from 55.6 to 70.9 %, if the hydrogen needed for the synthesis is provided from outside without using the internally converted hydrogen [56].

4.3.2.9. Hydrogen Production

The basic design of a nuclear plant for the hydrocarbon-hybrid or the "methane-methanol-methanal" process is schematically shown in Fig. 4-5 [9]. It is based on an HTGR to cogenerate low-temperature energy to be used in the steam generator and high-temperature energy to be used in the steam reformer. The latter is taken for methane splitting as the first step of the hybrid cycle to catalytically produce synthetic gas, a mixture of H_2 and CO. A certain fraction of the hydrogen contents is separated by a two-fold application of the shift reaction. The remaining synthesis gas is then consumed in the process of methanol production. In step (3), the methanol is split into methanal (= formaldehyd) and hydrogen. The heat required for this reaction is taken either from the steam generator or from the previous exothermal reaction. Both products methanal and hydrogen are fed into the electrolyzer to regain the methane which is recycled and to obtain the desired byproduct oxygen. According to a first design, 2.6 MW thermal power from an HTGR are required to generate 300,000 Nm^3/h of hydrogen [9].

Research work has been conducted at the Research Center Jülich on the Westinghouse sulfuric acid hybrid cycle. The heat consuming step of sulfuric acid splitting was successfully realized in bench-scale experiments under HTGR conditions at 4 MPa and with 950 °C heat from a furnace.

4.4. INDONESIA

4.4.1. Energy Situation in Indonesia

Indonesia is an oil and gas producing country with primary energy shares of 60 % and 33 %, respectively. Coal although abundantly available consists of low-quality lignite only; its share is about 6 %. The Indonesian domestic energy consumption rate is presently increasing by 15 % per year. In the 1970s, several giant natural gas fields have been discovered making natural gas a major export commodity. In 1994, the LNG production amounted to about 25 million t with 90 % of it exported to Japan, the residue to South Korea and Taiwan. The latest find, the off-shore **Natuna natural gas field**, is estimated to have an energy content of 1.5 TWy which would allow a production of 38 million t/yr of LNG over 20 years. Strong competition among international petrochemical companies is going on around this so-called "35 Billion plus" US $ project (with 10 Billion US $ needed for carbon dioxide extraction and re-injection). The Natuna gas feature of a very large content of CO_2 of 71 % is hoped to become not a burden but rather an economic challenge to introduce new technologies by means of gas processing to be the incentive for a rapid economic growth in South East Asia [2]. Proven gas reserves in Asia stand at some 10,650 billion Nm^3 with a share of 7.2 % of the world's total reserve. Hydro power is currently 1.7 GW restricted to Java island.

4.4.2. Experimental and Theoretical Activities in Indonesia

4.4.2.1. Exploitation of the Natuna Gas Field by Means of HTGR

A feasibility study has been initiated by the IAEA to investigate the application of the HTGR for cogeneration purposes of CO_2 conversion, desalination, and H_2 production in terms of economy and technology [17].

The prerequisite of minimal emission of CO_2 into the atmosphere has suggested the nuclear option in exploiting the **Natuna** gas field. Six alternatives have been identified as being feasible and economically competitive, distinguished by the desired product methanol or methane (or hydrogen) and by the CO_2 consumption [14]:

(a) steam and CO_2 reforming and H_2 from electrolysis for methanol synthesis with 15 % consumption of the Natuna CO_2,

(b) steam and CO_2 reforming and H_2 from electrolysis for methanol synthesis with 25 % consumption of the Natuna CO_2 (see Fig. 4-6 and Table 4-3),

(c) steam and CO_2 reforming and H_2 from electrolysis for methanol synthesis with 100 % consumption of the Natuna CO_2,

(d) CO_2 reforming and H_2 from electrolysis for methane and methanol production with 100 % consumption of the Natuna CO_2,

(e) Natuna gas and H_2 from electrolysis for methane production with 100 % consumption of the Natuna CO_2,

(f) separation of methane from the Natuna gas and H_2 from electrolysis plus Natuna CO_2 for methanol synthesis with 100 % consumption of the Natuna CO_2.

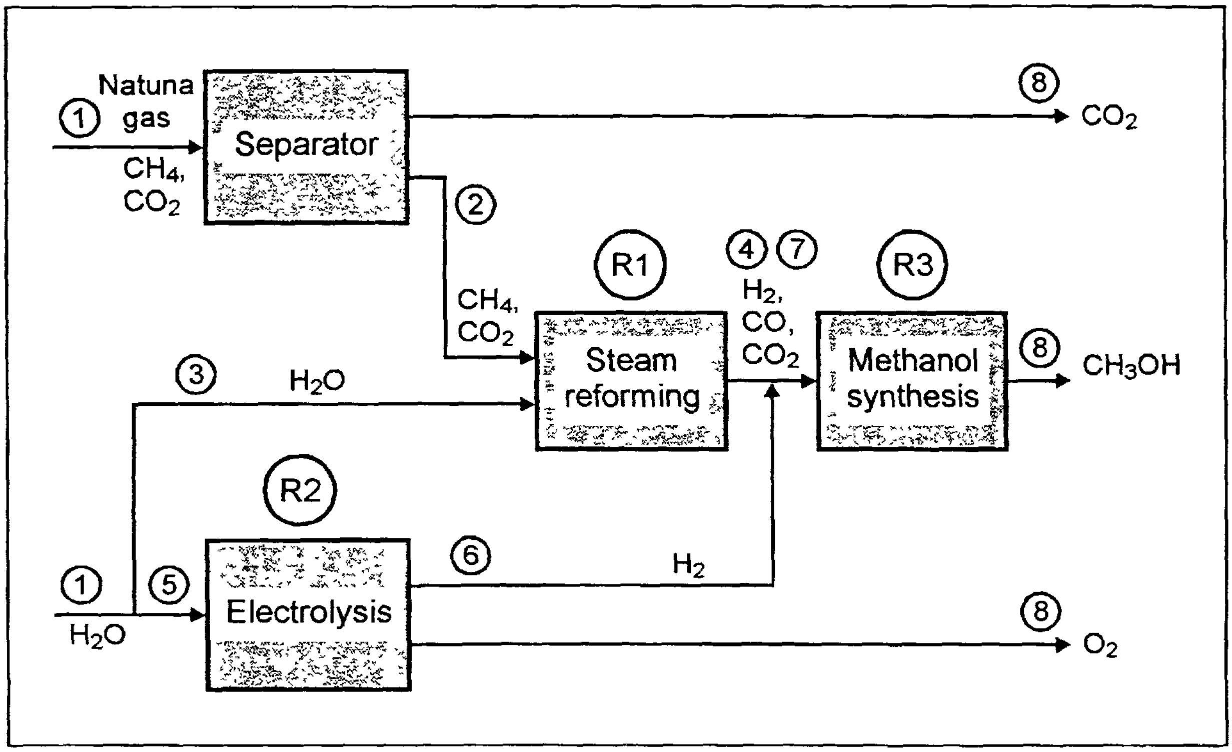

Fig. 4-6: Use of Natuna natural gas for methanol synthesis, variant (b) (see text), sources and sinks of species involved, from [14]

Table 4-3: Use of Natuna natural gas for methanol synthesis, variant (b) (see text), from [14]

	Species flow n, Δn [kmol/s]										
	1	2	3	R1	4	5	R2	6	7	R3	8
CH_4	+4.5	4.5		-4.5							
CO_2	+12	3		3	3				3	-3	9
H_2O	+9		4.5	-4.5		4.5	-4.5			+3	3
H_2				+13.5	13.5		+4.5	4.5	18	-18	
CO				+4.5	4.5				4.5	-4.5	
O_2							+2.25	2.25			2.25
M(1)										+7.5	7.5

(1) M = Methanol = CH_3OH

Another process is the production of formic acid, CH_2O_2, which would result in a complete conversion of the Natuna gas:

$$3\ CH_4 + 9\ CO_2 + 6\ H_2O \quad \rightarrow \quad 12\ CH_2O_2$$

Formic acid is a product of the chemical industry and could again attention as a future fuel for fuel cells [13].

An HTGR is proposed to be operated in cogeneration mode to provide the reaction heat for the reforming processes as well as electricity for water decomposition by electrolysis. Resulting products are the marketable fuels methanol as a motor fuel and, of lower value, methane as a heating fuel. Taking account of the huge size of the Natuna gas field, the thermal power of about 20 modular HTGRs with 200 MW(th) each is required [14].

A working group has been established by the National Atomic Energy Agency in Indonesia to concentrate on coal conversion to synfuel as a substitute for depleting oil or to synthetic natural gas or to synthesis gas, CO_2 conversion to methanol, hydrogen production, and enhanced oil recovery [1]. In connection with coal liquefaction, an HTGR could provide process heat for dewatering of the coal, thermal treatment of the slurry, and electricity production; this plan, however, needs further elaboration [29].

4.4.2.2. Oil Recovery by Means of HTGR

The thermally enhanced oil recovery process by steam flooding is a tertiary recovery method. A four-unit HTGR power plant with 200 MW(th) each for cogeneration of steam (530 °C, 15 MPa) and electricity (25 - 30 MW(e)) has been proposed to exploit the Duri oil field which currently represents the largest steam flood project in the world. Peak production has reached 300,000 bbl/d which requires 4,000 - 5,000 t/h of steam consuming 20 % of the oil produced. However, the present oil price development does not allow the economic employment of HTGRs for this type of oil recovery [57].

4.4.2.3. Hydrogen Production

Two hydrogen production plants are presently being operated in Indonesia used in oil refinery, ammonia synthesis, and methanol production. The capacities are $1.8*10^9$ Nm^3 and $2.1*10^9$ Nm^3, respectively. The H_2 is generated from steam reforming of natural gas. It is projected to replace fossil fuels in industrial processes, in the transportation sector, and in households.

4.5. JAPAN

4.5.1. Energy Situation in Japan

The significant growth of Japan's economy in the 1960s was based on cheap petroleum imports, which, however, ceased with the first oil crisis. The oil portion in primary energy consumption was lowered from 77 % in 1973 to 56 % in 1985, while shares of the alternatives nuclear and natural gas, also coal, were rising. It has become and is expected to remain the country with the most imports of LNG covering 70 % of the worldwide traded LNG. The Japanese energy consumption in 1993 of 507 million TOE (= $2.12*10^{13}$ MJ) was covered by oil (53 %), gas (17 %), coal (16 %), nuclear (11 %), and hydro (4 %) [61]. A portion of 60 % of the energy consumption in Japan is non-electric. About one third of the CO_2 emissions are from fossil-fueled power plants. The committment made on the Kyoto conference in 1997 for Japan is a reduction of the emissions by 6 % relative to 1990 compared with an observed increase of 8 % by 1995 [16]. According to MITI, however, even the minor goal of greenhouse gas reduction to the 1990 level increases Japan's nuclear dependence demanding 20 more units of the 1300 MW(e) class by 2010. Japan was the first industrial country to sign the Kyoto protocol.

The largest share in Japan's electricity production of $907*10^9$ kWh (1993) is provided by nuclear power with 34 % from 47 units; others are LNG (29 %), oil (18 %), hydro (11 %), and coal (8 %) [4, 61]. In mid 1997, Japan has operated 53 nuclear power stations; also Japan has the two largest nuclear sites of the world, Fukushima with 10 BWR units and a total of 9096 MW(e), and Kashiwazaki-Kariwa with 7 BWR units and a total of 8212 MW(e). Because of shortage of land, Japan has a preference for large nuclear power units with a strong and diverse program supported by the big industrial companies. The different designs for future reactors currently being pursued are considered promising and are expected to form Japan's next generation of reactors [33]. Reactors planned and under construction are expected to raise the nuclear share to 42 % by 2010 [46]. At present, however, the Japanese nuclear policy is being re-examined after the Monju accident which has aggravated the already serious difficulties of getting public acceptance [46].

Japan depends heavily on imported energy (84 % of the primary energy) and is thus highly energy-vulnerable. Therefore intensive research efforts are being conducted on new energy carriers. Fuel cell technology is considered one of the most important new energy technologies. The most likely chance for entry of SOFC based power generation plants is seen for Japan because of its very high gas and electricity price level combined with stringent emission requirements [8]. The WE-NET project focusing on hydrogen to follow LNG is one example, research on gas hydrates[14] is another one.

4.5.2. Experimental and Theoretical Activities in Japan

4.5.2.1. Process Heat from Light-Water Reactors

For the purpose of a stable, long-term energy security, promoting industries, and development of local areas, Japan is currently investigating the potential of light-water reactor process heat applications. The chemical industries in Japan occupy a share of about one sixth of the electricity which is mostly consumed in the form of heat. Designs have been presented to utilize steam from 1100 MW(e) class PWRs or BWRs.

The LWR is separated from the chemical plant by an intermediate circuit to minimize the risk of a radioactivity escape into the process gas circuit. A further advantage will be the accumulation of steam generated by cheap off-peak electricity. The basic technology

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[14] Gas hydrate is a mixture of methane embedded in ice crystals at -23 °C buried at the ground of the oceans. One m^3 of gas hydrate transforms under normal conditions into 164 m^3 of methane plus 0.8 m^3 of water.

is available. The demonstration of process heat applications is considered by using a small or medium-sized LWR [19].

The final goal of heat utilization of LWRs is described in a Japanese study [19] bypresenting the concept of a new city for approx. 50,000 inhabitants with the shape of half a circle and situated at the coast line. The nuclear energy supply center is located in the (circle) center to provide heat and electricity to belts of industries, greens, residences, arable land in a concentric arrangement. The energy center consists of four nuclear power units, two PWRs, two BWRs, with 1000 MW(e) each.

4.5.2.2. High-Temperature Reactors

Utilization of heat from the HTGR has been studied during the 1970s and 1980s in USA and Germany. In Japan, the experimental multi-purpose **VHTR** was designed by JAERI and a nuclear steel-making plant was studied supported by AIST. But the project was premature at that time and discontinued in 1980. Still the HTGR was and is considered a promising solution to meet the increased demand for clean energy on the basis of the energy carrier hydrogen to be used in industry and transportation. The Japanese market is foreseen to hold for 80 GW thermal power provided by HTGRs [34].

Starting in 1991, the **30 MW(th) High-Temperature Engineering Test Reactor, HTTR**, is being constructed in Oarai [58]. The main components are the reactor pressure vessel containing a prismatic core, a main cooling system with a 10 MW He-He intermediate heat exchanger (IHX), plus a 20 MW pressurized water cooler (PWC), and an auxiliary cooling system as well as a reactor vessel cooling system. In the first operation phase, the helium-cooled reactor will have an outlet temperature of 850 C. HTTR is planned to be critical in 1998.

With the introduction of the second core, the HTTR will be the first-of-its-kind nuclear reactor to be connected via a He-He heat exchanger to a high-temperature process heat utilization (natural gas steam reforming) system with an outlet temperature of 950 ^{0}C. The IHX is a counter-current and helically wound tube type shell-and-tube heat exchanger designed to provide helium of about 900 C at 4.1 MPa. Due to the high pressure and the low temperature of 800 C in the reformer, the CH_4 conversion rate is expected to be no higher than 65 %. Start of its operation in the HTTR is planned with the installation of the second core expected for 2002 [44]. Promoted by the International Atomic Energy Agency (IAEA), a Coordinated Research Program with international cooperation has been started in 1994 on the design and evaluation of heat utilization systems with the goal to identify the most promising technologies to be demonstrated at the HTTR.

The **FAPIG** (First Atomic Power Industry Group) representing 22 (now 18) Japanese industrial companies from different branches, organized a working group to study how to use heat from HTGRs to mitigate environmental and resource problems, to stabilize supply, and to promote effective use of energy. Three types of heat utilization plants based on HTGRs have been modelled, for each of which the system outline, basic plant layout, social effects, and technical issues were studied [35, 85]:

(i) a cogeneration plant for a typical chemical plant with two modular HTGRs of 450 MW(th) with a helium outlet temperature of 700 C, each to provide 640 t/h of steam of 200 °C plus 210 MW of electricity with an estimated overall efficiency of 74 %,

(ii) a coal gasification ammonia production plant with four modular HTGRs plus IHX of 170 MW(th) each and a coolant outlet temperature of 950 °C to produce 1700 t/d of ammonia, coal gasification rate is 2200 t/d in a fluidized bed, and

(iii) a hydrogen production plant with four 200 MW(th) modular HTGRs with a coolant outlet temperature up to 1050 °C and applying both the iodine-sulfur process and the high-temperature steam electrolysis process to produce 37,090 and 110,000, respectively, Nm^3/h of hydrogen.

The concept of an HTGR plant with a closed-cycle gas turbine is also being pursued by FAPIG and a proposal has been made for the construction of a demonstration test facility.

4.5.2.3. Hydrogen and Methanol Cogeneration by Steam Reforming

Top candidate to be tested by JAERI in connection with the HTTR is **steam reforming of natural gas** for hydrogen and **hydrogen/methanol coproduction** including carbon dioxide recycling [26]. The thermal energy of 10 MW is planned to be transferred to a secondary helium circuit via the IHX. The total power needed to provide the reforming process heat is 4.8 MW with 3.6 MW transferred from the helium gas to the steam reformer and 1.2 MW transferred from the outlet to the inlet process gas [82]. There are differences compared with a conventional fossil-fired system, in particular, a lower maximum temperature and a higher process gas pressure, so that a lower hydrogen production is expected. However, an optimization of the operation conditions should reach compatibility with the conventional system (see Table 4-4). The heat utilization efficiency is expected to be 78 % being close to the figure of 80 - 85 % of a conventional reforming system. The goal is the production of 3800 Nm^3/h of hydrogen or, in the cogeneration mode, 1390 Nm^3/h of hydrogen plus 1930 kg/h of methanol, while the input is 950 kg/h of natural gas plus 10 MW of process heat. A schematic of the coproduction process is shown in Fig. 4-7.

Prior to the installation of the steam reforming system in the HTTR, the operation of an out-of-pile plant downscaled to 1/20 - 1/30 of the size projected for the HTTR, is planned to investigate system characteristics, to verify operation and control technologies, and to confirm safety and performance under simulated HTTR operational conditions [49]. Pilot plant designing has started in 1995; its construction has begun and is expected to be completed in 1998.

4.5.2.4. Nuclear Coal Gasification

Another nuclear heat application system that offers reduction potential is the conversion of coal by gasification to other synthetic fuels. The gasification process selected is dependent on what type of fuel is desired. Hydro-gasification is appropriate for H_2 or CH_4 production, whereas partial oxidation and steam gasification are better suited for methanol production. The latter process has been proposed for a nuclear coal reforming system with methane reformer and steam gasifier based on a 450 MW(th) HTGR. With an input of 93 t/h of water and 34.5 t/h of coal and 27,490 Nm^3/h of methane, the methanol production rate would be 101 t/h plus 68 MW(e) electricity [31].

Table 4-4: Comparison of operation conditions and performance of conventional with nuclear-heated steam reformers, from [26]

	Steam reformer		
	Fossil-fired	**Helium-heated**	**Helium-heated (Improved design)**
Process gas pressure [MPa]	1 - 3 (depending on final products)	> 4	4.5 (at inlet)
Maximum process gas temperature [°C]	850 - 950	≤ 750	800
Maximum heat flux to catalyst zone [kW/m^2]	50 - 80	10 - 20	40
Efficiency [%]	80 - 85	≈ 50	78
CO_2 emission [t/h] (based on 10 MW)	3	0	0

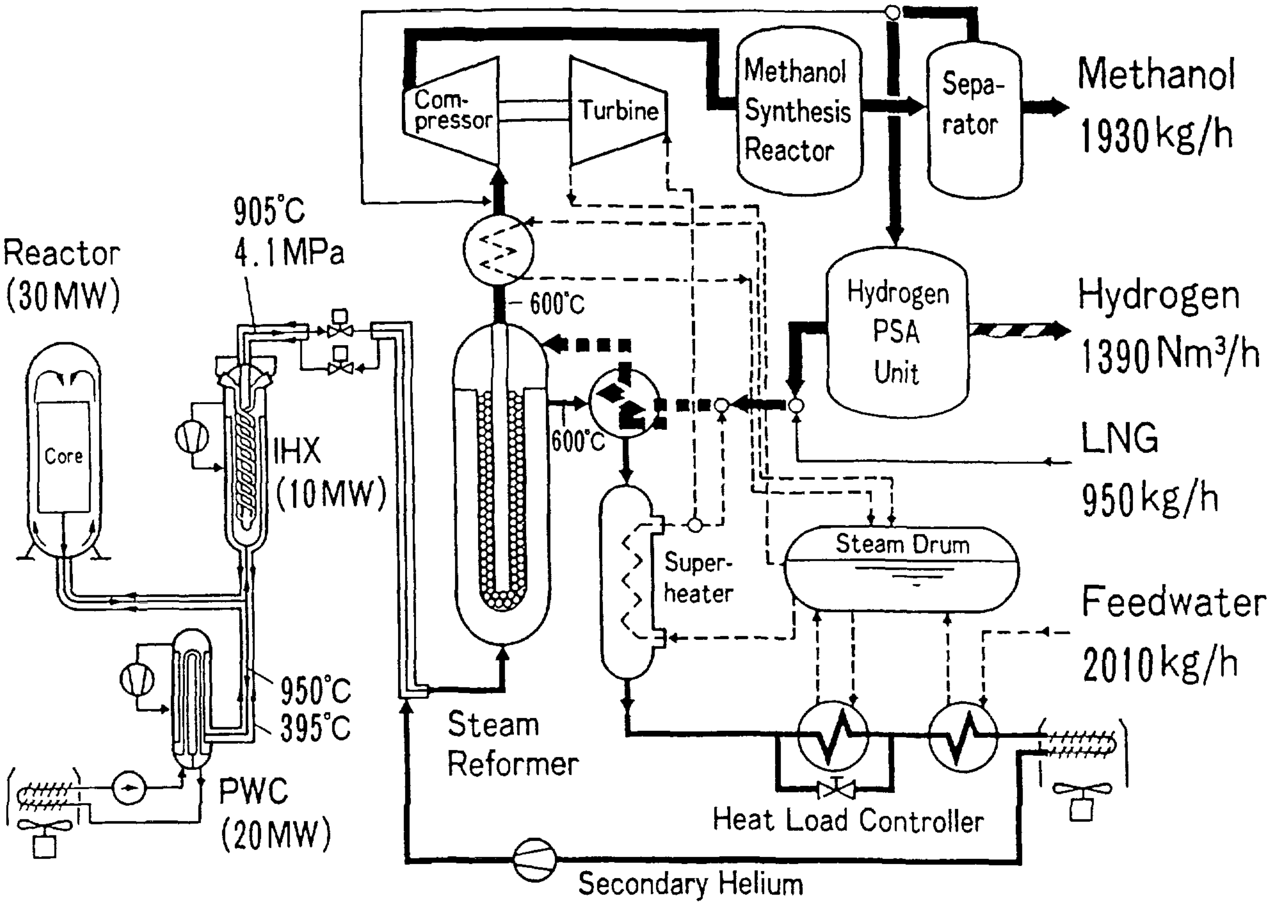

Fig. 4-7: Schematic of the HTTR steam reforming hydrogen / methanol coproduction system, from [25]

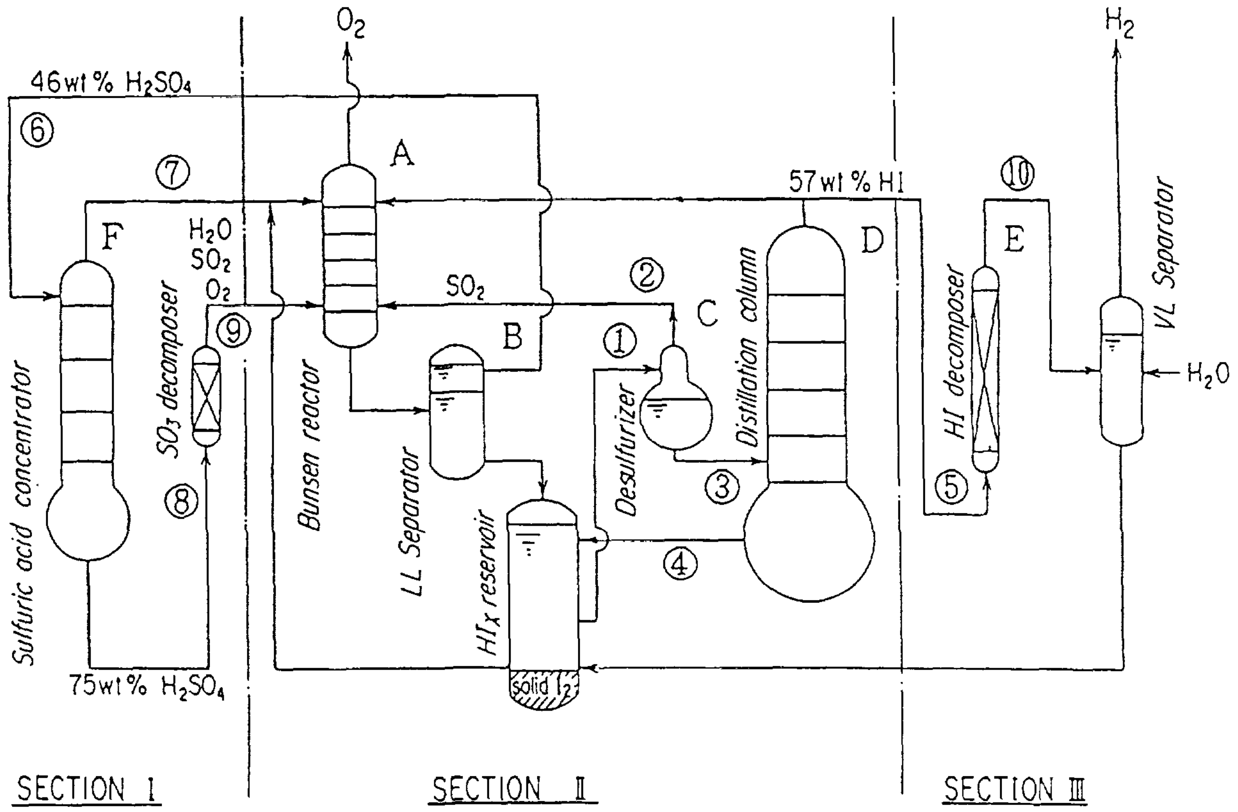

Fig. 4-8: Schematic of JAERI bench-scale apparatus for the "iodine-sulfur process" thermochemical cycle for hydrogen production (LL = liquid-liquid, VL = vapor-liquid), from [73]

The hydrogen production step of methane reforming could also be substituted by high-temperature electrolysis. The calculated balance here is 48 t/h of sea water plus 27 t/h of coal plus 15 t/h of air as input to yield 42 t/h of methanol. Excess hydrogen could be stored in tanks and retrieved for methanol synthesis, supposed the nuclear power needs to be used in peak periods [31].

4.5.2.5. Nuclear Hydrogen Production by Thermochemical Cycles

A bench-scale test facility for hydrogen production using the thermochemical **iodine-sulfur (IS) process** has been established at JAERI to verify the hydrogen production, to study the conditions for the reactions, and to gain experience for a large-scale plant [74]. The three reactions (see appendix A.2.3.) are performed in separate sections of the apparatus, the Bunsen reaction and the sulfuric acid decomposition at the same time to avoid SO_2 storage (see Fig. 4-8). The process requires temperatures of 800 to 900 °C. Its feasibility was successfully demonstrated in a glass, quartz, and teflon lab-scale apparatus. In the course of six cycles completed, the total amounts of H_2 and O_2 produced were 16.4 l and 9.9 l, respectively. The thermal efficiency achieved, however, was much smaller than the theoretical one of 47 - 50 % [44]. In late 1997, the continuous operation of the IS process cycle as a closed loop over 48 h resulted in the production of 44.8 l of H_2 [75].

Parallelly a simulation has been started to formulate a flow sheet for the cycle operation. The IS process and its characteristics have been verified. Agreement has been achieved between experimental data and the simulation model. A further improvement of the process is needed to acquire a higher thermal efficiency and to select better structural materials which are compatible on an industrial scale. Further demonstration steps are the employment of a metallic reactor for hydrogen production at a rate of 1 Nm^3/h and a scale-up process to a 100 Nm^3/h rate [44]. The IS process is one of the candidates to be connected to the HTTR following the steam reforming system.

The 4-step **UT-3 thermochemical cycle** with bromine-calcium-iron developed at Tokyo University is considered in Japan to be superior to many other thermochemical cycles. It has been successfully transferred into a bench-scale continuous model plant MASCOT. The system (Fig. 4-9) consists of four reactor furnaces containing the solid reactants $CaBr_2$, CaO, Fe_2O_3, and $FeBr_2$, respectively, which are manufactured as spherical pellets. Only gases are passed through the reactors which eases material flow control. Eleven cycles have been completed with a yield of 0.2 - 0.3 l of hydrogen per cycle [59, 90].

A **modified UT-3 cycle** has been developed where the reactions are carried out adiabatically. A process evaluation promises a higher thermochemical efficiency compared with the non-adiabatic version. The combination of the modified process with an HTGR for hydrogen and electricity cogeneration is one aspect of the current research efforts. The concept of a plant has been developed for the production of 30,000 Nm^3/h. The hydrogen production rate varies with the thermal efficiency and the nuclear heat input (see Fig. 4-10) [59].

The UT-3 cycle has also been studied based on solar as the thermal energy source. Its flow sheet needs to suit the intermittent characteristics of the heat source as day/night operation. Kinetic studies have shown that it takes about one hour for a complete cycle. Hydrogen generation rate is designed to be 2000 Nm^3/h. Surplus solar energy that is not immediately used could be stored and retrieved at night to allow a continuously running process. The calculated thermal efficiency of the solar cycle is 49.5 % [60].

4.5.2.6. Hydrogen Production by High-Temperature Electrolysis of Steam

Another candidate for nuclear process heat application is hydrogen production by means of **high-temperature electrolysis of steam**. It has already been tested by JAERI in a bench-scale facility. With the experience gained, design data on the process characteristics are to be derived. Experiments conducted in a serial arrangement of 12 tubular-type cells at a temperature of 850 °C resulted in a maximum yield of 4 Nl/h of hydrogen, which was increased to 7.6 Nl/h for a temperature of 950 °C. The maximum efficiency was with 80 % rather low. Tests have started with a planar-type cell. Hydrogen production densities were shown to agree well with the theoretical values, however, on a still very low efficiency level [54].

Next steps are the cell optimization, use of new construction materials, and completion of the system with ancillary equipment. The construction of a prototype system is planned with a capacity of 10 and later 100 Nm^3/h [30].

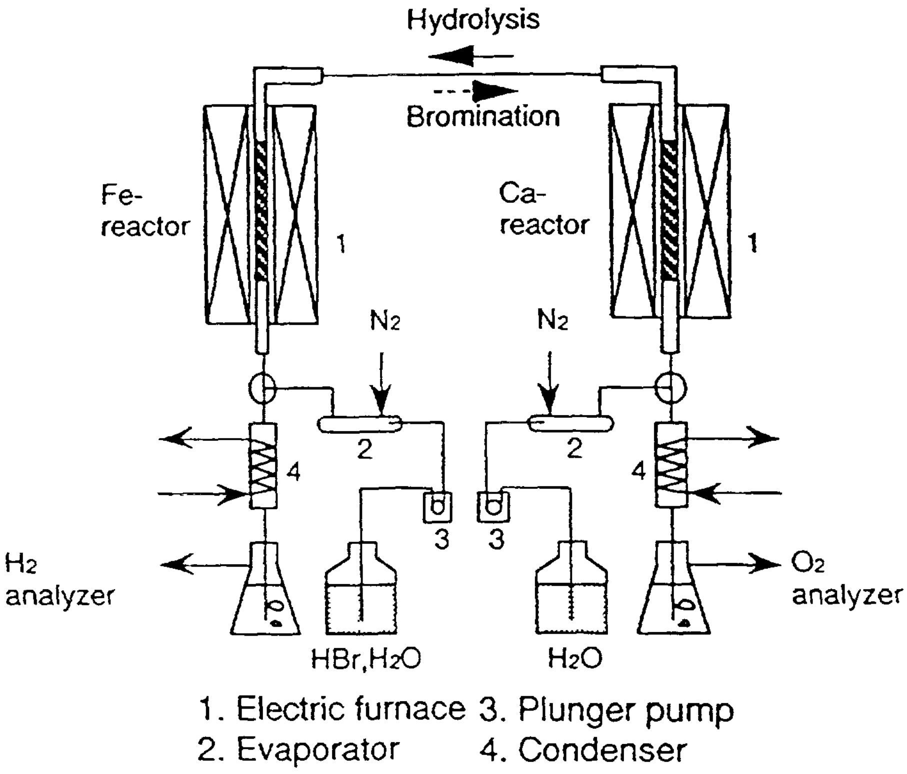

Fig. 4-9: UT-3 cycle system MASKOT, from [90]

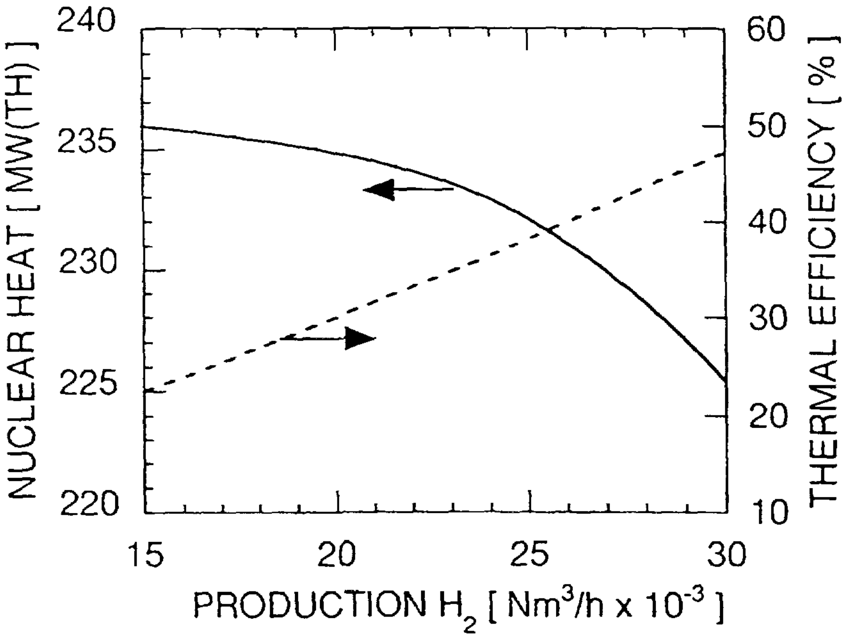

Fig. 4-10: Nuclear heat required and process thermal efficiency as a function of hydrogen production rate, from [59]

A 350 MW(th) HTGR is planned to be connected to 38 high-temperature steam electrolysis units, either one in a cylindrical vessel of 5 m height and 4 m diameter. The electric power required will be 139 MW resulting in a total hydrogen production of 39,000 Nm^3/h [48].

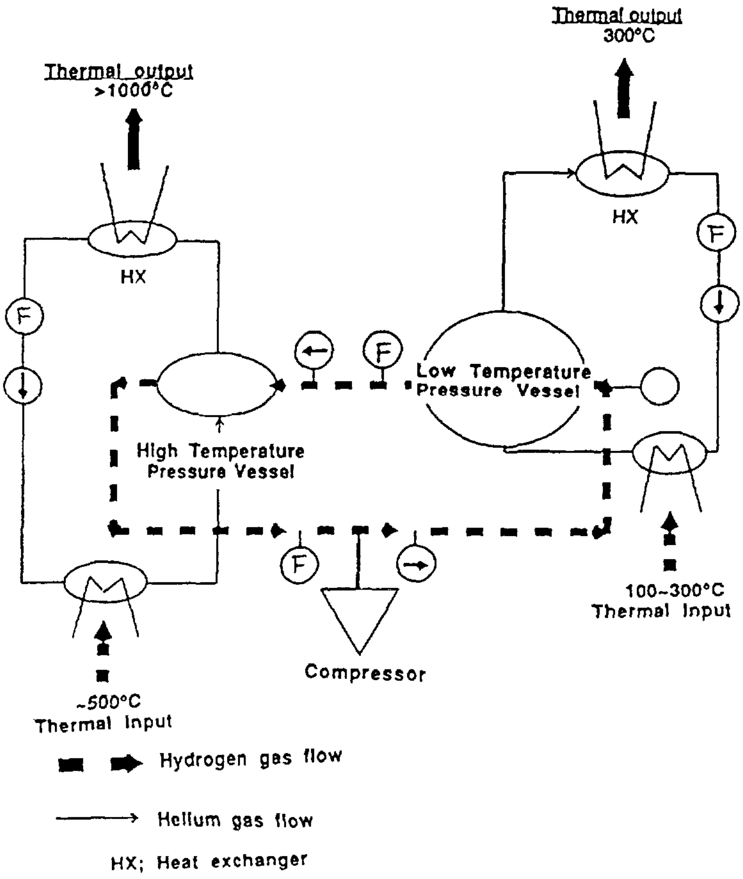

Fig. 4-11: High-temperature chemical heat pump test system at JAERI, from [36]

4.5.2.7. HTTR High-Temperature Chemical Heat Pump System

A **high-temperature chemical heat pump system** has been designed at JAERI to heat up waste heat of about 500 °C to above 1000 °C by using Ti/Cr metal hydride intermetallic compounds (Fig. 4-11). This method would improve the total energy efficiency of the hydrogen production system combined with the process heat provision by the HTTR. The system consists of a low-temperature and a high-temperature vessel with the metal hydride material. The exothermal process of hydrogen absorption by the metal is able to heat up helium to approx. 1000 °C as was demonstrated in a test system [36].

4.6. THE NETHERLANDS

Within the so-called **WHITE** ("Widely Applicable High Temperature Reactor") program, the design of a small-sized HTGR for combined heat and power generation, INCOGEN, is being developed. The reactor of choice is a 40 MW(th) direct-cycle pebble-bed reactor with a so-called peu-a-peu[15] loading scheme [67].

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[15] The peu-a-peu loading scheme is characterized by a slow, but steady fueling of the core resulting in just a small amount of surplus reactivity. One single loading cycle could encompass the whole reactor lifetime. For the INCOGEN concept, a 10-years cycle is considered.

4.7. RUSSIAN FEDERATION

4.7.1. Energy Situation in Russia

The energy economy in Russia is the largest provider of foreign exchange in international trading and usually considered the backbone of the Russian economy. It is also strongly influenced by the present economic crisis in the country. The region of the former USSR was the only in the world where the energy consumption was decreasing in 1996, minus 2.5 %, compared with the year before due to a lower demand by the domestic industries of the CIS[16] countries. Also the consumption per capita was reduced by a third in the past five years and has reached European level, approx. 3 TOE or 125 GJ [7]. The shares of electric capacity are 9 % nuclear, 22 % hydro, and 69 % fossil fuels [55]. The consequence has been a 30 % reduction of the CO_2 emissions compared with the 1990 level. According to the Kyoto agreement from 1997, Russia's greenhouse gas emissions have to stabilize at the 1990 level, thus seeming predestined to trade emission permits to the high-polluting countries.

The present economy crisis in Russia is thought of being a threat to energy supply security in the immediate future. The ongoing restructuring of the energy economy has led to a significant fraction of idle nuclear and hydro power capacity [55]. Current nuclear power in Russia allows the production of 20 GW electricity with a significant fraction dedicated for export to the other CIS countries or to the Scandinavian countries. However, within the next 10 years, about 60 % of the reactors are expected to reach the end of their lifetime. The Russian nuclear program is largely based on 1000 MW(e) units, but the 500 - 600 MW range is well represented in the development program. The nuclear option seems to have much better economics compared with conventional sources for application in remote areas, e.g. heating. The Russian Federation has also designs for HTGRs in the range of 50 - 400 MW(e). The VGM reactor with 200 MW(e) is intended for process heat application with helium outlet temperatures up to 900 °C [33].

4.7.2. Experimental and Theoretical Activities in Russia

Due to great experience in the development and construction of gas turbines, designs of HTGRs are being considered using a direct helium cycle, a cycle with intermediate heat exchanger, and the combined gas-steam cycle. The **MVGR-GT – 200 MW(th)** is a pebble bed HTGR in a closed-cycle gas turbine system. Helium coolant temperatures are 400 °C at the inlet and 850 - 950 °C at the outlet. The **HTGR-10 MW(th)** is thought of as being appropriate for decentralized power supply. Its design includes an intermediate loop and a combined gas-steam cycle.

The **GT-MHR – 600 MW(th)** concept of a direct cycle HTGR is a joint development by the US General Atomics and Russia's Minatom starting in 1995 and since 1997 supported by the French Framatome and Fuji Electric, Japan. It is planned to be built as modules of 250 - 285 MW(e) each with a prismatic core for commercial electricity generation and, in particular, for the burning of weapon-grade plutonium. A prototype and a plutonium

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[16] CIS - Community of Independent States is the successor of the USSR.

fuel production facility is intended to be constructed at the Siberian Chemical Collective Combine in Seversk [39].

The conceptual design of a 200 MW modular high-temperature gas-cooled reactor, **VGM**, has been developed and is intended to be used for process heat applications in various industrial branches including oil refineries, petrochemical plants, and the production of hydrogen, methanol, and synthetic fuels. To assure a high level of safety, the system is designed to have a helium-to-helium IHX and a helium-to-silicon oil process heat exchanger (PHX) [23]. The single-cycle variant, **VGMP**, with 215 MW(th) is completely orientated towards production of process heat. A design including three units has been made for connection to a standard oil-refinery plant [23].

4.8. SOUTH AFRICA

In 1996, the installed electricity capacity in South Africa was 38.5 GW with 90 % provided by coal-fired power plants. The only non-coal power station for base load is nuclear (two units of 965 MW(e) each). The fact of a continuously growing demand for more electricity in South Africa has raised serious consideration on installing new power plants. An alternative contestant to a conventional coal plant which must be erected near the coal mining, is a modular high-temperature direct-cycle reactor which could be erected in the electricity consuming coastal area and which is considered to increase diversity. The pre-conceptual design of a pebble bed HTGR with 900 C gas outlet and 558 C gas inlet temperature and a peu-a-peu loading scheme for pure electricity production is currently investigated. Reference size will be 100 MW(e) or 222 MW(th). The cost target fixed at < 1000 US $/kW is probably achievable only under series construction conditions (> 10 modules) [21, 52]. The option of a gasification system for upgrading the enormous domestic coal reserves should be given a thought.

The company Sasol operates a synthetic fuel production facility consisting of 48 coal gasification (Lurgi) units. The product gas is generated at a rate of 2.1 million Nm^3/h with a 38 % hydrogen share and is used for gasoline and diesel production by means of Fischer-Tropsch synthesis [78].

4.9. USA

4.9.1. Energy Situation

In 1994, electricity production in the United States winded up to $3*10^{12}$ kWh from a mix of energy sources with coal (55 %), nuclear (20 %), natural gas (11 %), hydro (9 %), oil (3 %) as the most significant energy sources. Renewable energies supply 2 % of the national electricity and 8 % of the energy demand, respectively, with 90 % of the current solar, wind, and geothermal generation residing in California [6]. The United States are ranking first in the annual energy consumption of more than 6 TOE per capita in 1996. With 20 %, the USA are also ranking first in the world's CO_2 emissions. Greenhouse gas emissions have increased in 1996 by 3.4 % along with the energy consumption (plus 3.2 %) compared with the year before and are 8.3 % above the 1990 level. The USA's obligation from the Kyoto summit in 1997 is a greenhouse gas emission reduction of 7 % below the 1990 level.

A fraction of 45 % of all industrial energy consumption in the US is used at temperatures below 300 C, a temperature compatible with LWRs. The huge hydrocarbon reserves that exist in the USA in the form of coal and natural gas could be easily used for effective alternate transportation fuel production.

Despite the fact that in the past 25 years no further nuclear power plant beyond the existing 107 units (1997) in the USA was licensed and no new plant is planned (for economic reasons), the US Department of Energy (DOE) has recently proposed to increase the budget for nuclear R&D efforts by 44 %. The transition to smaller nuclear power units is expected to reduce the financial risk of the US utilities and to provide a better adaptation to the demand for further electric power [37]. The current strategy aims at the prolongation for the operational license of the plants.

Renewable energies have been demonstrated to be technologically successful, however, they have to compete against the conventional energy carriers whose prizes are artificially kept on a low level. Photovoltaics (PV) is currently encountering a strongly increasing market for off-grid electric power needs in the USA and also internationally. Research continues to improve system performance and reduce system cost. Small PV systems for remote applications are commercialized. Large-scale systems involving units with up to 8 MW are currently in the demonstration phase; units of 100 MW are expected before the year 2000 [87].

4.9.2. Experimental / Theoretical Activities

The 115 MW(th) **Peach Bottom** HTGR operated successfully for seven years until it was shut down for decommissioning in 1974. It served as an excellent test bed for fuel development. An extensive R&D program was conducted with the goal of generating real-time integral data to validate HTGR design methods.

The **Fort St. Vrain** (FSV) HTGR was designed to produce 842 MW(th) and 330 MW(e). Its operation between 1979 and 1989 provided invaluable fuel performance, fission product release and plentiful data that have been used for further validation of respective calculational tools. Fort St. Vrain represents now the world's first successful decommissioning effort for a long-term operating commercial nuclear reactor.

Within the US HTGR program established by the Gas-Cooled Reactor Associates (GCRA), a reference conceptual design of an **1170 MW(th) HTGR** plant was developed based on a prismatic core for steam / electricity cogeneration, which is readily adaptable to various applications. Expected performance parameters for the reference design are coolant inlet / outlet temperatures of 318 and 686 °C at a system pressure of 7.2 MPa, a net electric output of 120 MW, and cogenerated process steam of 356 °C at 4.5 MPa with the amount of 1225 t/h. Multipurpose applications proposed for this design include [43]

- a "Sensible Energy Storage" (SES) system based on a molten salt (sodium nitrate, potassium nitrate) circuit for thermal energy storage and transport,
- a gas turbine cogeneration system utilizing the higher hot gas temperature of > 850 °C yielding a higher efficiency, and
- a process heat system employing the chemical reforming process with synthetic fuel or chemical feedstock as the principal output.

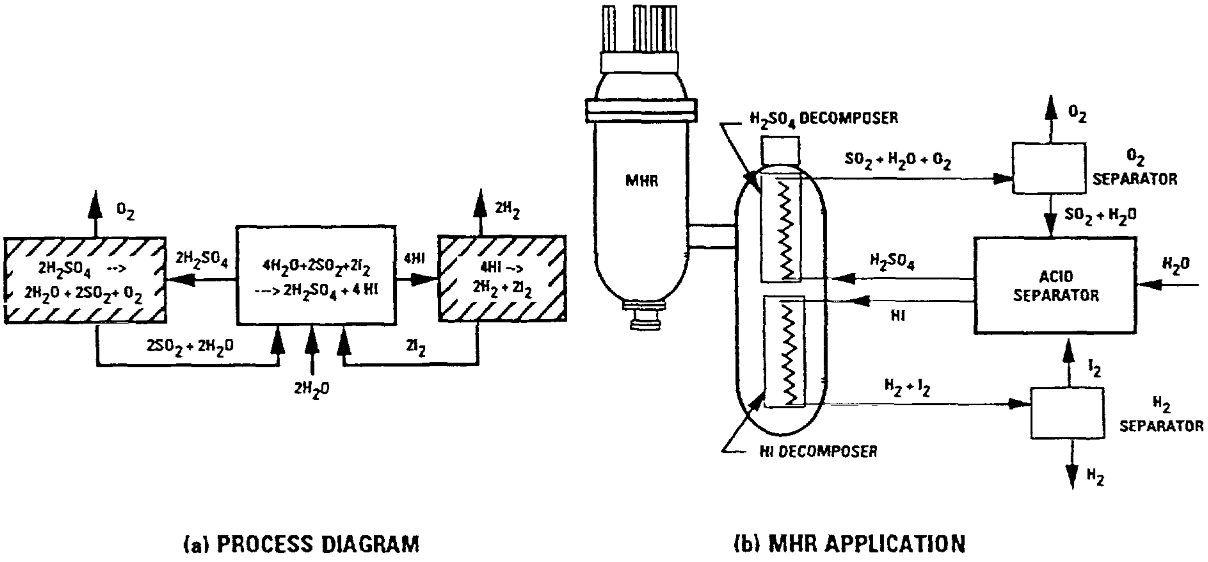

Fig. 4-12: Schematic of hydrogen production by the IS thermochemical cycle using MHR process heat, from [71]

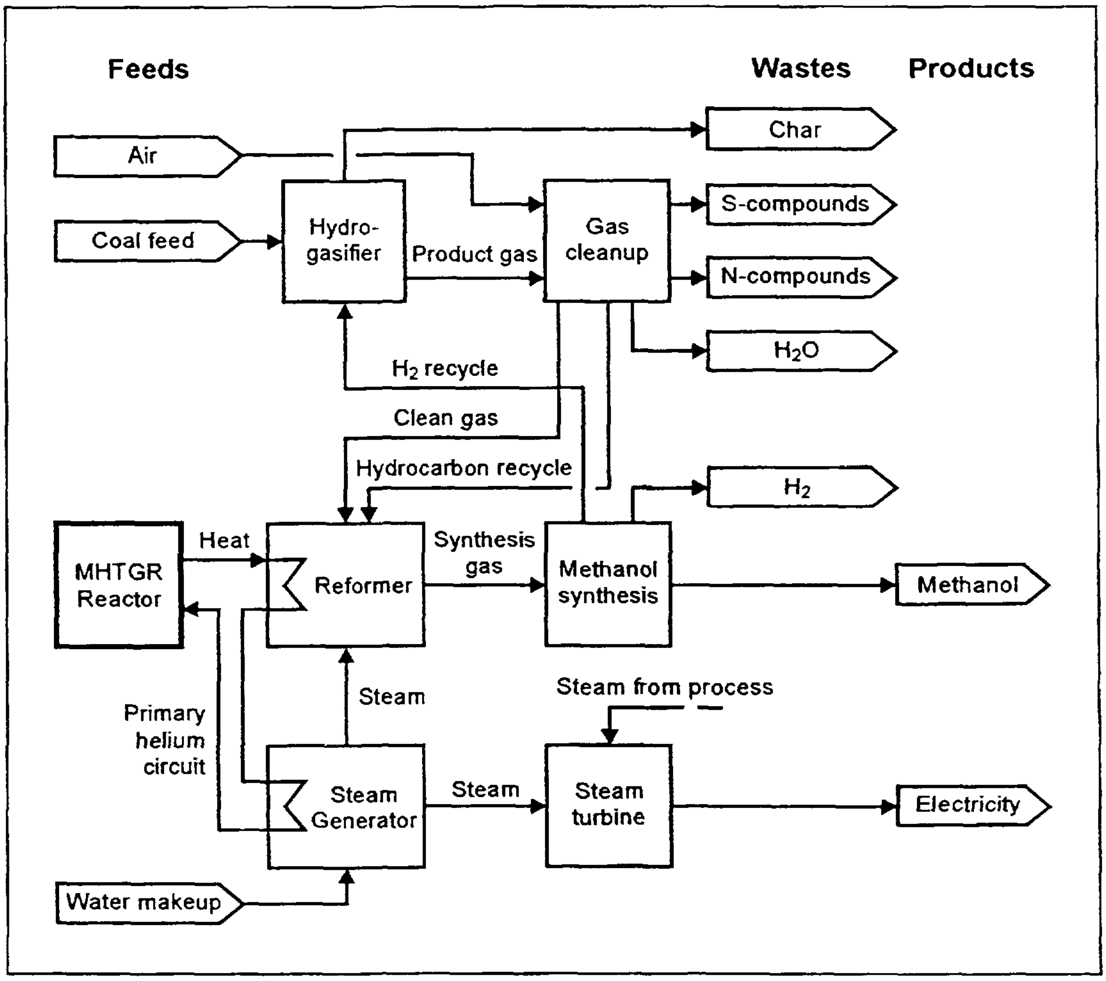

Fig. 4-13: Schematic of methanol processing based on a process heat MHTGR, from [63]

The **MHTGR-GT** is considered a second generation meltdown-proof nuclear power plant combining the experience of both gas-cooled reactor technology and industrial gas-turbine technology. The core consists of 84 columns of graphitic fuel elements in an annular arrangement. Helium inlet / outlet temperatures are 590 and 844 °C, and the reactor power is 450 MW(th) with a projected efficiency of 46 % if optimized for electricity production. A characteristic feature of the closed-loop Brayton cycle is its potential, besides electricity generation, for efficiently utilizing waste heat, e.g., for desalination, district heating, or steam generation.

The use of an MHTGR was studied for methanol synthesis from coal without CO_2 production. Besides coal and steam, the process requires a supplemental hydrocarbon feed or ideally hydrogen, also methane could be used, plus a non-combustion source of high-temperature heat which is ideally an HTGR. Based on coal with 60 % carbon content and a conversion rate of 80 %, a balance of the process was predicted such that with an input of 162 t/h of coal and 69.4 t/h of methane and an electric power of 300 MW yields 347 t/h of methanol [64].

A follow-up design is given in the **GT-MHR** (Modular Helium Reactor) (see also section 4.7.2.) with a higher power output of 600 MW(th). A standard plant is planned consisting of four of those units. Helium inlet/outlet temperatures are 485 and 850 °C, respectively. The cycle efficiency is predicted to be 47 % [51]. Follow-on evaluations which need to be done include the study of transient response of plant components to normal and off-normal events, impact of turbine contamination, and confirmation of plant efficiency [47].

The process steam/cogeneration variant of the MHR ("PS/C-MHR") has been studied at General Atomics for applications in heavy oil recovery, coal conversion, and in steel and aluminum processes. The process heat variant ("PH-MHR") provides the potential for fuels production including methane, synthetic gasoline, hydrogen, or methanol. The processes favored are hydro gasification of coal and methane reforming [72]. Also the employment of the iodine-sulfur (IS) thermochemical cycle for hydrogen production originally developed by General Atomics is conceived being applicable using MHR process heat; a respective diagram is depicted in Fig. 4-12 [71].

The generation of electrolytic hydrogen is achieved by selecting an MHR system in the electricity generation mode [72]. The two major safety aspects, higher operating temperatures and tritium permeation to the product gas, were evaluated and shown not to be a serious concern for the nuclear process heat plant [63].

A schematic of methanol processing on the basis of an MHTGR-PH is shown in Fig. 4-13, in this case with CH_4 as supplemental feed. The performance of the process components is depending on the operating conditions. Thermal efficiencies are expected in case studies to be up to 61 % [63].

The Advanced Pressurized Reactor **AP-600** (Westinghouse) final design certification by NRC is expected for 1998. A larger unit of an advanced PWR, the **System 80+**, with 1300 MW(e) is being developed by ABB/Construction Eng. [86]. These designs with enhanced passive safety features are pursued in the USA to provide additional electricity and replace retired plants.

Also the boiling water reactor is the basis for an innovative design with passive safety installations, sized approx. 1300 MW(e) for the "evolutionary" type designed by General Electric in cooperation with Hitachi/Toshiba and approx. 600 MW(e) for the passively safe reactor. Of the former type, two units have commenced commercial operation in Japan since 1996 [86].

4.10. VENEZUELA

Venezuela is one of the world's largest energy suppliers, in particular, of extra-heavy crude oils and bitumens. Continuous steam injection could raise the oil recovery rates. Studies have been conducted in Venezuela to apply a high-temperature gas-cooled reactor to the chemical processes of extracting and upgrading the domestic heavy crude oil resources, of the production of synthetic fuel, and of the gasification of extra heavy oil and the so-called Orimulsion (mixture of bitumens and water) fuel [18].

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Chapter 5

CONVENTIONAL AND ADVANCED HYDROGEN PRODUCTION METHODS

The most obvious pathways for the production of hydrogen from different primary energy sources are shown in Fig. 5-1. The efficiency of a conversion method is strongly dependent on the level of temperature at which the respective chemical reactions take place.

The world hydrogen production today is $500*10^9$ Nm^3 which corresponds to 2 % of the world's primary energy demand. Most part of it, 97 %, is produced from fossil fuels.

5.1. DECOMPOSITION AND GASIFICATION OF FOSSIL FUELS

5.1.1. Conversion of Natural Gas

5.1.1.1. Steam Reforming

The most widely used method of hydrogen generation is **steam reforming of natural gas**, which offers many advantages: Natural gas is available in large amounts; its commercial production in 1992 winded up to $2.1*10^{12}$ m^3. It is clean and can relatively easily be converted to hydrogen.

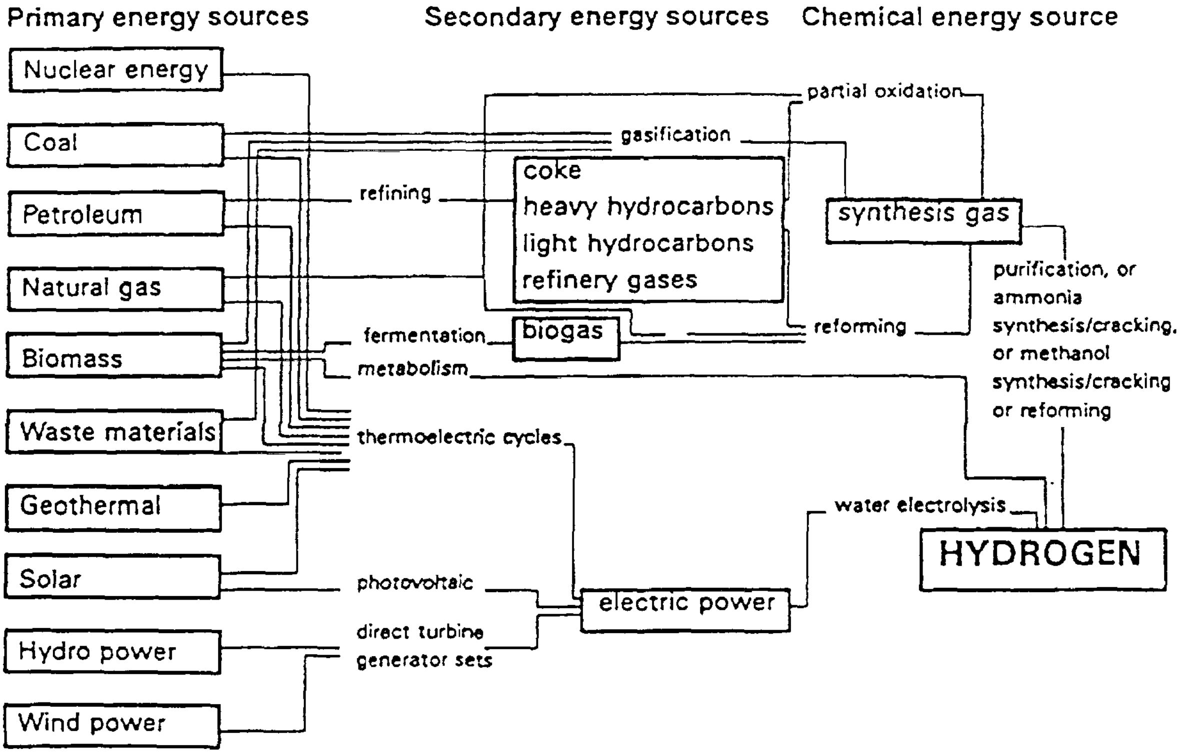

Fig. 5-1: Sources and production of hydrogen, from [21]

During the steam reforming process, natural gas is mixed with steam to react in a wide range of high temperatures, typically > 500 °C up to 950 °C, in the presence of a nickel catalyst. The **steam reforming reactions** are:

$$CH_4 + H_2O \longleftrightarrow CO + 3\ H_2 - 206\ \text{kJ/mol}$$
$$CH_4 + 2\ H_2O \longleftrightarrow CO_2 + 4\ H_2 - 165\ \text{kJ/mol}$$

or for light hydrocarbons in general:

$$C_nH_m + n\ H_2O \longleftrightarrow n\ CO + (1/2\ m + n)\ H_2$$

At a stoichiometric ratio, the conversion rate to the right-hand side is maximal for high temperatures and relatively low pressures. However, excess steam of 300 % away from the stoichiometric mixture is generally injected to move the equilibrium towards more CO_2 in the homogeneous **water-gas shift reaction**

$$CO + H_2O \longleftrightarrow CO_2 + H_2 + 41\ \text{kJ/mol}$$

in order to achieve a higher H_2 yield and to preclude carbon deposition due to the **Boudouard reaction** which is also catalyzed by nickel:

$$2\ CO \longleftrightarrow CO_2 + C + 172\ \text{kJ/mol}$$

The yield of the reforming process is a mixture of H_2, CO, CO_2, plus residual steam and still unreformed methane, the so-called reformer gas. The equilibrium composition of the gases depends on the process parameters temperature and pressure which are chosen according to the desired subsequent synthesis gas applications. The example shown in Fig. 5-2 is for a 4 MPa system pressure and a water to methane ratio of 2. The mixture of H_2 and CO left after purification is what is called **synthesis gas** which is an important feedstock in the chemical industry.

If the reforming reaction is carried out at additional presence of a selected adsorbent for CO_2, the reaction temperature is significantly lowered down to 300 - 500 °C while achieving the same conversion of methane to hydrogen plus the purity of the hydrogen is higher. This new process, **sorption-enhanced reaction** (SER), reduces the traditional downstream hydrogen purification step and could make small plants more economic [1].

5.1.1.2. CO_2 Reforming

If the steam is completely or partly replaced by carbon dioxide, the result is another H_2 to CO ratio, shifted towards a more CO-rich synthesis gas. The catalytic reforming of CH_4 with CO_2, first proposed in 1928 by Fischer and Tropsch, involves an environmental benefit, because two greenhouse gases are combined here resulting in a product gas which

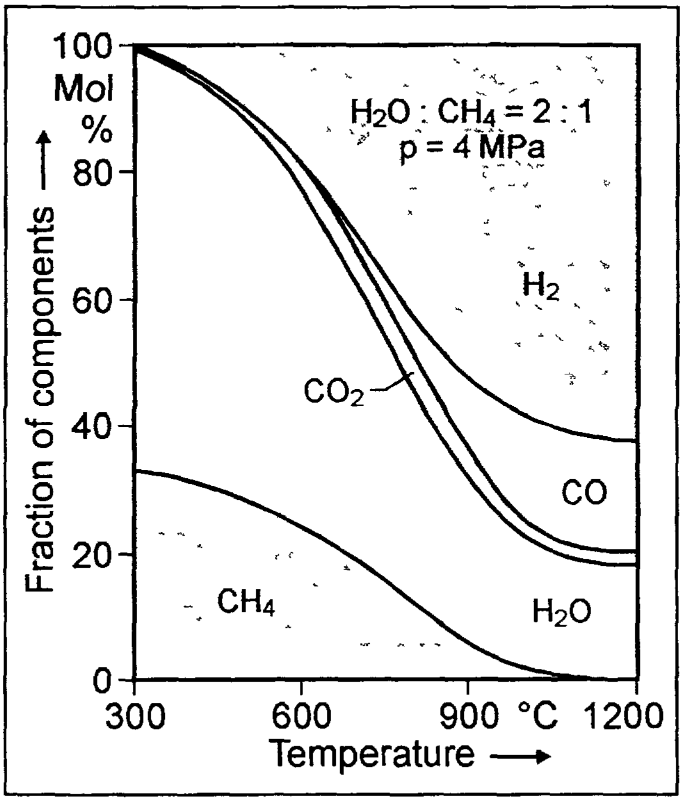

Fig. 5-2: Equilibrium composition of gases involved in the methane reforming process as a function of temperature, from [16]

might be more favorable for certain applications, e.g., the synthesis of valuable oxygenated chemicals [68].

$$CH_4 + CO_2 \longleftrightarrow 2\,CO + 2\,H_2 - 247\ \text{kJ/mol}$$

Side reactions are the reverse water gas shift reaction, the Boudouard reaction and methane cracking, where the former two are suppressed at temperatures > 820 °C and the latter two form carbon in the temperature range 550 - 700 °C [68].

However, currently no industrial technology for the CO_2 reforming of methane is established. The reasons for this are the rapid deactivation of conventional catalysts if used without the presence of steam, and the relatively high soot formation [68].

5.1.1.3. Partial Oxidation

Partial oxidation is able to convert methane and other hydrocarbons heavier than naphta, catalyzed or non-catalyzed, where steam reforming is not applicable:

$$CH_4 + 1/2\,O_2 \longleftrightarrow CO + 2\,H_2 + 71\ \text{kJ/mol}$$

or for hydrocarbons in general:

$$C_nH_m + 1/2\ n\ O_2 \longleftrightarrow n\ CO + 1/2\ m\ H_2$$

The catalytic process works at about 600 °C using methane or naphta feedstock. The non-catalytic process works at temperatures between 1100 and 1500 °C and in the pressure range 2 - 6 MPa using hydrocarbons from methane to heavy oil and coal. Pure oxygen from a preceding air decomposition step is taken because of the difficulty to clean the hydrogen from the nitrogen. Immediate feeding of water prevents undesired reverse reactions (quenching). Despite its lower efficiency of approx. 50 % compared with steam reforming, partial oxidation provides, on the other hand, exothermicity and a greater selectivity for synthesis gas production as well as advantages for certain applications such as compactness, rapid start-up or load change, and lower overall cost [21, 68].

If steam is added to the fuel and the oxidant, it is possible to heat balance the exothermal partial oxidation reaction with the endothermal reforming reaction. The reaction is then said to be **autothermal**, meaning that no external heat source is required what raises the efficiency.

A simulation model is currently applied to investigate the partial oxidation of methane in a fluidized bed of catalyst particles with some tenths of a millimeter diameter, rather than in a solid bed. This procedure is expected to provide a much better heat exchange. Total cost reduction is predicted to be about 20 %, which, however, still needs verification [72].

5.1.1.4. Reduction of Metal Oxides

In the temperature range 900 - 1100 °C, gallium (also tungsten) oxide is reduced to the metal by use of methane:

$$3\ CH_4 + Ga_2O_3 \longleftrightarrow 2\ Ga + 3\ CO + 6\ H_2$$

with the gallium oxide recycled in an oxygen-rich atmosphere. The problem in this reaction is that the activity of the metal decreases over repeated oxidation / reduction cycles [21].

5.1.1.5. Thermal Cracking

An alternative to the steam reforming of methane is single-step thermocatalytic decomposition or "**thermal cracking**". Methane and other hydrocarbons decompose at temperatures between 700 and 980 °C and, if no air is present, form hydrogen and carbon:

$$CH_4 \longleftrightarrow C + 2\ H_2 - 75\ kJ/mol$$

This process has been practiced over many years for the production of carbon black for rubber tire vulcanization and for the printing industry. Despite the advantage that no carbon dioxides are formed, it is often considered an unwanted reaction because of the formation of solid carbon [21].

Cracking was studied for various catalysts in both continuous flow and pulse catalytic reactors. Variations in the operational parameters were found to produce CH_4 - H_2 mixtures with a wide range of hydrogen concentrations, from 30 to 98 vol% [39].

For the thermal cracking, a tandem furnace can be operated where a methane-air flame is used to heatup firebrick to $\approx$ 1400 °C. The air is then turned off and the methane decomposes on the hot brick until the temperature drops below 800 °C. The H_2 enriched effluent gas stream is taken to heatup the second furnace. A continuous process is thought of as being possible also, but has not yet been practiced on a commercial scale [55]. A small-scale catalytic propane cracker has been realized at the Duisburg University, Germany (see section 9.4.).

The **Kvaerner process** is the non-catalized thermal decomposition of hydrocarbons with no emission of CO_2. Pyrolysis is done by means of an electrically heated plasma burner. Products are high-purity hydrogen plus carbon black, also an important industrial product. The specific energy demand is with 1.01 kWh/Nm^3 of hydrogen about a quarter of that of an advanced electrolyzer. A pilot plant based on the Kvaerner process is currently operated with a capacity of 8 million Nm^3 of H_2 and 2000 t of soot [60]. The construction of a larger facility in Canada is planned. It will be fueled by natural gas and optionally oil providing carbon black in the amount of 20,000 (later 90,000) t/yr and hydrogen in the amount of 50 (later 225) million Nm^3 [8].

High-temperature, non-catalytic reforming of hydrocarbons using plasma technology is investigated in the USA at the MIT Plasma Fusion Center. **Plasma reforming** is flexible in fuel because it consumes any hydrocarbon including heavy fractions. The fast kinetic rates can greatly reduce volume and weight of the reformer. An experimental facility was constructed and initial tests have been performed [18].

5.1.1.6. Methanol Dissociation

Methanol is endothermally cracked over a catalyst to produce synthesis gas plus traces of methanol, ether, and methane. A two-stage membrane separation system extracts the hydrogen from a CO-rich fuel that fires the cracker (see Fig. 5-3).

$$CH_3OH \quad \rightarrow \quad CO + 2\ H_2 - 91\ \text{kJ/mol}$$

The catalytic decomposition of methanol by steam reforming as taking place in methanol fuel cells at temperatures > 250 °C is described by the reaction:

$$CH_3OH + H_2O \quad \rightarrow \quad CO_2 + 3\ H_2 - 50\ \text{kJ/mol}$$

A water to methanol ratio of greater than 1 plus considering that also the methanol cracking process (see first reaction equation) occurs, the only significant products are H_2, CO_2, and CO.

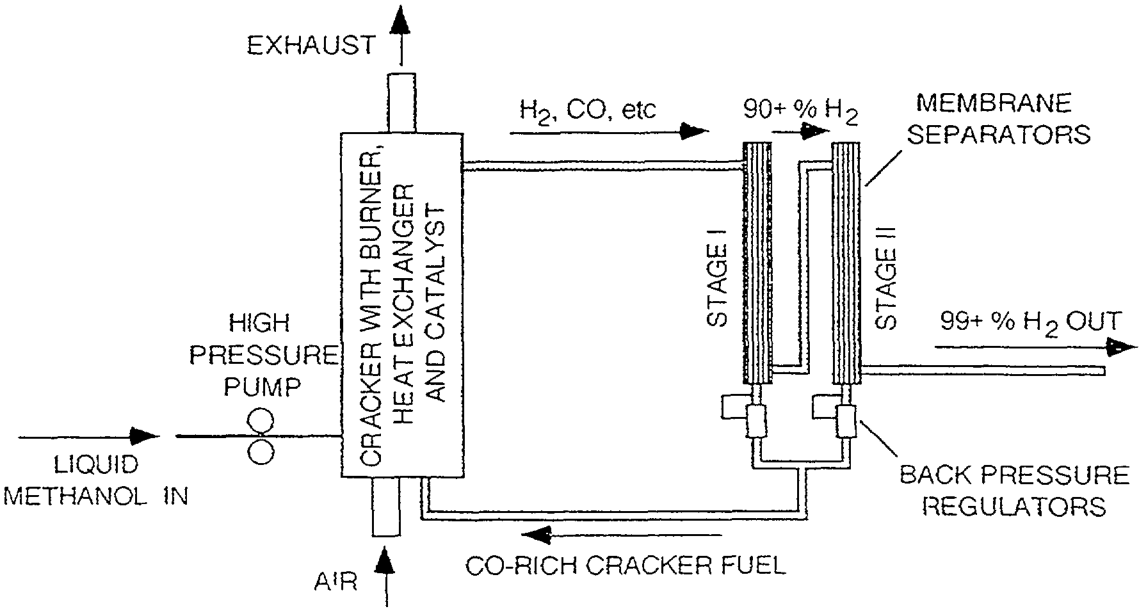

Fig. 5-3: Thermal cracking of methanol with a membrane separation system, from [34]

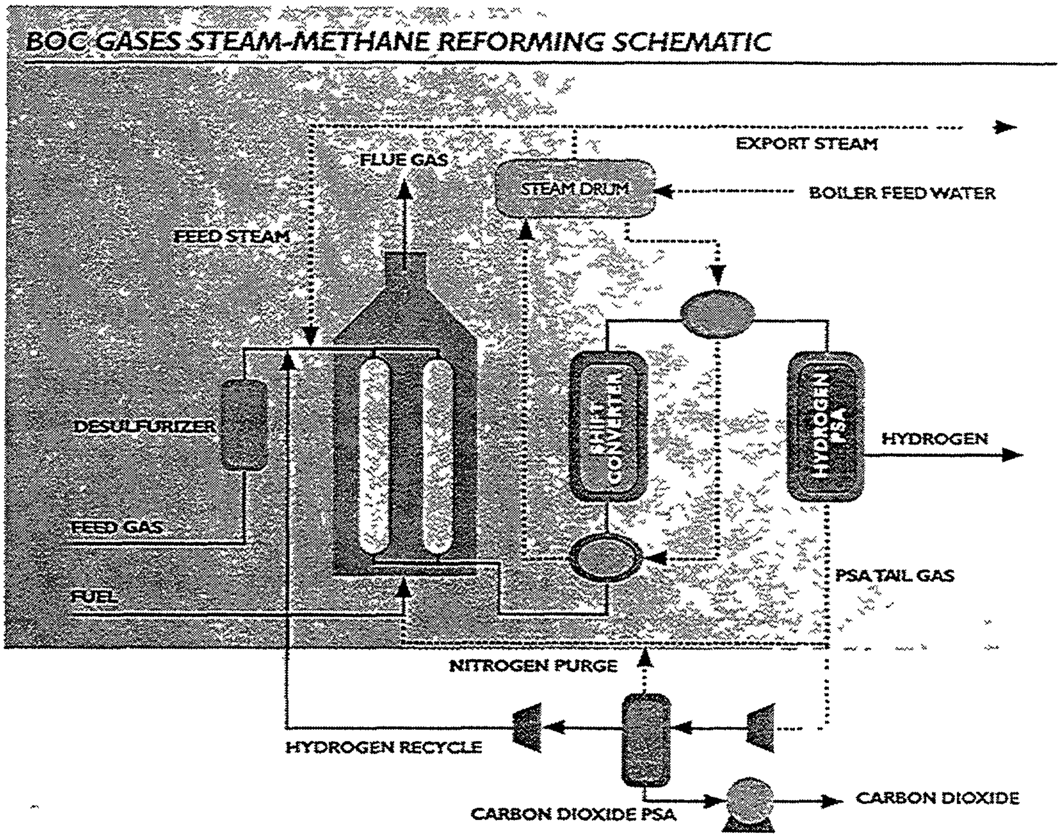

Fig. 5-4: Process flow sheet of hydrogen production from steam reforming of natural gas, from [BOC Gases]

5.1.1.7. Steam Reforming Process Technology

In the conventional steam reforming process (Fig. 5-4), the feed gas passes a desulfurization step to protect the catalyst against poisoning and is then routed to the steam reforming tubes which are externally heated mainly by heat radiation. The typical reforming temperature is 750 - 850 °C and the reforming pressure is 2 - 3 MPa depending on the application of the product gas. In the conventional process, the required energy is supplied by the combustion of light hydrocarbons. Combustion gases at a temperature of 1500 °C flow downwards through the steam reformer in parallel with the feed gas flow for the reforming process. Large amounts of heat are transferred in the upper section of the tube, but heat transfer decreases by about one order of magnitude from top to bottom. The average heat flux density is approx. 80 kW/m^2.

A typical reforming fraction in practice is 80 %. The CO in the gas mixture is converted after cooling in the shift reactor to CO_2. The gas mixture is then purified by passing special adsorber beds to obtain pure (> 99.99 %) hydrogen [38].

Steam reforming is a mature and well-established technology practiced on an industrial scale. Today's reformer plants for hydrogen production vary in size, from typically around 100 Nm^3/h capacity up to the largest currently existing with a maximum H_2 production rate of 140,000 Nm^3/h. Large-scale reformers could be used for H_2 supply to fuel cell applications at the 100 MW scale. Recent reformer improvement developments have focused on high efficiency, good load changing capability, and low cost through the use of cheaper materials and production methods [21].

A dominant problem for all synthesis gas processes is the **metal-dusting corrosion (MDC)** phenomenon. Further improvement of the reforming technology requires a minimization of MDC. Aging of the alloys and defects in the metal oxide layer as well as the gas atmosphere might explain this corrosion effect. A possibility for MDC prevention is the displacement of CO by a purge gas [28].

Membrane reformers take advantage of a useful feature of hydrogen, namely its ability to selectively permeate through Pd or Pd alloy membranes. As has been shown on a laboratory scale, the hydrogen is relatively clean and its continuous removal increases the methane conversion level [21].

Although **small-scale steam reformers** are commercially available today, relatively few small units have been constructed. Small size and suitability on a small scale makes them beneficial for integration into a fuel cell power plant. Fuel cell manufacturers are developing advanced miniaturized designs which are more compact for mobile applications.

A 50 kW multi-fuel partial oxidation processor coupled to an SPFC stack has been presented in October 1997 by Arthur D. Little Inc., USA, and test-operated in the meantime for more than 3000 h. The fuels that can be applied are gasoline, methanol, and ethanol; in a later stage, also diesel, oil, methane and propane processing will be possible [27]. In the UK, a bench-scale steam reformer system processing gasoline and diesel was successfully demonstrated for over 50 hours each. The H_2 concentration in the reformate was typically

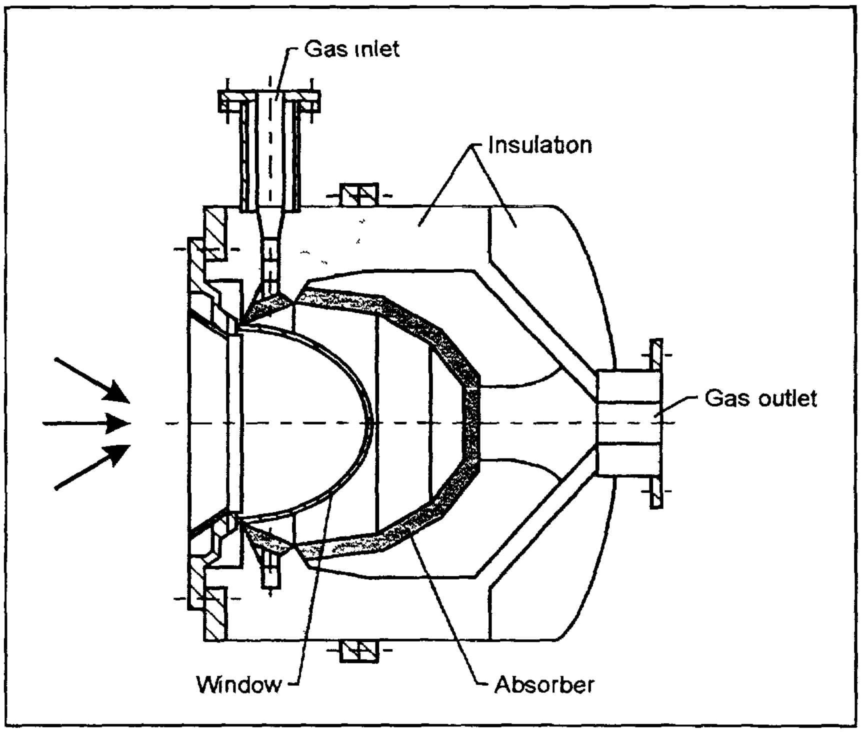

Fig. 5-5: Schematic of a directly absorbing receiver reactor, from [60]

76 %, the CO concentration less than 0.5 %. Both fuel processor developments are to be employed in fuel cell vehicles [7].

High temperature fuel cells (MCFC and SOFC) allow for the reforming process to take place inside the fuel cell stack which lowers the requirement for cell cooling and reduces cost due to absence of the external reformer vessel. A future SOFC application could also be the production of hydrogen (and electricity) by internal reforming of natural gas where more H_2 as a component of the synthesis gas is produced than can be converted electrochemically into electricity; the heat losses from the fuel cell operation would be used as the endothermal heat source for the reforming step [65].

A solar methane reforming process has been experimentally investigated in a joint German/Spanish project **ASTERIX** (Advanced Steam Reforming in Heat Exchange). Primary energy is solar at a temperature of 1000 °C. The convectively heated tube bundle reactor has a power of 80 - 170 kW. ASTERIX is designed for a product gas output of 115 Nm^3/h [60].

Other solar methane reforming projects are **CAESAR** (Catalytically enhanced Solar Absorption Receiver) in Germany with CO_2 reforming and **SCR** (Solar Chemical Reactor) in Israel. The latter is a directly absorbing receiver reactor (Fig. 5-5) with a power of 200 - 300 kW. The absorber structure allows an almost homogeneous distribution of solar flux and thus temperature. Conversion rates of 80 % have been achieved. Advantages are high heating rate and energy density, also the possibility to combine the external solar reformer gas to run a gas turbine, thus saving fuel up to 26 % [60].

5.1.2. Conversion of Coal

The most abundant fossil fuel on earth is coal. Its conversion to liquid and gaseous hydrocarbons has been commercially employed worldwide. In the first half of this century, it was the principal method of hydrogen production in the coke furnace process. The gas production from coal besides the anaerobic combustion process is realized by means of a gasification medium which reacts with the coal at temperatures > 800 °C. All organic constituents of the coal will be converted with long enough residence times. The gasification medium used is either steam ("steam-coal gasification") or hydrogen ("hydro-gasification"). If air or oxygen is injected into the gasifier, part of the coal is burnt directly leading to an autothermal reaction.

5.1.2.1. Steam-Coal Gasification

During steam-coal gasification, two consecutive chemical processes take place [30, 50]. The first process, the **pyrolysis reaction**

$$CH_xO_y \longleftrightarrow (1-y)\,C + y\,CO + x/2\,H_2$$

$$CH_xO_y \longleftrightarrow (1-y-x/8)\,C + y\,CO + x/4\,H_2 + x/8\,CH_4$$

is a very rapid expelling of all volatile constituents of the coal. In the subsequent, much slower step, steam of 600 - 1000 °C is needed to convert the residual organic solids in the heterogeneous water gas reaction:

$$C + H_2O \longleftrightarrow CO + H_2 - 163\ \text{kJ/mol}$$

with further increase of the H_2 yield in the shift reaction. The thermodynamic equilibrium composition of the product gas mixture is a function of temperature and pressure. As can be drawn from Fig. 5-6, the production of hydrogen and carbon monoxide is optimal at high temperatures and low pressures. The heat of the hot gas is recuperated for use in the production of high-pressure steam; the heat withdrawal must be quick to avoid reverse chemical reactions.

Despite its small hydrogen contents, coal gasification with oxygen and steam is used to generate about 18 % of the world hydrogen production. Also the production of methane or methanol or gasoline from the coal conversion step by modifying downstream treatment is conventional chemical engineering. Pulverized coal is rapidly partially oxidized by oxygen and steam in a fluidized bed at about atmospheric pressure. 30 - 40 % of the coal are transformed into CO_2 to supply splitting energy of water. The reaction rate strongly increases with temperature. Temperatures up to 2000 °C and pressures up to 3 MPa are typically chosen.

Pertinent criteria for applicability and economy of steam-coal gasification are the characteristics of the coal to be gasified. The (geologically) older the coal, the smaller is its reactivity and the higher is the temperature required [30]. Main disadvantages of coal gasification are the handling of solid material streams, which is generally more difficult

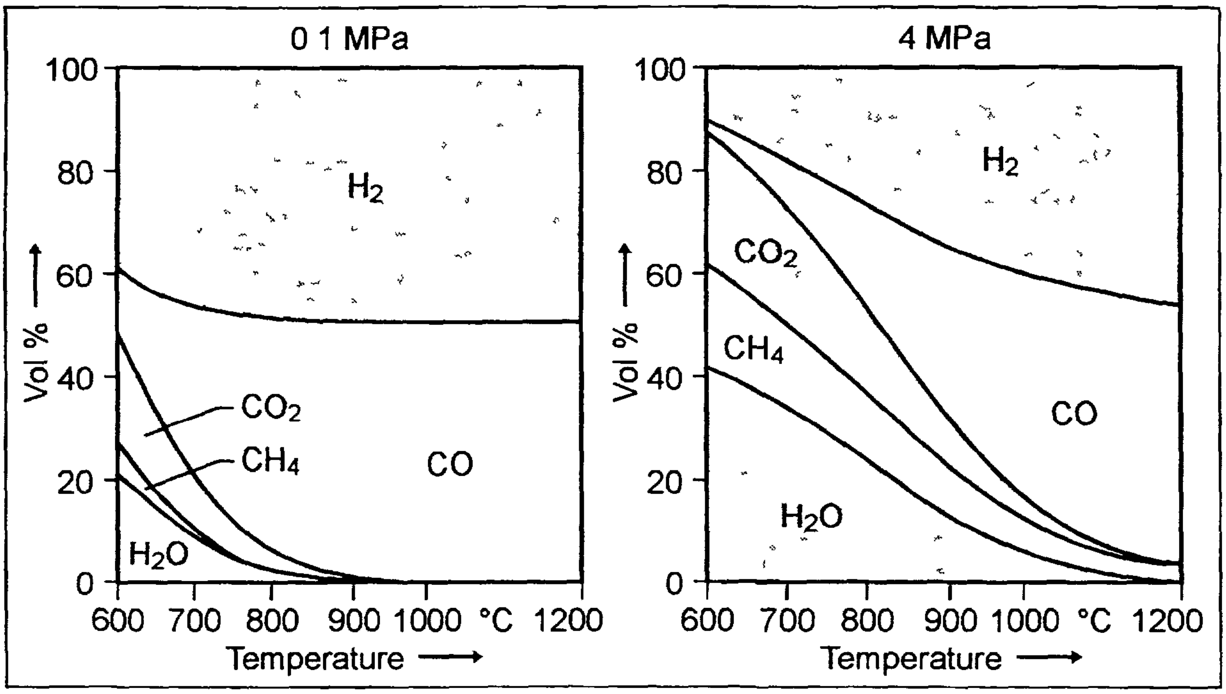

Fig. 5-6: Equilibrium composition of the product gas after steam-coal gasification as a function of temperature and (left) 0.1 MPa, (right) 4 MPa, from [30]

and more expensive than gaseous or liquid streams, and the large amounts of CO_2, SO_2, and ash produced during the process.

Different types of autothermal coal gasification processes used on a large scale are existent as shown in Fig. 5-7. Lurgi, Winkler, Koppers-Totzek, and their modifications, respectively. Their characteristic features are summarized in Table 5-1.

The **TEXACO** gasification process operates at high pressures ($\approx$ 5.5 MPa) and high steam contents. The synthesis gas typically contains 34 % H_2 and 48 % CO. Hydrogen of > 97 % purity is yielded at a pressure of 4 MPa to reduce energy consumption during H_2 pressurization [55].

At present, coal gasification is primarily used for ammonia synthesis in the fertilizer industry and for synthesis gas production to be employed in the hydrocarbon and methanol synthesis with large-scale production facilities, in particular, in the developing countries. Hydrogen production is of minor importance.

The option of integrating the steam-coal gasification process in a combined heat and power facility with a gas turbine step preceding the water/steam process, is currently considered the cleanest and most efficient (34 → 38 %) coal-fueled technique so far, and the combined-cycle portion could be switched to different fuels, e.g., natural gas or oil. The **Integrated Gasification Combined Cycle (IGCC)** technology with its intermediate stage of synthesis gas allows the removal of most carbon components before combustion. The separated CO_2 stream is of high purity and therefore suited for disposal. Adopting improvements in the turbine system, the overall efficiency is anticipated to be raised to 52 % [64]. Respective facilities have been realized so far in Germany and the United States

Table 5-1: Characteristic features of the steam-coal gasification processes after Lurgi, Winkler, Koppers-Totzek, from [30]

	Lurgi	**Winkler**	**Koppers-Totzek**
Reactor	Solid bed	Fluidized bed	Flue stream
Grain size [mm]	10 - 30	1 - 10	< 0.1
Steam over oygen ratio	9 - 5	2.5 - 1	0.5 - 0.02
Movement of fuel	countercurrent flow	vortex cocurrent flow	cocurrent flow
Residence time of fuel [*min*]	60 - 90	15 - 60	< 0.02
Requirements to fuel	must not bake or decay	high reactivity, must not decay	melting point of ash < 1450 °C
Maximum gas outlet temperature [°C]	370 - 600	800 - 950	1400 - 1600
Pressure [MPa]	2 - 3	atmospheric	atmospheric
Composition of product gas [vol%] $CO + H_2$ CH_4	 62 12	 84 2	 60 + 29 0.1
By-products	tar, oil, phenols, gasoline, waste water	none	none

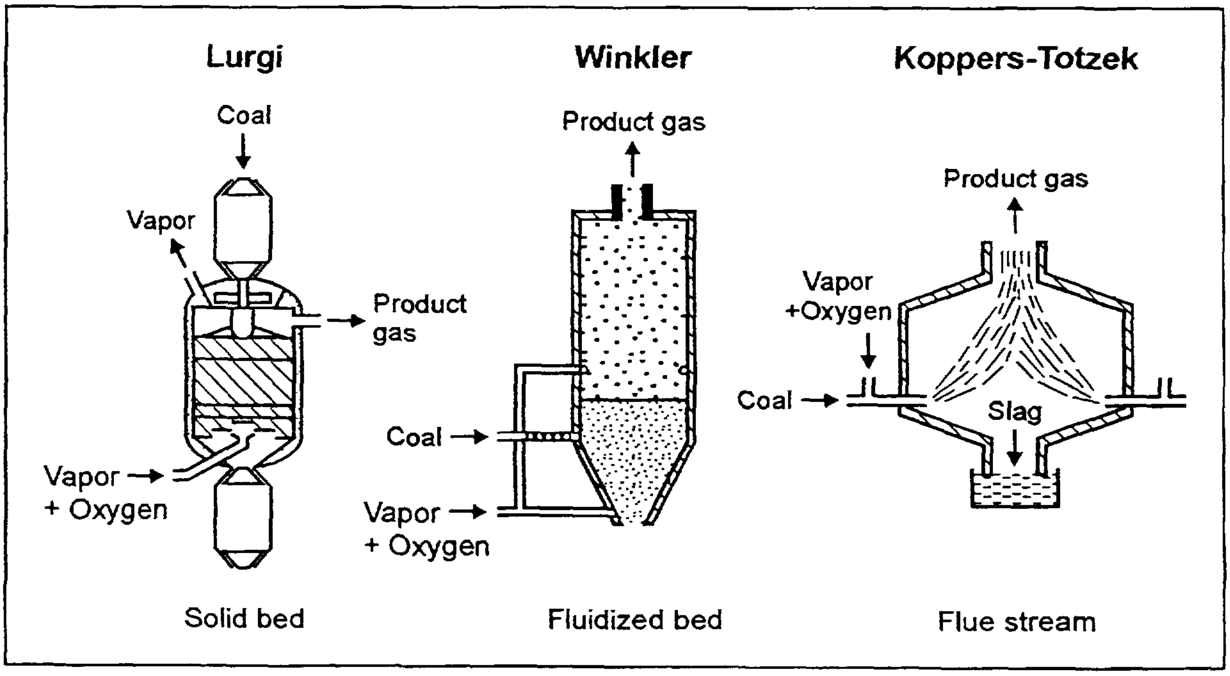

Fig. 5-7: Gas generator types for steam-coal gasification according to Lurgi (left), Winkler (middle), and Koppers-Totzek (right), from [66]

[30]. Some 4000 MW(e) of these IGCC power systems are planned for installation in the USA, Europe, and Asia [54]. The world's largest IGCC plant with 300 MW(e) is almost completed in Spain with an expected efficiency of 45 %.

A 300 MW IGCC power plant with electricity and methanol cogeneration has been proposed where 88 % of the carbon introduced by the coal can be extracted as CO_2 with an acceptable amount of energy and investment cost which is partially utilized in combination with H_2 from an external carbon-free source for methanol production. The overall balance for a 354 MW power plant (234 MW for the gas turbine and 120 MW for the steam generator) is an input of 2300 t of coal, 780 t of hydrogen, and 5500 t of CO_2 (as intermediate product) per day to achieve a daily output of 3800 t of methanol and a total net power output of 310 MW [44].

At a very early R&D level is the use of coal gasification integrated in a high-temperature **fuel cell** as a stationary power system (see section 7.2.2.3.).

5.1.2.2. Hydro-Gasification

In the hydro-gasification process, coal is converted to synthetic natural gas in a fluidized bed at temperatures of around 800 °C in an exothermal reaction:

$$C + 2\,H_2 \quad \rightarrow \quad CH_4 + 86\ \text{kJ/mol}$$

Parallel reactions are the steam reforming and the water-gas shift reactions to produce synthesis gas. The feed gas hydrogen could be taken either from a partial conversion of methane from the product gas in a steam reformer or from a conversion of the residual char with oxygen and steam in a high temperature Winkler process. A high gasification degree can be reached already with relatively short residence times (9 - 80 min) [50]. In order to obtain a high conversion rate of coal, the CH_4 fraction in the product gas of the reforming step (which will then be the feed gas for the hydro-gasification) should be no higher than 5 %, which requires a low-temperature separation step. Both reactions are carried out at system pressures of 4 MPa. The amount of 1.5 Nm^3 of hydrogen is required to produce 1 Nm^3 of synthetic natural gas [32].

After cleaning and separation, the methane is either utilized as a final product or fed into the reformer while the product hydrogen is available after the reforming process in the synthesis gas, subtracted by the portion that is required for the gasification step. The advantage of hydro-gasification compared with steam-coal gasification is its 200 K lower pre-heating temperature which reduces potential corrosive attack. A major drawback, however, is the relatively large amount of residual coke of up to 40 % [13]. Standardized reformer equipment for power industries is available.

5.1.2.3. Steam-Iron Process

The **steam-iron process** is another old hydrogen generation process. Although based on coal, it is actually a cycle process where hydrogen is generated from the decomposition of steam by reacting with iron oxide. The cycle, however, is not completely closed, since coal is consumed and CO_2 is emitted. The synthesis gas produced in the coal gasification step with steam is then reacted with iron oxide to generate reduced forms of iron oxides:

$$\begin{aligned} Fe_3O_4 + H_2 &\rightarrow 3\ FeO + H_2O \\ Fe_3O_4 + CO &\rightarrow 3\ FeO + CO_2 \\ FeO + H_2 &\rightarrow Fe + H_2O \\ FeO + CO &\rightarrow Fe + CO_2 \end{aligned}$$

In the following step, the reduced species are re-oxidized with water to form the original oxides plus a hydrogen enriched gas:

$$\begin{aligned} Fe + H_2O &\rightarrow FeO + H_2 \\ 3\ FeO + H_2O &\rightarrow Fe_3O_4 + H_2 \qquad 815 - 870\ °C \end{aligned}$$

Reduction and oxidation step in two separate reactors allow for a continuous hydrogen production. A major drawback is the small conversion rate of 60 % of the synthesis gas in the reduction step. The effluent from the steam-iron reactor contains 37 % H_2 plus 61 % steam and 96 % H_2, respectively, if the steam is condensed. The remaining heating value plus sensible heat at 825 °C, however, can be used to cogenerate electricity. With a plant capacity of 110,000 Nm^3/h of H_2, the byproduct electric power is 158 MW [55].

5.1.2.4. Gasification in a Molten-Iron Process

Temperatures of around 1400 °C in the **molten-iron process**, MIP, are capable of cracking almost any chemical compound, in particular that of coal. Product gases are CO and H_2. Other constituents are remaining as slag in the iron bath. Process heat is provided by the exothermal partial oxidation of C to CO. The MIP process is still in the development stage.

5.1.2.5. Coal Cracking Process

The **HYDROCARB** coal cracking is an advanced process where natural gas is synthesized from the hydrogenation of the carbon containing raw material. Coal is routed to a thermal cracker where it is decomposed to carbon black as a clean fuel and hydrogen as a byproduct fuel. HYDROCARB represents the possibility of a CO_2-free fossil-based hydrogen economy. The reaction in the hydropyrolyzer operating on bituminous coal is:

$$\begin{aligned} CH_{0.8}O_{0.08}S_{0.016}N_{0.015} + &\rightarrow C + 0.32\ H_2 + 0.08\ H_2O + 0.008\ N_2 + \\ ash + CaCO_3 \quad & \quad ash + 0.016\ CaS \end{aligned}$$

The HYDROCARB process is expected to become highly competitive with all other coal-based processes [55].

5.1.2.6. Byproduct from Coke Production

Coke furnace gas was formerly the major source for hydrogen until replaced by more efficient petroleum-based processes and by coal gasification. However, it is still an important and convenient method to obtain hydrogen on places where economically attractive.

$$CH_{0.8}O_{0.2} \quad \rightarrow \quad 0.8\ C + 0.2\ CO + 0.4\ H_2$$

Modern coke furnaces produce about 350 m^3 of coke furnace gas out of 1 ton of coal. Half of it is used to run the furnace at 750 - 850 °C and atmospheric pressure, the other half is processed for hydrogen extraction by means of either low temperature condensation or by pressure swing adsorption.

From the worldwide coke production from hard coal, an estimated (theoretical) 60 billion Nm^3 of hydrogen could be recovered [14].

5.1.3. Conversion of Oil

5.1.3.1. Partial Oxidation of Heavy Oils

The **partial oxidation of heavy oil**, in particular the remainder from crude oil distillation, is one of the most wide spread methods of hydrogen production. It involves the conversion of steam, oxygen, and hydrocarbons to hydrogen and carbon oxides with or without catalyst. The catalytic process appropriate for light hydrocarbons occurs at about 590 °C. The non-catalytic process includes also heavy oils and coal and works at temperatures of 1150 - 1315 °C and pressures of 1 - 10 MPa. Technological processes of oil gasification developed by Shell and Texaco operate at 8 MPa. The following reactions take place in a mixture of oil (residual oil: n=1, m=1.3; coal: n=1, m=0.8), oxygen and steam [55]:

$$\begin{aligned} C_nH_m + n/2\ O_2 &\rightarrow n\ CO + m/2\ H_2 \\ C_nH_m + n\ H_2O &\rightarrow n\ CO + (n+m)/2\ H_2 \\ CO + H_2O &\longleftrightarrow CO_2 + H_2 \end{aligned}$$

The partial oxidation delivers the energy for the steam splitting. The resulting synthesis gas with a typical composition of 46 % H_2, 46 % CO, 6 % CO_2, 1 % CH_4, 1 % N_2 + Ar at 6 MPa can be either used for methanol synthesis or is further catalytically converted to increase the H_2 yield. Purification is done in several steps. Maximum unit capacity is in the order of 80,000 Nm^3/h of H_2 [55].

5.1.3.2. Hydrocracking of Heavy Oil

Hydrocracking plants are used to convert heavy oils into lighter oil and gasoline (naphta) fractions. This process requires an input of hydrogen and heat where the former could be provided by naphta splitting. Different properties of raw materials imply the selection of different process conditions. Hydrocracking typically involves feedstock preparation by hydro-treating to remove metals, sulfur, nitrogen, and oxygen. The conversion process of the heavy feedstock is made in several hydrocracking stages which are high-pressure (10 MPa) catalytic processes in the temperature range of 320 - 400 °C. The mass balance is:

$$\begin{array}{lcl} \text{1 kg heavy oil} + 0.494 \text{ Nm}^3 \text{ H}_2 & \rightarrow & 4.22 \text{ Nm}^3 \text{ H}_2 + 0.041 \text{ kg H}_2\text{S} \\ + 34.4 \text{ MJ heat} & & + 0.104 \text{ kg residues} + 10.7 \text{ MJ heat} \end{array}$$

resulting in a net hydrogen production of 3.7 Nm^3 H_2 per kg heavy oil [35].

Partial oxidation of heavy oil is occasionally practiced on a large scale (> 55,000 Nm^3/h of H_2). Heavy oil is reacted with pure oxygen in a less than stoichiometric ratio. The product gas of CO and H_2 at temperatures of 1200 - 1350 °C is cooled and then subjected to the shift reaction to obtain pure hydrogen [37].

5.1.4. Conversion of Other Feedstocks

Thermal processes can also be applied to feedstocks or fuels others than natural gas and coal for hydrogen production. These include **municipal solid waste** and **biomass** such as peat, wood, gases, and agricultural residues. Its gasification leads to a low calory gas which is less convenient for H_2 production and better suited for heat or electricity production. Biomass acquires its H-atoms from water (with the release of O). In order to produce methanol with a higher content of H-atoms per C-atom, the input of energy is required. The amount of hydrogen produced during the conversion step depends on type of fuel/feedstock, the availability of steam and oxygen, and the temperature of the reaction. Besides the opportunity of a renewable clean energy supply, this process is CO_2-neutral. It is attractive for decentralized application.

$$CH_{1.8}O_{0.9} + 0.5\ H_2O + 0.3\ O_2 \longleftrightarrow CO_2 + 0.9\ H_2 + 92\ \text{kJ/mol}$$

The autothermal gasification of biomass in a fluidized bed results in a synthesis gas with about 30 % H_2, 30 % CO_2, 30 % CO, and 5 - 10 % CH_4 plus some higher hydrocarbons. For methanol synthesis, either H_2 needs to be added or CO converted in the shift reaction to CO_2 plus H_2 with separation of the CO_2 portion. The latter method is usually applied. A catalytically supported gasification of biomass (wood) has been reported to work in a fluidized bed at 650 °C. Experiments on a laboratory scale have shown, that 80 - 90 % of the feedstock were converted to synthesis gas consisting by 85 vol% of CO and H_2 [9]. Commercial plants for wood or waste biomass conversion are available already applying autothermal processes and using air instead of oxygen [49]. Other feedstocks like corn pulp, glucose or sugar cane juices were also found in experiments to produce hydrogen [48]. Under specific physical and chemical conditions, the H_2 or CH_4 concentration in the tail gas is sufficiently high for integration of a hydrogen or methane powered fuel cell plant into the gasification process.

A first-of-its-kind European power plant is planned in Bad Brückenau, Germany, to start its operation in 1999. The conversion of 2000 - 3000 t/yr of biomass to hydrogen-rich gas will allow an output of 600 kW of electricity from H_2 consuming fuel cells plus 800 kW of heat from combustion of the residual gas in an engine. The overall efficiency is expected to range between 50 and 60 % [6].

Methanol generation from biomass gasification is the heart of the Swiss project BIOMETH to be later extended by the introduction of electrolytic hydrogen for a complete conversion of the carbon oxides [56]. Gasification of biomass, where the heat for the endothermal reaction is externally provided, results in high heat value and high hydrogen contents of the product gas. It has been realized on a laboratory scale with a capacity of 2 kg biomass throughput per hour [31]. The Paul Scherrer Institute (PSI) has recently realized a demonstration plant with a capacity of 30,000 tons of dry wood to produce about 7500 t of methanol plus electricity and process heat [5].

In the USA, the erection of a pilot plant for methanol production applying the HYDROCARB process to biomass feedstock is planned. The designed capacity is 360 l/d of methanol to be used as a transportation fuel. The HYDROCARB appears to be superior to other biomass gasification processes [2].

Sewage waste usually generates in an anaerobic process methane as the major gas. However, its treatment with charged electrodes results in a hydrogen production. The process has been verified in two different types of lab-scale chemical reactors which allowed a continuous H_2 generation, if the sewage sludge was continuously supplied. The electric energy required is much smaller than in water electrolysis [48]. A first-of-its-kind fuel cell plant in Yokohama, Japan, has started its operation fueled by methane which is being derived from processed sewerage.

Fast pyrolysis is a process with no need of oxygen that converts biomass into a mixture of low-molecular weight oxygenates to be subsequently cracked and steam reformed. A hydrogen yield of 80 % of the theoretical maximum has been obtained in experimental studies. The marketing of the byproducts seems possible. Focus of research is being laid upon the catalytic reforming step to minimize carbon formation on the catalyst [19, 67].

Hydrogen sulfide, H_2S, is sometimes contained in natural gas with a fraction up to 25 % or is a byproduct of various petrochemical processes and is usually considered a waste gas. The widely used treatment of H_2S according to the Claus process only allows for sulfur production plus it leaves waste in the form of SO and polluted water. Therefore H_2S is projected to gain economic importance if decomposed in a waste-free process to hydrogen and sulfur. Achievable hydrogen from this resource is estimated to amount to 1 million tons per year [12]. The endothermal reaction

$$H_2S \quad \longleftrightarrow \quad H_2 + 1/2\ S_2 - 92\ \text{kJ/mol}$$

leads to an equilibrium conversion of 24 % when taking place at a temperature of 1100 °C. A yield of 35 % has been achieved in tests at 1200 °C. A calculation model has been used to optimize the design of a tubular heat exchanger type reactor. The “Zero Emissions Sulfur Process” catalytically decomposes H_2S in the presence of CO_2 at 900 - 1000 °C. The products are sulfur and CO-H_2 process gas [62]. Ceramic tubes will be required due to the corrosive nature of H_2S [20]. In Russian tests, an experimental electric arc reactor has been used to decompose H_2S at a temperature of about 2000 K. Different technologies that are being tested include thermal, thermochemical, electrochemical, photochemical, and plasmochemical methods.

Hydrogen production by **decomposition of H_2S** has been realized in Orenburg, Russia, in an experimental small-scale industrial plant of 1 MW power. Separating the CO_2/H_2S gas mixture from the natural gas exploited in a nearby gas field, the reforming reaction is:

$$2\,H_2S + CO_2 \quad \longleftrightarrow \quad H_2 + CO + H_2O + 2\,S$$

with low energy cost. Heat is provided by a plasma chemical unit containing two 500 kW plasmatrons. The plasma chemical technology allows the production of H_2 as a byproduct of the natural gas exploitation plus avoiding the emission of the greenhouse gas CO_2 into the atmosphere [10].

5.1.5. Recovery from Refinery Offgases

A significant component of refinery offgases is hydrogen which could be extracted for further use. Some examples of typical hydrogen concentrations in offgases are listed in Table 5-2. Presently the offgases in the petrochemical industries are usually flared because their utilization is either considered not economic or the infrastructure for their utilization is not existent. These byproduct gases, however, represent an attractive potential as a hydrogen source, in particular those from petrochemical reforming processes or olefin production. The British company BOC operates a cryogenic hydrogen and argon recovery unit for a large ammonia plant in Tulsa, USA.

The central recovery unit could be suitably designed also for hydrocarbon byproducts extraction [42]. Recovery methods for hydrogen are pressure swing adsorption, cryogenics, membrane, or a combination. Newly discovered polymer membranes which are stable up to 400 °C could help separate significant amounts of hydrogen to reduce energy consumption in the refineries and/or provide further revenues from selling the hydrogen [4].

Table 5-2: Typical hydrogen concentrations in various offgases, from [42]

Offgas source	Hydrogen contents [vol%]
Naphta reforming	65 - 90
Hydroprocessing	
High pressure	75 - 90
Low pressure	50 - 75
Fluid catalytic cracking	10 - 20
Toluene hydrodealkylation	50 - 60
Ethylene synthesis	70 - 90
Methanol synthesis	70 - 90

5.2. DECOMPOSITION OF WATER

5.2.1. Electrolysis

About 4 % of the world hydrogen production is made by electrolysis.

5.2.1.1. Principle

Water electrolysis is basically applied, if cheap electricity is available or high-purity hydrogen is required. The electrolytic decomposition of water with the cell reaction

$$H_2O \quad \rightarrow \quad H_2 + 1/2\ O_2 - 242\ \text{kJ/mol}$$

requires electric energy which is dependent on the reaction enthalpy (or gross heat of combustion), the reaction entropy, and the temperature. The ideal (reversible) voltage of decomposition is 1.229 V. But heat is also essential for the operation of an electrolysis cell. If this energy is to be supplied in electric form, the theoretical potential needs to be increased by another 0.252 V. Irreversible processes in the reaction mechanism at the electrodes and heat production imply the real decomposition voltage to be always higher. The excess voltage should be minimized to allow for a high electrolyzer efficiency. Typical cell voltages are about 1.85 to 2.05 V which translates into efficiencies of 72 - 80 %[17] [43]. The effective electricity consumption is approx. 4.5 kWh/Nm^3 at standard conditions. The electrolysis of distilled water takes place without any side reactions resulting in high-purity gases.

The principle of water splitting is described in Fig. 5-8. Two water molecules are reduced at the cathode to one molecule of hydrogen and two hydroxyl ions. The latter migrate under the influence of the electric field through a porous diaphragm to the anode where they are discharged to 1/2 molecule of oxygen and one molecule of water. Both oxygen and hydrogen escape from the electrodes as a gas.

The minimum feed water demand of an electrolyzer is 0.8 l/Nm^3 of hydrogen, in practice, about 1 l/Nm^3 is required. Sea water must be desalinated first which consumes an energy of 40 - 100 kWh/m^3 of water or in the order of 1 % of the H_2 heat of combustion.

5.2.1.2. Alkaline Water Electrolysis

Conventional electrolytic cells use aqueous solutions of KOH or NaOH or NaCl or use solid polymer matrices as the electrolyte. In industrial plants, the alkaline medium is preferred, because corrosion is more easily controlled and cheaper materials can be used than in acidic electrolysis technology. The alkaline water electrolysis using a 25 % potash lye as the electrolyte consumes about 4 kWh/Nm^3 including energy losses and related energy demands for ancillary equipment. It is a mature technology since decades.

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[17] The efficiency is the ratio of the energy content of the produced hydrogen to electric input. The given figure of 60 - 70 %, however, is dropped to 20 - 25 %, if the output is related to the input of primary energy.

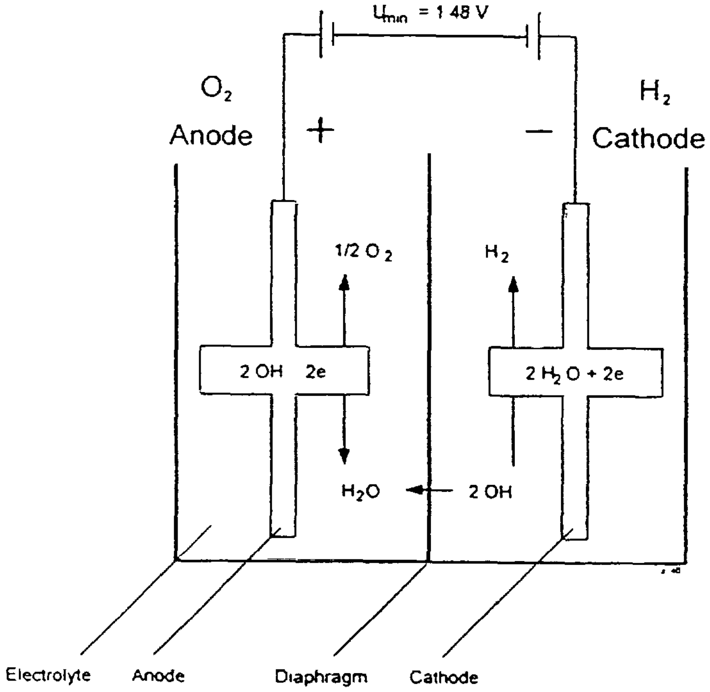


Fig. 5-8: Principle of water splitting process in an alkaline electrolyzer

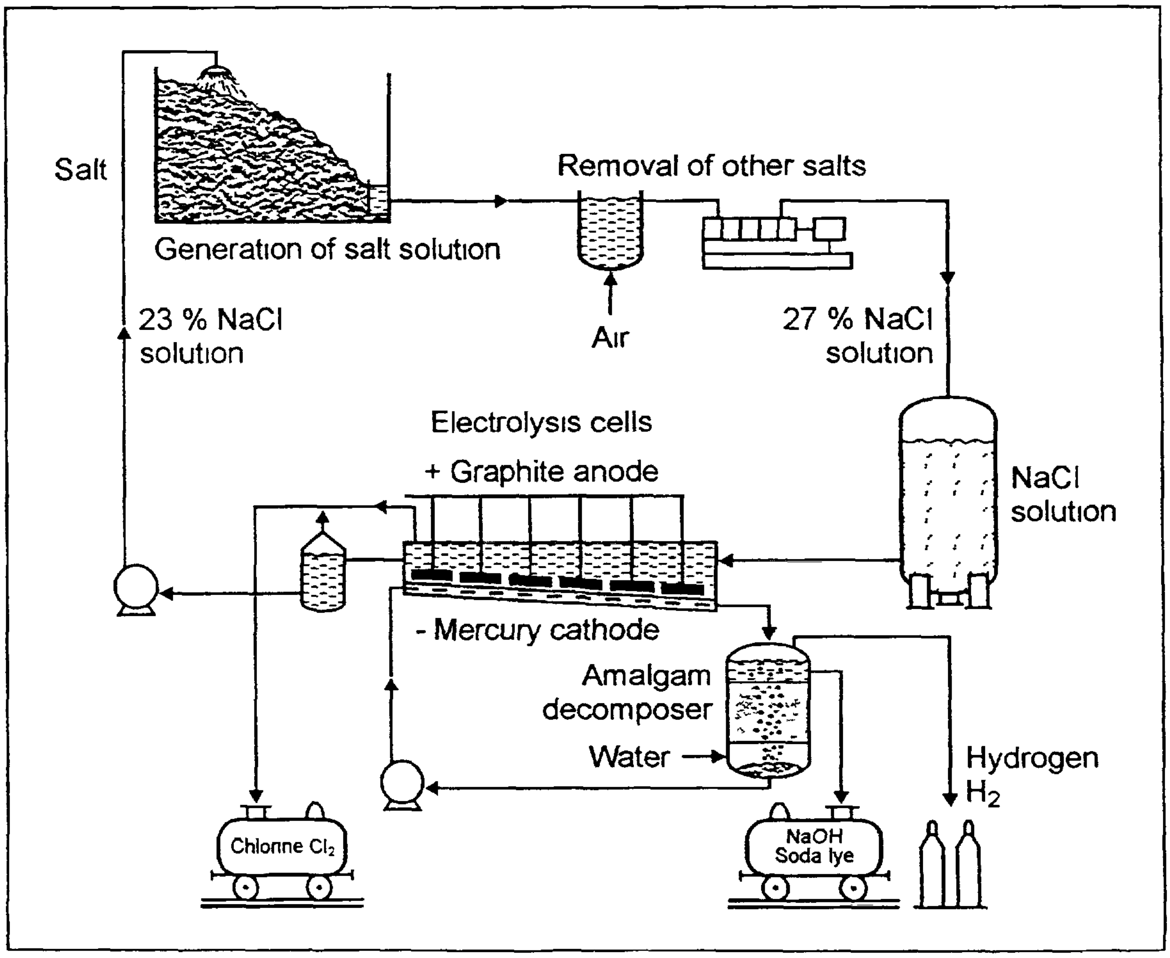


Fig. 5-9: Electrolytic chlorine (and hydrogen) production using the mercury process

The **chloralkali water electrolysis** is the only large-scale technological method to be commercialized, where the H_2 is actually a byproduct of the chlorine production and mostly used as the thermal energy source and substitute of natural gas. A solution of salt in water is electrolytically decomposed into hydrogen and soda lye (cathode) and chlorine (anode) as shown in Fig. 5-9 for the mercury process:

$$2\ NaCl + 2\ H_2O \quad \rightarrow \quad 2\ NaOH + H_2 + Cl_2 - \text{electricity}$$

During the annual production of 35 million t of chlorine worldwide, approx. 20 billion Nm^3 of hydrogen are being generated, which is more than the H_2 production by water electrolysis. Modern large-scale plants allow a production of 300,000 t/yr of chlorine with the byproduct hydrogen. In many cases, the hydrogen is vented to the atmosphere if not needed on site. A 1.6 MW fuel cell (PAFC) power plant is planned in Eastern Europe to be fueled by waste hydrogen from the chloralkali process. It is said, however, that industrial chlorine production does not have a sufficiently high electrolytic efficiency and productivity to form the basis of a large-scale hydrogen production.

Direct processes with the generation of hydrogen as a byproduct are the decomposition of HCl or HF.

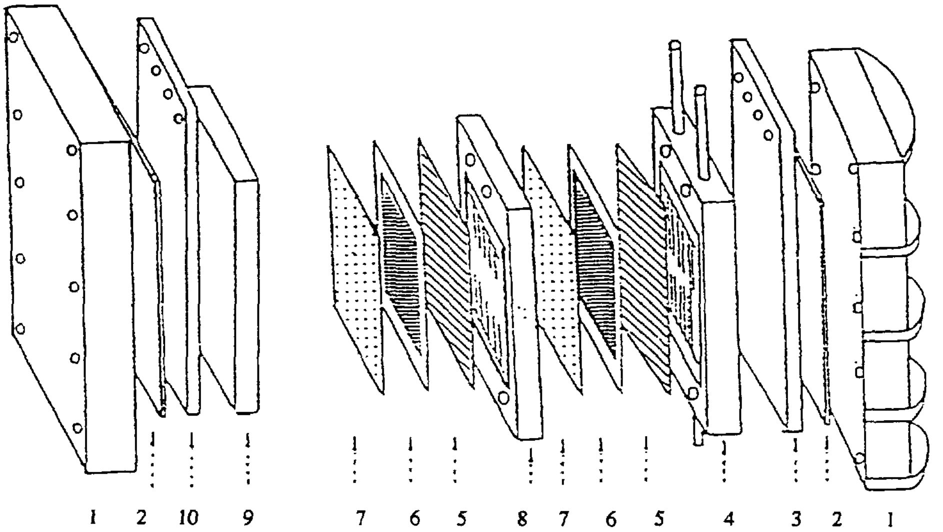
5.2.1.3. High-Pressure Electrolysis

Hydrogen and oxygen production under pressure, in the range between 0.6 and 20 MPa, has the advantages of smaller-sized gas separators, a reduced voltage loss increasing the current density reducing the electricity consumption by 20 % (Zdansky-Lonza process). For subsequent high-pressure storage of the produced hydrogen, the expensive first piston compression is saved. The main disadvantage is the more cost-intensive design of pressurized systems [66].

5.2.1.4. Solid Polymer Electrolyte Water Electrolysis

Solid polymer electrolyte water electrolysis (SPEWE) is considered to be a promising method because it can operate at high current densities due to the extreme volume reduction compared with the KOH electrolyte, and low cell alloys. It is based on the use of a proton conducting membrane of sulfonic acid type, Nafion, with a tenth of a millimeter thickness, which acts both as an acid and as a separating wall. In these membrane electrolyzers, only clean water is used. SPEWE has the advantages of cell compactness, simplicity in design and operation, lack of corrosion problem. A considerable handicap, however, is represented by the high cost of the membrane production and the need of noble metal primary electrodes. More than 40 polymeric materials known for their thermal and chemical resistance were examined, some of which showed good stability, some were even stable up to 300 °C. A schematic of the SPEWE module is shown in Fig. 5-10.

Efforts are made to test engineering polymer materials for intermediate temperatures 200 - 400 °C which are in the range of speeding-up kinetics at still reduced corrosive effects.



1: Flange for compression
2: Insulator plate
3: Cathode side bus bar
4: Cathodic end plate
5: Cathodic support collector
6: Membrane-electrodes composite
7: Anodic support collector
8: Bipolar collector
9: Anodic end plate
10: Anode side bus bar

Fig. 5-10: Schematic of a solid polymer electrolyte water electrolysis module consisting of 5 cells with a total electrode area of 500 cm^2, production capacity is 2 Nm^3/h, from [59]

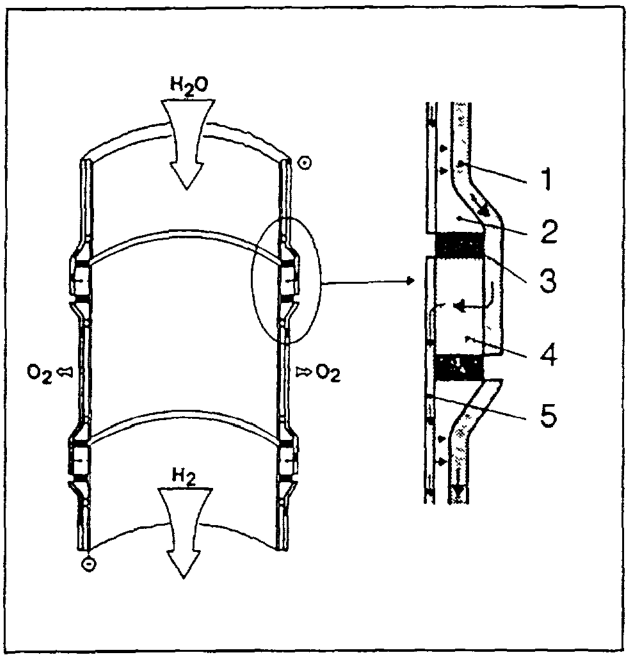
5.2.1.5. High-Temperature Electrolysis

The process of electrolysis of steam operated at higher temperatures (800 - 1000 °C) offers several advantages:

i. the thermodynamic electric energy required could be reduced, and
ii. the activation barriers at the electrolyte surfaces would be easier to overcome resulting in an improvement of the efficiency.

Very low electric energy consumption can be obtained if high-temperature heat and low-temperature heat or steam provided by HTGR or solar energy are fed to the system. The high-temperature water vapor electrolysis process could be realized with the development of metal oxide diaphragms as the solid, oxygen ionic conducting electrolyte. A water vapor electrolyzer is typically operated at 900 °C and consumes about 3 kWh of electricity for 1 Nm^3 of H_2 produced.

Zirconia-based ceramic membranes have been selected, which show a high conductivity for oxygen ions at operating temperatures. The electricity demand at 1000 °C is 30 % lower compared with that at room temperature. The most widely used solid oxide electrolyte is a calcium and yttrium stabilized zirconium oxide. It is formed as small tubes of about 2 cm diameter through which the hot steam is routed (see Fig. 5-11). The steam is split at the inside surface, the oxygen ions migrate through the ceramic, the hydrogen is enriched in the steam and is afterwards extracted. The principle of the high-temperature



1: anode	4: conducting material
2: solid electrolyte	5: cathode
3: electrically insulating material	

Fig. 5-11: Schematic of a high-temperature electrolysis tube (Hot Elly), from [70]

electrolysis of steam corresponds to the reverse operation of a solid oxide fuel cell. Some variations with tubular or brick-like cell forms have been developed and tested. Main goal of research is the low-cost production of efficient, reliable, and durable electrolysis cells.

5.2.1.6. Electrolyzer Technology

The technological development of electrolyzers started with a mono polar cell consisting of a cathode part and an anode part separated by a diaphragm. In multi-cell systems, bipolar plates are used carrying the cathode material for one cell and on its backside the anode material for the neighbor cell. The functions of the bipolar plate are the continuous supply of the membrane electrode with H_2 on one side and with O_2 or air on the other side and the regulation of the water balance by providing moisture for the membrane on the H_2 side and remove the product water on the O_2 side.

The development of electrolyzers is affected in particular by material problems. Cells need to be tight, electrically insulated, and resistant against corrosive attack. The reaction velocity is dependent on the electrodes' materials. The replacement of normal electrodes by catalyst electrodes reduces the specific energy consumption significantly. On the other hand, it is rising after some years of operation due to aging of the porous electrodes. The operation of an electrolysis plant is simple and can be interrupted according to the fluctuating energy demand [66].

Table 5-3: Present electrolyzer developments

Electrolyzer type	**Anode (A) Cathode (C)**	**Operating conditions**	**Cell efficiency [%]**	**Cell Voltage [V]**	**Current density [kA/m^2]**	**Energy consumption [kWh/Nm^3 H_2]**	**Remarks**
Alkaline (25-30 % KOH)	(A): Ni (C): Ni, steel	70 - 90 °C ambient pressure	77 - 80	1.84 - 2.25	1.3 - 2.5	4.3 - 4.9	Commercial large-scale units proven technology, simple, low efficiency, corrosive electrolyte
		80 °C ambient pressure	83	1.8	3	4.3	Norsk Hydro > 400 kW capacity 100-400 Nm3/h
		90 °C 3.2 MPa	79	1.7	4	4.2	Lurgi 25 MW capacity 5100 Nm3/h
		30 - 85 °C 0.3 - 0.9 MPa	69		3.5	5.0	Hysolar 350 kW
		100 °C 0.11 MPa	87	1.7	5	4.0	Research Center Jülich Hysolar 10 kW
		110 °C 0.5 MPa	90	1.7	5	3.9	Hydrogen Systems < 100 kW commercial 5-10 kW
		80 °C ambient pressure	80	1.9	2.5	4.4	Electrolyzer Corp. the only monopolar

Table 5-3: Present electrolyzer developments (continued)

Electrolyzer type	Anode (A) Cathode (C)	Operating conditions	Cell efficiency [%]	Cell Voltage [V]	Current density [kA/m^2]	Energy consumption [kWh/Nm^3 H$_2$]	Remarks
Advanced alkaline (25-40 % KOH)	(A): Ni (C): Ni	90 - 145 °C ≤ 4 MPa	80 - 90	1.5 - 3.0	2 - 20	3.8 - 4.3	Lab scale, prototype units, has commercialization potential, severe corrosion at higher temp.
		120 °C		1.5	2.5	3.8	Research Center Jülich several 10 kW
		< 150 °C > 3 MPa	82	1.8	10	4.1	100 kW prototype GHW
		150 - 250 °C, 3 - 10 MPa	70 - 80				
Inorganic Membrane alkaline (14 - 15 % NaOH)	(A): spinel oxide (C): NiS	90 - 120 °C ≤ 4 MPa	82 - 91	1.6 - 1.9	2 - 10	3.6 - 4.0	lab scale, prototype units, non-noble metal cat., membrane performance needs to be demonstrated
Solid polymer (Nafion)	(A): Ti (C): Carbon with Pt	80 - 150 °C < 4 MPa	85 - 90	1.4 - 2.0	2.5 - 20		100 kW compact, non-corrosive electrolyte, noble metal cat, expensive membrane
		100 - 130 °C ≤ 4 MPa	88	1.7	10		GIRI, Osaka, production rate 1.3 Nm^3/h

Table 5-3: Present electrolyzer developments (continued)

Electrolyzer type	**Anode (A) Cathode (C)**	**Operating conditions**	**Cell efficiency [%]**	**Cell Voltage [V]**	**Current density [kA/m^2]**	**Energy consumption [kWh/Nm^3 H_2]**	**Remarks**
Intermediate temperature Molten Carbonate (KOH/NaOH)	(A): Ni (C): Mb	300 - 600 °C	82 - 91	1.3 - 1.4	> 2		simple double cell configuration
High-temperature (solid Y_2O_3 stab. ZrO_2)	(A): Ni-NiO (C): Ni	800 - 1000 °C ≤ 3 MPa	90 - 100	0.95 - 1.3	3 - 10	3.5	very small lab scale units, non-corrosive electrolyte, severe materials and fabrication problem
			95 - 115		3.3	2.6 - 3.2	tubular 10 kW Hot Elly

Electrolyzers are being developed in various countries. Although very promising, they are still at an early stage of technology. An electrolysis plant can inherently operate over a wide range of capacities which is attractive for load leveling. Conventional alkaline water electrolysis is limited to small and medium-sized plants (0.5 - 5 MW corresponding to about 100 - 1000 Nm^3/h) unless cheap electricity is available. There are only a few large-scale facilities which have H_2 production capacities in the order of 33,000 Nm^3/h (approx. 150 MW), e.g. in Assuan, Egypt, with cheap hydro power used for the ammonia synthesis. The typical size is in the range of 100 - 1000 Nm^3/h corresponding to 0.5 - 5 MW. Some efforts are listed in Table 5-3.

One of the world leaders in electrolysis for H_2 production is the Norwegian company Norsk Hydro, which built the first electrolyzer in 1927 used in the ammonia production. Since then, the company has supplied a total of 461 electrolyzer units of different sizes (between 0.5 and 565 Nm^3/h of H_2) with a total capacity of approx. 30,000 Nm^3/h of hydrogen gas. The German Gesellschaft für Hochleistungselektrolyseure zur Wasserstofferzeugung mbH (GHW) has developed a 100 kW high-pressure, high-efficiency advanced alkaline pilot electrolyzer for both continuous and intermittent operation and operated it for more than 5000 h. Due to higher efficiencies, advanced alkaline electrolyzers can be smaller in size. Intermittent and part-load operation is possible. The positive experience allows a scale-up into the MW range [52].

Membrane electrolysis technology is well established and appropriate for smaller scale facilities. One application is its use as an oxygen generator in submarines, where the hydrogen is considered only a byproduct. Drawback is the high-cost membrane production [14].

In the high-temperature range, Westinghouse is leading the development of the thin layer tube concept with pilot plants up to 25 kW. Other companies pursuing the planar concept since the end 1980s, have reached the kW scale [23]. Test operation of high-temperature electrolysis cells basically confirm the predictions of achievable efficiencies.

The concept of a tubular solid oxide hot water vapor electrolysis (**Hot Elly**) has been investigated in Germany within the frame of a technology program between 1975 and 1987. It was terminated with the successful demonstration of a 2 kW lab-scale pilot plant [23]. The tubular concept was replaced by the planar concept, after respective ceramics production technologies were sufficiently developed.

The high-temperature technology is able to create so-called **regenerative cells** which can work either in the electrolyzer mode or in the fuel cell (SOFC) mode (see section 7.2.2.). Hot Elly efficiency is expected to rise up to 111 % in the future including the utilization of the process heat in the combined heat power operation mode [53].

A lower cost system is achieved if electricity and steam is generated from a coal-fired power plant and then routed to a high-temperature electrolysis plant for steam decomposition with an overall thermal efficiency of 35 - 38 % (based on 35 % efficiency of electricity production from coal) [55].

An advanced hybrid system combines high temperature electrolysis with coal gasification. The latter produces synthesis gas plus steam at a high temperature which is used for the electrolysis step. In return, the electrolytic oxygen is utilized in the gasification step. In the combined process, two thirds of the H_2 are produced in the gasifier and one third in the electrolyzer [55].

There are currently no comprehensive guidelines or codes for the design and installation of small and medium-sized electrolyzers. Considering future operation mainly by private users, international guidelines for quality criteria, safety requirements, licensing procedures, and testing methods should be implemented [57].

5.2.2. Thermochemical Cycles

Since a direct thermolysis of water, which requires temperatures of > 2500 °C, is not practicable under normal circumstances, the splitting process is subdivided into different partial reactions, each running on a lower temperature level. The thermal energy required is heat of 800 to 900 °C. Some 2000 - 3000 potential thermochemical cycles have been tested and checked in terms of appropriate reaction temperatures and velocities and in the economic respect. Thermochemical cycles are Carnot cycle-limited meaning that high temperatures could improve the conversion efficiency. Major problems arise due to the large material flows, the introduction of impurities, and the potential creation of toxic and environmentally unacceptable species. The main goal is to achieve satisfactory overall energy efficiencies which are currently not higher than around 40 % and, in connection with separation steps and severe materials and equipment design difficulties, do not allow large-scale thermochemical process applications so far [43]. Studies are focusing on reaction kinetics, thermodynamics, reactant separation, material stability, flow sheeting, and cost analysis.

Thermochemical multistage cycles are usually classified in families according to the chemicals involved. Cycles can consist of up to 8 equations, mainly 3 - 6, with up to 5 elements others than H_2 and O_2 involved [26].

The **thermochemical hybrid process** is a combined cycle process with both thermochemical and electrolytic reactions of water splitting. The hybrid process offers the possibility of running low-temperature reactions on electricity. The expectations for realization of hybrid processes are similar to those for purely thermochemical processes [13]. Various hybrid processes are energetically possible, but not always feasible. Important criteria are the minimum voltage for the electrolysis step, realizability, efficiency.

The most advanced and promising thermo(electro)chemical processes are described in more detail in appendix A.

5.2.3. Photolysis

In a photolytic process, light energy is directly absorbed to either convert the photon energy into electricity or store part of it as chemical energy in the water splitting reaction. This process is of great interest because solar energy can provide an unlimited energy source for hydrogen production.

5.2.3.1. Photoelectrochemical Systems

In **photoelectrochemical (PEC) systems**, inorganic materials are being used for direct conversion of (sun) light into hydrogen at a semiconductor-electrolyte contact [17]. The PEC direct water splitting by solar energy was first reported in 1972. The process is based on the band gap absorption of photons by which electrons are elevated from the valence band to the conducting band creating electron-hole pairs. Following this charge separation, the excitation energy is utilized for the splitting of water molecules at the n-type semiconducting anode surface. The band gap must be greater than the water decomposition potential (> 1.23 eV) to enable the necessary charge transfer. Constraints are given by the high voltage required for dissociation and the corrosiveness of the aqueous electrolytes. For some reason, only $SrTiO_3$ was found so far to be really able to directly split water [36]. Solid state devices with appropriate catalytic surfaces seem to widen working conditions [47]. Catalytic photo-decomposition of water is also possible using n-type semiconducting powders [73]. The theoretical limit for the solar conversion efficiency of PEC water splitting is 29 % [46].

In Japan, a photoelectrochemical system for outdoor operation, i.e., solar, has been constructed. Photoanodes were Ti plates with a 1 μm thick TiO_2 surface layer with a total area of 0.17 m^2, cathodes were of Pt, and the electrolyte was KCl. The result was an output of 1.1 l of hydrogen per day, the conversion efficiency was about 0.4 % which is considered relatively high compared with the small absorption wavelength range (3 % of the entire solar spectrum) by TiO_2 [25]. In a more recent effort using a multi-band gap PEC cell structure, an efficiency of 12.4 % has been achieved [3].

In another approach, semiconductor materials and devices which are stable in aqueous environment are taken to apply sunlight for direct water splitting. The conversion efficiency, however, is still insignificant, since only a very small portion of the solar spectrum is used. Photolytic response, however, could be shifted into the visible region using chomophores called sensitizers [73]. Research is focusing on the development of transparent and highly active catalysts and techniques of surface modification to increase lifetime and efficiency of PEC devices.

5.2.3.2. Photocatalytic Systems

Photocatalytic production of hydrogen can be realized from water in the presence of various types of catalysts. One system is the sulfide which is often found as the major constituent of natural gas:

$$H_2S \quad \rightarrow \quad H_2 + S - 0.21 \text{ eV/mol}$$

Another one is the use of alcohols with dispersed or supported catalysts [29]:

$$(R1)\,(R2) - CHOH \quad \rightarrow \quad (R1)\,(R2) - CO + H_2$$

In Japan, the carbonate method is being studied where the addition of carbonate was found to lead to a much more efficient decomposition of water.

5.2.3.3. Photobiological Systems

In **photobiological systems**, hydrogen is produced as a result of the way certain biological organisms use sunlight in an energy storing fuel production reaction. In principle, two ways are distinguished:

a) release of hydrogen from photolytical decomposition of water
b) extraction of hydrogen stored in biomass which serves as nutrition for the microorganisms

Photosynthesis reactions are:

$$\begin{aligned} H_2O + \text{light} &\rightarrow H_2 + 1/2\ O_2 \\ H_2 + CO_2 + \text{light} &\rightarrow \text{plant tissue} \\ CH_3COOH + 2\ H_2O + \text{light} &\rightarrow 4\ H_2 + 2\ CO_2 \end{aligned}$$

Some photosynthetic algae and bacteria, in particular the anaerobic ones, absorb energy from sunlight and use it for water splitting in the process of generating plant tissue or creating heavier hydrocarbons or oxygen for assimilation. The hydrogen production seems to be a precursor step from the anaerobic microorganism prior to fixing the hydrogen with carbon from its CO_2 uptake. Competent light-driven H_2 producers are cultured cyanobacteria and purple bacteria. Efficiencies under ideal conditions approach approx. 10 % [17].

The direct decomposition of water by bacteria has only a very low hydrogen yield and hydrogen extraction is difficult. The organic acids required as a substrate may be gained by organic waste conversion. Investigations have been made concerning the development of photoelectrolysis cells and the search for appropriate catalysts.

Among the biological options, systems of intact cells of photosynthetic bacteria are the most advanced. They evolve hydrogen from thermally gasified biomass (synthesis gas) using several different enzymatic mechanisms with near-term commercial potential for biological H_2 production from biomass. Research is now concentrating on maximization of bioactivity and durability [69].

The commercialization of the photosynthetic processes requires a drastic increase of the conversion efficiency as well as an improvement and upgrading of the microorganisms. The latter could be realized by genetic engineering and the development of mass cultivation techniques [58]. Other problems are the rapid separation of the produced oxygen and hydrogen to avoid explosion hazards and the removal of decayed microorganisms.

German scientists have discovered a suitable organism for H_2 production preferably in sunny climates. Within the “Erg-Chebbi project”, a photobioreactor, a so-called **heliomite**, has been developed which consists of a cone-shaped wooden construction (Fig. 5-12, left). The substrate with the bacteria is slowly led through glass tubes of 2.8 cm diameter which are radiated by solar (or artificial) light. The product gas contained 90 % H_2 and 6 % N_2. The highest production rate measured was 2.5 l of hydrogen per hour per m^2 of radiated reactor surface. Some 100 of such heliomites were deployed across a 60 by 60 m^2 area

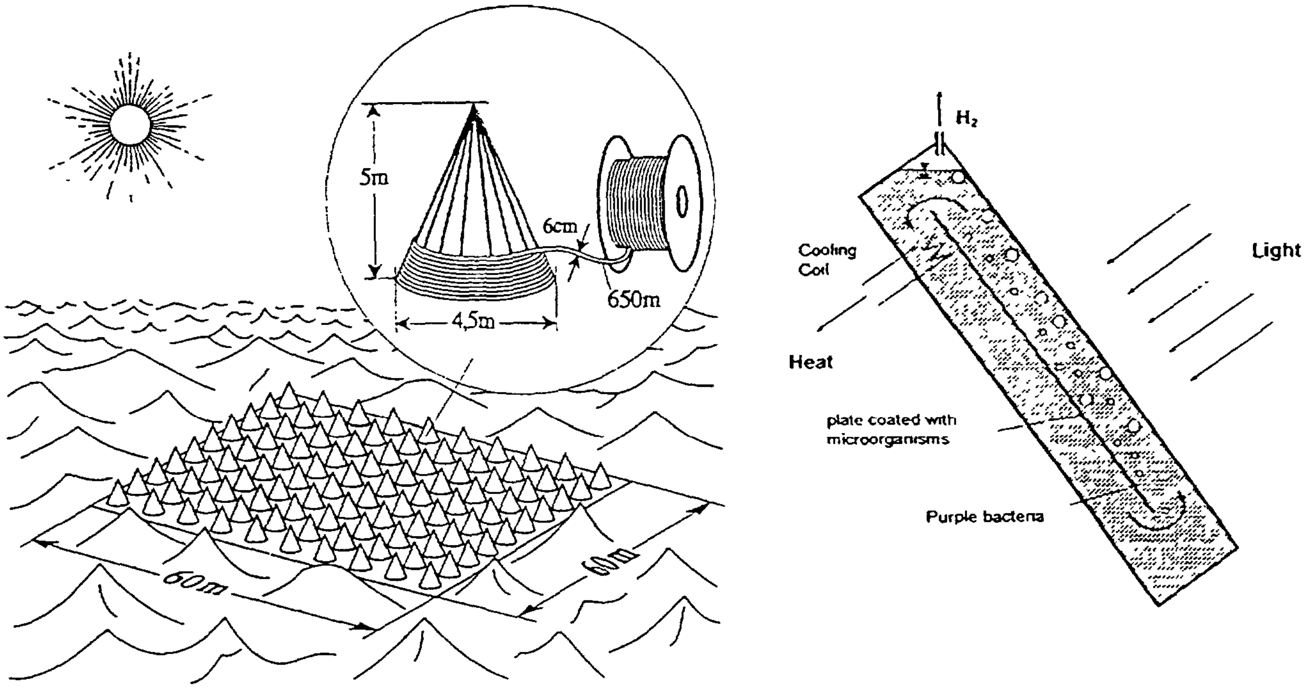


Fig. 5-12: Schematics of photobiological hydrogen production arrangements a heliomite farm (left) [45] and a plate loop reactor (right) [63]

reaching a yield of 285 l of hydrogen each. A 10 MW heliomite farm would require some 10,000 of such mini generators. A further development was the combination with green algae to form an artificial symbiosis, where the green algae react with the bacterial CO_2 to produce O_2 which in reverse serves as nutriment for the bacteria [45].

A plate loop or sandwich reactor for photobiological processes using purple nonsulfur bacteria has been designed at the RWTH Aachen (Fig. 5-12, right). The reactor is separated by a central plate on which the bacteria are growing. Solar insulation triggers a natural convection of the nutrition suspension to flush around the bacteria. In outdoor experiments, a hydrogen production rate of 2 $l/(h\ m^2)$ was achieved [63].

A two-stage process has been proposed [15] to use green algae cultivated in large open ponds to produce a high carbohydrate algal biomass which is then fed into a photobioreactor to produce hydrogen in a light-driven reaction. Such a fermentation device could be an arrangement of closed glas tubes of about 2.5 m in length and 3 - 5 cm in diameter.

5.2.4. Direct Water Splitting

The direct splitting of water requires a high energy input. In the **plasma arc process**, water is heated up to 5000 °C by an electric field resulting in the cracking products H, H_2, O, O_2, OH, HO_2, and H_2O. A fraction of 50 vol% of H and H_2 is possible. To avoid recombination, a rapid quenching of the plasma gases, e.g., by a cryogenic liquid, must be made. The process consumes a lot of energy and thus is very expensive [55].

5.3. COMPARISON OF HYDROGEN PRODUCTION METHODS

If hydrogen production processes are compared, the interdependence of efficiency, capital investment and value of the byproduct has to be taken into account. From the reaction equations, it can be derived that an essential part of the hydrogen is gained from water, e.g., 50 % in the case of steam reforming of natural gas plus CO conversion. On the other hand, all carbon in the raw materials is finally converted to CO_2 and released into the atmosphere; the least unfavorable process is steam reforming with a CO_2 to H_2 ratio of 0.25, the worst in coal gasification with a respective ratio of 1. The use of heavier raw materials is connected with a loss of efficiency since a larger mass of C-carriers and water need to be heated up to reaction temperatures [51].

Reforming of natural gas and partial oxidation of heavy oils are presently the least expensive and most frequently applied methods of hydrogen production (see Table 5-4). Methane cracking is considered in [55] to have even lower net H_2 production cost than reforming because of its very low capital investment which compensates the not very high efficiency. There is a high degression of cost if moving towards upscaling of the plant in contrast to electrolysis which is composed of many single cells. Electrolysis is the most expensive process unless cheap electricity is available [38].

The production of hydrogen (or methanol) from coal gasification and using a CO_2-free primary energy source (e.g., nuclear) is not an ideal alternative in terms of the necessary reduction of CO_2 emissions in the future, because the reduction is no higher than 20 - 30 % compared with the coal feed. In this respect, gasification of CO_2-neutral biomass would be the better alternative [11], although also non-CO_2 gases with a global warming potential are emitted with its combustion.

As can be seen from the reaction equations, the splitting of water requires different amounts of energy dependent on how much of the carbon contained in the (fossil) raw materials is converted into CO_2. The energy released during this conversion is consumed in the splitting process and does not need to be introduced from outside. The theoretical energies required for the production of 1 Nm^3 of hydrogen are listed in Table 5-4.

Electrolytic hydrogen has a small, but stable market. It is preferred if there is a fluctuating demand, a need for small amounts or the requirement for high-purity hydrogen [41]. It strongly competes with the direct use of electricity. From all electricity generating concepts, the most economic are hydro and wind compared with photovoltaics as the most expensive [71]. Cost from renewable sources, however, is projected to drop significantly in the next decade.

Hydrogen production in thermochemical (hybrid) cycles has been demonstrated to be feasible with an overall efficiency that can be higher than 35 %, however, is inherently less efficient than conventional processes. Technological improvements are still possible. A strong cost reduction, however, is not expected. Economic competitiveness appears to be likely, if nuclear heat (HTGR) could be used. Using solar primary energy promises high efficiency and no major technical problems although still connected to many uncertainties [26].

Table 5-4: Characteristics of splitting processes for hydrogen production (H_2 heat of combustion: 3.54 kWh/Nm^3), from [various sources, e.g. 26, 38, 51]

Splitting process	**Energy required [kWh/Nm^3 of H_2]**		**Status**	**Efficiency [%]**	**Costs relative to CH_4 steam reform.**(1)	**Fraction of production [%]**(2)
	in theory	**in practice**				
Methane steam reforming	0.78	2 - 2.5	mature	70 - 80	1	48
Methane cracking			mature	54	(0.9)	
Partial oxidation of heavy oil	0.94	4.9	mature	70	1.8 (1.6)	30
Naphta reforming			mature			
Coal gasification (TEXACO)	1.01	8.6	mature	60	1.4 - 2.6 (2.3)	18
Partial oxidation of coal			mature	55		
HYDROCARB			R&D		(0.9)	
Steam-iron			R&D	46	(1.9)	
Chloralkali electrolysis			mature		byproduct	4
Water electrolysis	3.54	4.9	R&D - mature	27(3)	5 - 10 (3.0)	
High-temperature electrolysis			R&D	48	(2.2)	
Thermochemical cycles			early R&D	35 - 45	6	
Biomass conversion			early R&D		2 - 2.4	-
Photolysis			early R&D	< 10		

(1) as estimated by DOE, 1993 [26], in parentheses estimation by Steinberg, 1987 [55]

(2) data from 1988 [51]

(3) electricity from fossils with 40 % efficiency

For solar hydrogen technologies, the efficiency is the key to a practical economic system. Systems with efficiencies less than 10 % will hardly have a chance to survive. Photoelectrochemical and photobiological devices have not exceeded yet the stage of laboratory outdoor demonstration and still need to show their potential fo economic H_2 generation [17]. Besides, renewable energy systems require much more land than fossil fuel systems providing the same amount of end-use energy. Land use and water requirements may be, in particular, a serious issue in the case of biomass energy systems [33].

Since coal is abundantly available in the world and thus should about maintain its cost level in the future, R&D efforts should concentrate on coal-based processes. The advanced processes of methane cracking and coal cracking (HYDROCARB) have a huge economic potential [55].

5.4. PRODUCTION OF LIQUID HYDROGEN

In contrast to the gases in air, the production and liquefaction of hydrogen is conducted in two separate energy-intensive steps. During the cooling process, condensation heat and heat of the ortho-para conversion are removed. The minimum work required for the liquefaction of hydrogen (at ortho-para equilibrium) is 3.92 kWh/kg. A realistic value, however, for the whole process of H_2 cooling from ambient to boiling point and condensing is 10 - 13 kWh/kg.

If an electric power of 500 MW is to be generated from hydrogen, the corresponding capacity of LH_2 production required is about 600 t/d.

5.4.1. LH_2 Production Methods

The **Linde-Hampson process** uses a thermodynamic process. Isothermal compression and subsequent cooling along an isobar is done in a heat exchanger. Joule-Thomson expansion connected with an irreversible change in entropy is used as the refrigeration procedure. Despite its simplicity and reliability, this method is now less attractive compared with new ones where cooling is primarily carried out in reversible processes (expander) and where less energy is required.

A commonly applied method in large-scale liquefaction plants is the **Claude process.** The necessary refrigeration is provided in four principal steps leading to the liquefaction of hydrogen (Fig. 5-13):

I. compression of hydrogen gas, removal of compression heat,
II. pre-cooling with liquid nitrogen (80 K),
III. expanding and thus cooling of a part of the hydrogen in an expander resulting in a further pre-cooling of the residual hydrogen (80 - 30 K),
IV. expanding of the residual hydrogen in a Joule-Thomson valve until liquefaction (30 - 20 K).

The first expansion process would be sufficient for liquefaction, however, Joule-Thomson expansion is applied for the final step (from approx. 26 K down) to avoid two-phase flow in the expander. Variations of the dual-pressure Claude process as a large-

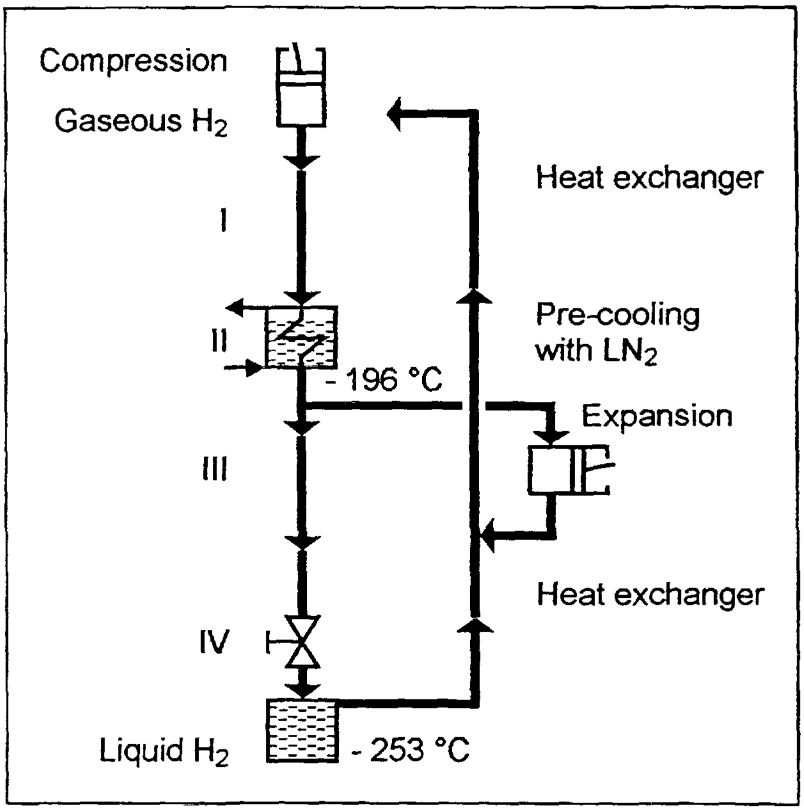


Fig. 5-13: Schematic of the Claude process for hydrogen liquefaction, from [Messer Griesheim]

scale liquefaction procedure has proven to be the optimal solution [43]. Maximum impurity level in the hydrogen gas is in the order of 1 ppm.

Magnetic refrigeration takes advantage of the entropy difference and the adiabatic temperature change upon application or removal of magnetic fields in the working material. It uses isentropic demagnetization of a ferromagnetic material as the cooling process. A respective plant has neither been built nor utilized; the method is still on a research stage. But it looks promising, because it offers a compact cooling system with an extremely long lifetime, lower capital investment since no expanders or compressors are required, an estimated liquefaction work of 7.3 kWh/kg, and it promises higher efficiencies [24].

5.4.2. Liquefaction Plants

A considerable amount of LH_2 was required starting with the US Apollo space program leading to the design and construction of large-scale plants. The liquefaction plants in the world are summarized in Table 5-5 presently revealing a total capacity of 265 tons of LH_2 per day, but not more than 19 t/d in Europe. Two major plants in the USA, West Palm Beach, FL, with a 31 t/d capacity and Sacramento, CA, with a 54 t/d capacity, ceased operation in the meantime.

Based on current experience, the construction of plants with a capacity of up to 250 t/d as an upper economic limit is expected to be feasible. The goal in the Japanese WE-NET

Table 5-5: Hydrogen liquefaction plants in the world

Place	Operator	Capacity [metric tons/day]	Operation since
America			
Montreal, Canada	Air Liquid Canada Inc.	10	1986
Montreal, Canada	BOC, USA	14	
Sarnia, Canada	Air Products, USA	30	1962
Kourou, French Guiana	L'Air Liquide, France	5	1990
McIntosh, USA	Praxair	24	1995
New Orleans, USA	Air Products, USA	68	1977
Niagara Falls, USA	Praxair	2 * 18	1981 / 1989
Ontario, USA	Praxair	20	1962
Pace, USA	Air Products, USA	30	1994
Sacramento, USA	Air Products, USA	6	1986
Europe			
Lille, France	L'Air Liquide, France	10	1987
Ingolstadt, Germany	Linde, Germany	4.4	1991
Rozenburg, The Netherlands	Air Products, USA	5	1987
Asia			
Amagasaki, Japan	Iwatani Gas, Japan	1.2	1978
Ooita, Japan	Pacific Hydrogen Co, Japan	1.4	1986

project is a plant capacity of 600 t/d. At present, the compression step limits the liquefaction capacity to 50 - 60 t/d, which appears to be a convenient module size. An assumed value for the liquefaction work of 10.8 kWh/kg representing approx. 30 % of the net heat of combustion of hydrogen is considered conservative, improvement of components could lead to a figure of 9.8 kWh/kg. A combined system of advanced pressurized electrolysis and liquefaction promises an improvement in efficiency.

5.4.3. Production of Slush Hydrogen

Most slush hydrogen has been produced so far by means of the **freeze-thaw method** [22]. In this technique the gaseous phase above the liquid hydrogen is pumped to pull a vacuum until the liquid is cooled down below the freezing point (13.8 K) and a film of solid hydrogen forms on the surface. The system pressure is then stopped and the solid phase allowed to settle into the liquid. After decreasing the pressure again, the formation of a new solid layer on the surface is initiated.

The time of the freezing period can be extended by spraying triple point liquid hydrogen onto the surface, the **spray / freeze method**, which could be a step towards a continuous process with no further need of a thawing period [40].

Some other production methods apply liquid helium for cooling. In the **Auger method**, a hollow cylinder is placed in liquid hydrogen. An annular interior of the cylinder is then cooled with liquid helium. Hydrogen freezes on the surface of the heat exchanger and is scraped off by means of a rotating auger. This method provides a stable, continuous, and contamination-free slush production. Another way is to have the cold helium bubbling through the liquid hydrogen.

A **Small Scale Slush Hydrogen Facility** has been constructed by NASA to study ways of optimizing the SLH_2 production process and provide a test bed for advanced instrumentation. The tank with a total volume of 0.76 m^3 is vacuum jacketed and wrapped in several inches multilayer insulation plus a liquid nitrogen shield in the upper tank part. A 1 kW heater is used to simulate a heat leak or a warming up. The tank also offers the option to install a liquid helium slush auger for research on this method of production. In a 17 m long and 0.05 m diameter vacuum jacketed transfer line, studies on flow characteristics and instrumentation can be conducted [40].

A smaller slush hydrogen production system has been constructed in Japan with a volume of 60 liters. Both the "freeze-thaw" and the "auger" production method have been investigated revealing the creation of finer fractions with a higher fluidity with the latter method [61].

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Chapter 6

STORAGE AND TRANSPORT OF HYDROGEN

The commercial provision of energy worldwide has turned into a very complex structure, not limited by national boundaries. A system for grid-bound energy carriers (electricity, gas) has evolved which represents 35 % of the final energy market. A major portion of 60 % is characterized as a storageable commodity. Storage represents the temporal decoupling of generation and consumption. Most countries are dependent on imports or exports of energy. Primary energies are transported sometimes over several thousands of km, whereas most of the secondary energies are transported over the shorter distance range of 50 - 500 km. The delivery to the consumer is usually made in a distribution system with distances < 50 km. The consumer expects a supply with energy which suits his spatial and temporal needs ("supply security"). This situation translates then into a question of storability of energy. Unlike primary energies, secondary energy carriers exhibit high transportation losses, comparatively poor storability, and higher transportation cost (see Table 6-1) [39].

Table 6-1: Energy carrier transportation, from [64]

Energy carrier	**Energy contents [kWh/kg]⁽¹⁾**	**Transportation properties**			**Typical distance [km]**
		Speed	**Losses**	**Storage capability**	
Primary energy carriers					
Oil	9 - 11	slow / fast	small	good	$\geq 10^3$
Natural gas	9 - 11	fast	high	medium	$\geq 10^2$
Hard coal	8	slow	small	good	$\geq 10^2$
Lignite	2 - 3	slow	small	good	10^1 - 10^2
Secondary energy carriers					
Electricity	≤ 600 kV	very fast	high	none	10 - 10^4
Gaseous hydrogen	33	fast	high	medium	$\geq 10^2$
Liquid hydrogen	33	slow	small	poor	$\geq 10^3$
Steam	≤ 300 °C	fast	high	none	1 - 10
Hot water	300 °C (ΔT)	medium	high	poor	10^{-1} - 10
Solid biomass	3 - 5	slow	small	good	≥ 10
Liquid biomass	8 - 10	slow / fast	small	good	$\geq 10^3$
Gaseous biomass	4 - 7 MJ/m^3	fast	high	medium	$\geq 10^2$

(1) unless otherwise indicated

6.1. STORAGE OF HYDROGEN

The storage of hydrogen can increase the cost of hydrogen by 30 - 300 %, which means that there must be some benefit in order to give economic viability [61]. Possibilities of storage of hydrogen include physical storage via compression or liquefaction, chemical storage in hydrogen carriers (e.g., metal or liquid hydrides), and gas-on-solid adsorption.

6.1.1. Gaseous Hydrogen Storage

6.1.1.1. Pressure Vessel

Gaseous hydrogen at ambient temperature can be compressed in high pressure tanks which are easy to handle. Pressures range from < 1 MPa to around 30 MPa. The high pressure is the dangerous aspect for this type of storage tanks. They must be periodically tested and inspected to ensure their safety. Pressure vessels are economically operated only on the basis of short refilling cycles. Pressure vessel materials are low carbon steels or special alloys or high-strength non-metal composites. The Al/carbon composite is the lightest and strongest, but also the most expensive. Advanced designs use composite pressure vessels with a metallic liner and attainable pressures of 30 MPa. Cooling the compressed gas to cryogenic temperatures ("cryo-hydrogen"), e.g., by using liquid nitrogen, results in an increase of the storage density by up to a factor of 3.5 [33]. High-pressure tube storage, however, is confined to relatively small gas volumes.

Typical pressure vessels, e.g., as provided by the German gas company Messer Griesheim, are 50 l steel bottles containing 8.9 Nm^3 at a pressure of 20 MPa. For a large-scale consumption ($\approx$ 250 Nm^3), bundles of 28 bottles are used interconnected by high-pressure piping. Compressed natural gas (CNG) storage systems in cars have an experience of more than 3 million vehicle years of use with an excellent safety record [21]. The data base for H_2-fueled vehicles is very limited thus far.

6.1.1.2. Mass Storage

Natural gas pipeline grids are usually subdivided into a high-pressure grid (> 1.6 MPa), a low-pressure grid, and a third one for special industrial companies only. For gas storage, the high-pressure grid is used. The pipeline diameter is about 0.8 m and system pressure around 7 MPa meaning that the pipeline system itself has already an enormous storage capability.

Seasonal fluctuations of gas supply on interregional basis require a storage capacity in the order of some 10^8 to 10^9 Nm^3 which can be economically realized only in **no-vessel underground mass storage** used during peak consumption periods: (i) porous storage and (ii) cavern storage. Geological formations with the porous structure ($\approx$ 1 μm) of permeable layers underneath a gas-tight blanket, which can be either an aquifer or a depleted natural gas resource or a specifically formed cavern in a salt mine. Caverns are usually constructed and operated in salt formations in which large open void spaces are introduced by a process where water is pumped through a bore hole into a salt layer and exits as a brine. A cavern volume is in the order of 300,000 m^3. The storage capacity is dependent on void volume and the allowable pressure which is determined by the strength of the surrounding body.

A minimum pressure is required to serve as a support of the void which is independent of the gas stored and is usually in the range of 15 - 30 % of the total capacity [57]. Maximum pressures can be up to 4 MPa. Storage rates are in the order of 75,000 Nm^3/h, release rates are in the order of 320,000 Nm^3/h. Gas losses are in the order of 1 - 3 % per year. Typical ratios of the capacities of a 100 km high-pressure pipeline section to cavern storage to porous storage are 70 to 1300 to 20,000.

The operation of underground natural gas storage sites started in the USA in the 1950s. Today in continental Europe, there are 80 underground storage sites for natural gas with a total capacity of $40*10^9$ Nm^3. In Germany, the first cavern for natural gas started its operation in 1966. In 1993, 11 caverns, aquifers, and porous storage sites were operated in Germany for short-term peak consumption with a total capacity of $9*10^9$ Nm^3 [17, 57].

A large-scale hydrogen economy would need a similar large-scale underground storage method which, however, is expected to exhibit higher specific storage cost and somewhat higher gas losses. The basic feasibility of **H_2 underground storage** has been demonstrated. Experience exists with an aquifer at Beynes, France, operated with no problems from 1957 to 1974 where town gas containing 50 % hydrogen was stored. The capacity was $330*10^6$ Nm^3. Since 1971, the city of Kiel, FRG, uses a salt cavern in 1300 m depth as a storage site for town gas with 65 % hydrogen contents at pressures of 8 - 16 MPa. In Teeside, UK, the British company ICI operates three salt caverns in 366 m depth for hydrogen gas storage with a system pressure of 5 MPa [61]; storage capacity is of the order of 2 million Nm^3 each. Various other porous underground storage sites were in use already during the coke gas era [15].

6.1.2. Liquid Hydrogen Storage

Hydrogen is in its liquid state (LH_2) at a temperature as low as 20 K. It requires about 30 % of its energy for cooling and liquefaction. LH_2 must be stored in a superinsulated tank, called "dewar" or "cryostat", and even then, depending on the insulation quality and the surface-to-volume ratio, a certain fraction is an unavoidable boiloff to keep the rest cold. Safety is another concern. Energy can potentially be recovered when the cryogen is vaporized. The theoretical maximum is 10 % of the liquefaction energy. There are many opportunities of recovery; its realization is part of downstream engineering consideration [61].

6.1.2.1. Basic Design of a Cryogenic Tank

A storage tank to hold a cryogenic liquid requires an effective insulation since temperature difference is the driving force for heat to enter the tank. It usually means a second vessel around the fluid container [13]. A supporting structure and interconnections between the two vessels have to assure that the inner shell can freely undergo contraction / expansion, also for numerous temperature cycles (refills) that may occur during its lifetime. An even more complicated structural design is necessary for large vessels. Typical materials used for a cryogenic tank are carbon steel for the outer shell and stainless steel or aluminum for the inner vessel. Tubing from the inner vessel to the outside is generally made from stainless steel with vacuum-sealed transition joints on the cold side [51].

A multilayer insulation consisting of a reflective foil fixed on the outside of the inner vessel is usually chosen to minimize the transport of radiation heat. With increasing number of radiation shields, however, additional heat transfer is introduced due to conduction via physical contact. An optimal number is between about 60 and 100 layers [51]. The whole remainder of the intermediate space, in larger vessels about 1 m in thickness, serves as a vacuum jacket to avoid heat transport by convection or residual gas conduction. A typical pressure value in this space is < 0.013 Pa. Appropriate getter materials help maintain the vacuum over longer times.

An alternative which is used for large capacity tanks, is to fill the annular space with perlite powder of reflective particles. Tiny spaces in between avoid heat convection resulting in a less demanding vacuum of < 1.3 Pa. On the other hand, a shifting of the perlite powder during contraction of the inner vessel, a phenomenon called "perlite compaction" needs to be prevented in order to avoid breakage of the supporting structure [13]. A further decrease in heat conduction compared with the powder can be achieved by using hollow glass microspheres of boron silicate which have diameters in the range of 15 - 150 μm and a very low weight [51].

In large containers, the boiloff rate as a result of heat leakage can be significantly reduced by cooling the insulation with cold venting gas. For this purpose, metallic shields are installed with the insulation. In smaller containers, also liquid nitrogen cooling is being successfully used for boiloff reduction, but they are not as handy as the vapor-cooled container because of their weight and periodic refilling [51]. Multilayer super-insulation tanks exist at sizes of 300 m^3 with around 100 radiation shields. Storage and transport containers for LH_2 have been developed practically for all sizes. The autonomy of the system, i.e., the time with no loss of the product, is typically 30 days.

Further improvement is foreseen with the introduction of high-temperature supraconducting materials which allow the contact-free placement of the inner vessel in the outer container ("magnetic levitation") [33].

6.1.2.2. Passenger Car Tanks

The schematic of an LH_2 (or LNG) tank for a passenger car is shown in Fig. 6-1. The tank materials typically used are austenitic steel and cold-tough aluminum alloys. A minimum wall thickness of 2 mm is prescribed in Germany. The tanks are checked upon fabrication in leakage and pressure tests [50]. Present cylindrical double-walled storage tanks have a capacity of up to 150 l. The 30 mm thick insulation consists of 70 layers of aluminum foil and glass fibers allowing a boiloff loss of not more than 1.5 %/d. The total weight is 50 - 60 kg. Maximum operation pressure is 0.6 MPa.

An extensive experimental study as a part of the Euro-Quebec project has been conducted by **BMW** to investigate the safety of LH_2 storage tanks for passenger cars [50]. In particular, vibration and acceleration testing, air flooding of the vacuum, vessel deformation and perforation, and fire testing have been made to check the stability of the supporting structure and the performance in conceivable traffic accidents (see Fig. 6-2). Burst tests revealed a safety factor for the LH_2 tank walls of more than 14. The results have been used for design improvement. Preparation of the tanks with a safety burst

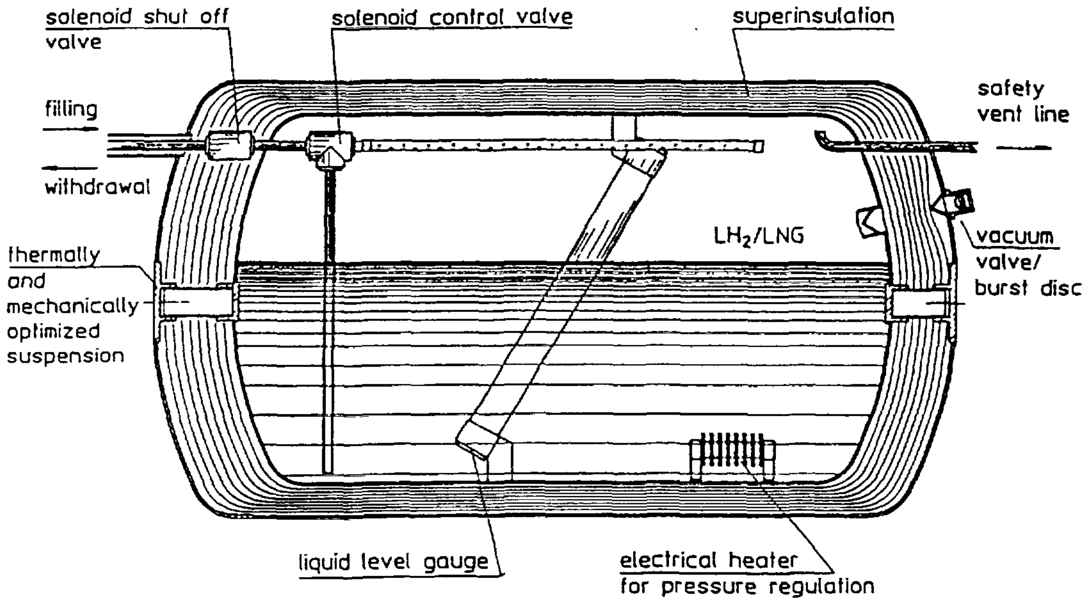

Fig. 6-1: Schematic of LH_2 tank for passenger cars, from [Messer Griesheim]

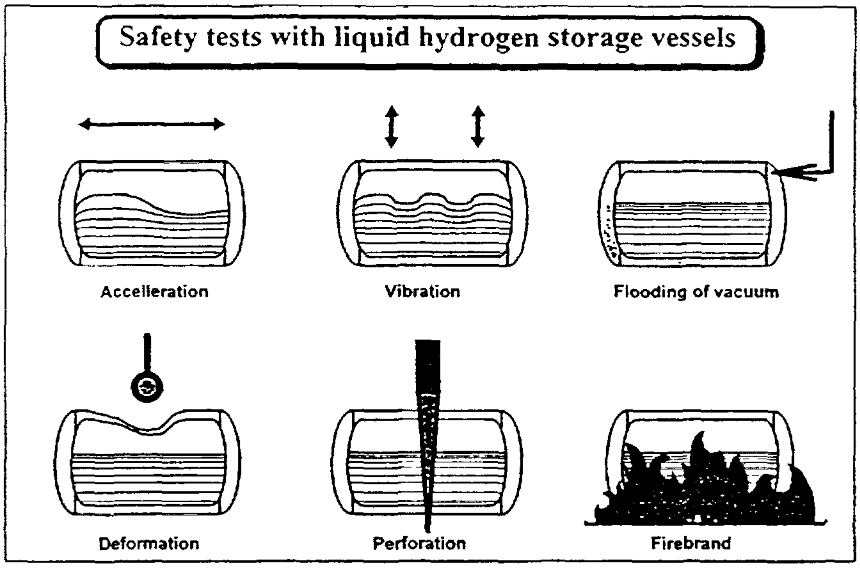

Fig. 6-2: BMW safety testing on LH_2 (or LNG) tanks for passenger cars, from [42]

device, a circular notch, prevented the catastrophic failure and rather dampened flow and pressure relief, but its reliability over the whole lifetime has yet to be proven. Fire tests meeting IAEA requirements have exposed the tank to a temperature of 900 °C. Safety valves opened after 4 minutes. The LH_2 was completely vaporized after 10 more minutes before the inner aluminum tank started to melt while the outer tank hardly exhibited any changes. The tanks have demonstrated good-natured behavior during depressurization via the safety valve. Neither test resulted in LH_2 pool formation.

6.1.2.3. LH_2 Model Container for Maritime Transportation

Within the frame of the Euro-Quebec project various technical concepts for the transportation and distribution of liquid hydrogen have been developed. A **61 m^3 model container** has been constructed in a joint effort between the Federal Institute of Materials Research and Testing (BAM), Berlin, responsible for infrastructure and tank operation, and the Germanischer Lloyd (GL), Hamburg, taking care of the scientific program including the evaluation of the test results. Its purpose is to demonstrate the safe storage and transport of large quantities of LH_2 [69]. It serves as a model simulating a future tank for maritime transport and storage. The cylindrical double-walled tank has a diameter of approx. 5 m and a length of 9 m with a designed system pressure of 0.5 MPa. The insulation between inner and outer tank consists of 30 layers of aluminum foil at the inside plus another 0.5 m vacuum space. For instrumentation, 67 temperature and pressure sensors are deployed to examine the thermal behavior of the tank.

Tests were conducted, the first with an LH_2 tank of such a size, to investigate the thermodynamic behavior of the liquid hydrogen in the tank. One important goal was to examine the pressure rise in the closed tank. Three test series were conducted [52, 69]:

- Open vaporization at atmospheric pressure to determine the energy input into the tank from the boiloff quantities and provide a homogeneous temperature distribution for subsequent tests
- Closure of tank and measurements of pressure increase rates simulating conditions of a maritime transport
- Intentional pressure increase by means of a vaporizer device to investigate the energy input by hydrogen preheated in a heat exchanger

The boiloff rate was measured to be approx. 1.3 %/d (about 0.7 m^3/d) for the filled open tank, while it was decreasing to 0.6 %/d at filling levels below 40 %. The decrease of the boiloff rate is attributed to the stronger heat uptake of the steel at higher temperatures which occur when in contact with the gas phase. In the self-pressurization tests, mass transfer from liquid to gas was found to have a dominant influence. The tests with the model tank on the BAM test site near Berlin have been terminated in the meantime, the tank is now being offered to third parties for further experimentation.

The fluiddynamic processes in a tank are very complex and are currently subject of investigation. A calculation model has been developed to enable the simulation of all conceivable states of the tank. The heat transfer from outside into the inner tank was measured to be 200 W whereas a value of 97 W was predicted [69].

6.1.2.4. Large-Scale Stationary Storage Tanks

For a large-scale liquid hydrogen storage, tanks of spherical shape are used to minimize boiloff losses. Two spherical dewars with a capacity of 190 m^3 of LH_2 plus 10 % ullage each were components at the Nuclear Rocket Development Station, Nevada, during the ROVER project starting in 1955 (see section 9.5.1.). The insulation consisted of a vacuum jacket and a 0.9 m perlite powder layer allowing an estimated boiloff rate of

0.3 %/d [11]. Later a 1900 m^3 LH_2 dewar was in use with an evacuated perlite insulation and a boiloff rate down to 0.08 %/d.

The largest LH_2 tank constructed so far is the **NASA** 3407 m^3 vacuum perlite-insulated spherical storage tank at the Kennedy Space Center, Florida, used in the US space shuttle program. The outer sphere is made from carbon steel with an inside diameter of 21.34 m and the inner sphere is made from austenitic stainless steel with an inside diameter of 18.75 m; the ullage is about 10 %. The tank has a boiloff rate of 0.03 % or approx. 800 l per day [51]. For comparison purposes: the LH_2 storage tank within the External Tank (47 m height, 8.4 m diameter) of the US Space Shuttle has a volume of almost 1600 m^3.

The largest stationary LH_2 storage in Japan is at the Tanegashima space center in two spherical double-walled tanks with an outer diameter of 12.6 m and a capacity of 540 m^3 each.

The Baikal-1 nuclear rocket test facility in Semipalatinsk, Kazakhstan, is reported to have constructed in the 1970s three large underground tanks for LH_2 storage with an estimated 18 m in diameter. In 1982, one of the tanks developed a leak and became unusable [53].

6.1.2.5. Future Storage Tank Designs

A concept of a composite LH_2 container has been developed in Canada where the outer shell is fabricated from fiber reinforced plastics. The tank volume is 60 m^3. Such vessels of which a first set has been manufactured already, are to be used for the transportation of smaller amounts of LH_2 onboard conventional container ships, railway carriers, or as a storage medium near power or refueling stations [34, 35].

The LH_2 storage container considered for the **Euro-Quebec barge carrier** is designed as a cylindrical pressure vessel type with a volume similar to that of the NASA tank. Geometric data are a length of 22 m outside and 18.7 m inside, a diameter of 14.7 m outside and 14.0 m inside. The total weight is 1000 tons including 213 tons of LH_2. To keep the vessel at cryogenic temperatures, 5 % of the LH_2 contents is left in the vessel on its way back to Canada. The tank must guarantee a stand-alone period of more than 25 days. The containers are designed to serve both as a transportation vessel and as an onshore storage vessel in order to avoid the undesired losses of LH_2 if it were to be pumped from one into another container. This concept eases at the same time the operation of the ships [18, 35].

Improved concepts of insulations have been developed for future large-size LH_2 storage tanks, e.g. a spherical tank with inner / outer diameters of 36 m and 40 m, respectively, which means a volume of about 24,400 m^3 or six times the NASA tank volume. The characteristic feature of the new insulation design is the partition of the interspace volume of approx. 9000 m^3 into many (some 10^4) small insulation boxes which can be arranged as a combination of vacuum and foam layers on the inner tank wall. The insulation character is maintained even if a single box has lost its vacuum. Target boiloff is 0.1 % per day. Experimental and theoretical investigations have been conducted for design optimization, in particular, the design of the supporting structure which is subjected to dynamic loads during maritime transportation. The new insulation concept was found to exhibit a thermal conductivity which is on the average one order of magnitude lower than that of conventional foam insulations [40].

Tank specifications for a large-scale LH_2 storage tank as projected within the **WE-NET** project, are a storage capacity of 50,000 m^3 with a target boiloff rate of 0.1 % per day. Various insulation concepts are currently being under investigation [32].

Also within the WE-NET project, a metal hydride/LH_2 hybrid storage system is proposed, where a hydrogen storage alloy serves as a buffer for a liquid hydrogen storage for the sake of ensuring a stable supply plus it absorbs flash hydrogen and boiloff losses [47].

6.1.3. Hydrogen Storage as a Metal Hydride

Metal hydride (MeH) is an intermetallic compound that traps hydrogen at moderate pressures. Large amounts of hydrogen can be stored in an exothermal diffusional process.

$$\mathrm{Me} + \mathrm{n}/2\ \mathrm{H_2} \quad \rightarrow \quad \mathrm{MeH_n} + \mathrm{heat}$$

The gas/solid reaction can take place at any temperature in the wide range between -80 and +600 °C. Storage temperature is at ambient, storage pressure between 3 and 6 MPa. Heating is required to restore the hydrogen. Some drawbacks are its cost and its heavy weight, and its requirement for very pure hydrogen. Metal hydride advantages include convenience, compactness, stable storage, and its intrinsic safety. Its specific storage capacity of 700 Nl of H_2 per l of system volume is higher than that of liquid hydrogen. In order to obtain alloys suitable for different applications, the properties of hydrides can be controlled by changing the composition and microscopic structure or by treating the surface, e.g., substituting or adding other metal elements. Examples of appropriate materials are FeTiH, $LaNiH_6$, MgH_2, or $MgNiH_4$. Container designs vary from simple low-pressure vessels to high-pressure, high-temperature heat exchangers. After repeated use, the metal alloy disintegrates into very fine powder which is toxic. Current research activities are concentrating on improving the performance both of the alloy, e.g., increase of capacity, lifetime, reactivity, and of the container, e.g., decrease of volume and weight, improvement of durability.

A new class of hydrogen absorbing alloys are **nanocrystalline metal hydrides**. These are polycrystals with a typical grain size < 20 nm. Their advantages are to maintain their integrity upon cycling and to show enhanced absorption / desorption kinetics. Examples of materials which can be synthesized easily by mechanical alloying, are FeTi and Mg_2Ti. A major drawback is the reduced maximum capacity [58].

Metal hydrides can serve as a purification system for hydrogen. Charging a hydride container with impure hydrogen allows only the hydrogen to reversibly react with the alloy while the impurities are concentrated in the void spaces. Venting a small fraction of the hydrogen removes the impurities and makes a flow of ultrahigh purity hydrogen available [49].

Ni-metal hydride batteries are a highly promising approach to a small and medium-scale energy storage for portable appliances. The first of its kind were designed for space applications in the 1980s. The basic electrochemical net reaction is

$$H_2 + 2\ NiOOH \quad \longleftrightarrow \quad 2\ Ni(OH)_2$$

The Ni-hydrogen battery has the advantages of high capacity, long lifetime, high energy and power density, recyclability and thus environmental acceptability. Typical energy densities are 50 - 70 Wh/kg [37]. The NiMeH battery is rechargeable up to 1200 times. Disadvantages are a high self-discharging, long charging times, its sensibility towards temperature and over-charging as well as complex and expensive manufacture [5].

A storage device that couples a high-temperature hydride to a phase change material has been tested by Arthur D. Little Inc. This system uses the heat released during hydrogenation to melt the material. In the reverse process, the released solidification energy is taken to liberate the hydrogen from the hydride compound. The material used is a Mg powder coated with Ni by means of chemical vapor deposition. The system was successfully tested as an essentially isothermal and isobaric process [29].

6.1.4. Others

6.1.4.1. Glass Microspheres

New high-strength **glass microspheres** with 25 - 500 μm in diameter and with 1 μm wall thickness are loaded in a high-pressure bath of hydrogen ($\approx$ 60 MPa) at higher temperatures where the tiny bubbles are highly permeable to hydrogen. After cooling the hydrogen is trapped. Once stored, the pressure in the carrying tank can be low. They are inert, resistant to contamination and only require moderate heat to release the hydrogen. Experiments are being done with crushing the spheres to increase the hydrogen release rate. The most advanced glass microspheres exhibit a burst pressure of 1000 MPa [38]. Engineered microspheres could make storage and transport of large amounts of hydrogen much more efficient and, if transported by rail, even could economically compete with liquid hydrogen [55].

6.1.4.2. Zeolites

Zeolite is an aluminum-silicate with a 3D structure which contains pores and voids. The storage principle of zeolites is that guest molecules (= hydrogen) are forced into the hollow spaces of the host material at high temperatures and high pressures. After cooling and relaxation, the hydrogen is encapsuled in intracristalline voids. It is recovered in a heatup process [66]. Tests have shown that no permanent storage was possible unless cooled down to temperatures < 120 K. Then the storage capacity was found to be 45 cm^3

hydrogen per gram dry zeolite (corresponding to 0.4 wt%). Experiments at the Taiyuan University of Technology in China have reached 1.9 wt% [66]. Zeolites can be effectively used for purification of hydrogen gas.

6.1.4.3. Gas-on-solid Adsorption

Activated Carbon is prepared from special biological or mineralogical carbonaceous materials by chemical activation, low-temperature (400 - 500 °C) carbonization to remove volatile organics, and high-temperature (800 - 1000 °C) oxidation to develop porosity and surface areas of 300 - 2500 m^2/g [3]. The effect of physisorption of the hydrogen is most pronounced at cryogenic temperatures. Adsorption properties are dependent on the pore size distribution. The principal capacity is originating in particular from the micropores (< 2 nm). The mesopores' contribution is not more than 5 - 10 %, whereas that of the macropores (> 50 nm) is insignificant. A volumetric density of 50 g/l of H_2 has been verified at 77 K and 3.5 MPa [7]. One of the best currently available carbons contained in a carbon fiber-wrapped pressure vessel at 87 K and 6 MPa would store hydrogen at 4.2 wt% and 16.8 kg/m^3 [3]. Latent heats of sorption must be removed during charging and supplied while discharging the container. Equilibrium times are less than 5 minutes.

A recently discovered option of hydrogen storage is adsorption on a material known as **carbon nanotubules**. These tiny tube-like configurations have a very large surface per unit weight, minimal macroporosity, uniform and tailored microporosity, and high thermal conductivity [3]. The amount of hydrogen stored was observed to be 10 wt% on the single-wall nanotubes (SWNT) weight basis. SWNTs are found, e.g., in arc-generated soots. Acting adsorption forces could lead to effective H_2 storage under ambient temperature conditions. Research is concentrating on SWNT production at a high yield [10].

The carbon sorption system is claimed to offer higher gravimetric and volumetric density of pressurized hydrogen with minimal cost as well as a high degree of dormancy and safety. Efficiency, however, is reduced when introducing impurities. The need of cooling system and vessel working under high pressures and low temperatures may complicate the whole system [45].

A new storage system consisting of graphite layers was reported in early 1997 by US scientists to store 30 l of molecular hydrogen per gram. This corresponds to about 75 % hydrogen storage per weight, which could represent a breakthrough compared with the figures of 4 % valid for nanotubes. The material is a densily packed structure of graphite fibers of 5 - 100 mm length and 5 - 100 nm diameter. Storage pressure is about 4 - 5 MPa. Filling time is between 4 and 24 hours. This tremendous storage capability is still unexplained; it would give a hydrogen-fueled car a range of as much as 8000 km (!) [26]. Attempts will be made in near future to verify these results with masses of 200 mg to 1 kg.

6.1.4.4. Liquid Carrier Storage

Hydrogen can be reversibly stored in a chemical compound in a liquid state with, for example, methanol, toluene (methylcyclohexane), ammonia as the carrier from which it must be extracted (dehydrogenation) prior to utilization unless the products are used directly (see section 6.3).

6.1.5. Comparison of Storage Systems

Table 6-2 summarizes pros and cons associated with the various types of hydrogen storage. The Bentley plot in Fig. 6-3 gives some perspective on volumetric versus gravimetric energy densities of different hydrogen storage systems (which include vessel, heat exchangers, insulation etc.) compared with conventional liquid fuels and future storage designs [28]. The DOE goal for vehicular hydrogen storage systems is 6.5 wt% and 65 kg/m^3. If the above mentioned recently discovered graphite material with 75 % hydrogen storage per weight and its technological feasibility could be verified, it would mean a tremendous qualitative step forward.

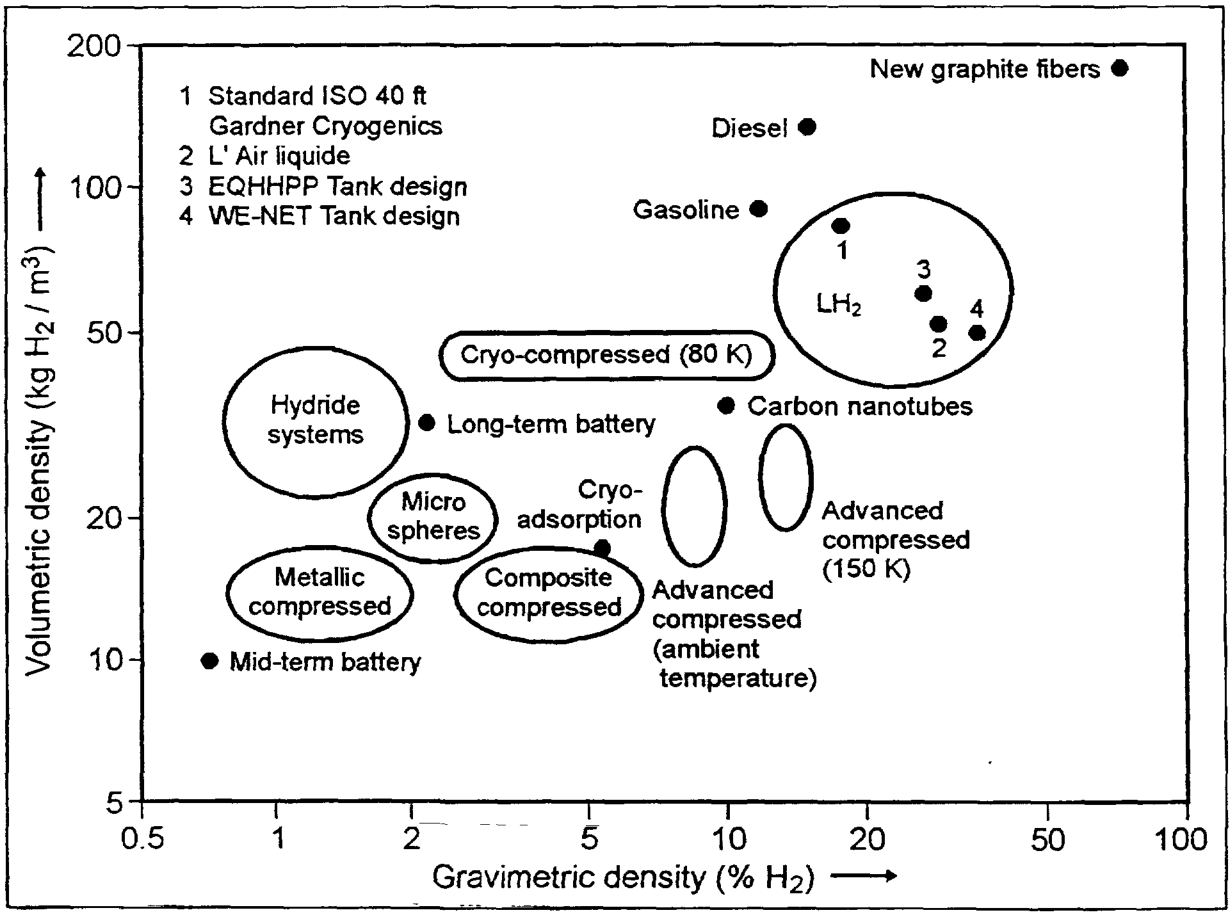

Fig. 6-3: Gravimetric and volumetric hydrogen (and other fuels) storage systems, from [28, 33, 71]

Table 6-2: Advantages and disadvantages of hydrogen storage technologies, from [3]

H_2 storage type	Advantages	Disadvantages
Compressed gas	Mature technology High gravimetric density dormancy	Bulky compression costs safety
Cryogenic Liquid	High volumetric and gravimetric density Purity	Liquefaction costs Boiloff loss Poor performance in small systems
Metal hydride	High volumetric density Safety	Poor gravimetric density High dissociation temperature Impurities
Gas-on-solid adsorption	Fair volumetric and gravimetric density Potentially low costs	Compression and cooling costs Complexity
Chemical storage	High gravimetric density Unlimited storage	Toxicity Impurities Rehydrogenation reaction Conversion limitation

6.2. TRANSPORT AND DISTRIBUTION OF GASEOUS AND LIQUID HYDROGEN

Larger distances between the locations of heat production (power plant) and heat demand (consumer) require tanks and methods of transportation of heat/energy to distribution systems.

6.2.1. Pipeline System

6.2.1.1. Gas Pipeline Grid

In most countries, gas pipeline systems serve both transportation and distribution purposes. An exception is the Russian Federation whose **natural gas** pipeline is a pure long-distance transportation. An important component of a gas grid are the compressor stations to maintain the necessary system pressure. Their energy consumption corresponds to about 0.2 - 0.5 % of the amount of gas transported per compressor station which amounts to the order of 10 % for the long-distance gas transportation [39]. Design specifications of a future natural gas pipeline are a diameter of 1.6 m, the deployment of an inner coating, a system pressure of 12 MPa, and an annual transport capacity of $54*10^9$ Nm^3. Compressor consumption will be down to 5 % on a length of 6000 km [57].

The net heat of combustion of hydrogen per unit volume is by a factor of 3.3 lower than that of methane. The transport of the same energy quantity thus requires a correspondingly increased compression for H_2 propulsion, in reality a factor of 3.3 - 3.8. Differences between natural gas and hydrogen are given by different energy transport capacities (Wobbe index) and the different compressibility behavior as a function of pressure resulting in higher friction losses for hydrogen. Furthermore the H_2 compression necessitates multi-step compressors whereas natural gas compression is usually designed for one step. A simplification is given in that no pre-heating is required because of the positive Thomson-Joule effect liberating heat upon hydrogen depressurization [15]. Economic operation implies the transport of very large quantities.

The transport of **gaseous hydrogen** in a pipeline system is a technology, which has long been applied. More than 750 km of hydrogen pipelines (as of 1990) have been put in place worldwide [43], an estimation of 700 miles is given in [46]. The German company Hüls AG has started as early as 1938 to operate a H_2 distribution grid in the Rhine/Ruhr region. This pipeline system, since 1993 being operated by the British BOC, with a total length of 250 km and connecting 14 H_2 producing and consuming companies, is the largest in Europe. The hydrogen is provided by steam reforming and as a byproduct from the chlorine production by the chlorine-alkali electrolysis process. The pipe diameter varies between 0.17 and 0.27 m and the throughput is $250*10^6$ m^3/yr at a system pressure of 2.2 MPa. Since 1969, the US company Air Products is operating a 232 km hydrogen pipeline in Houston, USA, with a pipe diameter of 0.15 - 0.2 m diameter at a pressure of 6 MPa. The company operates two more H_2 grids in New Orleans, USA, with 96 km and in Rotterdam, The Netherlands, with 48 km. L'Air Liquide in France operates since 1966 a H_2 pipeline network which has reached today an extension of about 600 km connecting North France, Belgium, and The Netherlands. Another one in South Africa is of 80 km length [43]. Circumferential stresses of < 56 N/mm^2 and the relatively low degree of purity of the piped hydrogen are reasons for the good performance of the existing H_2 pipelines so far. Long-distance pipeline transportation of hydrogen gas has not reached an intercontinental dimension up to now.

The use of the existing natural gas pipeline grid for the transportation of pure hydrogen would require tremendous modification efforts. But the technical problems of increased propulsion or material degradation appear to be solvable [15]. Safety requirements for H_2 pipeline transportation are more stringent compared with natural gas. The question whether the existing natural gas pipeline grid can be used for hydrogen, cannot finally be answered since the presently used steel, StE480.7TM, has not yet been proven to guarantee safe operation under hydrogen transportation conditions. Another disadvantage is that hydrogen is more prone to leaking than natural gas; grid losses are expected to be 3 % for hydrogen compared with 2 % for natural gas. If hydrogen, however, is added to the natural gas up to a fraction of 5 vol%, the existing pipe infrastructure can be used without changes [39]. Minimal changes are required for blends with up to 20 %.

The project of a "Trans-Asian Gas Pipeline Network" has been proposed connecting natural gas fields with consumer markets of 19 supplying, consuming, and transit countries with a total length of 46,200 km. It is small compared with the existing NG pipeline grids in the European Community with 800,000 km (1990) or in the USA with 440,000 km. The Asian pipeline is designed to transport natural gas in first stage, but is apt to be converted to hydrogen in the future [25].

Summarizing, it can be stated that a large-scale hydrogen transport and distribution is technically feasible taking account of the peculiarities of hydrogen (physical, material-specific) compared with natural gas. Transportation cost is expected to be in the same order as natural gas for regional distribution and to be higher for a large-scale transportation [15]. In the long term for large geographically concentrated demands, pipeline distribution might ultimately yield the lowest delivered fuel cost [48].

6.2.1.2. Pipeline Grid for Cryogenic Liquids

An alternative to the gas transport is **liquid natural gas** (LNG) transportation. A much higher density is gained at the expense of additional losses due to liquefaction, ship transport, and boiloff, estimated to be in the range of 12 - 20 % [39]. Relay bases as distribution systems are being operated for LH_2, LNG, and LPG. These satellites bases are usually smaller than the primary bases.

Pipeline transportation of **liquid hydrogen** is realized on a small scale and short range. Stainless steel is usually taken for the inner line with low heat conduction spacers as a support in the vacuum jacket. The Kennedy Space Center in Florida uses an LH_2 and LOX pipeline of 500 m length with an inner pipe diameter of 0.15 m. Flow rates achieved are up to 250 m^3 LH_2 per minute and 100 m^3 LOX per minute, respectively [12]. Transfer is realized by applying pressure, no pumps. Major concerns besides heat leakage is the mechanical stress imposed on the inner line due to contraction / expansion, pressure oscillations upon cooldown, or two-phase flow.

In the German city of Jena, a 5 km **liquid helium** pipeline is operated to provide consumers with 25 m^3/yr of LHe which is at a temperature of 4 K.

6.2.2. Vehicle Transportation

The type of storage system to be chosen largely depends on size, driving cycle, and range of the vehicle. A low mass is required, if acceleration plays a significant role, e.g., in aviation, while it is of less importance for trains or ships. Also tank geometry for onboard H_2 storage needs to be compatible with the vehicle structure aiming at a minimum of surface-to-volume ratio. The lifetime of the storage system should suit the vehicle lifetime.

6.2.2.1. Road Transportation

Loads of **LH_2 tank trucks** are in the range of 30 to 70 m^3 with boiloff rates of 0.3 - 0.5 % per day. Due to restrictions in the tank size, the upper limit of the diameter is around 2.5 m. Cylindrical vessels are used with surface to volume ratios of only 10 % more than that of a sphere [59]. Messer Griesheim trucks have a transport capacity of 30,800 m^3 (at 0.1 MPa, 15 °C) of hydrogen, corresponding to 42 m^3 of LH_2. Road transport capacities of Gardner Cryogenics are ranging from 5.7 up to 64 m^3 of liquid hydrogen with normal boiloff losses less than 0.2 % per day.

In 1994 hydrogen transportation on European roads amounted to 311.2 million Nm^3, about 40 % of which were transported in Germany translating into 50,000 deliveries per year or about 200 per working day [62]. The number of liquid hydrogen deliveries is lower; estimations are approx. 2300 LH_2 deliveries per year to customer sites. In North

America, the number of LH_2 truck deliveries is estimated to be 15,000 per year providing approx. 180 (metric) tons of LH_2 to customers [8, 63].

Substituting conventional gasoline fuel by liquid hydrogen would increase the number of tank truck transports for distribution by a factor of three.

Gaseous hydrogen transportation is generally realized in 20 MPa pressure vessels. Common practice is the use of trailers loaded with either gas bottle bundles with a capacity of 4000 Nm^3 or a set of 9 large bottle vessels with a total capacity of 4300 Nm^3. A new development of a trailer is now in operation holding 200 single bottles with a transport capacity of 6000 m^3 (at 0.1 MPa, 15 °C) of hydrogen and a filling pressure limited to 20 MPa. In Germany, several hundred hydrogen trailers are being operated [62]. In North America, the amount of hydrogen gas transported by truck is estimated to be around 10 % of the liquid volume [8].

6.2.2.2. Ship Transportation

LNG maritime transportation is a since long applied technology on a large-scale base. In 1992, 76 LNG tank ships were operated with an average capacity of 100,000 m^3 of LNG [35]. Commercial transportation of liquid hydrogen via pipeline does not appear realistic [68]. A tank ship transport of LH_2 is reasonable especially if transported over long distances. The comparatively low volumetric energy density of LH_2, however, requires very large tank ships and a much higher fraction of the hydrogen transported is needed for the transport itself and is estimated to be in the range of 23 - 38 % of the energy transported compared with about 5 % for an LNG tank ship [68]. In terms of safety, LH_2 ship designs may principally capitalize on the broad long-term experience with LNG and LPG maritime transportation.

Liquid hydrogen barges for fuel supply in the French and US space programs. Barges with 900 m^3 of LH_2 storage containers were used during the NASA Apollo project. The European Ariane project was supplied with LH_2 by overseas transportation from New Orleans to Kourou, French Guiana, in 20 m^3 storage vessels with either LN_2 or vapor cooled multilayer insulation [51]. Maritime LH_2 transports to Kourou have been discontinued with beginning of the on-site liquefaction plant operation in 1990 [6].

The barge carrier considered within the **Euro-Quebec project** to transport LH_2 to Europe is designed as a dock ship with a total length of 180 m and a width of 29 m carrying 5 barges to contain a total of 15,000 m^3 of LH_2. Its remarkable safety features are a double-walled hull, a distance of 6.5 m between side shell and barge, and a distance of 11 m between ship bottom and vessel. The ship is powered by 10 MW diesel engines and reaches a speed of $\approx$ 18 kt[18] (which is about 33 km/h). The LH_2 tank consists of two concentric vessels with a total length of 22 m and 18.7 m, respectively, for the outer and inner vessel and with an outer/inner diameter of 14.7 m and 14 m, respectively. The net volume of the tank is 3047 m^3 (corresponding to 213 tons of LH with an ullage of 15 %. The cargo is stored at an initial pressure of 0.125 MPa; the upper design limit for the tank is 0.5 MPa [18, 35].

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[18] 1 kt = 1 knot = unit of speed of one nautical mile an hour = 1.852 km/h.

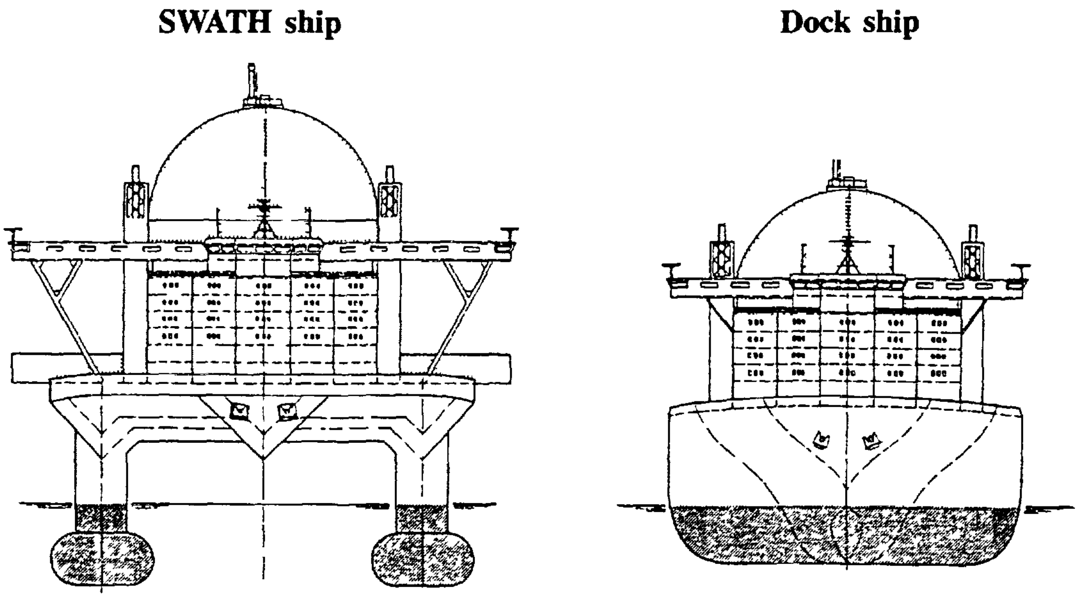
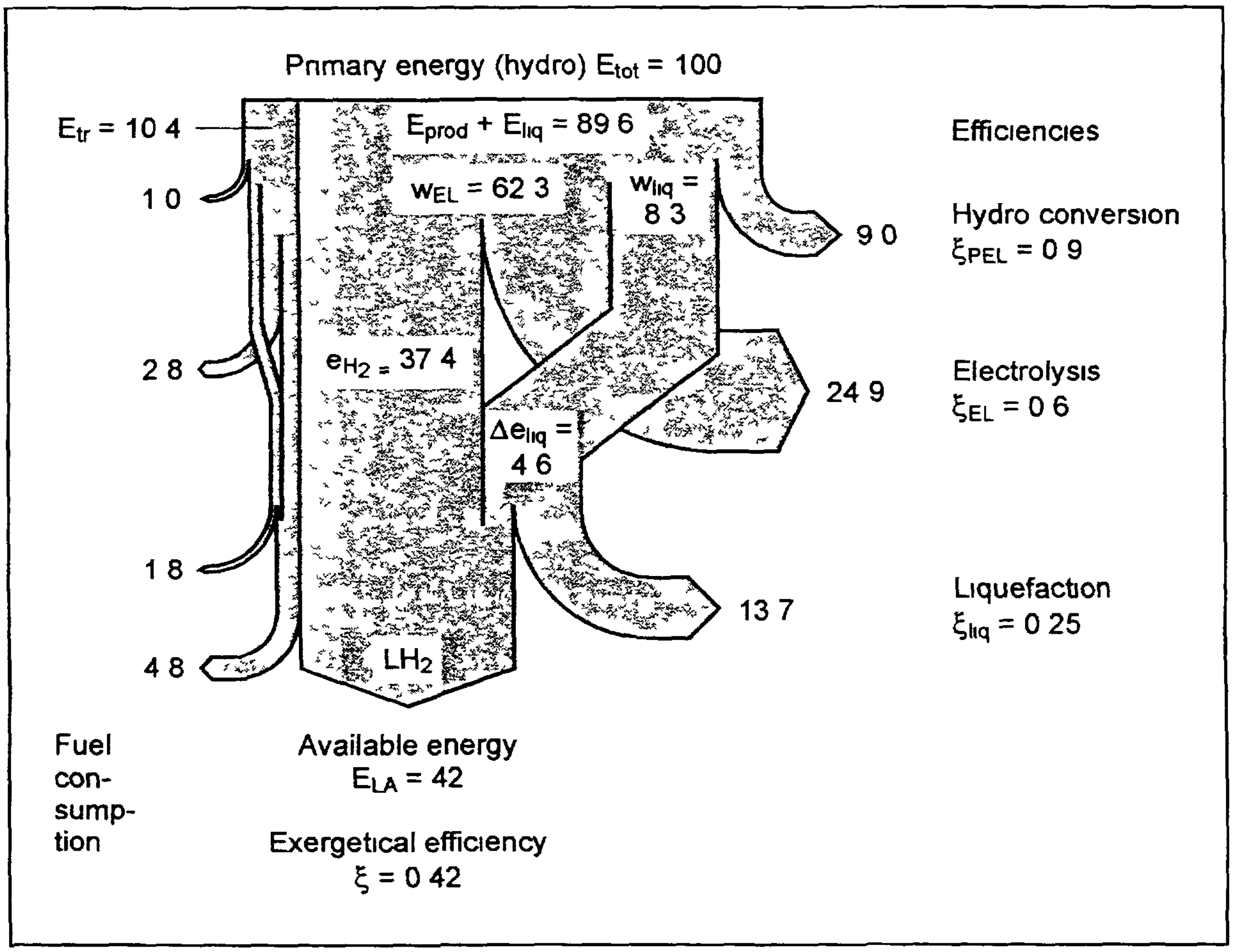


Fig. 6-4: Liquid hydrogen tank ship design of the SWATH ship and the dock ship, from [35]



E_{tr}, E_{liq} = energy portion of transportation, production, liquefaction
w_{el}, w_{liq} = work requirement for electrolysis, liquefaction
e_{H2} = chemical exergy, Δe_{liq} = thermal exergy

Fig. 6-5: Exergy flow diagram for SWATH ship transportation of liquid hydrogen based on E_{tot} corresponding to 310 MJ/kg H_2, modified from [35]

Two follow-on LH_2 tank ship designs, the **SWATH (Small Waterplane Area Twin Hull) ship** and the **dock ship**, have been developed by the German companies Howaldtswerke Deutsche Werft, Noell-LGA Gastechnik, and Germanischer Lloyd. Both ships have a load capacity of 125,000 m^3 corresponding to a weight of 8,150 tons (see Fig. 6-4). The ships are hydrogen-fueled for which liquid hydrogen as well as the unavoidable boiloff losses ($\approx$ 0.1 % per day) are used. The SWATH ship is superior to the dock ship in terms of lower weight and lower energy consumption per sea mile. The SWATH ship with a length of more than 300 m carries four spherical LH_2 tanks. As the propulsion system, a gas turbine with steam injection of 41 MW has been proposed. This system allows to regain a part of the technical work that was introduced into the liquefaction process ("Enhanced Cryogen Exergy Recovery System", ECERS). Waste gas energy is utilized for steam generation. The efficiency is estimated to be 51 %. Although this type of propulsion system is known in its single components, it has not yet been realized. However, the technical feasibility was proven [68]. A flow diagram of the exergy (= energy that can be converted with no restriction into another form of energy) for a maritime LH_2 transport with the SWATH ship is shown in Fig. 6-5. The overall exergetic efficiency is estimated to be 42 % [35].

Studies on a future hydrogen sea transportation system in Japan is based on its broad experience on large-scale LNG transportation with the first tanker ship starting in 1959. Within the **Japanese WE-NET project**, two preliminary concepts of a cryogenic tank ship have been proposed based on the assumption of fueling a 1000 MW(e) power plant which consumes 1200 t/d of LH_2. Furthermore assuming two ships to travel 6000 nautical miles within 10 days, the load capacity will be 200,000 m^3 of LH_2. The two concepts are distinguished by different tank structure designs. One is the ISI SPB self-supporting prismatic tank system, the other one the MOSS self-supporting spherical tank system with capacities of 100,000 and 50,000 m^3, respectively. The boiloff losses of estimated 0.2 - 0.4 % per day are designed to be utilized for the H_2 propulsion system of the twin hull ship, whose power is calculated in first approximation to be provided by two 30 MW engines to allow a speed of 20 - 25 kt ($\approx$ 37 - 47 km/h) [1].

The Japanese Ship Research Institute in the Ministry of Transport has developed within the PORSHE project (see section 9.2.4) a concept of a 125,000 m^3 LH_2 tank ship. An internal reheat hydrogen gas turbine has been designed as an engine for an ultra-high speed marine vehicle. The engine must have a power of > 300 MW to transport a total weight of 5000 t at a speed level of 100 kt ($\approx$ 185 km/h) [24].

6.2.2.3. Railway Transportation

Transportation of LH_2 in rail cars has started in the 1960s by the Linde company using a 107 m^3 tank with a multiple layer insulation. The measured boiloff rate was 0.2 %/d. The US company Praxair operates a fleet with 16 hydrogen railcars. The hydrogen is saturated at a working overpressure of the tank of 55 kPa with a pressure control system to open the relief valve at an overpressure of 117 kPa. The amounts of LH_2 transported in railcars in recent years were approx. 70 tons or about 10 railcar loads per month [8].

6.2.2.4. Aircraft Transportation

The transportation of liquid hydrogen as a payload onboard an aircraft is being considered an alternative delivery scheme to the ship transport including the option of a cryo-fueling of the aircraft itself. The advantages of air transportation is the light weight of LH_2, a reduced boiloff loss, the short duration of an aircraft roundtrip, the direct accessibility of the production site, and the reduced buffer storage required. Drawback is the large number of deliveries in a large-scale supply connected with an extensive ground infrastructure [41] and last, but not least, the lack of any practical experience.

In phase I of the **Euro-Quebec project**, air transportation of LH_2 across the Atlantic was considered a possible option. The full payload potential of an Airbus A300-600 would cover the entire daily production of 42.7 t of LH_2. The overall energy yield, however, was estimated to be down to 35 % compared with a 10 points higher yield for LH_2 transportation by ship. The fact that the energy demand of transportation in an aircraft was as high as the payload, was deemed unacceptable [9].

Within the **WE-NET project** the aircraft transportation capacity based on 5000 km distance was investigated in a study to correspond to a payload of 454 tons and a speed of 400 kt ($\approx$ 740 km/h) to allow two airplanes to operate a 1000 MW power plant. For a payload of 1500 t and a speed of 300 kt ($\approx$ 560 km/h), one plane would be sufficient [47].

6.3. CHEMICAL ENERGY TRANSMISSION SYSTEMS

The key components of a chemical energy transmission system (CETS) or a chemical heat pipe are a primary energy source (fossil, renewable, nuclear) to provide heat to an input catalyst reactor. In this reactor, a mixture of appropriate materials is chosen for the desired endothermal reaction, i.e., to store energy in the newly created products. After transportation of the product gas mixture at ambient temperatures, the reverse exothermal chemical reaction in an output catalyst converter helps to extract the stored heat for consumption as high-grade or low-grade heat or in a turbine. In a closed cycle, product materials are then returned to the heat source. Unlike liquid hydrogen, chemical compounds with hydrogen provide an economic method of a seasonal storage of energy [60].

The reactions must be reversible, rapid, and as complete as possible to avoid unwanted secondary products. They should have a high efficiency and a high reaction enthalpy in order to minimize the masses to be transported, plant and pipe sizes as well as operating cost. They must be controlable to allow intermittent storage/retrieval operation. Furthermore, educts and products should be inexpensive, non-corrosive, non-toxic, and easy and safe to handle [19]. CETS have to compete against hydrogen pipeline systems or the electricity grid.

Several candidates for a closed-loop reversible chemical energy system with varying operating temperature ranges and storage capabilities have been detected and are listed in Table 6-3 [20]. Certain limitations of the long-distance heat transport are given by its restricted storage capabilities, by the limited temperature ranges and by the complex distribution systems required [2].

Table 6-3: Organic systems with hydrogen as the energy carrier as CETS candidates, from [20]

Closed-Loop CETS			Temperature range [°C]	Reaction enthalpy [kJ/mol]
$CO + 3\ H_2$	$\longleftrightarrow$	$CH_4 + H_2O$	700 - 1200	250
$2\ CO + 2\ H_2$	$\longleftrightarrow$	$CH_4 + CO_2$	700 - 1200	247
$C_2H_2 + H_2O$	$\longleftrightarrow$	CH_3CHO		134
$C_2H_4 + H_2$	$\longleftrightarrow$	C_2H_6		138
$C_6H_6 + 3\ H_2$	$\longleftrightarrow$	C_6H_{12}	500 - 750	207
$C_7H_8 + 3\ H_2$	$\longleftrightarrow$	C_7H_{14}	450 - 700	215
$C_7H_8 + 4\ H_2$	$\longleftrightarrow$	C_7H_{16}		252
$C_{10}H_8 + 5\ H_2$	$\longleftrightarrow$	$C_{10}H_{18}$	450 - 700	359

Some of the important CETS are

- steam reforming system with natural gas
  theoretically and experimentally investigated and demonstrated at the Research Center Jülich, known as the EVA/ADAM system to prove the ability of the HTGR as a primary energy provider,
- CO_2 reforming system with natural gas
  studied as a closed cycle in Israel based on solar primary energy,
- methanol system
  as CO_2-neutral cycle, if atmospheric CO_2 is used as the carbon source,
- methylcyclohexane (MCH) - toluene cycle
  as transportation or seasonal storage method considered as one option in the Euro-Quebec project and the WE-NET project,
- ammonia system
  investigated in Australia as a closed cycle system based on solar primary energy.

The above CETS systems are described in more detail in appendix B.

Japan has made a **comparison of the transmission efficiencies** (= ratio of output energy to input energy) for various hydrogenation - dehydrogenation systems. Based on the assumptions of 4000 MW hydro power, electrolysis with a 90 % efficiency, and a maritime transportation distance of 5000 km, transmission efficiencies have been derived as listed in Table 6-4. The table, however, does not reflect production cost or environmental aspects [70].

Within the conceptual design of the WE-NET project, a comparison was made between the methanol system and the liquid hydrogen system. The energy balance over the whole path from electricity over the steps electrolysis, methanol synthesis, transportation, reforming to hydrogen, combustion turbine power output reveals an overall efficiency of

Table 6-4: Transmission efficiencies for various types of vectorization, from [16, 70]

Vector	Energy density [kWh/kg$^{(1)}$]	Storage capacity [wt%]	Working temperature [K]	Energy needed for storage [%$^{(2)}$]	Transmission efficiency [%]
Liquid hydrogen	33.3	100	20	25 - 33	70
Long distance pipeline	33.3	100	> 273		88 - 92
Methanol / Methyl - Formate$^{(2)}$		2.9			69
Methanol / CO_2	5.6	12.0	> 273	28	68
Ammonia	5.14	17.6	> 240	22 - 28	68
Methanol / CO	5.6	12.5	> 273		66
Cyclohexane	2.03	6.2	> 573	30	60

(1) in relation to net heat of combustion

(2) in relation to gross heat of combustion

about 25 % compared with 38 % in the LH_2 system. On the other hand, LH_2 facility cost is expected to be higher because of the need for heat insulation. Nevertheless, the LH_2 system was deemed superior to the methanol system [47].

6.4. CHEMICAL HEAT PUMP SYSTEMS

Chemical heat pump systems are important, if the utilization of low-quality heats (≈ 80 °C), e.g., solar or geothermal or nuclear (LWR) heat, waste heat in factories, is considered for heat storage and temperature upgrading to improve the total efficiency of the system. Among the many chemical cycles that have been considered to store and transport heat energy in the form of chemical reaction enthalpy, the coupled processes of hydrogenation / dehydrogenation can be adapted here.

A chemical heat pump system consists in principle of two reactors H and L where the following processes proceed:

$$\text{H:} \quad A(s) + C(g) \longleftrightarrow AC(s) + Q_H$$

$$\text{L:} \quad B(s) + C(g) \longleftrightarrow BC(s) + Q_L$$

Reactor L contains the compound BC where heat is added to cause an endothermal reaction liberating C as a gas. C is routed to the reactor H which contains A to undergo an exothermal reaction where high-temperature heat becomes available.

The reactions are of either liquid-gas (wet) or solid-gas (dry) type. Dry processes show high reaction rates enabling compactness, but a poor heat and mass transfer behavior compared with wet processes [19]. The examples of the 2-propanol - acetone system [44, 56], the cyclohexane-benzene system [31], the hydride system [30], and the sponge iron system [54] are given in more detail in appendix C.

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Chapter 7

APPLICATIONS OF HYDROGEN

Hydrogen has many and versatile uses as a secondary energy carrier and a secondary raw material: With 48 % consumption, it plays a significant role in non-energetic applications as a chemical raw material and intermediate product for industrial and petrochemical processes. Furthermore, it is largely used in energetic applications indirectly, e.g., in the production of clean synthetic fuels (20 %) or directly as a fuel for producing process heat in the chemical industries (32 %) [45]. From the annual world production of approx. $500*10^9$ Nm^3 of hydrogen, about 70 % are consumed in the chemical industries. It possesses, however, a huge potential to generate mechanical energy, heat, or electricity for a future large-scale use.

7.1. HYDROGEN AS A RAW MATERIAL IN CHEMICAL PROCESSES

The chemical hydrogen economy started already at the turn to the 20th century when coke furnaces generated process gas and town gas with an up to 60 % hydrogen component. Since then a whole variety of non-energic and indirectly energetic applications has been developed for hydrogen as a part of the synthesis gas such as

- ammonia synthesis
- methanol synthesis
- direct reduction of iron ore
- fossil fuel processing (hydro cracking)
- Fischer-Tropsch synthesis
- methanation in long-distance energy transportation (see section 4.3.2.3. and appendix B)
- hydro-gasification (see section 5.1.2.2.)

7.1.1. Ammonia Synthesis

More than half of the hydrogen used in the chemical industries or 40 % of the world production, approx. $200*10^9$ Nm^3, is consumed in ammonia synthesis

$$N_2 + 3\,H_2 \quad \rightarrow \quad 2\,NH_3 + 46\ \text{kJ/mol}$$

Feed gas for the steam reformer is methane or gasoline. High dilution with steam is chosen to keep the methane contents on a low level. Adding air in a secondary reformer leads to partial oxidation of the residual methane and of the CO. After separation of the CO_2, the product gas is a mixture of nitrogen and hydrogen whose ratio (desired 1:3) is adjusted by the operating conditions. The system pressure is about 5 MPa, the synthesis temperature is 400 °C [27].

The production of one ton of ammonia requires about 2000 Nm^3 hydrogen as well as approx. 800 kWh for compression of the synthesis gas and provision of the nitrogen (by air liquefaction).

Modern industrial production of ammonia in the so-called Haber-Bosch process allows a daily output of 1000 - 2000 t of liquid NH_3 corresponding to a hydrogen consumption of 80,000 - 160,000 Nm^3/h. The use of high gasification pressures makes the subsequent compression step superfluous. Ammonia is worldwide used as a fertilizer with facilities for storage, safe handling, transportation, and distribution being available. It could also be used as a fuel for automobile transportation to replace CO_2 producing fuels.

7.1.2. Methanol Synthesis

The world production of methanol is currently estimated to be about 27 million (metric) tons per year (1995). The methanol synthesis consumes about 5 % of the world hydrogen production. Methanol is basically used in the chemical industry as an intermediate product ("C_1 chemistry"). It is gaining further attention as a secondary energy carrier with less CO_2 emission, e.g., as a direct vehicle fuel or as a basis for the production of hydrogen-rich gas to feed fuel cells.

The formation of methanol from synthesis gas can be described by the two independent reverse reactions that were given in section 5.1.1.6. for the methanol splitting process by high temperatures or steam reforming. In the conventional method, a mixture of CO, CO_2, and H_2 is compressed to about 10 MPa and introduced into a fixed-bed catalytic reactor at temperatures of 220 - 280 °C and pressures of 5 - 20 MPa [27].

$$CO + 2\,H_2 \rightarrow CH_3OH + 91\text{ kJ/mol}$$

$$CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O + 50\text{ kJ/mol}$$

The reactions are exothermal and volume-reducing, thus low temperatures and high overpressures are desirable. A catalyst is required to maximize methanol output. The specific consumption is 2300 Nm^3 of CO and H_2 per ton of methanol. A processing scheme has been proposed by Lurgi (see Fig. 7-1). Nowadays conventional synthesis reactors have a capacity of up to 3000 t/d of methanol.

Methanol production generates a surplus of hydrogen which can, by adding CO_2, be utilized to increase the methanol yield and thus reduce CO_2 emission into the atmosphere:

$$3\,CH_4 + 2\,H_2O + CO_2 \rightarrow 4\,CH_3OH$$

In a subsequent step, hydrocarbon fuel synthesis can be made:

$$n\,CH_3OH \rightarrow (CH_2)_n + n\,H_2$$

A CO_2-neutral solution is obtained if the CO_2 released during combustion of the methanol is recovered from the ambient during the methanol production step. A CO_2-free coal-to-methanol production is given by taking H_2 as a supplemental feed and a non-fossil source of high temperature heat (e.g., nuclear).

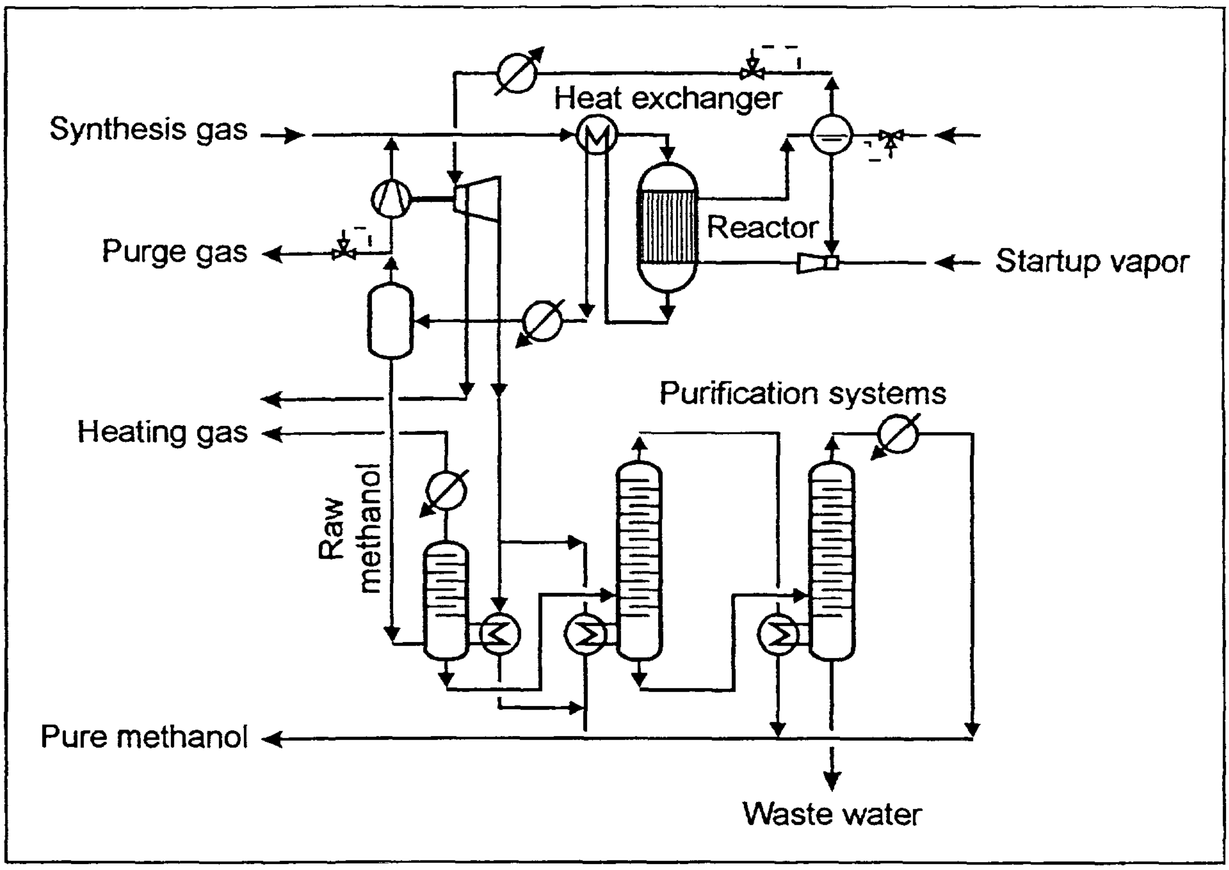

Fig. 7-1: Chemical processing flow chart of the Lurgi low-pressure methanol synthesis, from [38]

In the low-temperature liquid phase process, the use of a highly active liquid catalyst results in an efficiency of 90 % compared with 40 % in the conventional process. A 10 t/d unit has been constructed and continuously operated for 320 h. Next step is the realization of a 100 t/d pilot plant [2].

The development of a new catalyst allows the methanol synthesis to take place at lower temperatures (80 - 120 °C) and lower pressures (1 - 5 MPa). A drawback is the rapid deactivation of the catalyst in the presence of strong lyes [33].

In Japan, the conventional method of methanol synthesis has been modified by adopting a fluidized granular catalyst bed rather than a fixed bed which allows the possibility to enlarge the scale of the reactor, to reduce the power required, and to exchange the catalyst during operation [2].

7.1.3. Direct Reduction of Iron Ore

Blast furnace technology is used for more than a century for raw iron production. The stack gas generated during the process was usually considered a waste gas. Its constituents and typical fractions are CO (≈ 40 %), N_2 (≈ 40 %), CO_2 (≈ 12 %), H_2O (≈ 6 %), and H_2 (≈ 2 %).

Direct reduction of iron ore to sponge iron which can then be converted to steel in an electric arc furnace is a process that takes place outside a blast furnace avoiding the use of coke. This process is more favorable than the traditional raw iron production by means of coke. The chemical reactions are:

(a)	$Fe_2O_3 + 3\ H_2$	$\rightarrow$	$2\ Fe + 3\ H_2O$ - 91 kJ/mol
(b)	$Fe_2O_3 + 3\ H_2$	$\rightarrow$	$2\ Fe + 3\ H_2O$ - 91 kJ/mol
	$Fe_2O_3 + 3\ CO$	$\rightarrow$	$2\ Fe + 3\ CO_2$ + 32 kJ/mol

translated into demands of 610 Nm^3 of hydrogen or 604 Nm^3 of carbon monoxide per ton of iron. Process (a), the **H-iron process**, operates at 500 °C temperature and 3 - 4 MPa pressure and needs pure hydrogen (98 %) and a high dilution of the reformer feed gas with steam. Process (b), the **Korf-Midland-Ross process**, operates at 800 °C temperature and 0.3 MPa pressure and requires low steam dilution ratio to prevent carbon deposition and a low methane level (< 2 %) in the reformer product gas [27]. The optimal H_2 to CO ratio is a compromise between a favorable energy balance of the endothermal and exothermal reaction, and reaction kinetics as well as environmental impact by the CO_2 produced [32].

Heat treatment of ferrous metals is made in a hydrogen-nitrogen atmosphere with 3 - 30 % H_2 to increase metal ductility, improve machinability, and alter electric and magnetic properties.

7.1.4. Fossil Fuel Processing

Steady utilization of hydrogen in refineries commenced more than 50 years ago. It is mainly used for **hydro-cracking** and fuel burning of excess byproduct and **hydro-treating** comprising pre-treatment of reformer feed and treatment of heavier streams in upgrading processes including the removal of sulfur compounds, halides, metals, nitrogen or oxygen, the saturation of olefins, diolefins, cyclo-olefins, or aromatics, the decyclization or ring-opening. The cracking of heavy crude oil is made to produce lighter hydrocarbons or refined products such as high-octane gasoline [41].

In the process of **coal hydrogenation** which is a high-pressure (30 - 70 MPa) catalytic process at a temperature of 500 °C, hydrogen is used to convert coal to gasoline

$$C + H_2 \rightarrow -CH_2-$$

and to remove sulfur, oxygen, and nitrogen. Rigid specifications concerning the contents of the catalyst poison CO (< 10 ppm) have to be met. A purity of 98 % hydrogen is desirable. With an input of 2000 - 2600 Nm^3 of hydrogen and 1.7 t of coal, an output of 1 t of gasoline is obtained. In addition, 600 kWh of electricity are necessary for H_2 compression and coal preparation [27].

The **oxo synthesis** is an exothermal catalytic process in which a H_2-CO mixture, as the product gas of the steam reforming process, is used to produce aldehydes which are then hydrided to the respective alcohols. The oxo process works at 3 - 30 MPa and 100 - 180 °C.

The hydrogen demand in cleaning and upgrading of coal and oil is listed in Table 7-1 for various processes.

Table 7-1: Hydrogen demand for coal upgrading or product improvement, from [6]

Process	**Hydrogen demand [mol H_2 per mol CH_2 (CH_3OH)]**
Crude oil desulfurization	2 - 5
Hydrotreatment	5 - 10
Hydrocracking	15 - 30
Residue hydrogenation	25 - 30
Very heavy oil → syncrude	30 - 40
Oil sand → syncrude	30 - 45
Oil shale → liquid products	80 - 125
Coal gasification (CH_3OH)	100 - 160

7.1.5. Fischer-Tropsch Synthesis

The catalytic hydrogenation of carbon monoxide resulting in the formation of paraffin-olefin mixtures of different C-numbers is what is called the Fischer-Tropsch synthesis. The product spectrum depends on the operating conditions and the catalysts applied and on the partial pressures of CO and H_2 in the synthesis gas:

$$CO + 2\,H_2 \rightarrow (-\,CH_2\,-) + H_2O + 165\ \text{kJ/mol}$$

for Co catalyst

$$2\,CO + H_2 \rightarrow (-\,CH_2\,-) + CO_2 + 205\ \text{kJ/mol}$$

for Fe catalyst

The resulting hydrocarbons are characterized by the strong arrangement of the C-atoms used as a raw material in the petrochemical industry or for the production of synthetic hydrocarbons [13].

Until now the Fischer-Tropsch technology has never been able to compete economically with conventional fuel and was limited to very isolated cases. Recent process innovations, however, give hope to a comeback for the exploitation of untapped gas fields in remote regions as an alternative to LNG processing. Shell and Sasol are currently the only companies to operate Fischer-Tropsch plants on a commercial basis.

7.1.6. Others

A significant application of hydrogen with a large-scale technological importance is in the food industry the hardening of fats and oils by catalytic hydrogenation for the purpose of extended durability. The process takes place at pressures of 20 - 40 MPa and at temperatures of 200 - 400 °C.

Other fields of hydrogen applications are in the metallurgical industry as the reducing medium for the nickel production, for autogeneous welding and cutting, in the glass industry when clean combustion is required, or in the electronics industry for the epitaxial growth of polysilicon. For the fabrication of semiconductor elements, vaporized liquid hydrogen is used as a doping gas because of its cleanness.

A field with growing interest is the ability of hydrogen of scavenging oxygen, e.g., in boiling water reactors where traces of oxygen in the feed water which were found to cause intergranular stress corrosion cracking, are removed by the injection of hydrogen down to a level of < 100 ppb [41].

7.2. HYDROGEN AS A FUEL

The first application of hydrogen as a "fuel" was starting in the late 18th century when it was tried to utilize the physical property of low density for flying balloons. The Frenchman Charles realized in 1783 the first liftoff of an H_2 balloon ("Charliere") filled with 40 m^3 of H_2 which he produced by spilling sulfuric acid onto iron. The balloon traveled a distance of 25 km in a height of up to about 1 km.

7.2.1. Heating

Catalytic or flameless combustion of hydrogen exhibits many advantages in comparison with flame combustion. It occurs at low temperatures (ambient - 800 K), is safe and leads to a very high conversion of the burning gas (99.9 %). The NOX formation which usually occurs in conventional combustion at temperatures of about 1700 K, is here almost completely suppressed. The catalytic combustion in diffusion burners (Fig. 7-2) occurs in the presence of small amounts of Pt or Pd catalysts. It is adequate, e.g., for kitchen appliances such as cooker, oven, water heater, space heater. Drawbacks are the possible non-uniformity of the temperature distribution at the catalyst surface, rapid changes in the operational state, and relatively small heat flux densities [47].

7.2.2. Fuel Cells

7.2.2.1. Principle

The fuel cell is an energy conversion device that works in reverse of electrolysis. In the cell, the energy of a fuel is directly converted by an electrochemical reaction

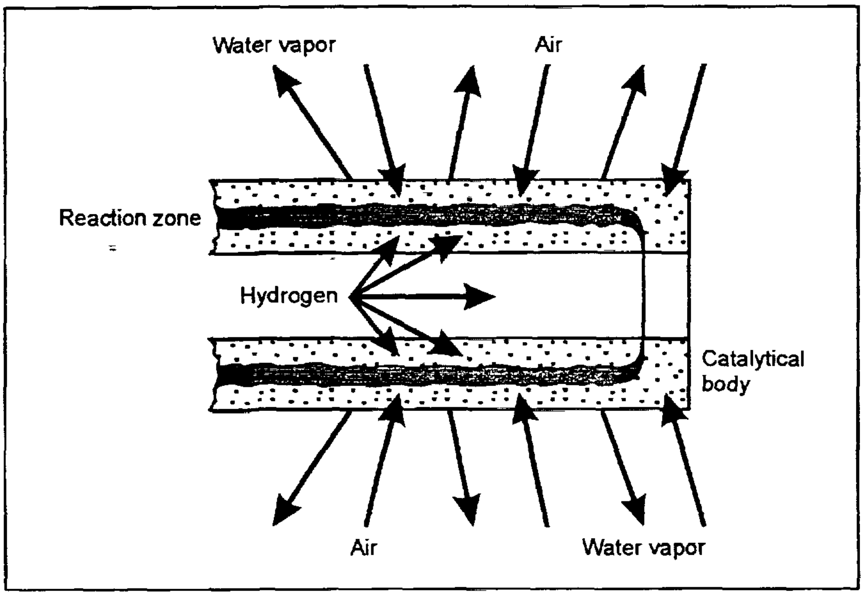

Fig. 7-2: Schematic of a hydrogen diffusion burner, from [14]

into D.C. electricity. Streams of hydrogen and oxidizer pass through porous metal plates separated by an electrolyte with partial pressure differences as the driving force. Outside the electrolyte, the plates are electrically connected. The hydrogen plate (anode) converts hydrogen molecules into ions and electrons where the former migrate into the electrolyte. The oxidizer plate (cathode) separates oxygen molecules into oxygen atoms. They also migrate into the electrolyte where they recombine with the hydrogen ions and anode electrons to create water and heat. Electricity can be captured from the circuit and put to useful work. Water and heat are expelled from the electrolyte to be further used or recycled. The principal advantages of a fuel cell in comparison with the indirect energy conversion (which goes via heat first) are its high efficiency and its cleanness. Practical cells typically generate a voltage of around 0.7 - 0.8 V per cell and a power output of a few tens or hundreds of watts.

Of all fuels that have been tested in fuel cells, hydrogen has the highest reactivity. At temperatures < 300 °C, most hydrocarbons and alcohols show low catalytic reaction rates and often unwanted secondary products. At high temperatures, direct electrochemical oxidation may be feasible. Fuel cells convert stored energy to electricity with an approx. 60 -70 % efficiency (based on lower heating value), a higher is thought to be theoretically possible [11]. The efficiency is nearly constant independent of size, thus configurations of power plants could range from watts to megawatts. Internal reforming gives an increase in efficiency as compared with external reforming. Heat from the electrochemical reaction is available for cogeneration application.

A detailed description of all different kinds of fuel cells, their techniques and applications can be found in [30].

Table 7-2: Fuel cell characteristics, from [25, 29, 49]

Type of fuel cell	**Operation temperature [°C]**	**Fuel**	**Typical efficiency [%]**	**Anode reaction**	**Cathode reaction**
PEFC⁽¹⁾	50 - 140	H_2, (no CO)	50 - 60	$H_2 \rightarrow 2\ H^+ + 2\ e^-$	$O_2 + 4\ H + 4\ e^- \rightarrow 2\ H_2O$
AFC⁽²⁾	25 - 120	H_2 (no CO_2)	50 - 65	$H_2 + 2\ OH^- \rightarrow 2\ H_2O + 2\ e^-$	$O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$
DMFC or SPFC⁽³⁾	80 - 130	CH_3OH	24 - 40	$CH_3OH + H_2O \rightarrow CO_2 + 6\ H^+ + 6\ e^-$	$3/2\ O_2 + 6\ H^+ + 6\ e^- \rightarrow 3\ H_2O$
PAFC⁽⁴⁾	60 - 210	H_2 (no CO)	35 - 45	$H_2 \rightarrow 2\ H^+ + 2\ e^-$	$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$
MCFC⁽⁵⁾	620 - 660	H_2 CO	45 - 60	$H_2 + CO_3^{--} \rightarrow H_2O + CO_2 + 2\ e^-$ $CO + CO_3^{--} \rightarrow 2\ CO_2 + 2\ e^-$	$O_2 + 2\ CO_2 + 4\ e^- \rightarrow 2\ CO_3^{--}$
SOFC⁽⁶⁾	800 - 1000	H_2 CO CH_4	50 - 60	$H_2 + O^{--} \rightarrow H_2O + 2\ e^-$ $CO + O^{--} \rightarrow CO_2 + 2\ e^-$ $CH_4 + 4\ O^{--} \rightarrow 2\ H_2O + CO_2 + 8\ e^-$	$O_2 + 4\ e^- \rightarrow 2\ O^{--}$

(1) PEFC = Polymer Electrolyte Fuel Cell or PEM-FC = Proton Exchange Membrane Fuel Cell

(2) AFC = Alkaline Fuel Cell (4) PAFC = Phosphoric Acid Fuel Cell

(3) DMFC = Direct Methanol Fuel Cell or SPFC = Solid Polymer Electrolyte Fuel Cell

(5) MCFC = Molten Carbonate Fuel Cell (6) SOFC = Solid Oxide Fuel Cell

7.2.2.2. Fuel Cell Types

Various fuel cell types have been developed usually classified according to the electrolyte used. In Table 7-2, fuel cell types are listed with their operating temperatures and anode / cathode reactions.

Certain constraints to the fuel cell do apply depending on the type of fuel cell. In low-temperature fuel cells, noble metal electrodes are necessary to increase the reactivity. Poisoning of electrodes can be avoided by purification of natural gas. Various methods have been developed to remove sulfur which is a poison to nickel steam reforming catalysts and to many anode catalysts incl. platinum: high-temperature based hydro-desulfurization for a large-scale hydrogen production (with a small quantity of H_2) and low-temperature based desulfurization adsorption processes that do not need H_2 [11]. The high-temperature fuel cell designs avoid expensive noble metal catalysts, thermal activation is insensible to pollutants. Drawbacks are the short lifetime and expensive plant components. To avoid dilution of the electrolyte by the product water, it must be removed by evaporation or vaporization. In high-temperature fuel cell systems, the water is steamed off anyway.

If carbon-containing fuel gases are used instead of pure hydrogen, oxidation must be realized first in a reforming reaction. Internal reforming has the advantage that there is no requirement for hydrogen storage. Incomplete reaction at lower temperatures results in presence of carbon monoxide which is a catalyst poison and must be removed, at the expense of efficiency. CO causes no trouble at high operating temperatures since reforming can take place internally. Attempts of a direct conversion of coal or oil in an integrated gasification fuel cell system are presently at an early R&D stage, but they are considered potential primary fuels in the long run.

The **Polymer Electrolyte Fuel Cell**, PEFC, or **Proton Exchange Membrane Fuel Cell**, PEM-FC, is an efficient, compact, robust, and quiet method of generating electricity. A diagram is shown in Fig. 7-3. It has a 0.1 mm thick proton conducting foil as a solid electrolyte. It has the highest power density of all cell types, a relatively low operating temperature and thus long cell lifetime, good load change behavior and good efficiency at partial load, and a good standby performance, thus being ideally appropriate for mobile applications. A problem in PEFC is the necessity to keep the polymer electrolyte membrane in a wet state and at higher operating temperatures to prevent a dry-out by means of external wetting [37]. Applicable fuels are hydrogen, reformed methanol or methane with purity requirements of < 10 ppm of CO, < 1 ppm of NH_3, and < 0.1 ppm of H_2S. The development is concentrating on improvement of catalysts and reduction of CO poisoning effects [15].

The **Alkaline Fuel Cell**, AFC, is the most efficient low-temperature fuel cell presently available with a very high power density, therefore ideally appropriate for mobile applications. The AFC shows a similar performance as the PEFC, but with a much more demanding process control which is complicated because of the requirements of fuel purity (no CO_2) and of the corrosive liquid electrolyte. Efficiencies of more than 60 % have been achieved with clean hydrogen and oxygen and noble electrode materials. The AFC was demonstrated to also work with a hydrogen-air system, in a 1 kW stack in Japan and in a 6 kW Russian system with more than 5000 h lifetime [34]. PEFC and AFC may play a role where pure and inexpensive hydrogen is available [29]. Unsatisfactory is its observed power decrease with operation time, by 20 % after 5000 h [51].

The **Direct Methanol Fuel Cell**, DMFC, (see Fig. 7-6 in section 7.2.2.4.) is another low temperature fuel cell enjoying a renaissance after significant improvements in current density. The DMFC runs on either liquid or, with better performance but higher system complexity, on gaseous methanol and is normally based on a solid polymer electrolyte (**SPFC**). Pt-Ru catalysts were found to produce best oxidation results at the anode, still the power density is relatively low [5, 29]. Conversion rates up to 34 % of the energy content into electricity were measured, an efficiency of 45 % is expected to be feasible in the future. SPFC in the power order of several kW to be used in automobile applications are currently in the development phase.

Most practical experience has been gained in the operation of **Phosphoric Acid Fuel Cells**, PAFC. Because of its higher operating temperature, it has a minor CO poisoning problem plus it offers operation in the CHP mode providing good quality steam of approx. 200 °C. Fuel is hydrogen or reformed methane plus CO converter. The principal poison for the Pt catalysts is sulfur carried in the reformate stream as H_2S.

A **Molten Carbonate Fuel Cell**, MCFC, is being operated at > 600 °C temperatures with porous Ni catalysts. Carbon dioxide which is yielded at the anode, needs to be fed back to the cathode where it is consumed. Besides hydrogen, the MCFC can be operated with methanol or methane or coal gas with external or with partial or full internal reformation, the possibility of internal naphta reforming is also investigated. In the future the synthesis gas from (internal) coal gasification systems may be linked to MCFC electricity generation inducing a further increase of the coal conversion efficiency up to 55 % with 60 % expected to be possible [37, 46]. Drawbacks of this fuel cell type are its low current and power densities. A problem often observed in MCFCs is the strong corrosivity of the electrolyte and its leakage through gaskets. Also the high serial resistance of the electrolyte limits the efficiency at low 40 % [34].

The **Solid Oxide Fuel Cell**, SOFC, (Fig. 7-4) is attractive – and difficult at the same time – because of its very high temperature which allows fast chemical reactions, but on the other hand implies stringent requirements for materials and construction. Without any further modifications, the SOFC can be operated either in the electrolysis or in the fuel cell mode. Two different stack design are currently pursued using tubular or flat cell geometry. Typical dimensions of the tubular design are: support (= cathode) with inner diameter of 12 - 22 mm, 2.2 mm wall thickness, and a length up to 1500 mm, an electrolyte layer of 20 - 40 μm, and outside the anode with 100 μm thickness. For a flat cell, the typical data are: a gastight electrolyte of 150 - 200 μm thickness, electrodes with 50 μm thickness and 30 - 50 % porosity. SOFCs convert gaseous hydrocarbons either directly or after internal reforming with a very low emission level. Utilization of the high-temperature waste heat raises the overall efficiency to a maximum. Furthermore the waste gas at the anode consisting of CO_2, H_2O, CO, and residual H_2 could be utilized for methanol, ethylene, or ammonium synthesis. On the other hand, heat release during internal reforming creating sharp temperature gradients, is difficult to control. A combination of 25 % internal and 75 % external reforming was found to work best for the (Westinghouse tubular) SOFC design [29]. Goal of the future development is the reduction of the operating temperature.

Little fundamental knowledge is yet available on the mechanisms of degradation in the ceramic and metallic components during cell operation. Long-term stability is currently subject to research activities within the IEA SOFC cooperation [36].

7.2.2.3. Stationary Fuel Cell Applications

The complete **fuel cell power generation system** consists of a fuel processing system to convert raw fuel gas into a hydrogen rich gas, the cell stack assembly for electric energy production, a power conditioning system to connect the electricity to the regulated A.C. grid supply, plus some form of heat recovery if used in the CHP mode. The core part of a fuel cell system is the fuel cell stack which consists of layered unit cells and in which hydrogen-rich gas and air are continuously supplied. Stationary applications embrace a large-scale central power generation, distributed generation, and cogeneration. The potential of fuel cell power plants is strongly related to the global demand for new power and heat capacity. A cogeneration system with waste heat recovery can achieve efficiencies of up to 80 %. Both high-temperature and low-temperature fuel cells are suitable for stationary applications and also convenient in all sizes from medium-sized units on the order of MW down to space heat supply for single rooms on the order of W.

State-of-the-art **AFC** units are in the range of 50 to 100 kW. Within the smaller-scale commercial sector, considerable potential is believed to exist for **SPFC** based systems because of their advantages in terms of low noise and vibrations and favorable emission characteristics [5].

PAFC, MCFC, and SOFC are currently the strongest contenders for commercial stationary power generation. **PAFC** power plants are presently at the pre-commercial demonstration stage for small, decentralized on-site power plants of 200 kW. When operated in the cogeneration mode, the overall efficiency could amount to 80 %. A fleet of 67 phosphoric acid systems has already accumulated in excess of 1,000,000 fleet hours of in-service operation at a sustained high level of availability [19] including use of external reforming of either methane or naphta. State-of-the-art is an 11 MW power plant operated in Ichihara, Japan, since 1991. It was shutdown in March 1997 having attained 16,000 h of operation time up to 1995 with an efficiency of 49 % and demonstrating a smaller performance decay rate than expected (7 % loss of efficiency over 40,000 hours). "Bestseller" on a commercial basis is the 200 kW(e) unit, PC25, by the US company ONSI, the only commercially available plant with an availability of 95 %. Operating times have reached 20,000 hours for a single unit [4, 50]. Worldwide 150 demonstration power plants are currently (mid 1997) being operated with a total power of 40 MW(e).

MCFC have reached a high developmental level and are expected to be ready for market entry before 2000. The MCFC is approaching the stage of the first, pre-commercial demonstration units [5]. Present prototypes have a power of 300 kW; large units have been operated for more than 40,000 hours. Power plants in the range of 0.25 - 1 MW are in development in Japan and the US. The world's largest MCFC demonstration power plant with 2 MW has begun its operation in Santa Clara, California, in April 1996 [19]. The construction of a 3 MW unit in New York State has been initiated [4]. MCFC are unlikely to be commercialized below $\approx$ 500 kW because of system complexity [29].

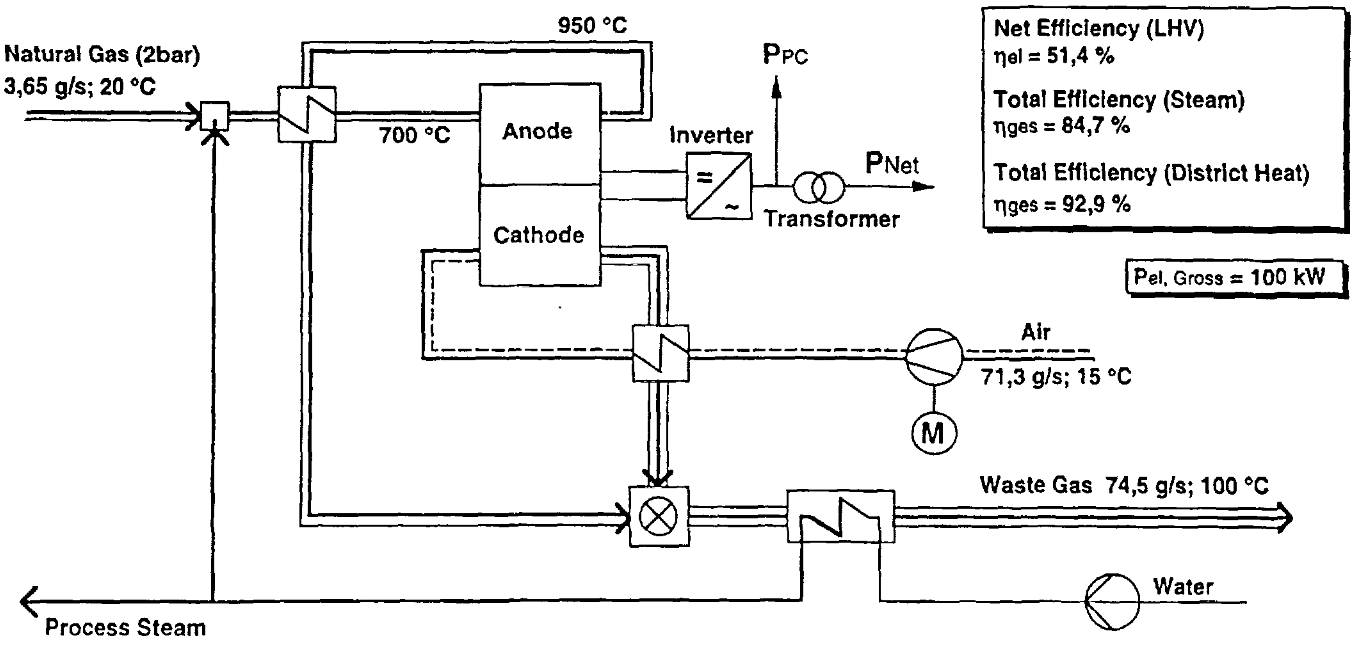

Fig. 7-5: Siemens design of a 100 kW SOFC combined heat and power plant, from [12]

SOFC-based power plants appear to be the most interesting alternative because of a simpler system technique, high efficiency, and the option of utilizing the waste heat in a gas turbine for electricity generation with an effective system efficiency of about 77 % [53]. The most advanced concept is the tubular version by the US company Westinghouse, which has developed a large SOFC unit of 44 kW. A growing number of SOFC is being tested in different cell configurations, different materials and different experimental conditions. More and more cells are being operated for longer testing times, i.e., > 1000 h [36]. A world record[19] has been achieved by Westinghouse with a 25 kW stack operated for 13,200 hours including a 6500 h period of nonstop operation with 10 cycles and a 92 % availability [3]. Although several demonstration units in the 10 to 25 kW(e) size range are existing already, the solid oxide system is still essentially at the research stage. The main risks of SOFC at present are unknown degradation of the fuel stack and operating performance of the balance of plant. Startup and shutdown operations impact the stack because of thermo-mechanical tensions [29].

SOFC are foreseen to phase out the classical Combined Heat and Power (CHP) for stationary applications with flexible power to cogeneration heat ratios, although it is believed to have no significant chance on the central power generation market up to 2010 [5]. The SOFC still needs to demonstrate its competitiveness in power generation. Their most pertinent competition are gas and diesel engine and gas turbine based systems in the 1 - 3 MW power range which find wide spread application in industrial cogeneration schemes, where their characteristics are in line with process requirements [5]. A significant chance is seen for SOFC and MCFC in distributed generation systems. The general trend

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[19] As can be seen world records are moving targets: The most recent information from October 1997 considered an SOFC world record is about Westinghouse's generation of 120 kW on their SOFC cogeneration unit [28].

towards smaller units and increasing cost of transmission and distribution capacity make an advanced SOFC power plant (Fig. 7-5), owned and operated by the utility likely to offer significant advantages over the existing slow speed diesel engine systems in this sector [5]. For the cogeneration or combined heat and power application, the market uptake was found to be highly dependent on the national legislative / regulatory framework and thus may be strongly country, site, and situation specific. The SOFC offers only a poor heat to power ratio of less than 1, whereas the industrial sectors are typically heat demand led with a heat to power ratio required of at least 2 or greater [5]. A potential niche market for SOFC may be the so-called micro-CHP for household applications in the order of 1 kW [29].

The **integration of fuel cell and coal gasification** technologies is expected to raise efficiencies significantly by utilizing hot exhaust and unused fuel gas in a steam turbine. The US DOE has launched an Integrated Gasification Fuel Cell (IGFC) Program with the goal to achieve the operation of an IGFC commercial-scale power plant with a net system efficiency of greater than 60 % by 2010. Pilot-scale gasification and gas stream cleanup facilities are planned to be completed by 1998 [52]. In Japan, a study is underway on a coal gasification combined power generation system based on MCFC. The preliminary target is a single 500 MW coal gasifier facility, an 18 stacks arrangement, four expansion turbines and two steam turbines.

7.2.2.4. Mobile Fuel Cell Applications

The first successful applications of fuel cells were made in the US space missions Gemini in 1963 (PEFC) and Apollo in 1969 (7 kW AFC with a life time of more than 7000 h). Due to this experience, the most advanced AFC, however, not commercially viable, are found in space and military applications (satellites) with requirements of 65 % efficiency for 10,000 hours. The Space Shuttle employs three stacks with 12.5 kW each. Nevertheless, the AFC has recently lost its important role in the context of terrestrial development [29].

Fuel cell systems have gained increased interest as an automobile propulsion system fostered by the new regulations in California ("Clean Air Act") for emission reduction. Fuel cell-based propulsion is efficient, has a high energy density, consumes comparatively less energy, and, in particular, reduces the emission levels of all relevant pollutants. Hydrogen powered fuel cell cars would represent true zero-mission vehicles (ZEV). The most significant development goals which need to be reached for market introduction is a wider cruising range, larger long-term stability and lower cost. A large-scale fuel cell application in the road traffic needs, in addition, a grid of refueling stations with hydrogen or methanol. From all low-temperature fuel cells, the PEFC is favored.

Using methanol as the energy carrier and hydrogen as the feed gas for a fuel cell, methanol combined with a reforming process offers better capabilities for storage in mobile systems with respect to tank size and weight. The entire unit should be small and light and provide a high conversion rate. Methanol reforming with/without water vapor is used on an industrial scale. The thermal splitting reaction does not suit the low-temperature fuel cells' need of a very low CO content in the feed gas [22]. Two fueling systems are being developed: hydrogen and methanol reformate or **indirect methanol fuel cell (IMFC)**. Compared with hydrogen, methanol has the higher storage density and is easier to handle. Also the existing infrastructure for fuel transport, storage, and distribution could

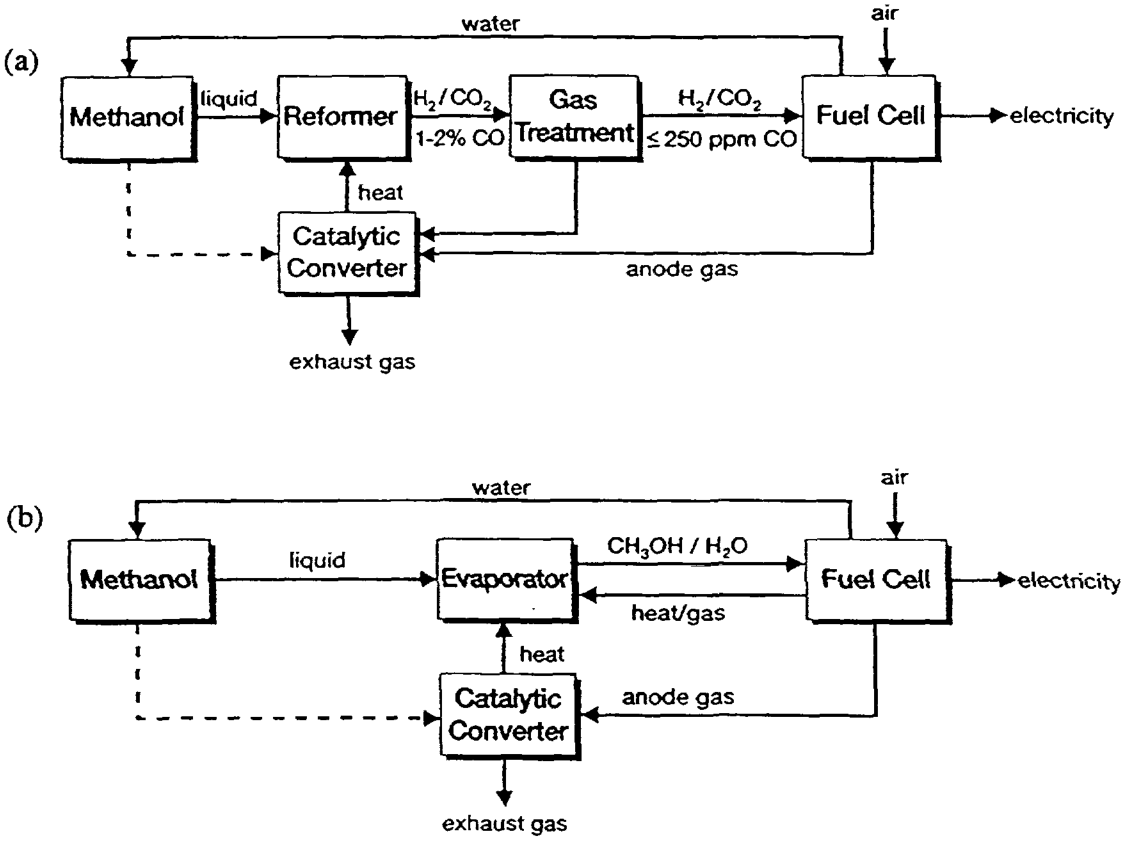

Fig. 7-6: Schematics of the processes in a PEM fuel cell system using methanol (a) indirect methanol fuel cell and (b) direct methanol fuel cell, from [43]

be utilized. The methanol option appears to offer the safer concept, but does tolerate only a very low CO level. Procedures for CO reduction are CO-methanation, selective CO-oxidation, and membrane separation [8]. An analysis of the emissions of an IMFC propulsion system at the Research Center Jülich exhibited its advantages compared with a conventional combustion engine by meeting the ULEV standard [35]. Works have started on **ethanol** fuel as an alternative to methanol with the advantage of an easy bioproduction.

A serious candidate for transportation application is also the "**direct methanol fuel cell (DMFC)**" which has been realized already on a laboratory scale. A catalytic burner is required to evaporate the methanol/water mixture and to burn the exhaust gas at the anode [43]. Considering the complete energy chain, a PEFC is by 50 % more efficient than a diesel engine which consumes 4 l per 100 km; this is also valid for a natural gas driven engine [37]. Fig. 7-6 presents the processing schematics of both IMFC and DMFC. The DMFC offers a much simpler system than the PEFC. The DMFC is currently at an early development stage. It is perceived to offer improved solutions to the need for a small-scale power supply. A program for the construction of a 30 kW stack has recently started [29].

Also a **gasoline** driven fuel cell has been developed recently in a joint effort between leading car and oil companies in the USA demonstrating a much lower CO_2 emission level than a conventional engine. Vehicles with a gasoline fuel cell drive are hoped to double the cruising range compared with conventional drive with emissions lower than ULEV standard [21].

The critical issues in designing a vehicular fuel cell power system are the selection of an optimal operating pressure, oxidant flow rate and the choice of an adequate control strategy. Computer models have been developed to simulate fuel cell performance under various operating conditions.

An interesting statement to fuel cell technology was made by a fuel cell sales director on a seminar in November 1996 telling that fuel cells have the potential of changing the accepted pattern of the electric utility and other industries and fuel cell technology could lead to the demise of combustion technology as a means of powering land and sea transportation, with the potential of disrupting automotive and petroleum industries as they exist today [20].

7.2.3. Hydrogen Powered Vehicles

The properties of a high heat of combustion and a high specific heat as well as the clean combustion product has made hydrogen very attractive to be used as a fuel in mobile applications.

7.2.3.1. Cars

Internal combustion engines (ICE) that run on hydrogen are on the order of 25 - 30 % more efficient than gasoline ICE, because they take advantage of the fast-burn and far-lean combustion characteristics of hydrogen. ICE for earth-bound vehicles is seen by many to be superior to battery or fuel cell powered vehicles in terms of range, acceleration, and power-to-weight ratio with no substantial improvement in the near future [40]. Internal combustion engines extract about 30 % of the stored fuel energy. Consideration of hydrogen as an ideal fuel for the internal combustion engine has started in the early 1920s. The operation with hydrogen is possible in a wide range of mixtures with air. At extremely lean conditions, it provides a low emission level and a high thermal efficiency in the low power range. In addition, cryogenic hydrogen provides a high density storage and a considerable cooling effect. From the works done so far it can be concluded that successful hydrogen fueled direct injection engines are feasible (see Fig. 7-7). Limitations are given by the present storage technology and, in principle, by lack of suitable applications [7].

A Ford pickup truck is reported to be the first LH_2/LOX-fueled car by Perris Smogless Automotive Association in 1971 in the USA. The first European car running on LH_2 was demonstrated by the German DFVLR (now DLR) in 1979, who also built the first LH_2 system for vehicle refueling [48]. Many automobile companies have designed and operated prototypes of cars or trucks. This is a rapidly changing field. A recent study by the Japanese Musashi Institute of Technology has shown that the most practicable solution for cars, trucks or buses in terms of onboard H_2 storage is liquid hydrogen compared with hydrides or electric drive [54]. Detailed description of LH_2 use in vehicles can be found in [39]. Major hydrogen fueled vehicle R&D programs in the world are listed in [26, 31].

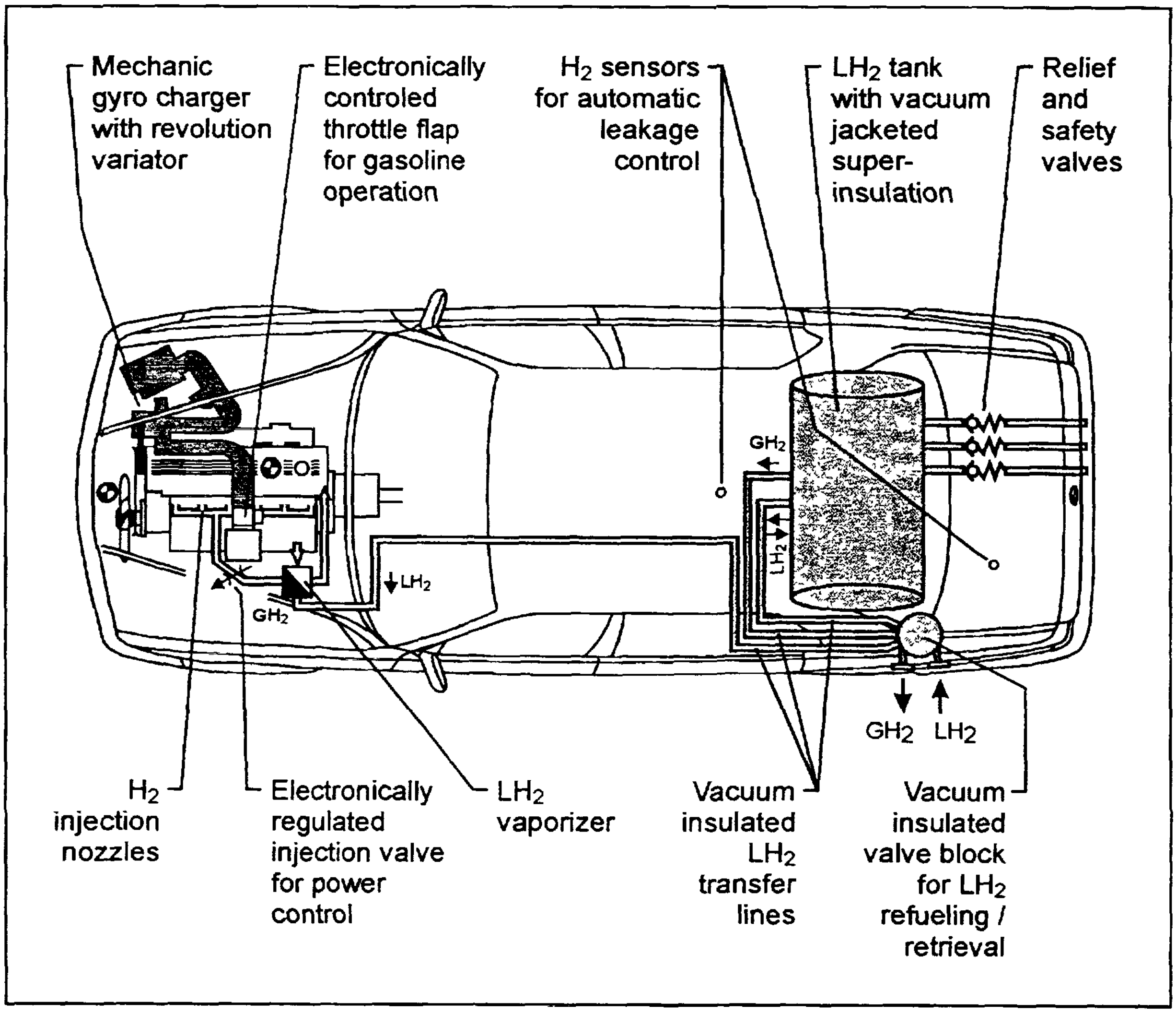

Fig. 7-7: Arrangement of main components in the BMW 735i LH_2 test vehicle with internal combustion engine, from [42]

Computationally assisted engine development is conducted focusing on optimization of fuel efficiency and low emissions with respect to operating conditions and combustion chamber geometry. Fluid dynamics in lean premixed combustion are examined for complete oxidation of the fuel in a safe and clean way [24].

Ground-based vehicles with PEM fuel cell systems are foreseen to appear on the market by the year 2004. Various prototype cars and buses have been presented already, the first in the USA in 1991 (see section 9.5.2.). The critical aspect is the on-board storage of the hydrogen fuel which can be provided as compressed gas, cryogen, or metal hydride.

A mid-term goal for fuel cell cars is the employment of a reformer in which any hydrocarbon, including gasoline, is processed by steam reforming or partial oxidation to generate hydrogen, which is then consumed in the fuel cell. One appropriate, easy-to-handle energy carrier is methanol. A comparison of representative vehicle fuels in terms of mass and volume requirements yields the amount of 30 kg (40 l) of gasoline to be equivalent to 60 kg (70 l) of methanol or 24 kg (57 l) of LNG or 24 kg (110 l at 30 MPa) of CNG or 10 kg (141 l) of LH_2 or 10 kg (370 l at 30 MPa) of compressed hydrogen.

A hydrogen hybrid electric vehicle represents a transitional step between a gasoline ICE vehicle and a fuel cell vehicle. Hydrogen is burnt in a small optimized engine which runs a generator to charge a battery. The total efficiency is estimated to be 39 %. Not more than 3.3 kg of hydrogen would allow a theoretical cruising range of 480 km [31].

7.2.3.2. Aviation

Liquid hydrogen was early recognized to be an important rocket fuel for use in space flights. The H_2 / O_2 system together with the H_2 / F_2 system belongs to the most energetic propellants allowing for exhaust velocities sufficiently high to escape the earth gravity or reach earth orbit [39]. The Japanese LE-7 is a two-stage combustion engine (see also Fig. 9-9). LH_2 and LOX are pressurized by a pump and burnt in a preburner chamber (stage 1). The resulting high-temperature high-pressure gas operates the pump. The exhaust gas from the pump is routed to the main combustion chamber where it is burnt once again using remaining LOX (stage 2). Ram engines for future reusable space transportation can be operated with atmosphere oxygen up to a height of 40 km. Air-breathing engines with supersonic combustion, scramjet, offer an excellent thrust potential. Fig. 7-8 shows the schematic of a scramjet. Hydrogen in space transportation is being used by the USA, Russia, Europe, China, Japan, and India.

Considering weight and volume restrictions in aviation, liquid hydrogen has been shown to be particularly attractive as an aircraft fuel. The wide range of flammability of hydrogen in air enables a stable combustion chamber operation far beyond the limits of hydrocarbons. The lighter fuel load compared with conventional fuel results in a gross weight reduction allowing the use of a smaller engine. Together with its high combustion heat per mass unit, fast ignition and high heat sink capacity, hydrogen is a perfect candidate, in particular, for supersonic applications. In addition, it avoids all pollutants of fossil fuels except for NOX. Compared with kerosene, the flight-related energy content of LH_2 is nearly 2.8 times larger on a mass basis and it could be used as a coolant. Also the engine life time is expected to be higher and maintenance requirements to be reduced. The main penalty, however, is the storage volume of the hydrogen tanks which is by a factor of about 4 larger than kerosene [9, 39].

Also in terms of safety, liquid hydrogen is superior to kerosene. A fuel fire is expected to be less dangerous, the endangered area is much smaller, a kerosene fire lasts much longer [10].

7.2.3.3. Ships

A specialist field of application of hydrogen is seen in ship propulsion using low-temperature fuel cells. The operation of submarines powered by SPFC systems has been successfully demonstrated. The German submarine class U212 is equipped with an air-independent Siemens PEM fuel cell drive. The hydrogen is stored as titanium hydride in cylindric vessels attached to the inner hull. The first four units were ordered in 1994 and are planned to go into operation from 2003 [18]. Japan is investigating a two times 500 kW PEFC system operating on methanol reformate gas. US research is focusing on 250 kW and 2.5 MW shipboard power units [20]. Naval applications are being realized in Australia, Canada, and Germany.

Within the Euro-Quebec project, a passenger boat is currently under construction equipped with a PEFC electric drive and three 200 l LH_2 storage tanks [15].

The German Howaldtswerke Deutsche Werft AG, Kiel, has recently investigated in an internal feasibility study the use of fuel cells in powering merchant ships [44].

7.2.3.4. Locomotives

A fuel cell propulsion system for locomotives is being reconsidered one option in future railroad technology. A new emission standard for locomotives, which will be effective in the year 2000, has led to a revival of respective research activities from the past [1].

7.2.4. Stationary Gas Turbines

Hydrogen is an ideal fuel for gas turbines. Due to its rapid mixing with air, a smaller combustion chamber is sufficient and the efficiency is higher compared with conventional fuels. Gas turbines modified for liquid hydrogen operation yield an up to 10 % higher thermal efficiency and output compared with fossil-fueled turbines. For systems with advanced heat exchange, efficiencies of more than 50 % are estimated to be achievable. The remainder-free combustion is stable and favorable for lifetime and maintenance. Of disadvantage is NOX production. No particular difficulties are expected for a conversion of a stationary gas turbine to H_2 fuel [51].

The schematic of a **hydrogen-oxygen gas turbine** system with recirculating argon gas as the working fluid is shown in Fig. 7-9. The internal stoichiometric combustion of hydrogen and oxygen heats up the argon gas which actuates the turbine for power generation. The water vapor produced is condensed and removed from the circuit while the argon is returned to the combustor. Innovative developments of gas turbines capitalize on the experience of aerospace propulsion systems. Performance goals are control of combustion temperature by pre-mixing steam and operational flexibility [17].

A modified gas turbine cycle, a H_2-fueled chemical-looping combustion, has been proposed in Japan. The oxidizer air or oxygen is replaced by a solid metal oxide, e.g., NiO. An increase in the efficiency up to 66.8 % is predicted compared with 61.6 % as the best figure for H_2/O_2 cycles [23].

The **hydrogen-oxygen steam generator** is a novel power plant component derived from rocket technology to provide instantaneously spinning reserve capacity upon demand. H_2 and O_2 stored in high-pressure tanks are injected into a combustion chamber and ignited. Combustion takes place at pressures of 2 - 20 MPa. The reaction heat is directly transferred to additional feedwater introduced. Steam of the required temperature of 500 - 1000 °C is obtained and routed to the intermediate pressure steam turbine, thus being capable of increasing the electric power by 20 MW within seconds [16]. However, lack of demand for such direct power reserve and relatively high cost have made DLR to abandon this development. Respective research projects are presently pursued only in Japan and Russia.

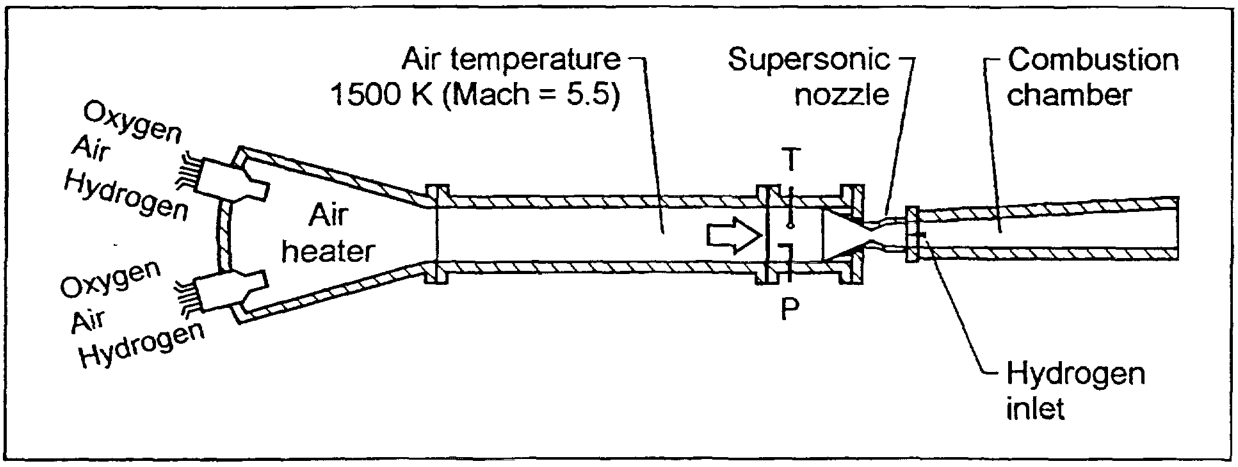

Fig. 7-8: Schematic of a model combustion chamber of a scramjet, from [DLR]

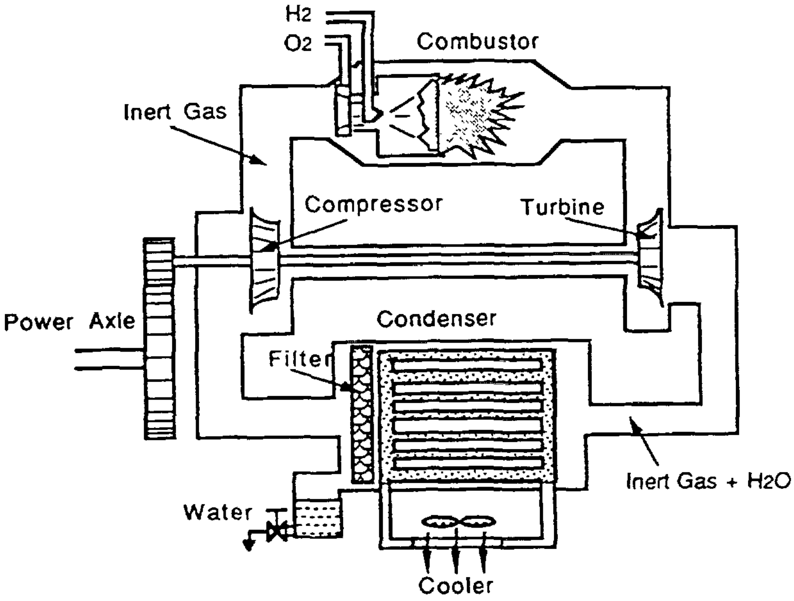

Fig. 7-9: Inert gas recirculating hydrogen-oxygen gas turbine system, from [17]

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Chapter 8

SAFETY RISKS OF A LARGE-SCALE HYDROGEN APPLICATION

With increasing significance of hydrogen as an energy carrier, the risk of an accident in a production plant or during storage and transport or while being applied will rise as well. The broad introduction of hydrogen thus requires a concomitant and prognostic evaluation of safety and risk. The inadvertant release of hydrogen caused by a leak or spillage creates a local atmosphere that is depleted in oxygen and, thus, does not support life. Furthermore, the explosion hazards associated with hydrogen when mixed with air, the **assessment of conceivable risks** and its hazard potential after an inadvertant release is mandatory. The tools for such a deterministic analysis of the risk are calculation models to simulate all the steps of an accident scenario as realistically as possible. Model validation is based on the evaluation of experiments and postexamination of previous accidents [120].

8.1. PROPERTIES OF HYDROGEN

Hydrogen gas is colorless, odorless, tasteless, non-toxic, and undetectable for human senses. If released in a confined area, hydrogen can cause suffocation by dilution of the oxygen content. Gaseous hydrogen at its boiling point (20 K) is heavier than air. At a temperature > 22 K, it becomes buoyant and tends to rise in the ambient air. Hydrogen coexists in two phases, para and ortho hydrogen, whose partition depends on the temperature. At low temperatures, $< \approx 80$ K, the para phase presents the more stable form. Hydrogen exhibits in part a positive "Thomson-Joule effect" meaning a positive temperature change upon pressure decrease. The effect is found for hydrogen at temperatures > 200 K, for example, an increase of 6 degrees when released from 20 MPa to ambient conditions.

Mixtures of hydrogen with oxygen are flammable over a wide range of concentrations, 4 - 75 vol%. A stoichiometric hydrogen-air mixture contains 29.5 vol% H_2. Despite its relatively high autoignition temperature, the minimum energy required for an ignition (0.02 mJ) is very low, further reduced by increasing temperature or pressure or oxygen content. Catalytically active surfaces can ignite hydrogen-air mixtures even at much lower temperatures. The hydrogen flame is nonluminous, comparatively hot, but hardly radiates any heat.

Liquid hydrogen (LH_2) has the advantages of economic transportation in large amounts, simple conversion technology, extreme cleanness, convenient consumption. Major drawbacks are given by the enormous energy consumption of liquefaction which is around 30 % of its heat of combustion and the unavoidable boiloff losses during storage and handling, which can total 40 % of its available combustion energy [105]. Most experience in handling LH_2 has been gained for decades in the space programs of the USA, the Russian Federation, Europe, Japan, and China.

Slush hydrogen (SLH_2) is a homogeneous mixture of liquid and solid H_2. A fraction of 50 wt% results in a 16 % higher density and an 18 % higher heat capacity compared with the liquid phase. Both effects reduce volume and thus tankage weight in possible applications, e.g., in aircraft, improving transportation efficiency. A reduced vaporization loss is given at the expense of a storage at higher pressures up to 1.3 MPa.

Table 8-1: Properties of hydrogen, from [37, 88, 101]

Molecular weight	2.01594	g/mol
Gas constant	4.1245	kJ/(kg K)
Normal boiling point	20.268	K
Heat of combustion, gross (including thermal energy of water vapor)	286.0 141.86	kJ/mol MJ/kg
Heat of combustion, net	241.8 119.93	kJ/mol MJ/kg
Latent heat of vaporization	445.59 31.78	kJ/kg MJ/m^3 liquid
Vapor density @ Standard Temperature Pressure (STP)	0.083764	kg/m^3
Vapor density @ Normal Boiling Point (NBP)	1.338	kg/m^3
Liquid density @ NBP	70.78	kg/m^3
Slush density @ Triple Point (TP) (50 wt% solid)	81.50	kg/m^3
Solid density @ TP	86.50	kg/m^3
Liquid-to-gas expansion ratio	845	
Specific heat capacity of gas @ STP	14.89	kJ/(kg K)
Dynamic Viscosity of gas @ STP	87.5	10^{-7} kg/(m s)
Thermal conductivity of gas @ STP	189.7	10^{-3} W/(m K)
Diffusivity of gas @ STP	6.1	10^{-5} m^2/s
Adiabatic speed of sound in air @ STP	1294	m/s
Stoichiometric composition in air	29.53	vol%
Limits of flammability in air	4.0 - 75.0	vol%
Limits of detonability in air	13. - 65.	vol%
Minimum ignition energy in air (stoich.)	0.019	mJ
Auto-ignition temperature in air	858	K
Flame temperature (stoich.)	2318	K
Flame temperature (maximum)	2403	K (at 31.6 vol%)
Emissivity	< 0.1	
Quenching distance in air @ STP (stoich.)	0.64	mm
Laminar burning velocity in air (stoich.)	2.37	m/s
Laminar burning velocity in air (maximum)	3.46	m/s
Flame front velocity (spherical gas cloud)	18.6	m/s
Detonation velocity (Chapman-Jouguet)	1968	m/s
TNT equivalent	2.22	kg TNT/Nm^3 gas

The subatmospheric vapor pressure of (slush) hydrogen at 13.8 K can cause the total system pressure to drop below that of the local atmosphere, requiring precautions to avoid air entrainment into the system, which would solidify the air and warm up the system. Another safety concern is electric charge accumulation in SLH_2 flows since it involves solid particles; this effect needs further investigation. NASA has studied SLH_2 characteristics under conditions of production, storage, and transfer [81, 109].

Various property data of hydrogen are summarized in Table 8-1. A more detailed description of the properties is given, e.g., in [45, 120].

8.2. SAFETY MEASURES IN HANDLING (CRYOGENIC) HYDROGEN

8.2.1. Physiological Hazards

Direct contact with liquid hydrogen or surfaces on very low temperature causes cryogenic "burns", i.e., freezing of living tissue, except for very brief contact periods where the temperature difference between cryogen and skin is still high (film boiling regime) and heat transfer small. Prolonged exposure to cold temperatures after a large spill lowers the body temperature resulting in hypothermia, organ dysfunction, and respiratory depression [43].

Vaporization of released liquid hydrogen affects the local atmosphere by diluting the oxygen in the air. A fraction of less than 19.5 % is considered by NASA to be dangerous to humans causing asphyxication; less than 8 % will be lethal within minutes.

Physiological effects as anticipated upon the explosion of a flammable gas mixture are listed in Table 8-2; the effects arising from the accidental release and combustion of hydrogen are treated in section 8.4..

Table 8-2: Physiological Effects of blast overpressures, from [43]

Maximum overpressure [kPa]	Effect on personnel
7	Knock personnel down
35	Eardrum damage
100	Lung damage
240	Threshold for fatalities
345	50 % fatalities
450	99 % fatalities

8.2.2. Safety Measures

Safety of a system must be considered in all phases from design to fabrication and its operation, sufficient instrumentation, safety analysis to assess consequences of untoward

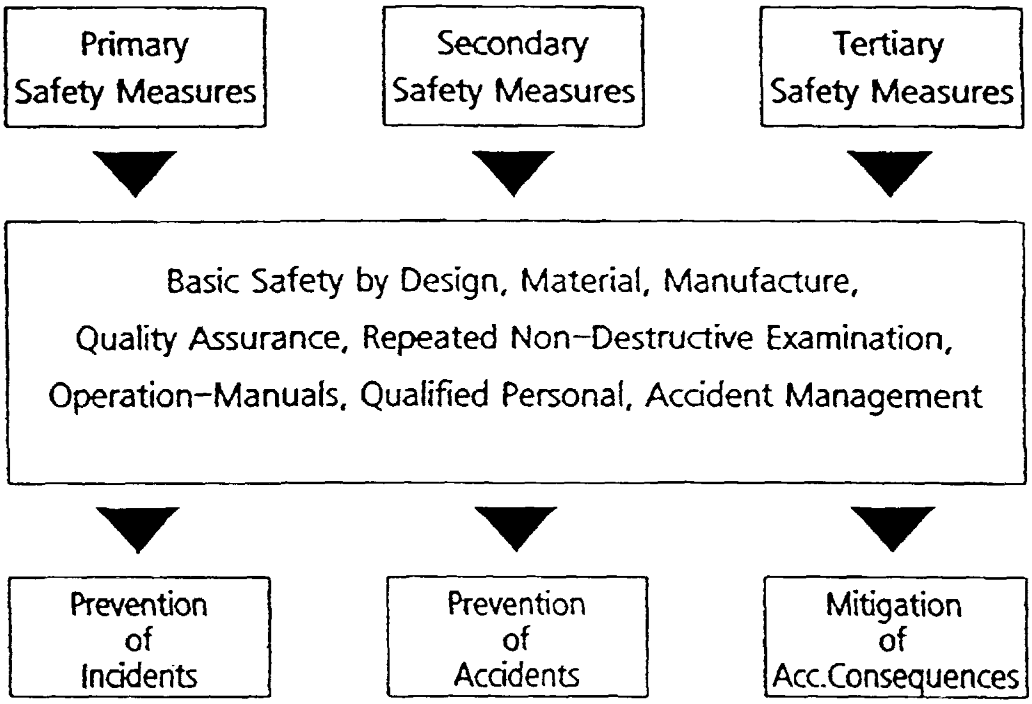


Fig. 8-1: Safety approach for handling hydrogen in the industries, from [10]

events, plant maintenance and documentation, well-trained and knowledgeable personnel [43]. The investigation of the combustion behavior of hydrogen connected with the pressure development under accident conditions is the basis of all safety-related considerations.

NASA experience with hydrogen began in the 1950s, when hydrogen was considered the principal liquid rocket fuel. Safety engineering soon started to address hydrogen hazards and to develop procedures for the safe operation of equipment and facilities. NASA also determined the need for rigorous training and certification programs for personnel.

The large-scale industrial application of hydrogen has led to a safety concept with a scale of safety measures aimed at minimizing risks by preventive safety measures and by mitigation measures. A basic safety approach that can be applied to hydrogen energy technologies is outlined in Fig. 8-1. Some examples are [45]

1. for primary measures (design):
   welding as a basic principle of construction, metal gaskets for connectible parts, selection of proper materials, waste or leakage or relief valve piping leading into the open atmosphere, sufficient ventilation in closed buildings, handling of LH_2 in closed systems only, leak detection, regular check, training of personnel;
2. for secondary measures (avoidance of ignition sources):
   prohibition of open fire, avoidance of electric or mechanically generated sparks, avoidance of electrostatic charge, flame barrier or N_2 inertialization system in large plants;
3. for tertiary measures (mitigation of consequences):
   quick shutdown system with cutoff of H_2 feed lines, explosion-proof construction of

components (e.g., stack), avoidance of a transition from deflagration to detonation, safety distance, flare rather than extinguish hydrogen fire.

Measures to be applied are defined and fixed in rules and regulations or in respective recommended industrial standards or company internal rules.

8.3. EFFECT OF HYDROGEN ON MATERIALS

The stress which a structural material is able to withstand is determined by its **ductility** (see Fig. 8-2). A material is elastic if, after being elongated under stress, it returns to its original shape as soon as the stress is removed. At a certain strain, it departs from linearity meaning that the material will retain a permanent elongation; the applied stress is called "yield stress". A further increase of the strain eventually reaches the "ultimate or tensile stress" beyond which the stress decreases finally leading to rupture. In contrast, a brittle material does not exhibit the phase of permanent elongation. The material abruptly breaks without any warning as soon as it is exposed to its tensile stress [43].

Metals that work successfully at low temperatures include aluminum and its alloys, copper and its alloys, nickel and some of its alloys, as well as austenitic stainless steels.

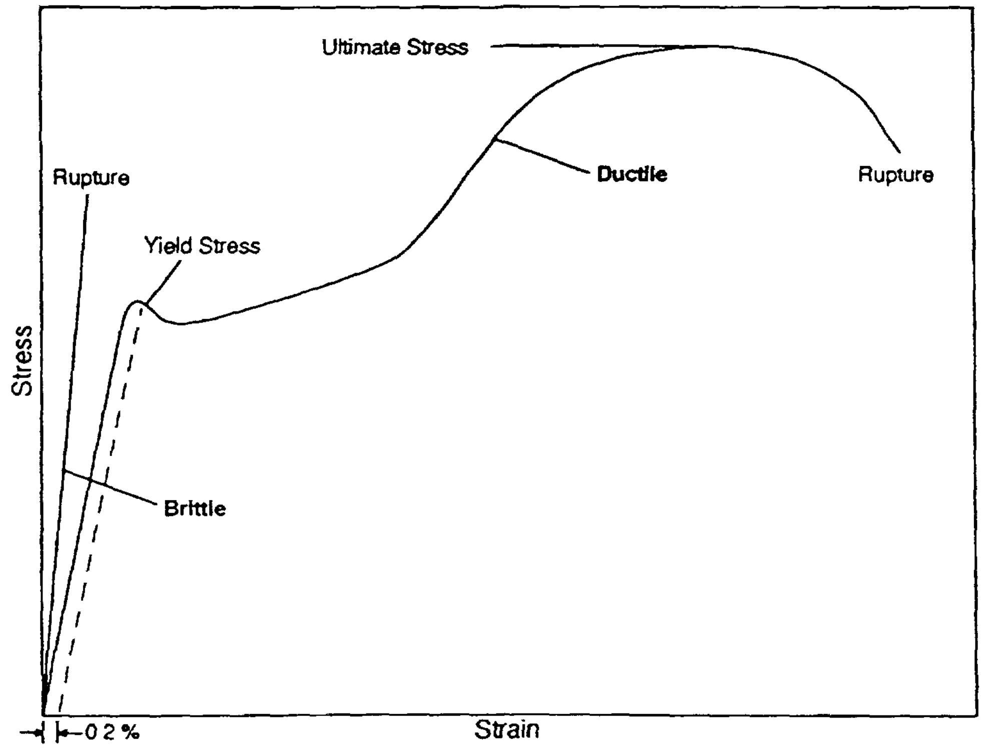


Fig. 8-2: Ductile and brittle behavior, from [43]

8.3.1. Hydrogen Embrittlement

8.3.1.1. Phenomena

Hydrogen has long been recognized to have a deleterious effect on some metals by changing their physical properties. It is basically due to the presence of hydrogen atoms dissolved in the metal grid and accumulating in disturbed lattice regions. Research on this **embrittlement effect** has led to the definition of three different categories [39, 43]:

a. **Hydrogen Reaction Embrittlement**
   Hydrogen reaction embrittlement is a phenomenon in which the hydrogen chemically reacts with a constituent of the metal to form a new microstructural element or phase such as a hydride or gas bubbles ("blistering"), e.g., methane gas if combined with carbon, or steam if combined with oxygen. These reactions usually occur at higher temperatures. They result in the formation of blisters or expansions from which cracks may start to weaken the metal.
b. **Internal Hydrogen Embrittlement**
   Internal hydrogen embrittlement means that hydrogen is introduced into the metal during its processing, e.g., chemical reactions with water to form metal oxide and liberate hydrogen. It is a phenomenon that may lead to the structural failure of material that never has been exposed to hydrogen before. Internal cracks are initiated showing a discontinuous growth. Not more than 0.1 - 10 ppm hydrogen in the average are involved. The effect is observed in the temperature range between -100 and +100 °C and is most severe near room temperature.
c. **Environmental Hydrogen Embrittlement**
   Environmental hydrogen embrittlement means that the material was subjected to a hydrogen atmosphere, e.g., storage tanks. Absorbed and/or adsorbed hydrogen modifies the mechanical response of the material without necessarily forming a second phase. The effect occurs when the amount of hydrogen that is present, is more than the amount that is dissolved in the metal. The effect strongly depends on the stress imposed on the metal. It also maximizes at around room temperature.

8.3.1.2. Mechanisms

To which extent metal is degraded by hydrogen is influenced by strain (tension, frequency, stretch velocity), specimen geometry (notches, bad welds, geometric inhomogeneities), the medium (pressure variation, temperature, impurities), and material (chemical composition, fabrication, heat treatment, welding joints) [67].

Several mechanisms have been proposed which might explain at least partially the degradation of metal by hydrogen embrittlement and which might act simultaneously:

- The formation of hydrides can lead to **new hydrogen-related phases** which may be brittle and also may have a lower density than the pure metal leading to internal stress.
- The hydrogen distribution in a metal under stress is highly non-uniform which can lead to locally increased **hydrogen-enhanced plasticity** causing local microscopic deformation and eventually a failure.

- The **lattice decohesion effect** is presumed to cause embrittlement by a decrease in the atomic bonding strength in the presence of hydrogen. A fracture occurs when the stress exceeds the cohesive stress.

Molecular hydrogen precipitation forming high pressures and compound formation are other mechanisms identified.

The above ideas help understand the observations that whether a metal is susceptible to embrittlement by hydrogen or a hydrogen compound or whether not, depends on the metal and also its metallurgical history which affect the migration behavior of hydrogen within the metal. The embrittlement is strongly connected with locally high hydrogen concentrations which can be caused by stress-enhanced diffusion rates to lattice defects and reaction sites to initiate cracks [62]. Cracks grow when hydrogen concentrations reach a critical level; crack growth stops when the crack has grown through the H_2-enriched region. The ability to explain the observations, however, was not accompanied by the development of non-destructive methods to detect early stages of degradation and the ability to predict with certainty the susceptibility of new alloys to hydrogen [71].

8.3.2. Low-Temperature Influence

Cryogenic temperatures can affect structural materials. With decreasing temperature, ultimate stress and yield stress increase for most metals, generally connected with a corresponding drop in fracture toughness which is a measure of the material's ability to resist crack propagation. The lower the toughness, the smaller is the tolerable crack length. A material can **change from ductile to brittle behavior** as soon as the temperature falls below its "nil-ductility temperature" which is sometimes considerably higher than the temperature of the cryogen. It is a particular problem in cryogenic equipment exposed to periodic temperature changes. Several accidents with failure of a cryogen storage tank have been traced to originate from cold embrittlement, for example the severe accident with the rupture of a 4250 m^3 LNG tank in Cleveland, USA, in 1944 [131].

Low temperatures can also affect materials by **thermal contraction**. The thermal expansion coefficient is a function of temperature. For many materials, which are cooled down from room to cryogenic temperature, more than 90 % of the total contraction experienced will have already taken place at 77 K. Rule-of-thumb figures of thermal contraction are 0.3 % in iron-based alloys, 0.4 % in aluminum, or over 1 % in many plastics [43]. Cryogenic vessels or piping systems must account for this contraction to avoid large thermal stresses.

The components of a cryogenic system usually undergo a **thermal gradient**, some only during cool-down or warm-up phases, others even at steady state of operation. Strong gradients, particularly if non-linear, result in stresses which under certain circumstances may lead to rupture. Thermal gradients are of particular significance in systems with stratified two-phase flows of cryogenics.

8.3.3. Materials Questions

Materials for hydrogen containing components have to meet the requirements of high strength and high ductility to enable a high system pressure and have to be appropriate for welding. Respective materials are ultrafine grain steels and thermomechanically treated steels. Usually applied dense coatings on the surface of the ferritic steels containing gaseous hydrogen prevent the adsorption of hydrogen unless they are damaged by plastic deformation. Other sensitive areas are welding seems and surface quality. Also a high degree of purity of the hydrogen favors embrittlement which could be influenced by adding gaseous promotors (e.g., H_2S) or inhibitors (e.g., O_2 and CO) or inert gases (N_2 and noble gases) depending on the specific operating conditions [67].

An additional requirement for materials containing liquid hydrogen is a sufficient fracture viscosity. Adequate materials are aluminum alloys, austenitic steels and steels with a high Ni fraction. The need for weight reduction in mobile applications has led to

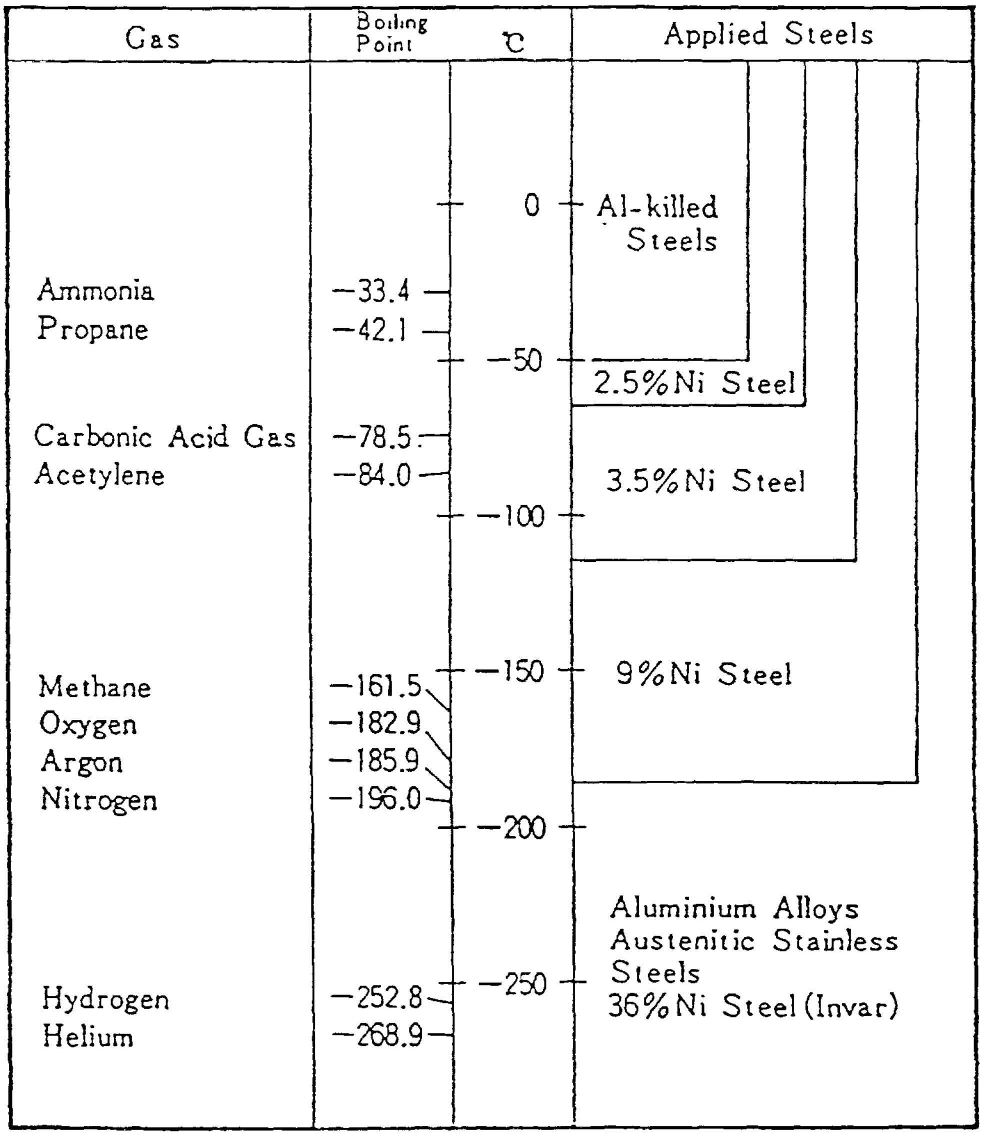


Fig. 8-3: Materials for containers of cryogenic liquids, from [45]

the development of **composite materials**, a matrix of plastic or metal in which glass or carbon fibers are embedded. Qualities of the composites are a higher strength compared with steel, a lower heat conductivity and almost no thermal expansion in fiber direction. With decreasing temperature, however, composites are prone to enhanced embrittlement and lower strength as well as a higher thermal expansion perpendicular to the fiber direction. Fig. 8-3 shows which materials are appropriate as containers for various media at different temperatures.

Two special materials testing systems have recently gone into operation at the University of Stuttgart, FRG, to investigate storage vessel materials behavior at cryogenic temperatures down to the helium boiling point of 4 K. The systems are suitable for tensile, fracture mechanics and fatigue tests which are conducted at pressures up to 20 MPa [32].

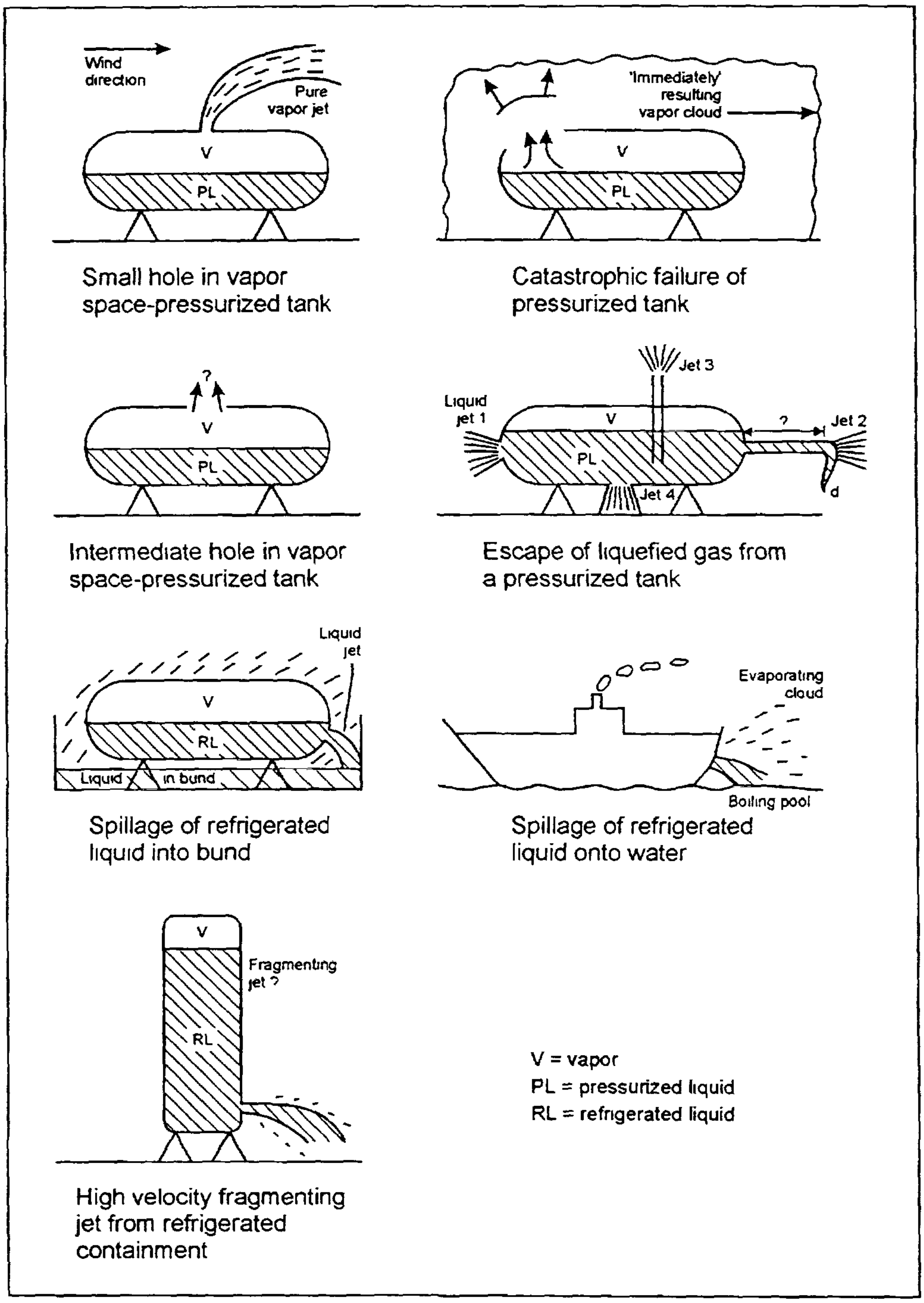
A materials test equipment has been developed in Japan within the WE-NET project to investigate the environmental hydrogen embrittlement of specimens in high-pressure hydrogen up to 10 MPa at different temperature levels between 20 K and 1500 K. Additions of various gaseous inhibitors have been examined as a preventive technique to arrest crack growth in the materials [129].

Based on many years experience, a material related safety concept for hydrogen technology has been developed in Germany applying so-called "**basis safety**" and independent redundancies. Goal of the "basis safety" concept as has been successfully applied in the field of nuclear energy, is the evaluation and validation of information on critical leak size, brittle and ductile behavior including the leak-before-rupture criterion of pipelines and pressure vessels in accordance with the state-of-the-art. With respect to a large-scale hydrogen economy, material development and optimization must be continued [67].

8.4. THEORETICAL AND EXPERIMENTAL INVESTIGATION OF ACCIDENTAL RELEASE OF HYDROGEN

The technical risks which are existent when handling hydrogen, also include the uncontroled release into the environment under accidental conditions. Three categories of **release types** are distinguished:

- Vaporization of a liquid hydrogen pool on the ground
  As a rule, the vaporized hydrogen escapes upwards, away from the site of release and from ignition sources, an advantage which, however, does not hold for confined or obstructed areas. The smaller the specific vaporization rate, the larger is the pool and the more extended and shallow is the evolved gas cloud. An LH_2 pool exhibits a decrease in depth of 0.4 - 0.8 mm/s which is high compared with other liquid fuels [41].
- Jet stream of liquid or gas through a small opening in a pressurized system
  A liquefied gas is widely sprayed from the exit developing a multi-phase mixture. In the opening, a narrow, so-called "flashing zone" is formed in which a certain fraction of the liquid depending on its thermodynamic conditions is spontaneously (flash-) vaporized. Adjacent zones are the zone of flow establishment characterized by a dilution of the jet stream from its boundaries and the zone of established flow with the full development of the plume interacting with the ambient [84].



Small hole in vapor space-pressurized tank

Catastrophic failure of pressurized tank

Intermediate hole in vapor space-pressurized tank

Escape of liquefied gas from a pressurized tank

Spillage of refrigerated liquid into bund

Spillage of refrigerated liquid onto water

High velocity fragmenting jet from refrigerated containment

Fig. 8-4: Conceivable release mechanisms from tanks containing liquefied gas, from [50]

- Catastrophic failure of a pressure vessel

The explosion-like expansion of a gas stored under pressure is characterized by its rapidity, the high energy release, and the high chance of ignition. The positive effect with respect to hydrogen is that a rapidly rising cloud is formed with a strong release-induced turbulence.

In Fig. 8-4, illustration of some conceivable release mechanisms is given. Release types include venting, leaks, or pipeline ruptures showing that the medium could escape as a gas, liquid, or two-phase mixture. The figure also demonstrates that the specification of the source term for an accidentally released liquefied gas is of particular importance for the accurate modeling of the gas cloud evolution and its atmospheric dispersion. The conditions and configuration of the source determine such features as release height, initial plume distribution, gas cloud dimensions as well as temperature, composition, and energy balances [50, 56].

8.4.1. LH_2 Pool Formation, Spreading, and Vaporization

8.4.1.1. Phenomena

If hydrogen is released in its liquid form, it can accumulate and form a pool on the ground and immediately starts to vaporize. A growing pool surface area implies an enhanced vaporization rate. After the initial phase, a state is reached which is characterized by the incoming mass to equal the vaporized mass. This, however, does not necessarily mean a constant pool radius: on solid grounds, the pool surface area will continue to rise due to the fact that the heat transport to the pool becomes smaller, the lower the ground temperature, thus decreasing the vaporization rate per unit area. The temperature of the cryogen itself corresponds to its boiling point and remains unchanged. A cutoff of the mass input results in a breakup of the pool from the central release point creating an inner pool front. The ring-shaped pool then recedes from both sides until it has completely died away. The physical phenomena arising with LH_2 spillage are depicted in Fig. 8-5.

LH_2 vaporization is determined by **heat transport into the pool**. The principal heat sources are conduction from the "hot" ground, atmospheric convection (wind), and radiation from the ambient (sun, fire). Of all contributions, heat transfer by conduction plays the dominant role; the error introduced by neglecting all other heat fluxes is in the order of 10 - 20 % for liquid hydrogen [34]. Due to the large temperature difference between ground and cryogen during the initial phase, a vapor film is formed inhibiting heat transport (film boiling regime). Vapor that cannot escape to the sides due to friction forces rises as bubbles disturbing the liquid layer. Cooling of the ground reduces the generation rate of vapor leading to an unstable and partially collapsing vapor film which immediately improves the heat transport between ground and liquid (nucleate boiling regime) connected with a rapid cooling of the ground. The processes are similar if the LH_2 is spilled on a liquid surface, e.g., water, except that the pool penetrates the surface to a certain degree, thus reducing the effective height responsible for the spreading; for instance, 7 % of an LH_2 pool on water are underneath the water surface while it is 80 % for an LN_2 pool. Cooling of the liquid ground leads to a natural convection flow transporting warmer water to the surface. A further decrease of the water temperature eventually leads to ice formation.

Thermal interactions between the cryogen and water at ambient temperature can induce vapor explosions or so-called **rapid phase transitions**. A spontaneous phase change occurs due to a sudden improvement of heat transfer between the two liquids. Under certain circumstances, an essential fraction of the thermal energy could be transformed into

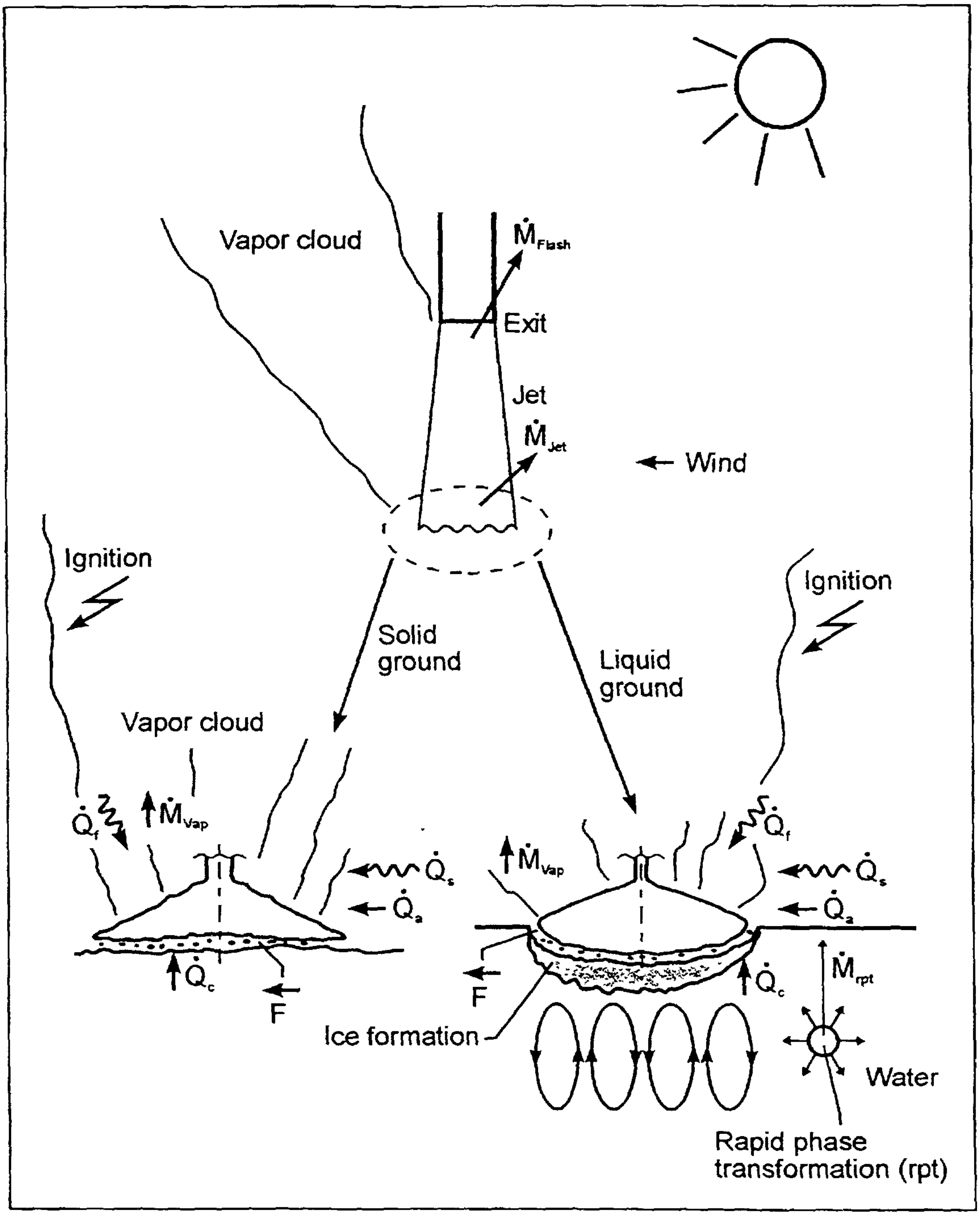


Fig. 8-5: Physical phenomena after the accidental spillage of liquid hydrogen, from [121]

mechanical energy. Besides, large amounts of gaseous hydrogen could be released into the atmosphere within a short period of time.

The result of most interest in this initial stage of an accident is the temporal and spatial production rate of gaseous hydrogen to be a boundary condition for describing the dilution by atmospheric dispersion of the hydrogen-air gas mixture and the determination of the flammable fractions within the concentration distribution of the gas cloud.

8.4.1.2. Experimental Investigation of Cryogenic Pool Spreading and Vaporization

Starting from a large-scale liquid fuel (LNG, LPG) maritime transportation and application in the 1970s, interest increased in the assessment of the consequences of spill accidents.

Many experiments have been conducted in the past with cryogenic liquids, mostly LNG, LPG, or the non-hazardous LN_2, to examine transient cryogenic pool behavior on both solid and liquid surfaces [e.g., 24, 25, 34, 38, 64, 65]. Main goals were the examination of the transient pool behavior under different release conditions on different surfaces and the verification of the thermal phenomena. Only a few data are available on LH_2 pool behavior.

The **NASA** hydrogen release tests with the spillage of 5.7 m^3 LH_2 with the purpose of investigating dispersion behavior [26] revealed a few coarse data about the pool size on the ground which was compacted sand. The data revealed a much smaller pool size than predicted with a simple model explained by a strong release-induced vaporization and by ignoring the flash vaporization effect and possible percolation into the sand [26, 120].

The most detailed investigation of LH_2 pool spreading so far was conducted by the **Research Center Jülich** [34] while conducting the hydrogen dispersion experiments under BAM direction in 1994 near Cottbus, Germany [102]. In four spill experiments, two on water and two on an aluminum sheet, the LH_2 pool size was measured as a function of time and location. Release rates were 5 l/s over 62 s for the water tests and 6 l/s over 62 s for the Al tests. A pulsation-like release behavior resulted in a pool front moving in the range between 0.4 - 0.6 m for the tests on water and between 0.3 - 0.5 for the tests on aluminum, respectively. LH_2 spillage onto the water created a massive ice layer with radial ice tracks attached that resembled very much the structures as observed in continuous LN_2 release experiments [34].

Within the WE-NET project (see section 9.2.1.), **Mitsubishi Heavy Industries** is planning to conduct small-scale LH_2 spill experiments for a detailed investigation of the vaporization phenomena with the purpose to develop and validate respective computer models [29].

8.4.1.3. Modeling of Cryogenic Pool Spreading and Vaporization

A concomitant effort of all experimental work on cryogenic pool spreading behavior has always been its simulation by calculation models. The development of mathematical models has passed several qualitative steps over the years. First approaches were of pure empirical nature correlating pool surface and maximum diameter with time or mass released [e.g., 24]. These model equations are only applicable to the material released. In an improved class of models, a **mechanistic approach** is used where the pool is represented in a cylindrical shape and the conservation equations for mass and energy were applied [e.g., 23, 47]. This kind of model is mostly used at present for safety analyses purposes.

State-of-the-art modeling, however, is based on the solution of the so-called **shallow-layer equations**, a non-linear differential equation system which takes into account the conservation of mass and momentum. This allows the tracking of the dynamic behavior

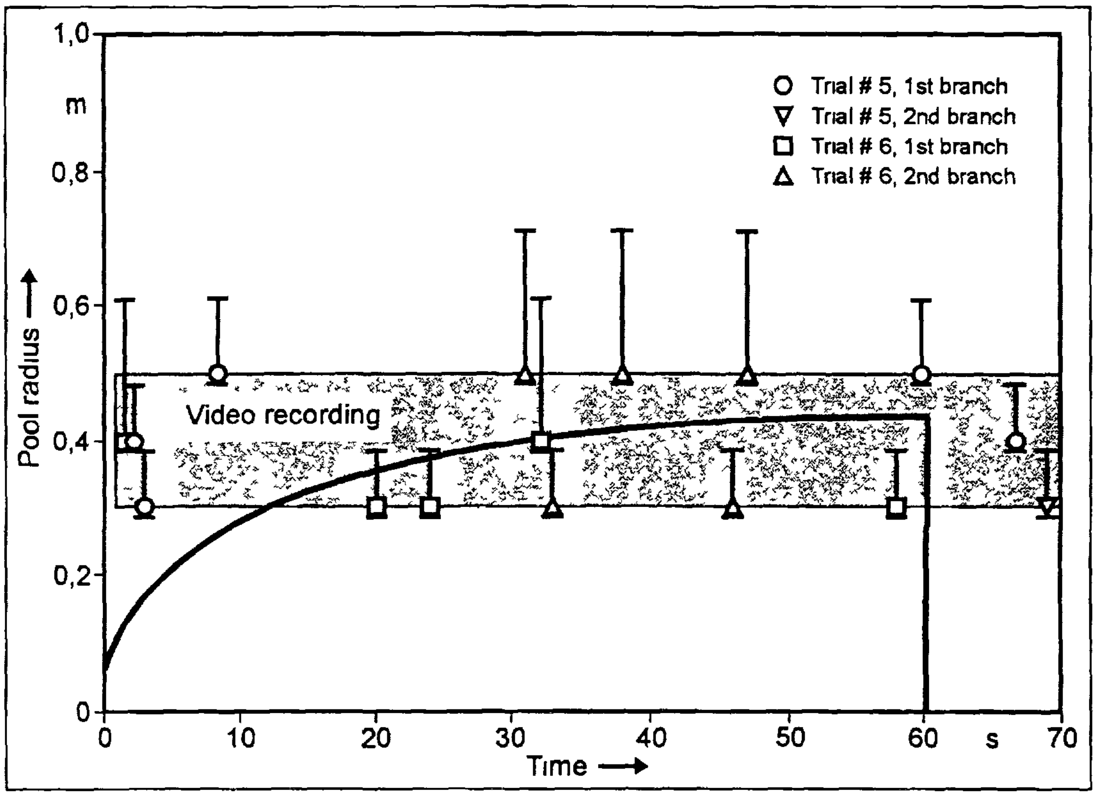


Fig. 8-6: Comparison between experimental data of the continuous LH_2 release at a rate of 0.006 m^3/s onto an aluminum sheet and corresponding postcalculation, from [121]

of pool growth and recession and calculates pool height and velocity as a function of time and location. Respective calculation models with successful performance have been implemented in the British **GASP** code [125, 126] and recently in the **LAUV** code [34] of the Research Center Jülich. The latter contains, in addition, a submodel for ice formation on a water surface. Validation of the LAUV model was made by postcalculation of LN_2 spill experiments conducted in Jülich and the above described LH_2 spill experiments and of examples from the literature [34]. The calculation of a Jülich experiment is shown in Fig. 8-6.

8.4.2. Atmospheric Dispersion of Hydrogen

8.4.2.1. Phenomena

The accidental release of gaseous hydrogen or the spillage of liquid hydrogen leads to the evolution and dispersion of a gas cloud whose shape is influenced by the type and rate of release and by the atmospheric conditions as well as by topography. Liquid hydrogen at 20 K which immediately starts to vaporize upon release, behaves like a heavier-than-air gas in the very first phase ("cold sink effect"). This short phase of negative buoyancy with a reduced heat and mass transfer due to the stable stratification effects is replaced by an enhanced positive buoyancy as soon as, due to continuous air entrainment from outside into the gas cloud, the cloud temperature has been raised to > 22 K. The dilution with ambient air makes the hydrogen cloud pass through the whole broad flammable range from high to low concentrations. The density of the hydrogen-air gas cloud is a function of time. Condensation of the always available humidity in the ambient air, which makes the hydrogen cloud visible, reduces the cloud density and liberates latent heat, both effects supporting the positive buoyancy. The strong buoyancy of hydrogen connected with a rapid mixing with the ambient air significantly reduces the lifetime of the flammable gas cloud. While for small release amounts, the dynamics of the atmosphere is dominant, a large gas cloud is observed to be capable of affecting the convective conditions, in particular, if wind velocities are small [76].

8.4.2.2. Experimental Studies

Pioneering experimentation with liquid hydrogen started way back in the late 1950s to examine hydrogen dispersion behavior as a consequence of its increasing application in space aviation. Test series conducted by **Arthur D. Little** [7] confirmed the decelerated buoyant behavior of vaporized but still cold hydrogen and its tendency of a horizontal spreading and revealed strong concentration fluctuations.

The first significant experiments to study the dispersion behavior of a hydrogen gas cloud was the **NASA** series of seven spill tests in 1980 with the release of 5.7 m^3 LH_2 per test within a period of 35 - 120 s [26]. Instrumentation allowed for concentration measurements at various positions (see Fig. 8-9). High release rates in connection with release-induced turbulence resulted in intensive cloud formation and rapid mixing with ambient air. The tests demonstrated that the hydrogen cloud was existent for a couple of 100 m downwind, especially if the ground was able to cool sufficiently.

In 1994, the Federal Institute for Materials Research and Testing (**BAM**), Berlin, conducted some spill tests with LH_2 and LPG to compare the dispersion behavior of both liquefied gases. Of special interest was the influence of adjacent buildings on the dispersion. The amounts released were 0.5 - 1 m^3 LH_2 at a rate of approx. 0.8 kg/s and about 0.2 m^3 LPG at a rate of approx. 0.25 kg/s. The tests revealed the completely different dispersion behavior of the "light" hydrogen and the "heavy" propane and demonstrated that hydrogen rapidly disappears upwards away from most ignition sources and does not accumulate around the location of release [102]. Typical hydrogen gas cloud formations under the given somewhat fuzzy wind conditions are shown in Fig. 8-7.

Test data have been collected for mixing and dispersion characteristics of methane and hydrogen leaking into the interior of a passenger car. Non-vented cars were found to hold flammable gas mixtures about 10 times longer than vented cars. Potential flammable ranges were identified as a function of leak rate and (roof) vented area. An integral design of the fuel system isolated from the passenger compartment incl. gas warning system was recommended for future gas-fueled vehicles [8].

A whole variety of other experimental series involving many liquids or gases of different densities, both on a laboratory scale in wind tunnels and on a large scale in field trials, instantaneously or continuously, have been conducted in the past with the prime goals to observe their behavior and to validate the performance of respective simulation models [120].

Fig. 8-7: Hydrogen cloud formation during the BAM LH_2 spill experiments as indicated by condensed water vapor in the atmosphere, from [Research Center Jülich, ISR]

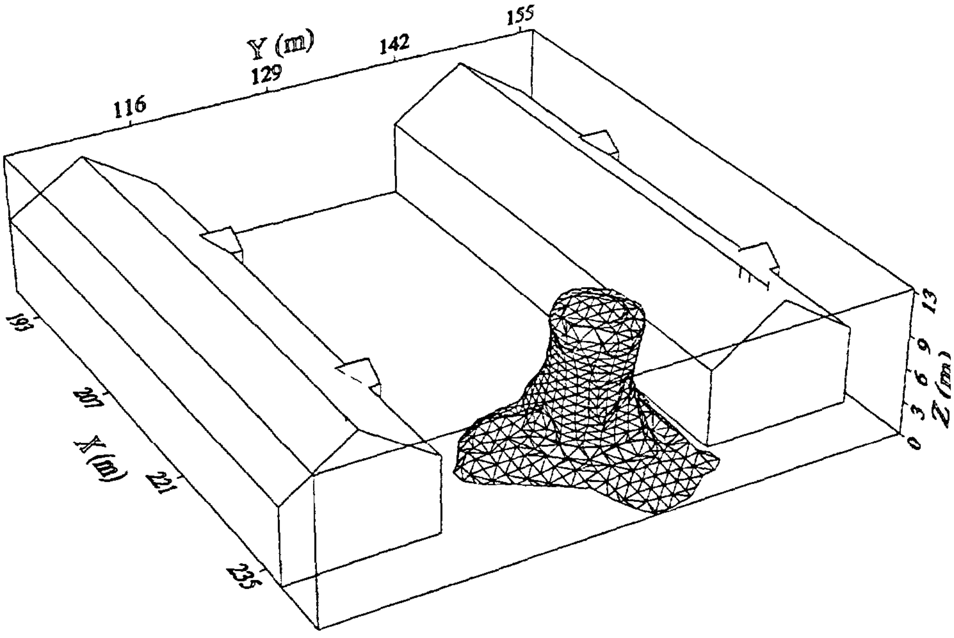


Fig. 8-8: Three-dimensional calculation of the 4 % hydrogen concentration isosurface for trial #6 of the BAM LH_2 spill experiments with the JRC Ispra code ADREA-HF, from [111]

8.4.2.3. Calculational Methods

The need to simulate the atmospheric dispersion of a gas cloud in order to determine extension and lifetime the flammable portions as realistically as possible has led to a lot of approaches, however, with different degrees of success in reaching the ideal profile of a mathematical model.

A classical approach is being made in the **Gaussian plume model** to simulate the spreading of neutral (sufficiently diluted) gases or pollutants, e.g., radioactivity. It is a simple model describing the concentration profile as a solution of the diffusion / advection differential equation with empirical spreading coefficients depending on the atmospheric conditions [87]. The Gauss model is inappropriate for treating the buoyant behavior of light or heavy gases.

In box or **slab models**, the released gas cloud is assumed to be of cylindrical shape. The processes of advection, i.e., the transport by the mean wind field, of air entrainment, and of gravitational spreading are implemented in empirical correlations derived from experiments. Box models were basically developed to simulate the behavior of a heavier-than-air gas cloud with averaged (in later developments vertical profiles of) temperature and concentration. Acknowledged (extended) box models are, e.g., the US code DEGADIS [57] and the British code HEGADAS [75].

Many dispersion models, such as, for example, the software packages HGSYSTEM or DEGADIS are accompanied by a **jet model** to calculate the dispersion of releases with significant momentum flux (the dominant parameter for jets). The jet behavior falls into two main zones: a region of adjustment from storage conditions to atmospheric pressure followed by "conventional" jet dispersion at atmospheric pressure. As noted above, many failure scenarios produce jet releases, which may be liquid, gas, or two-phase. If the storage conditions are pressurized, an initial zone of adjustment to atmospheric pressure would be expected possibly including flashing for a liquid or choked two-phase jet. The conventional jet dispersion region begins with a so-called region of flow establishment, in which similarity profiles for the concentration and axial velocity evolve; following this the jet evolves with self-similar profiles. The main features distinguishing the various jet models in this part of the flow are the treatment of the entrainment of ambient air and the choice of similarity profile (top-hat, Gaussian).

State-of-the-art modeling of the transient behavior of gases with positive or negative buoyancy in the atmosphere is provided by **computer fluid dynamics (CFD) models** which simulate complex flow processes by solving the Navier-Stokes equations in an Eulerian three-dimensional calculation grid structure. This approach comprises the conservation equations of mass, momentum, and energy. Besides their need for immense computer time and storage capacity which can only be realized by the current computer generation, these models require a detailed input of initial and boundary conditions for the calculation grid. In the **two-equation k-ϵ turbulence model**, special partial differential equations are solved to describe the transport of turbulence as well as its generation and dissipation. The standard k-ϵ model has been modified in [97] such that the influence of thermal stratification can be taken account of by introducing and additional expression of turbulence generation/dissipation.

Of all the approaches, the k-ϵ model offers the highest relative independence of empirical relations. It appears to be the only one to allow a proper simulation of hydrogen dispersion, because it meets the requirements of describing effects such as turbulence energy in the gas cloud, interaction of the cloud with the atmospheric wind field, the characteristic positive buoyancy, transient sources with initial momentum, and last but not least, gas flow in a complex geometry (buildings, terrain). K-ϵ modeling has been realized in a variety of computer codes distinguished by the choice of the numerical solution method which was found to have a significant effect on the calculation procedure.

Only a few theoretical efforts have been made to simulate the dispersion of hydrogen gas mostly due to scanty experimental data. Early efforts were made in the late 1970s by the Los Alamos National Laboratory on a box model for hydrogen taking account of heat transport from the ground into the cloud [42] and later applying the Gaussian model for neutral and buoyant dispersion as a part of the World Bank software package **WHAZAN** [112].

The NASA has developed the dispersion code **AFGASDM** applicable to LH_2 and other aviation fuels [22], which is in a sort of interim stage between a Gaussian model and an Eulerian grid model. The model solves the conservation equations following a gas "parcel" released as a puff until its dilution below the flammability limits. It takes account of air entrainment and phase changes.

A 2D version of the **BITC** model [122] developed by the Solvay company, Belgium, for heavy gas dispersion has also once been used for hydrogen to demonstrate its basic applicability for light gases. It uses a Lagrange approach of tracking "marked" particles representing the statistics of turbulence transport.

The 3D finite volume code **ADREA-HF** was developed for the computation of the atmospheric dispersion of heavy gas clouds in complex terrain. It contains a one-equation turbulence submodel taking account of two-phase processes [3]. The code has been applied to ammonia, propane, chlorine, and also buoyant releases. It has recently been tested against the BAM hydrogen release experiments. The calculational results for one of the trials are given in Fig. 8-8 showing the hydrogen dispersion near buildings [111].

Mitsubishi Heavy Industries' computer code **CHAMPAGNE** is a multi-phase, multi-component thermodynamics model originally created for the assessment of severe accidents in fast breeder nuclear power reactors. It was recently modified to also treat the formation and spreading of hydrogen gas clouds. CHAMPAGNE has been successfully applied both as a 2D and 3D version to the NASA LH_2 spill tests from 1980 (Fig. 8-9) [30].

A k-ϵ atmospheric dispersion model **POLLUT** was developed at the TU München [93] to describe hot gas plumes escaping from stacks of power plants. The code was used in a DLR study [45] to investigate hydrogen dispersion upon accidents with LH_2 powered cars releasing their tank contents both in open terrain and in a road tunnel.

The Battelle k-ϵ model **BASSIM** originally designed for hydrogen combustion in nuclear containments (see section 3.4.5.) was also applied to the above mentioned LH_2 spill experiments conducted by the BAM, Berlin, for predictive calculations providing reasonable qualitative results for 3D effects of hydrogen dispersion behavior [94].

The commercial CFD code **CFX** by AEA Technology [1] (see section 3.4.5.) has been taken to predict the hydrogen gas distribution inside the ELBA fuel cell demonstration vehicle (see section 9.5.2.2.) under H_2 leakage conditions. It has, however, not (yet) been applied to H_2 dispersion in the open atmosphere, but according to its profile, it should be an appropriate tool of simulation.

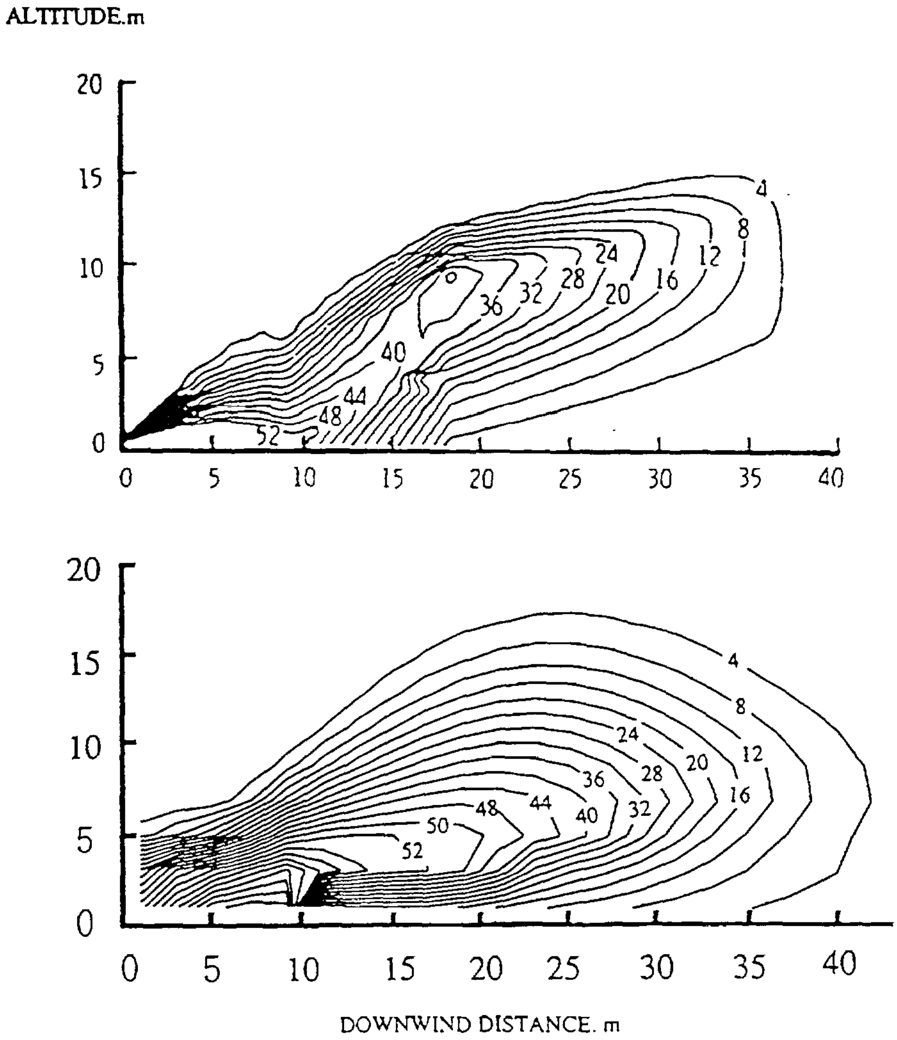


Fig. 8-9: Hydrogen concentration measurements during the NASA LH_2 spill experiment #6 (top) and corresponding 2D postcalculation with the Japanese CHAMPAGNE model (bottom), from [30]

8.5. COMBUSTION BEHAVIOR OF HYDROGEN

8.5.1. Flame Propagation, Deflagration

8.5.1.1. Phenomena

According to the evaluation of explosion accidents in the past, only a small portion of the energy of a hydrogen cloud is expected to be liberated in an open air explosion; it is estimated to be in the range of 0.1 - 10 %, mostly < 1 % [68].

The lower **flammability limit** of a hydrogen-air mixture was observed to be a function of temperature expressed by the empirical Burgess-Wheeler law [131]. The respective value near the boiling point (20 K) is 7.7 vol% and as low as 2.3 vol% at a temperature of 723 K. Because of its strong buoyancy connected with a rapid mixing with air, a hydrogen gas cloud soon reaches concentrations in the flammable range, but is on the other hand also soon diluted below its lower flammability limit. In most accidental situations, the lean limit is the most relevant one.

The ignition of a gas cloud always requires an ignition source. Under normal circumstances, a spreading cloud is ignited at its perimeter. According to accident statistics, the most probable reasons for the ignition of hydrogen gas clouds are autoignition on hot surfaces, an electric spark, or an electric discharge. The positive Thomson-Joule effect does, in principle, not lead to an ignition. In practice, however, ignition is observed in almost all cases of sudden expansion due to electric charging by dust particles during the release process [61].

The laminar **burning velocity** which is defined by the reaction rate of volume of unburnt mixture per square unit surface or the velocity of the reaction front relative to the coordinate system that follows the fluid motion, is a material property which increases with increasing temperature. For a stoichiometric hydrogen-air mixture at room temperature, the burning velocity is 2.37 m/s with a maximum of 3.46 m/s for a 42.5 vol% concentration. In an H_2/O_2 mixture, it is even as high as 9.4 m/s. The flame front velocity is defined by the burning velocity multiplied with the expansion ratio leading to a figure for hydrogen in air of about 24 m/s.

The turbulent burning velocity is significantly higher due to small-scale turbulence and flame instabilities reaching the order of several hundred m/s. Most realistic flames are turbulent. Turbulence causes an increase of both energy transfer and flame surface, thus enhancing the burning process (positive feedback), plus it forms new ignition centers. At present, the turbulent velocity cannot be sufficiently determined on a theoretical base, but must be deduced from experience [2, 45].

Deflagration is the type of combustion with a subsonic burning velocity level. It occurs under non-adiabatic conditions and at densities lower than that of the unburnt mixture. Its propagation mechanism is conduction heating and free radical diffusion. Only fuel-air gas clouds at around stoichiometric mixture imply high flame front velocities and maximum expansion upon ignition, i.e., the ratio of the density of unburnt mixture to that of the reaction products, which is about 7 - 8 for hydrocarbons (in reality smaller by up to 50 % because of non-ideal micro-mixture), but < 1 for hydrogen.

As a rule, the ignition of an unconfined vapor cloud leads to flame front velocities small enough to preclude a fast deflagration and a pressure wave. In such a flash fire, the burning energy is almost completely transferred into thermal energy. The so-called "**Unconfined Vapor Cloud Explosion**" (UVCE) is the explosive type of deflagration where about 60 % of the burning energy is expressed as kinetic energy in the form of pressure waves [54]. The flame front consists of a preheating zone and a reaction zone. Heat transport by conduction and diffusion from the reaction zone into the preheating zone enables the propagation of the flame.

Experience with explosion accidents has shown that whenever hydrogen was involved, a shock wave was created, however, a comparatively weak one because only a portion of the gas cloud actually did explode. One reason might be the pinch effect, a flame deceleration in a less dense mixture causing an isolation of the flame from the main cloud [54]. A near-ground deflagration results in a hemispherical fireball which subsequently gains a spherical shape due to buoyant forces. Depleting fuel terminates the radial spreading and the buoyant forces allow for a liftoff of the fireball resulting in the typical mushroom shape.

"**Boiling Liquid Expanding Vapor Explosion**" (BLEVE) characterizes the failure mechanism of a liquid gas container where the major part of the contents are released by flash vaporization and explode while the remainder forms a pool which burns down. Three conditions need to be met: (i) the liquid is superheated, (ii) a sudden pressure drop occurs, (iii) pressure and temperature conditions are such that flash vaporization is possible. This type of explosion is caused if a storage tank is exposed to a heat source from outside. A tank structure weakened by the high temperatures, a high inner pressure, and tensions in the container wall near the gas / liquid boundary layer eventually results in the catastrophic failure, however, merely causing pressure waves. An intact safety valve could delay, but possibly not prevent the vapor explosion [73].

An even stronger explosion is represented by a "**Boiling Liquid Compressed Bubble Explosion**" or BLCBE which runs in two steps. Starting with a partial failure of the container by a crack growth, there is a spontaneous expansion of a two-phase mixture which makes the pressure rise again up to its starting value. This then causes the vapor bubbles to collapse creating pressure waves of 100 - 300 MPa. It finally results in a rapid crack growth and a total failure of the tank with the whole contents to be violently and uniformly distributed as a fine, high-turbulent aerosol. This failure mechanism was experimentally verified [119].

The thermal emission of a burning gas cloud can induce further damages in the neighborhood by igniting other objects. The thermal radiation of a hydrogen flame is low (emission coefficient $\epsilon < 0.1$) compared with that of conventional gaseous fuels ($\epsilon \approx 1$) leading to a much smaller thermal impact.

If an ignition occurs above an LH_2 pool, heat transport develops from the burning gaseous cloud by conduction, convection, and radiation enhancing the vaporization rate. The pool regression rate is dependent on the radius: For small radii, heat conduction from the perimeter dominates meaning that the burning rate decreases with incresaing radius. For large radii, radiation is dominant causing the burning rate to increase with increasing radius. Burning rates have been measured in the range of about 0.3 - 1.1 mm/s [131].

If liquid hydrogen is released in ambient air with a high humidity content, the flammable fraction of the gas cloud is generally enclosed in the visible cloud, while under conditions of a dry atmosphere, flammable fractions could also exist outside the visible cloud. These observations show that the visible cloud is not a precise indicator for the flammable zone of the gas cloud [130]. The 4 % lower limit coincides with the perimeter of the visible cloud at temperatures of about 270 - 300 K and humidities of about 50 - 57 %, but with strong fluctuations in the concentration which affect the capability of flame maintenance.

Condensation and solidification of air in liquid hydrogen is always connected with an oxygen enrichment. It leads to local combustion if ignited. If the oxygen fraction exceeds 40 %, the ignition immediately results in a detonation [108].

8.5.1.2. Experimental Studies

The first experiments conducted in the late 1950s by Arthur D. Little Inc. [7], Lockheed-California Co. [96], and the US Federal Bureau of Mines [130] with the release of up to 19 m^3 liquid hydrogen and subsequent ignition have been used to find empirical correlations for flame height and width in order to define safety distances. The more delayed the ignition, the larger was the fire ball. The hydrogen flames were restricted to the pool area, but far extended in vertical direction with flame height up to 50 m. It was also observed that the fire ball could ignite flammable portions of the gas mixture separated from the main cloud.

Ballistic tests and lightning strike tests have been conducted in the USA to investigate the impact on LH_2 and conventional JP-4 fueled areas of an aircraft. Test specimen with dimensions of 40.6 x 2.5 x 30.5 cm^3 and 5 cm thickness filled with fuel were subjected to projectiles and artificial arcs. In the case of LH_2, moderate fire balls were observed and a deflagration of hydrogen vent gases with no evidence of a detonation. Hazards associated with LH_2 fuel appear to be less severe compared with JP-4 [70].

In Japan in the early 1980s, tests with ignition of LH_2 in an open dewar of 0.3 m diameter were conducted. A steady flame above the pool was observed higher and wider than a respective gasoline flame. The burning rate expressed as a liquid level regression was measured to be 0.4 mm/s or 6.5 times larger than for gasoline. Abnormal burning with very high flames was observed when the burning LH_2 came into contact with solidified oxygen from the air in the LH_2 [116]. Tests with burning LH_2 pools have also been used to examine different methods of extinguishing pool fires [59].

Within the so-called "Hydrogen Oxygen Vertical Impact", **HOVI**, project, the national space institutions of the US (NASA) and Japan (NASDA) have recently conducted a series of explosion experiments on the NASA White Sands Test Facility. In these tests, LH_2 and LOX tanks were dropped from a 70 m tall tower and exploded upon touchdown. Explosion pressures have been measured to derive a TNT equivalent.

Ignition of the cone-shaped hydrogen gas cloud evolving from the leakage off a compressed gas tank for vehicles is being investigated at the University of Miami with the goal to improve the design of vehicle storage systems. Resulting overpressures were greater than in the case of methane, however, still relatively low [114].

8.5.1.3. Modeling

Early explosion tests with gas clouds were used to derive simple empirical correlations concerning flame extension or lifetime as a function of fuel mass released, e.g., **WHAZAN**, a software package of the World Bank [115]. Other approaches are subjected to a turbulent jet flame [74] or the dynamics of a rising and expanding fire ball or the impact by the heat radiation flux [31]. Common to all models is the fact that they are based on a more or less empirical approach with a contentious capability of predicting the consequences of an explosion.

Detailed chemical mechanisms for combustion processes, in particular in gas mixtures, comprise a large number of species and elementary reactions, a respective detailed coding would not be practicable. Therefore a systematic reduction of the chemical mechanisms down to a three-step or two-step reaction process is being made with different degrees of approximation, e.g., the assumption of partial equilibria or the neglecting of highly reactive species whose concentrations thus are small [86].

The **flamelet model** for diffusion flames has been developed at the RWTH Aachen describing in a simplified manner the flame front of a multi-dimensional flow. The flame front is assumed to be locally one-dimensional. By introducing an appropriate coordinate, e.g., fuel-mass ratio, the determination of flame structure and of flame front propagation can be separated [79].

The above mentioned CFD code **BASSIM** of the Battelle Institute was originally written to simulate hydrogen deflagration in confined 2D geometries with combustion in a one-step process. It has been successfully applied to calculate jet ignition and the influence of water vapor on the deflagration [29].

The German DLR has been using a computer code to simulate 3D turbulent reacting flows by solving the Navier-Stokes equations and using the k-ϵ turbulence model in a Lagrange approach. The modeling of the chemical kinetics of hydrogen-air combustion was realized by considering 12 elementary reactions with 9 species including the NOX formation mechanism. The code is intensively used for testing and optimizing hypersonic propulsion concepts (Fig. 8-10) [80].

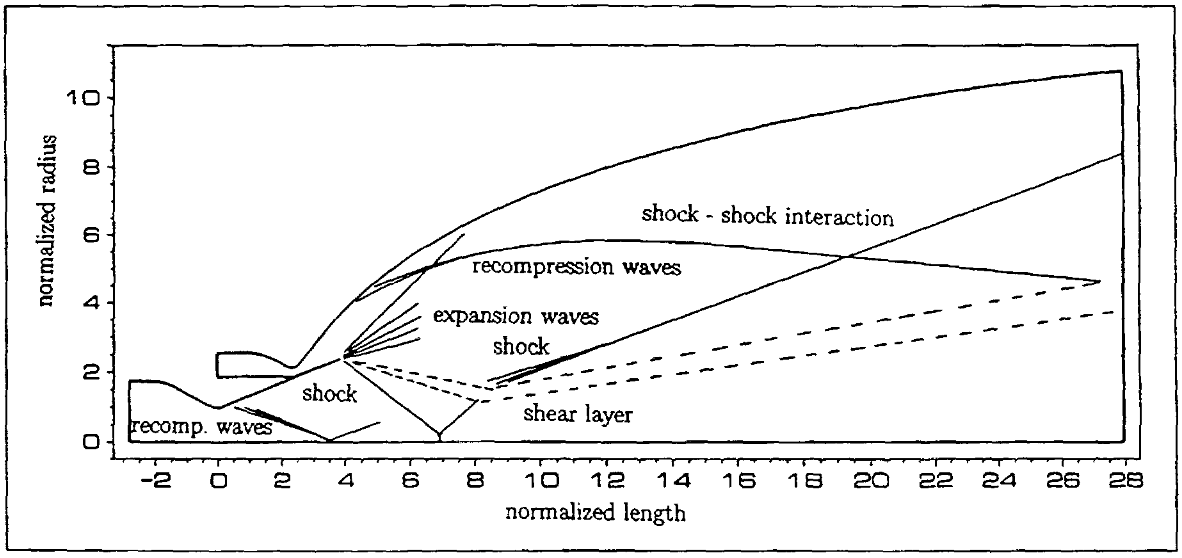


Fig. 8-10: Phenomenological diagram of the complex flow field in an advanced rocket thrust chamber and nozzle, from [DLR]

8.5.2. Flame Acceleration and Detonation

8.5.2.1. Phenomena

In contrast to a deflagration, the chemical reaction in a detonation is faster by several orders of magnitude where the reaction front propagates at a supersonic speed in the order of several km/s. The flammable gas mixture is compressed connected with a temperature increase and autoignition of the still unburnt mixture. The release of the chemical energy keeps the shock wave going. The detonation is a rare event, but the damage potential is much stronger than in a deflagration.

The shock front possesses a 3D cellular structure characteristic of the fuel-air mixture. The higher its reactivity, the smaller is the cell. In general, the detonation cell size, λ, is proportional to the characteristic chemical reaction time for the mixture. It can also be related to other key quantities, such as detonability limits, confinement, geometry, critical tube diameter[20], chemical induction length, whereas the run-up distance does not appear to be of fundamental importance. With 15 mm, the λ of hydrogen is smaller compared with other fuels meaning that detonation of a hydrogen gas cloud can occur even in small geometries. The critical diameter in a stoichiometric mixture corresponds to $\approx 13*\lambda$ or about 0.2 m. Deviation from stoichiometry increases the detonation cell size, e.g., λ = 50 mm at 20 vol% H_2 [55, 77]. The same effect results from the addition of diluents; a 10, 20, 30 % steam fraction was found to result in a λ enlarged by a factor of 6, 20, and 60, respectively [15]. Also the addition of 8 % methane to a stoichiometric hydrogen-air mixture was found to act as an inhibitor for DDT [44].

The range of detonability of a hydrogen-air mixture is from 18 to 59 vol% with the most hazardous range between 35 and 40 %, measured in detonation tubes with diameters of the order of a few centimeters. In larger experimental facilities (see section 8.5.2.2.), even values as low as 15 % (FLAME) and 12.5 % (RUT) as the lower detonability limit in air have been observed [21]. Depending on the strength of the ignition source, the limits of detonability can even coincide with the flammability limits [98]. In pure oxygen, the detonation range of hydrogen is 15 - 90 vol%. A mixture of gaseous hydrogen with solid oxygen has the quality of an explosive and can easily detonate.

The detonation of a gas cloud occurs either directly by detonative ignition (explosive, turbulent jet) or starting from a deflagration by flame acceleration. During the **transition from deflagration to detonation (DDT)**, two phases are distinguished:

1. Occurrence of a local explosion (hot spot) leading to a shock wave
   The area in front of the reaction zone is ideally prepared for autoignition. Hot spots are being created by focussing of weak waves behind obstacles.
2. Amplification of the shock wave until autoignition and transition to detonation by means of an effective mechanism
   One DDT mechanism is **SWACER** ("Shock Wave Amplification by Coherent Energy Release") based on a stimulated release of the chemical energy which goes synchronous with the shock wave.

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[20] Critical tube diameter is the minimum diameter of a tube that will permit a detonation wave to continue propagating into an open volume as a spherically expanding wave.

The decisive criterion for flame acceleration is the state of turbulence in the gas cloud defined by intensity and characteristic length and time of the spectrum. Main effects on the flame speed are given by:

- **partial confinement**
  Geometric arrangement, e.g., a lane, or interaction with (a series of) obstacles might induces high turbulence. A positive feedback effect (enlarged flame surface area → enlarged reaction rate → enlarged flame front velocity) leads to a continuous flame acceleration. An upper limit for the flame front velocity is given when the effect of rapid mixing levels the effect of temperature decrease due to the mixing. Hydrogen flames have been observed to soon reach the stage of a quasi-steady velocity.
- **Rayleigh-Taylor instability**
  If the boundary layer between two fluids of different densities is accelerated towards the higher density fluid (like reaction products towards unburnt mixture), disturbances are amplified causing an enhanced reaction rate (and vice versa).
- **Markstein-Taylor instability**
  Pressure waves of local explosions can accelerate a preceding slower flame front leading to a sudden increase of burning rate and flame velocity.
- **turbulence prior to ignition**
  Turbulence created during a release process does not have a long lifetime. However, if an ignition hits this narrow time window of ideal turbulence and concentration distribution, a high flame speed can be reached.
- **type of release**
  If ignition in a confined area leads to an expelling of the unburnt mixture through a relief opening into a gas mixture outside, the result could be a spontaneous (jet) ignition, which is even more probable, if obstruction is available inside or outside.
- **dust**
  whirled-up dust can absorb thermal radiation from the flame front increasing the flame speed. The heatup effect can then lead to autoignition with initiation of a detonation. This effect, however, needs a certain size of the gas cloud and a certain loading with dust.
- **gas cloud shape and size**
  The velocity of the flame front becomes smaller when it intersects the cloud perimeter. Larger clouds exhibit a slightly higher flame speed.

All above effects have in common a generation of turbulence as the dominant mechanism for flame acceleration. In addition, large-scale experiments have revealed that also effects of scale and geometry have a strong influence on the probability of DDT. In the whole detonation range, hydrogen appears to be much more sensitive to a transition to detonation than the hydrocarbon fuels. DDT behavior can be influenced by introducing inhibitors, which are non-reacting components such as nitrogen or water vapor or even slow-burning hydrocarbons.

The explosion of an **unconfined hydrogen gas cloud** in the presence of a weak ignition source was never observed to have turned into a detonation [45]. The ignition energy required for a direct detonation can only be provided by either an intensive turbulent hot gas jet or by an explosive. For a stoichiometric mixture, the minimum energy was experimentally determined to be 4.7 kJ ($\approx$ 1 g TNT). A methane-air mixture even requires at least 22 kg of an explosive for detonation [89]. This type of explosion, however, is irrelevant under realistic accident conditions. A real gas cloud evolved after a release, normally has a concentration gradient which tremendously diminishes the strength of an explosion as it were in a well-mixed cloud. Only an estimated 17 % of a real gas cloud behave like a stoichiometrically premixed cloud [89].

8.5.2.2. Experimental Studies

Numerous large-scale and small-scale test facilities have been used to investigate flame acceleration and the deflagration-to-detonation transition as well as the relevant detonation parameters (e.g., blockage ratio, obstacle distance). The most dangerous configurations were, as expected, those with (partial) confinement and obstruction. But spontaneous transition has also been observed with a weak ignition source and at H_2 concentrations relatively far from stoichiometry (0.6 - 1.6 equivalence ratio). Key similarity is the turbulence generation. A good survey on the worldwide experimental work is given in [79].

The initiation of a detonation by means of a jet ignition has been demonstrated in experiments for the first time at the end of the 1970s. An essential result was the rule of thumb according to which the high flame front velocity and the overpressure have decayed within the distance of 10 times the characteristic length of the vessel [113].

Within the nuclear power plant safety program and the PNP gas cloud program, the German **Fraunhofer Institute for Chemical Technology** (ICT) has conducted different test series involving mixtures of propane, ethylene, methane, and hydrogen with air to investigate detonation and DDT in spherical, hemispherical, and tube geometries. Unconfined, hemispherically shaped H_2-air mixtures were investigated at volumes between 7.5 and 2100 m^3 with a measured maximum overpressure of 6.3 kPa corresponding to 84 m/s flame velocity [35]. A series of six balloon tests was conducted in 1991 with hydrogen-air mixtures at concentrations of 20 and 29.6 vol%, respectively [91]. The hemispherically shaped gas cloud of 50 m^3 volume was ignited in the center on the ground by an explosive to trigger a detonation. Pressures were measured at various positions inside and outside the balloon. Visually measured detonation speed agreed well with the theoretical value [20].

Tests with two interconnected balloons have shown that the detonation in one balloon did initiate not more than a fast deflagration in the other, unless a tube connection was chosen which was shown to pass on a detonative combustion. The geometry of the gas cloud seems to play an essential role. DDT was examined using various igniters in balloon volumes up to 500 m^3. Plastic tubes with up to 25 m length were found to have the higher degree of turbulence. Flame acceleration in all tests was far away from yielding a DDT.

Other balloon tests with up to 15 m^3 volume and tests in plastic tubes with ethylene-air gas mixtures were found to detonate by means of 8 g of an explosive, however, not with a 100 J heated wire. Minimum mass of explosive is 80 g for propane-air mixtures, and as much as 22 kg for methane-air mixtures. For real gas clouds, the required explosive mass is even higher: 300 g did not initiate a detonation of a flash-depressurized propylene gas cloud, where 20 g would suffice for a stoichiometric mixture.

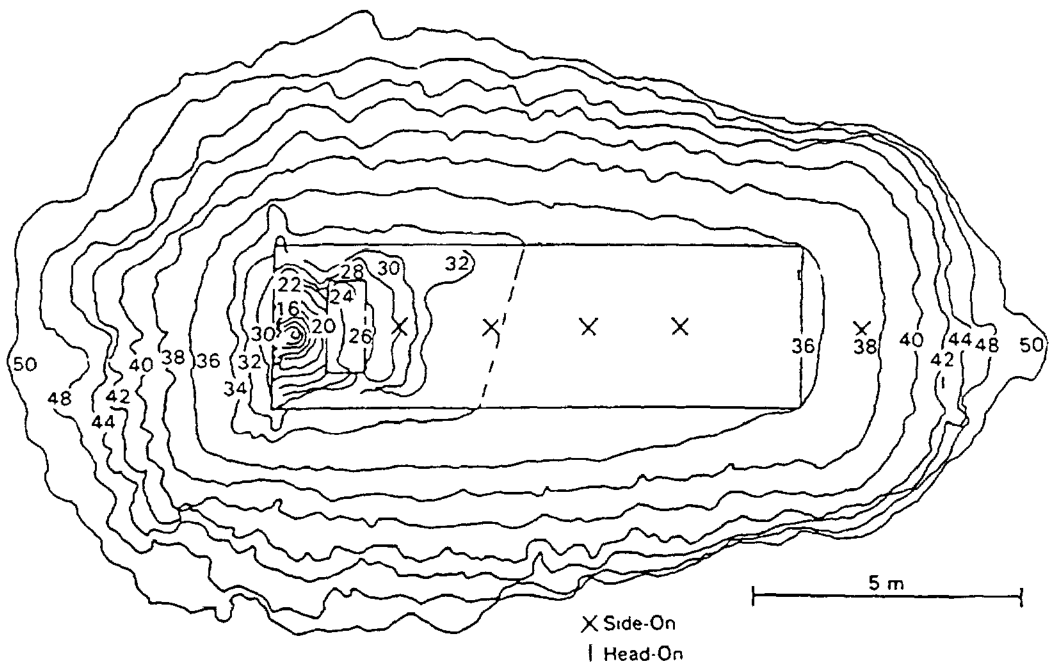


Fig. 8-11: Measured flame front profiles for the ICT test "GHT41". The rectangular-shaped body in the center represents the balloon with a 40 % H_2-air mixture. Ignition point is near the left wall. The vertical rectangular box on the left-hand side describes the position of the fan, the crosses are measurement positions. The numbers on the contour lines represent time in milliseconds. DDT occurs approx. 2 m past the fan, from [15]

A series of 17 tests was carried out by the ICT with ignition of pancake-shaped, free, homogeneous, near-stoichiometric methane-air or propane-air gas clouds of up to 13,000 m^3 volume. The generation of additional turbulence due to obstacles or entries/exits was observed to result in locally higher flame speed (up to 80 m/s) and overpressures (up to 8 kPa) compared with undisturbed clouds with respective figures of 6 - 8 m/s and 0.1 - 0.2 kPa [90].

More ICT tests were conducted under conditions of partial confinement (two parallel walls forming a 10 x 3 x 3 m^3 lane) and with rich (36 - 41 vol%) H_2-air mixtures. With full fan-induced turbulence, flame acceleration was observed until DDT occurred resulting in pressures and velocities exceeding the Chapman-Joguet values (see next section) [35]. Flame and detonation front profiles for one of the tests are plotted in Fig. 8-11 clearly showing the sudden transition to detonation shortly past the fan.

Shock tube experiments with hydrogen-air mixtures conducted at the **RWTH Aachen** have shown different modes of self-ignition. At lower temperatures (< 1150 K), randomly distributed hot spot mild ignition leads to a deflagrative type of combustion [16].

The **Research Center Karlsruhe** has conducted combustion test series with premixed stoichiometric hydrogen-air mixtures both in a 12 m long cylindrical tube of 0.35 m diameter and in a rectangular channel with 0.1 x 0.1 m^2 cross section and 3 - 6 m length. Different degrees of obstruction allowed the examination of the whole spectrum of turbulent flames and their reflection and diffraction at obstacles and system boundaries [20].

DDT experiments at the **Technical University Munich** have been carried out in a 66 mm diameter and 6 m long closed test tube with a 3 m acceleration section. The degree of obstruction was varied between 30 and 70 %. Mixtures with < 10 vol% H_2 could not be ignited reliably. High flame speeds were observed at 10 - 13 % H_2 concentrations in the obstructed section. At > 20 vol%, detonations occurred; a lower H_2 concentration is sufficient the smaller the initial temperature. For high blockage ratios, the flame was found to be strongly accelerated at the beginning, but then eventually quenched [11].

Another facility to investigate DDT in hydrogen-air-steam mixtures has been operated at the **Battelle Institute**, Frankfurt, with the goal to examine the influence of steam as a possible inhibitor of a detonation. Two series of experiments have been conducted under conditions simulating a core meltdown accident in an LWR: (i) at 100 °C and 0.1 - 0.2 MPa with a homogeneous mixture (9 tests) and (ii) at 120 - 130 °C and 0.2 - 0.3 MPa with a high steam fraction and H_2 concentration gradient (12 tests). The experimental setup consisted of a tube of 10 m length and 0.4 m diameter installed in a closed steel vessel with 5.4 m^3 total volume. The flame front passes a 2 m acceleration section with obstacles, propagates upwards through the inner tube, and then after exiting u-turns down in the outer vessel. The significant change of geometry in the upper part makes the combustion process rather complex enhancing turbulence in connection with a quenching of the flame. In four out of the 21 tests, DDT was observed [14].

A small-scale test facility, **FAST**, was erected at the TNO research center, The Netherlands, to investigate the influence of obstruction, inerting, and multicompartment arrangement on hydrogen explosions under LWR accident conditions. It consisted of an 8 m long duct with a 0.5 x 0.25 m^2 cross section. A total of 450 tests with a H_2-air mixture were conducted. A higher blockage reduced the flame speed. Partial inerting was found to increase pressure wave duration and to decrease the amplitude [123].

With the **HDT** (Heated Detonation Tube) facility, the **Sandia National Laboratory** has constructed a 0.43 m inner diameter tube capable of operating at temperatures above 100 °C. Detonations were observed in the H_2 concentration range between 13.5 and 70 vol% at room temperature confirming the tendency towards lower figures in scaled-up experimental arrangements. At 100 °C, the lean detonability limit was down to 13 %. Detonation was even observed at a 30 % steam diluted mixture [15].

More large-scale tests were conducted at Sandia in the two channels, **FLAME** (Flame Acceleration Measurements and Experiments) [110] with the dimensions 30.5 * 1.8 * 2.4 m^3 and **MINI-FLAME**, reduced in size by a factor of 8, with one open end and movable top and including obstacles. The FLAME facility had an open end; its top could vary from fully closed to 50 % open with intermediate open spaces. A total of 28 tests were carried out in FLAME with variation of H_2 concentration (12 - 30 vol%), obstacle blockage (0 - 33 %), top venting. The observed lower detonability limit was at 15 vol% H_2 with and at 25 vol% without obstacles. DDT also occurred for 24.8 vol% H_2 and a 13 % open top. Top venting was found to have two counteracting effects: increase of burning rate due to turbulence dominant at low venting rates, flame speed reduction due to loss of gas for large venting rates [128].

Hydrogen-air detonation in a 3D geometry has been investigated in the **Russian facility RUT** (Rocket Shock Tube). The channel used has a variable cross section with a length of 69.5 m and a total volume of 480 m^3, representing presently the largest facility for such experiments in the world. Ignition was made by detonators. Test series conducted were with a premixed hydrogen-air atmosphere (1993), with dynamic H_2 injection in air (1994), and, relevant for nuclear containments, with a premixed hydrogen-air-steam atmosphere at elevated temperature level (100 °C). One of the key results in RUT was the observation of a 12.5 vol% H_2 lower detonability limit, demonstrating that larger-scale facilities seem to extend the detonability range of a flammable gas mixture [20, 79]. The Russian **UTR** facility, an up to 3 m long tube with 66 mm diameter was taken for systematic studies of the effect of different DDT locations on peak pressure and impulse using a $2H_2$-O_2-$1.75N_2$ gas mixture [20].

8.5.2.3. Modeling

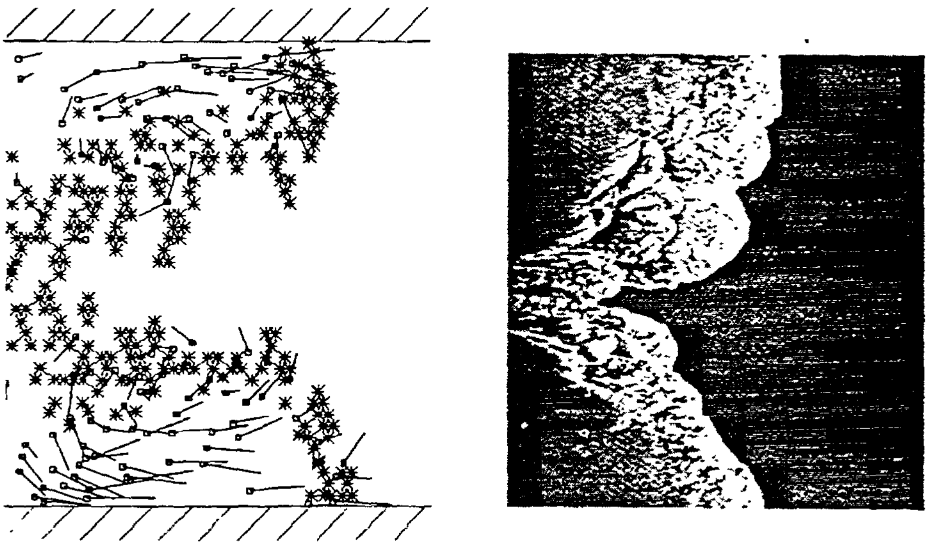
The classical theory of detonation is formulated in the **ZND model** (Zeldovich, Von Neumann, Döring) assuming that the propagation mechanism of a detonation is ignition by shock-induced adiabatic compression.

The **Chapman-Joguet model** [113] offers the opportunity to approximate the parameters of the complex dynamic process of a detonation such as detonation velocity, pressure, and transformed energy. For a stoichiometric hydrogen mixture, these parameters are: 1968 m/s, 1.6 MPa, and 2.82 MJ/kg, respectively.

The **TNT equivalent model** is often used as a simple method of estimating the mass of TNT per mass unit fuel gas whose detonation results in the same blast wave at the same distance. One kg of TNT translates into an energy of 4520 kJ. The equivalent for hydrogen is 2.22 kg TNT per Nm^3 gas. The weakness of this model is to ignore the pressure-time characteristic differences between a gas cloud and a detonative TNT explosion. In the short range, the model overestimates the pressure. Furthermore the model does not take into account the influence of turbulence and confinement [113].

A better approach is given by the numerical calculation models. Detonation codes have been developed at the Research Center Karlsruhe, **DET1D** and **D3D**, to determine the characteristic parameters within the reaction zone and outside in the unburnt mixture [20, 95, 100]. These models consider a homogeneous mixture of H_2, O_2, N_2, H_2O and are mainly applied to examine the load on a nuclear reactor containment. Validation was made against the above mentioned balloon tests of the Fraunhofer Institute and the Russian RUT experiments. Parameter calculations of 3D detonation have shown that the 3D structure is unimportant for the pressure load and that a relatively coarse grid provides sufficient accuracy [20].

The **Multi-Energy method** developed by TNO and coded in REAGAS [117] considers a vapor cloud explosion to be composed of a number of sub-explosions. Portions of the gas cloud which are confined up to a certain extent, are correlated with an initial


(a) Numerical

(b) Schlieren record

Fig. 8-12: “Tulip” flame in a closed channel, from [48]

pressure value. The strength of the explosion blast is expressed as a number between 1 and 10 representing categories of “insignificant” (= 1) to “detonative” (= 10). These cloud portions are responsible for the pressure buildup. The model simulates the feedback in the interaction between combustion and reaction products flow as a consequence of heat transfer and turbulence. Turbulent combustion is realized in a one-step process.

State-of-the-art are the **CFD models**, which are similar to the dispersion models, based on the Navier-Stokes equations for momentum conservation with a k-ϵ approach to deal with turbulence. They need, however, to be adapted to the characteristic spatial and temporal lengths for chemical reactions. Typical time steps for hydrodynamic flow calculation are in the order of 10^{-6} s and for the H_2-O_2 reaction mechanism 10^{-10} s occurring on the 10^{-4} m scale [20]. Most approaches are based on the assumption of incompressible flows or are restricted to slow deflagrations or to pure detonations. The assumption of incompressible gases in fast deflagrations with Mach numbers > 0.3, however, is not applicable since the pressure waves caused by the flame front are no longer negligible. Numerical simulation methods are applied to study turbulent combustion, flame acceleration processes, and (re-initiation of) detonations. Today's modeling and simulation show a good agreement with a variety of fast combustion phenomena [48].

The **DLR Stuttgart** has developed a 2D algorithm to model the flame folding in the early phase of the process after ignition and the acceleration process in obstacle areas which can lead to detonation. The method of approximate mapping functions is introduced to allow the simulation of more complex geometries. Also the detonation propagation and the quenching of a detonation and an eventual re-ignition are numerically simulated. The numerical analysis of flame acceleration is based on the random vortex modeling the turbulent eddy movement. What is not yet possible is the adequate modeling at the link between deflagration and detonation (DDT). The results obtained with the calculation model are in quite good agreement with the Schlieren pictures taken from experiments (see

Fig. 8-12) [66]. The results of CFD calculations were used to optimize the design of a detonation arrestor geometry [48].

A 2D calculation code has been developed at the **RWTH Aachen** to simulate fast turbulent flame propagation in hydrogen-air explosions in large-scale geometries. The trubulent flame front is considered as a reactive discontinuity. The model is based on the solution of the compressible Navier-Stokes equations with chemical source terms and buoyancy forces using a k-ϵ turbulence submodel. Validation work was made against the hydrogen combustion tests in the Russian RUT facility showing good agreement between experimental and calculational results for the flame propagation in the obstructed channel section, except for the fact that the DDT observed in the expanded part of RUT could not be reproduced. This is explained by a still insufficient grid resolution and/or inaccurate initial turbulence distribution in the simulation [79].

The 3D CFD computer code **FLACS** (Flame Acceleration Simulator) developed at the Christian-Michelson Institute in Bergen, Norway, is able to handle complete chemical processing plants down to the level of piping. The code treats spreading and combustion of flammable gases and determines concentration distributions and the impact on structures from explosions. Its main application is the prediction of explosion effects in offshore geometries [118].

The Harwell code **CFX** has been described already in the section on dispersion models. The chemical kinetics submodel specifies a chemical system of several species and reactions with an offered selection of different combustion models. Heat transfer is accounted for by convection, conduction, and radiation [1]. Examples calculated at the Research Center Jülich include Russian RUT tests and combustion experiments conducted in a Swiss railroad tunnel.

8.5.3. Pressure Impact and Damage Analysis

8.5.3.1. Phenomena

Combustion waves generate pressure waves. In a deflagration, the volume expansion of the burnt products reacts like a piston pushing the unburnt gas mixture aside. The pressure is in principle uniform and static. At the cloud perimeter, expansion waves are created which both run backwards into the cloud or follow the shock wave. Pressure and density decrease in the wave direction.

The **static pressure** loading in slow deflagration processes is conservatively described by the adiabatic, isochoric, complete combustion (AICC) pressure representing an upper bound in a closed volume. Analytical load functions approaching the AICC pressure in the long term are presented in [19]. Mitigation of the (theoretical) AICC pressure is given by incomplete combustion, venting, heat losses, and/or the addition of diluents. Therefore, the maximum static pressure will be generally lower than the AICC pressure. For combustion at atmospheric pressure, the AICC peak pressure is 0.8 MPa enough for many building structures to exceed their failure limits.

In contrast, a detonation generates a compression wave. Its pressure-time behavior is characterized by a distinct increase ("Von Neumann spike") and a subsequent exponential decay. Behind the shock wave, a pressure discontinuity is observed where the pressure drops below the atmospheric pressure evoked by the so-called "molecular collapse" due to the much denser oxidation product water upon hydrogen combustion. The peak overpressure increases with increasing flame speed. **Transient pressures** can be locally higher thean the AICC pressure. Inhomogeneities can result in local detonations decaying to deflagrations. When the detonation wave leaves the cloud, it will become an expanding, decaying wave. Overpressures drop fairly rapidly in a spherical expansion. In the far distance, deflagration and detonation show about the same pressure shape. An example from nature is the flash in a thunderstorm with a typical peak overpressure of 50 MPa.

In the intermediate stage of a fast deflagration, the peak overpressure is not so high, but the pressure drop is over a larger time period making the impulse, i.e., the integral of pressure over time, which is a measure for the load on a building structure, about the same in both cases [12].

Dynamic loads of fast transient pressures are imposed in the presence of inhomogeneously distributed combustion energy and are specific to the structure geometry. The response to an incident shock wave could be a movement of solid objects [60].

The essential parameters are peak overpressure and positive / negative phase of the specific impulse which are dependent on the liberated explosion energy which itself is dependent on pressure and volume of the container, on the type of gas, and on the distance. Deflagration overpressures for an unconfined hydrogen gas cloud are in the order of 10 kPa. As a rule, an overpressure of 2 kPa is considered safe although about 10 % of the window panes could be ruptured [108]. An 11 vol% H_2 mixture suffices to cause damage to human beings and buildings [46].

Gas explosions in a vessel which is connected by a small opening to another vessel produce peak pressures and pressure increase rates in the second vessel much higher than in a single vessel explosion, a phenomenon referred to as **pressure piling**. A pressure in excess of 3.5 MPa was measured in a two-chamber vessel for a stoichiometric hydrocarbon mixture, where 0.8 MPa were expected for a single vessel. From experiments with stoichiometric methane and propane-air mixtures, it could be concluded that in front of the propagating flame incl. the secondary chamber, a higher turbulence level is created which leads to an accelerated flame speed into the tube and the second chamber with a large overpressure. Unlike the length of the interconnecting tube, its diameter has a significant influence on the overpressure. An empirical model has been developed to predict explosion pressures in interconnected vessels up to a volume of a few hundred liters [106].

Series of tests concerning the simulation of heat fluxes and temperature loadings on equipment, pressures, and moisture conditions during multiple hydrogen burns were conducted in **CRTF** (Central Receiver Test Facility) and in **SCETCH** (Severe Combined Environment Test Chamber [60].

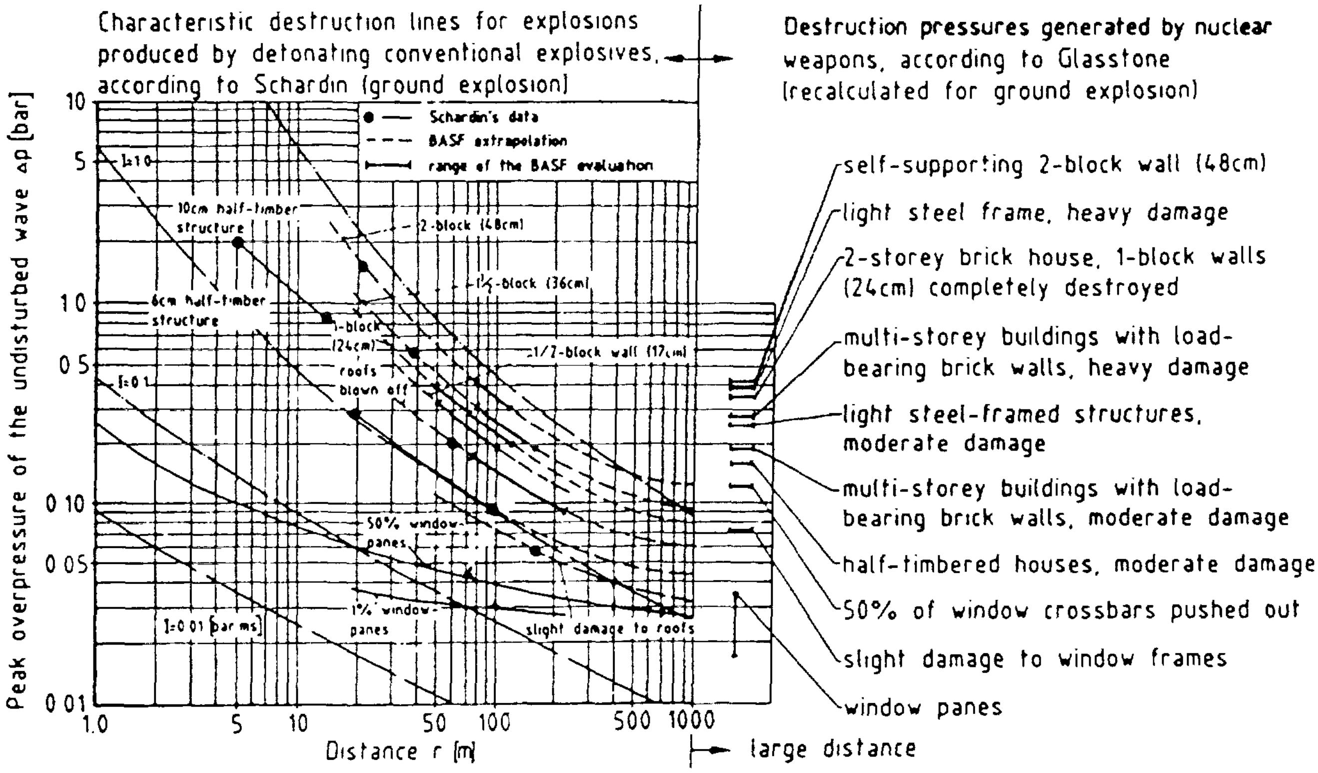


Fig. 8-13: Characteristic destruction lines for explosions produced by detonative conventional explosives according to Schardin (ground explosion), from [52]

8.5.3.2. Modeling

In the post-combustion modeling, the partial transformation of combustion energy into mechanical energy is treated reproducing the complicated structure of a shock wave and determining the pressure distribution on buildings. Pressure loads depend on the mutual orientation of the incoming wave and the loaded surface.

In general, it is possible in a first approximation to deduce the strength of the destroying pressure waves from the evaluation of damage. Charts with characteristic destruction lines give peak overpressures of a damage-equivalent pressure wave as a function of the distance (“**Scharding criteria**”) [52] as shown in Fig. 8-13. “Experimental” data were derived from explosives and nuclear weapon explosions (which both are detonations). The Scharding criteria, however, are only partially applicable to a deflagration. Here for a deflagration to be expected in an unconfined explosion, the relation between mass of flammable mixture and pressure wave is derived from an evaluation of damages that occurred in accidents in the past.

In a joint French/Italian benchmark study, measured pressure histories from detonation tube tests with stoichiometric H_2-air mixtures have been compared with the codes DET1D, D3D, and PLEXUS. The agreement in pressure amplitudes and speed was quite satisfactory [20].

Computer simulation techniques have been developed by SRI International in the USA for analyzing the explosion of a pressurized hydrogen tank and the response of structures and humans exposed to the resulting blast environment. The SRI equilibrium thermodynamic code **TIGER** is used to calculate explosion pressures and expansion characteristics of the explosion products. After obtaining the pressure contour plots, the **DYNA3D** model is taken to determine structural response. A simplification of the blast load damage analysis has led to the development of the **Pressure-Impulse (PI) methodology**. Its basis is the observation that for a broad range of structures subjected to simple pulse loads, the final damage state depends on peak pressure (P) and total impulse intensity (I) only. For a specific level of damage, the corresponding load varies between high pressures with short duration pulses and low pressures with long duration pulses. Focus is laid upon the development of a PC-based algorithm, AACA (Accident Analysis Computer Algorithm), for quick and easy evaluation of accident scenarios, which includes a continuously growing library of pressure-impulse load and damage curves that are based on either experimental data or computer simulations [99].

Combustion of unconfined hydrogen-air clouds have shown to result in simple deflagrations with typical overpressures no higher than 7 kPa, but high enough to knock down personnel [43] (see also Table 8-2).

8.5.4. Safety Distance

The **safety distance** as defined in Germany is the required distance between the location of a gas leakage and the object to be protected which takes account of the evolving flammable atmosphere as well as of the pressure and heat wave resulting from a possible ignition. The distance can be fixed according to physically defined criteria, e.g., the dose of thermal radiation or peak overpressure, to have reached a certain threshold value. A minimum safety distance is desirable for economic purposes. A basic prerequisite is knowledge of the source term which is dependent on leak size and thermodynamic conditions of the leaking material. A problem is given by non-quantifiable leakages, e.g., from cracks in welding seams. Minimum safety distances between LH_2 storage systems and inhabited buildings are shown in Fig. 8-14 as a function of LH_2 mass. The curves illustrate the variation in conservativism of different institutions that generate safety criteria. The safety distances are different for people and for less demanding equipment, e.g., adjacent storage tanks, working buildings, or distinguished with respect to fireballs, shrapnel, structural response or physiological effects (Fig. 8-15).

A formula for the safety distance is generally acknowledged to have the form

$$R = k * M^{1/3}$$

with R the distance in m and M the mass in kg. The formula is extended by damping parameters, if some protective measures, e.g., wall or earth coverage, are being applied. In Germany, k values have been fixed as listed in Table 8-3, depending on what object is to be protected. For the more relevant cases where the safety of people is of primary concern and material-related damage of secondary order, the k-factor of the above formula has been defined based on a pressure shock wave of 15 kPa for a human to be tolerable [35].

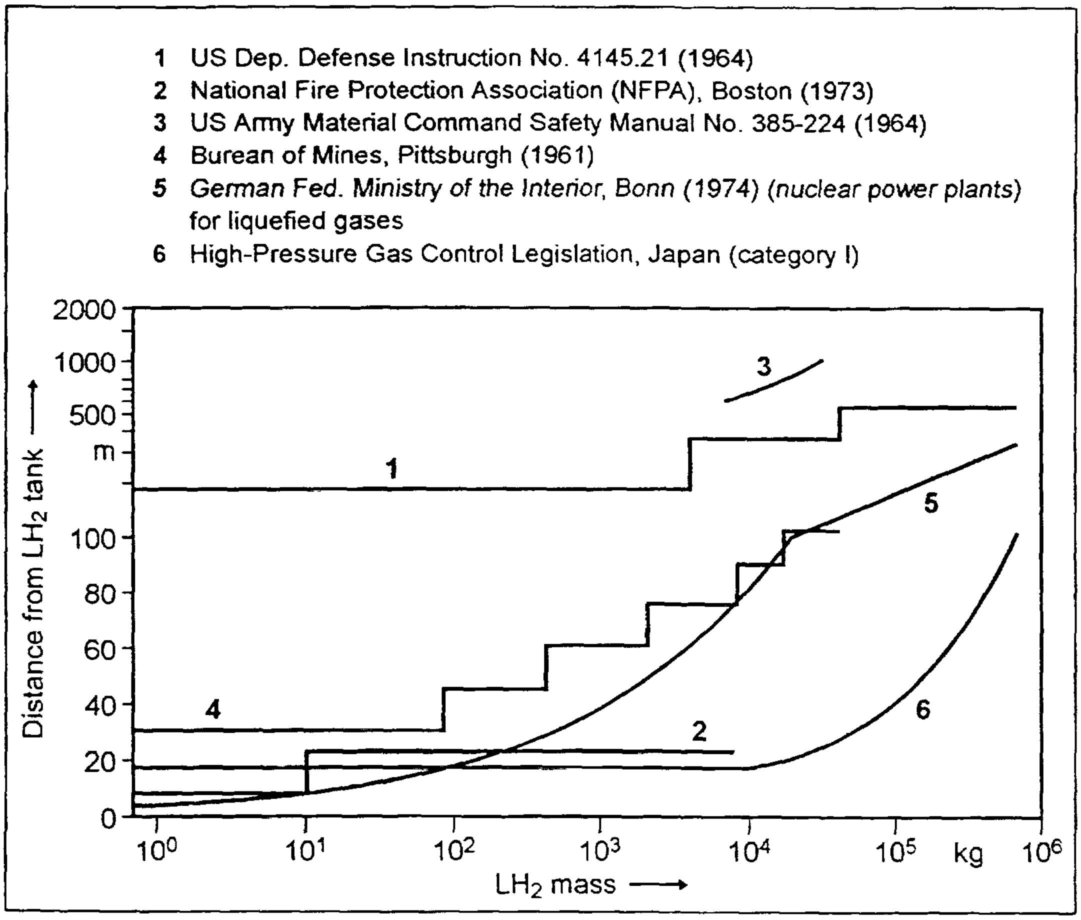


Fig. 8-14: Safety distances diagram (please note the scale change on the ordinate!) #1 and #3 from [40], #2 and #6 from [4], #4 from [130], #5 from [36]

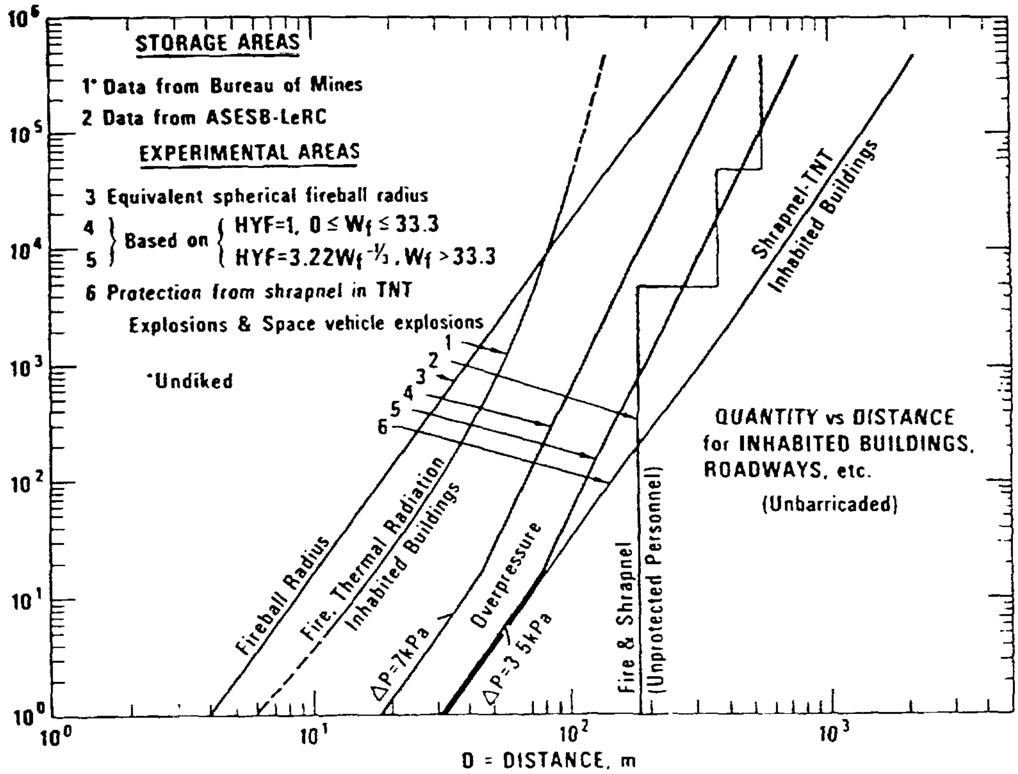


Fig. 8-15: Safety distances diagram, HYF = Hydrogen Yield Factor in g TNT/g H_2, W_f = Fuel Weight, from [58]

Table 8-3: K-factor of the safety distance formula according to official regulations in Germany, from [35]

Object	K-factor in safety distance formula $R = k * M^{1/3}$ [$m/kg^{1/3}$]
Working building	2.5 - 8
Neutral building	8 - 22
Residential building	22
No damage	200

The German regulation TRB 810 No. 25 proposes a safety distance of 120 m for > 300 tons of liquid gas storage tanks. The difficulty arising with this figure is the enormous consumption of land which turned out to be not practical in all cases. Therefore an additional rule was released saying that the safety distance could also be determined by considering the traveling distance of an accidentally released flammable (heavy) gas cloud [9]. The computational model **VDI 3783** is an acknowledged guideline in Germany to allow for a conservative estimation of such a safety distance [53]. Another rule says that the safety distance can be cut to half, if additional measures are applied, e.g., earth coverage, rupture discs, far-distance emergency shutdown, or warning systems to initiate deluge or spray devices [9].

The deployment of protection walls could have a counteracting influence on the accident consequences. The effects of obstruction and turbulence generation can usually lead to enhanced flame speed and pressure increase. Therefore gastight fences or walls should not be generally applied and should be restricted to special cases only [53].

The safety distance between LH_2 and LOX tanks at the Tanegashima Space Center was set to be 167 m according to the US Air Force Standard for blast wave pressure [83].

8.6. EXPERIENCE IN HANDLING HYDROGEN

Within the distribution system of pressurized hydrogen, cases of damage were observed in terms of leakage due to structural defects on the inside surface of the vessel, or of catastrophic failures as a consequence of frequent pressure fluctuations due to refilling procedures.

The first spectacular damage reported was as early as 1894 where at least 70 out of 1000 H_2 pressure bottles exploded. Little knowledge was available at that time on the embrittlement phenomena. Further failures occurred in NASA pressurized hydrogen storage tanks at 35 MPa occurred as well as in hydrogen tube trailers in Germany in the 1960s and 1970s.

The **Hindenburg** accident in 1937 at Lakehurst is very familiar to the public if the talk is on hydrogen. In fact, the 220 tons Zeppelin LZ-129 Hindenburg, the largest airship ever built filled with 200,000 Nm^3 of hydrogen in 16 gas cells, did not explode, it tragically caught fire when docking. At that time practice was to allow hydrogen to be stored in highly combustible materials [33, 82]. This accident has put a preliminary end to the development of airships as a means of transportation.

The accident of the **Challenger Space Shuttle** evoked a wide range of deeply felt public responses. The catastrophe was said by NASA officials to be caused by the failure of an O-ring rubber seal in one of the two solid rocket boosters due to erosion by hot gases. Later a steady flame developed which was directed towards the surface of the LH_2 and LOX containing external tank (ET). The flame eventually breached the tank resulting in an explosive burn of the hydrogen and oxygen [6]. The above explosion root theory has been questioned recently. According to [27, 28], so-called "phantom" fires resulting from undetected small cryogenic hydrogen leakages ($<$ 1.4 kg/s) from the ET and their early (i.e., at low altitude) ignition by the anomalous plume from the rocket booster have caused the quick deterioration of the ET structural elements. The analysis indicated that LH_2 leaks occur in all missions meaning that the shuttle may explode again, if the leaking LH_2 were ignited again by unforeseeable ignition sources.

The spectacular accident in **Hanau** in 1991 demonstrated the consequences to be expected from the catastrophic failure of a tank with pressurized hydrogen. The 100 m^3 cylindrical hydrogen pressure vessel with 2.8 m diameter, 16 m total height, and 22 mm wall thickness was exposed to a cyclic inner pressure between 1.5 (empty) and 4.5 (full) MPa. The explosion was caused by a fatigue rupture near a longitudinal welding seam [13]. Clarification of the causes resulted in a significant progress in terms of safety [103].

The **evaluation of reports and statistics of accidents with hydrogen** in industrial facilities in the period 1965 - 1977 exhibit that [132] (see Tables 8-4, 8-5, and 8-6)

- accidents were mainly caused by leakage or insufficient purging or venting,
- in 38 % of the accidents, the evolution of a flammable hydrogen-air mixture remained undetected,
- The average damage per accident was independent of the state of the hydrogen,
- most releases finally lead to ignition,
- in partially obstructed areas most cases result in an explosion caused by a fast deflagration or even a detonation,
- spontaneous ignition is also possible by jets escaping from a burst disk or a safety valve.

From a total of 409 accidents investigated, 78.5 % were related to gaseous hydrogen, 20.8 % to liquid hydrogen, and 0.7 % to hydrides.

Another study evaluating 96 mishaps in **NASA** hydrogen operations has come to the following conclusions [49]:

- Valve malfunctions or leaks caused more than 20 % of the mishaps.
- Leaks were mainly due to personnel not following prescribed procedures.
- Ignition occurred in 60 % of the atmosphere releases and in all cases of release into enclosed areas.
- Improper system purging was the cause in 25 % of the mishaps.

Table 8-4: Statistics of hydrogen accident reports between 1965 and 1977 on primary causes of combustible mixtures, from [132]

	Number of incidents	**Percentage**
External leak	71	17.4
Internal leak	30	7.3
Inadequate purging	26	6.4
Inadequate ventilation	29	7.1
Vessel or pipe rupture	69	16.9
Venting incident	54	13.2
Exposure to fire	4	1.0
Collision or puncture	5	1.2
Excessive vacuum	3	0.7
Intentional operation	33	8.1
Electrolysis malfunction	18	4.4
Battery charging	5	1.2
Operator negligence	35	8.6
Other	7	1.7
Σ	409⁽¹⁾	

(1) The above table is as given in [132]. Although not explained, the total sum of incidents in the table is 389, not 409 as indicated. Therefore the overall percentage does not wind up to 100 %.

Table 8-5: Consequences of accidents involving hydrogen in industrial applications, from [132]

	Number of cases	**Casualties**	**Percentage**
Fire	117	16	28.6
Exlosion	211	90	51.6
Pressure rupture	25	1	6.1
Unignited release	39	5	9.5
Other	17	11	4.2
Σ	409	123	100

Table 8-6: NASA statistics on accidents with release of hydrogen, from [85]

	Number	**Percentage**
Accidents with H_2 release	80	83
Release to atmosphere	66(1)	69
Release to containment	20(1)	21
Ignition of release to atmosphere	41(2)	62
Ignition of release to enclosure	20	21

(1) In 6 mishaps, hydrogen was released to both atmosphere and enclosure
(2) In 25 mishaps, hydrogen released to atmosphere did not ignite

- Some cases were due to air entrainment into LH_2 systems.

Hydrogen leaks typically originate from valves, flanges, diaphragms, gaskets, seals, fittings.

Considering hydrogen accidents during transportation, in 71 % of the inadvertant hydrogen release cases recorded, no ignition was observed, a trend that is also confirmed by NASA experience [104].

A couple of hydrogen accidents were associated with the chlorine production by chloralkali electrolysis, which are included in Table 8-4 under "Electrolysis malfunction". Fire or explosion occurred when for some reason, for example a reversal of cell polarity, the hydrogen entered the chlorine processing equipment downstream of the electrolysis cells [104].

A recent inquiry of accidents involving hydrogen by **Mitsubishi Heavy Industries** within the WE-NET project has revealed a number of accidents in the order of a few cases per year. Most accidents were caused by electric sparks. The maximum amount of hydrogen released was 4000 Nm^3 (Hanau accident), and 1300 Nm^3 referring to accidents in Japan [29].

Although hydrogen has a reputation as a particularly dangerous fuel, the overall statement was made that despite the fact that some metals can become brittle to hydrogen or hydrogen compounds, the technology of handling hydrogen as a high-pressure gas or as a liquid is successful and safe [43]. Explanations of this good record are possibly the facts of conservative assumptions for the design stress and of a scheduled retesting of the vessels. Further measures for accident prevention are the appropriate choice of materials, coatings, adsorption layers, the deployment of stainless steel liners in composite vessels and piping, and proper welding procedures. Although the excellent safety record should not be extrapolated to a large-scale use in a hydrogen economy, since experience so far is based mainly on the existence of well-trained personnel and extreme concern about system reliability. If handled properly, hydrogen will be a safe alternative to fossil fuels. The hazards of hydrogen are generally recognized to be different than those of petroleum fuels, but not necessarily greater [69].

8.7. SAFETY AND RISK ASSESSMENT FOR HYDROGEN CONTAINING SYSTEMS

8.7.1. General Methodology

Technical systems which contain material representing a hazard potential must be treated under controled, safe conditions. A respective design of the facility and its operational modes is checked by different kinds of safety considerations. In addition to the consequences of normal operation, the system behavior under accident conditions has to be considered in terms of sufficient measures for controling accidents. Assumptions are being made based upon experience which has been achieved in the course of the technical development and which has resulted in a system of laws, regulations, rules, guidelines, and recommendations, e.g., for the design of components, for quality assurance, for fire protection and also for accident prevention measures.

Not only is the selection of accident scenarios made on the basis of experiences, but also on the basis of intuition. It comprises both the reliability of the technical systems and the consequences of uncontroled accidents. Problems arise if conceivable accident scenarios start to leave the realm of direct experience and if the possible damage is getting high.

It was typically in the nuclear technology that systematic prognosis procedures for the event and the consequences of uncontroled accidents were applied. They have been significantly improved over the last 25 years and are now an essential part of the valuation process of nuclear power plants in the form of **probabilistic safety and risk assessments** (PSA and PRA).

The methodology of PSA is in principle a combination of **event tree** and **fault tree** analyses. The target of the analysis decisively determines the selection and the definition of modes in which the technical system is at the end of an event sequence. These modes comprise both the safe ones resulting from successful safety measures and also those unwanted ones characterized by a certain release of hazardous materials. A PSA is extended to a PRA, if the consequences of the different system modes are determined and linked with the event frequencies of those modes.

The single steps of a PSA are:

(i) the identification of **hazardous potentials** by searching for sensitive areas and processes which contain toxic or flammable materials;

(ii) the identification of **accident-initiating events**, e.g., the failure of components. Starting from such an event, the (non-) availability of safety installations and measures are questioned in an event tree resulting in a ramification, where every branch represents an event sequence. Sequences with similar consequences are summarized in categories.

For the initiating event, frequencies per operation year are determined, as a rule, by evaluation of statistics, or, if no experience is available, by justified assessments. The probability of non-availablities of safety installations or measures is determined by fault trees or immediately by values derived from operational experiences. The total frequencies of the event sequences are then calculated by multiplication of the frequency of the initiating event with those of the non-availabilities.

8.7.2. Examples

The spectrum of hydrogen quantities that might be released into the atmosphere varies from small amounts in a vehicle tank to the large capacity of a stationary storage tank. Table 8-7 lists typical LH_2 quantities together with the corresponding volumes of a (stoichiometric) mixture gas cloud and the (theoretical) TNT equivalent.

8.7.2.1. Liquid Hydrogen River Transportation

Ship transportation is considered an economic method to carry large amounts of hazardous cargo. In case of an accident, however, it turns into a major safety problem with possibly disastrous consequences for the environment. The coarse procedure for a risk assessment focusing on the inland navigation of a large-scale LH_2 cargo on a 15,000 m^3 capacity barge carrier has been demonstrated in [17, 72].

Table 8-7: Typical liquid hydrogen quantities and hazardous potential, from [120]

	Liquid hydrogen contents [m^3]	**Hydrogen-air mixture [m^3]**	**TNT equivalent [t TNT]**
Passenger car tank	0.15	433	0.28
Bus tank	0.6	1,730	1.13
Tank truck load	40	115,400	75.2
Railway transport tank	100	288,300	188
Aircraft tank (Airbus)	240	692,000	451
Ship barge	3800	10,950,000	7,140
Ship barge (WE-NET)	33,000	95,100,000	62,000
Stationary storage tank	130,000	375,000,000	244,400

The initiating event of an inadvertent LH_2 release from a ship could be of internal or external nature. Internal initiating events are caused by technical failure (tank rupture) or by human error. External events comprise maritime events, i.e., a collision with any obstruction (ground, other ship), and general hazards such as natural hazards or sabotage. A collision may result in a sinking of the barge carrier by which the barges could be set free and float on the water under no control possibly risking a subsequent damage.

For the period 1983 - 1989, the number of ship movements on the Elbe river amounted to about 65,000 per year with an approximate 30 % fraction ($\approx$ 19,500) assumed to be large enough to have the potential of significantly damaging the carrier ship. The total maritime accident probability is then approximated by summing up the single probabilities for different river sections characterized by geometry, traffic volume, and the nearby population density. Multiplication with the number of trips of the barge carrier per year finally yields the frequency of an initiating event. It was found to be largest for grounding/stranding, followed by an encountering collision, a crossing collision, and the extremely unlikely event of technical vessel failure.

Conceivable accident scenarios identified result in consequences which can be grouped in different release categories:

- continuous release of gaseous hydrogen through safety valve, e.g., due to loss of insulation or failure of safety valve in open position
- quasi-continuous or instantaneous release of a small fraction of the tank contents, e.g., due to pipe rupture
- continuous release of a large amount of the tank contents, e.g., due to a leak in the vessel
- instantaneous release of the complete tank contents, due to catastrophic vessel failure

The spill of a small amount of LH_2 is more likely to occur than the release of the complete vessel contents (leak-before-failure construction rule). The conceivable ignition of the flammable gas cloud reveals the actual hazardous potential for the environment. A delayed ignition represents the worst case with a certain chance for deflagration or even detonation, connected with the formation of a blast wave and heat radiation. Corresponding relations connect received radiation dose or pressure impact with the probability for a fatality resulting in certain individual risk levels.

Qualitative conclusions can be drawn:

- The highest societal risk is found on-shore for the population of Hamburg city, the highest individual risk is found on water for the ship crew
- Collision with an encountering ship causes the highest total risk.
- Collision with a crossing ship causes the highest risk for the on-shore population

The quantitative evaluation given in [72] is deemed preliminary, because many assumptions were based upon either conservative estimates where no better data could be acquired or too simple modeling methods which do not realistically account for the specific behavior of gaseous or liquid hydrogen. Nevertheless, the study has given a feeling for the specific aspect of a liquid hydrogen river transportation and demonstrated a viable procedure for a probabilistic risk assessment.

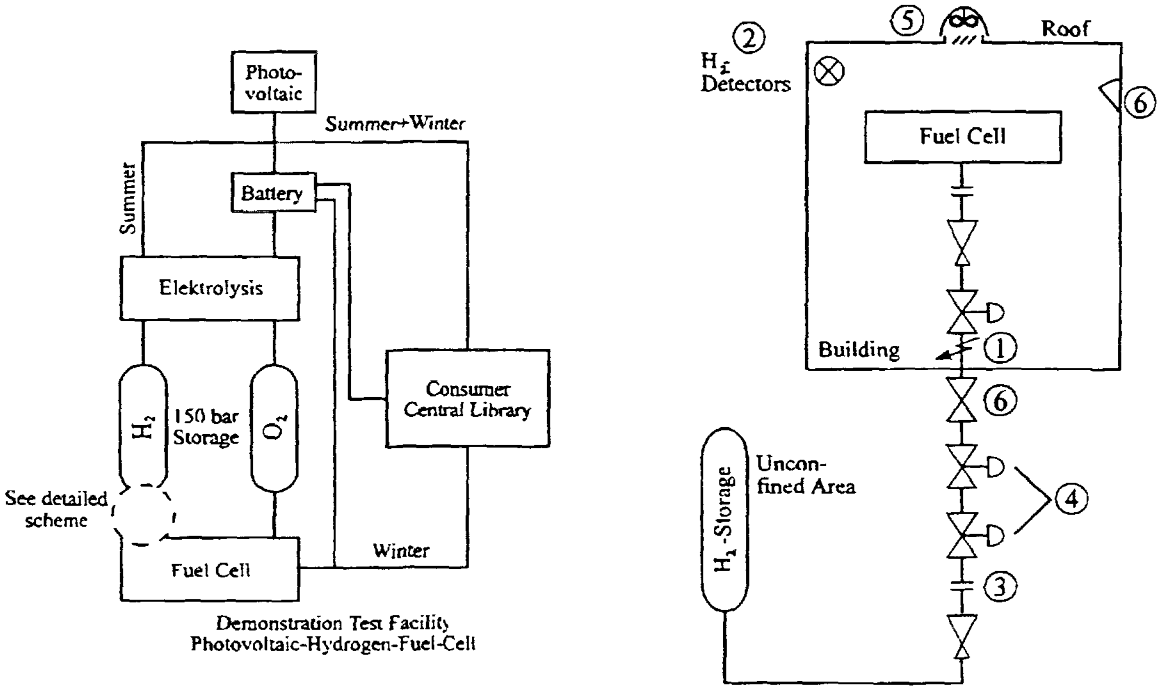
8.7.2.2. PHOEBUS

The prognostic procedures for a risk assessment as have been used at the Research Center Jülich for safety analyses for nuclear power plants, have been applied to the Photovoltaic Hydrogen Fuel Cell Demonstration Facility, PHOEBUS [18].

8.7.2.2.1. Safety Concept

The **safety concept** of PHOEBUS is composed of several active and passive measures which are basically directed against hydrogen release inside the building (Fig. 8-16):

- **hydrogen gas warning system**
  with a total of 8 detectors immediately above the sensitive components and, in addition, at the ceiling of the building. Alarm is given, if the H_2 concentration reaches a level of 0.4 vol%. At an 0.8 vol% level, the gas lines between building and outdoors storage are automatically closed off as well as gas and energy provision of the respective component. Also air ventilators in the ceiling are started. At the same time, alarm is given to the security service of the Research Center Jülich.



Demonstration Test Facility
Photovoltaic-Hydrogen-Fuel-Cell

Detail: Connection between
H_2 - storage and fuel cell

1: position of leak assumed
2: H_2 control
3: flow control

4: automatic shutoff
5: automatic venting
6: emergency manual shutoff

Fig. 8-16: Schematic of the safety concept in the PHOEBUS facility, from [17]

- **gas throughput and pressure supervision system**
  to disconnect gas lines leading into the building, if limits are exceeded.
- **stainless steel piping**
  with a maximum pressure of 0.7 MPa indoors. High pressure pipes up to 15 MPa (H_2) and 7 MPa (O_2), respectively, are operated only outdoors.

8.7.2.2.2. Conceivable Accident Scenarios

The final state of an accident sequence with a hydrogen release comprises the formation of a flammable gas mixture either inside H_2 carrying components or inside the building or outside in the open atmosphere.

- **Flammable H_2-O_2 mixtures in components**
  are conceivable in the electrolyzer and the fuel cell. Component-internal leakages, e.g., after a diaphragm fracture, however, do lead to relatively small amounts of gas mixtures. Only the failure of the protective measures, i.e., an erroneous continuation of operation, allows a larger amount of the mixture to be routed into the oxygen storage vessel where, however, there is no ignition source.
- **Flammable H_2-air mixtures inside the building**
  is possible after leakage of H_2 carrying components. Three categories of leaks have been defined:
  1. small leaks with a leakage rate less than 10 Nm^3/h, which is the lower throughput supervision limit,
  2. medium leaks with leakage rates up to 120 Nm^3/h, which is the maximum escape rate from the high-pressure storage with still working high-pressure reduction system, and
  3. large leaks with a maximum leakage rate of 600 Nm^3/h, if also the pressure reduction system fails

  In the case of small leaks, the natural air exchange in the hall is sufficient to prevent flammable mixtures. For medium leaks, flammable mixtures on a large scale can be precluded, however, not on a smaller scale, e.g., in the vicinity of the leak. Large leaks which are not actively ruled can lead to large flammable gas mixtures.
- **Flammable H_2-air mixtures in the open atmosphere**
  is given upon the catastrophic failure of the outdoor high-pressure storage vessel. The sudden release of 3000 Nm^3 of hydrogen represents in principle the greatest hazard potential, whereas leaking hydrogen does not cause a serious problem due to its strong buoyancy.

8.7.2.2.3. Frequencies of Initiating Events

Because of the prototype character of the PHOEBUS facility, hardly any direct operation experience could be utilized. Therefore generic data, also assessments, have been used implying a relatively large uncertainty range.

Operational experience has been taken to derive reliability parameters for the various components and safety systems in order to determine the frequencies for possible accident

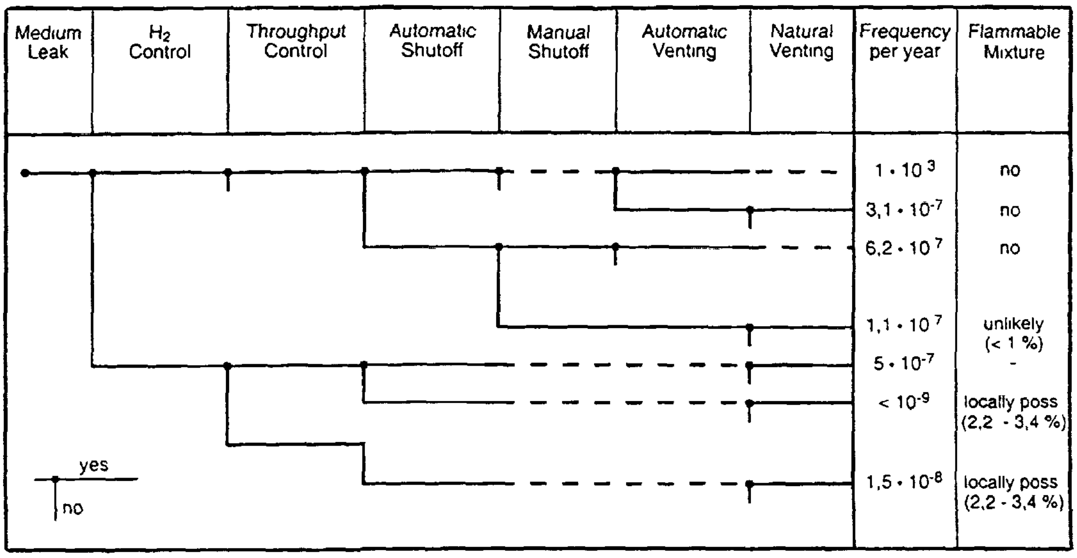


Fig. 8-17: Event tree for medium-sized H_2 leak in the PHOEBUS plant, from [17]

Table 8-8: Classification into groups of hydrogen release events in the open atmosphere, from [17]

Event group		Reacting H_2 mass [kg]	Frequency [10^{-5}/yr]
1	Rupture of one vessel energy conversion 1 %	0.2	2.3
2	Rupture of one vessel energy conversion 25 %	1.5 - 4.0	1.8
3	Vessel rupture with subsequent emptying of a battery of nine vessels energy conversion 25 %	15 - 35	0.2
4	Vessel rupture with subsequent emptying of both batteries of 18 vessels energy conversion 25 %	65	0.001

sequences. As an example, the event tree for a medium-sized hydrogen leak inside the experimental hall is presented in Fig. 8-17 showing that for two of the final states reached, locally flammable mixtures cannot be excluded. The respective frequencies, however, are extremely small.

For accidents outside the hall, no active measures are planned. Ramification of the event trees is developed by subsequent failures or conditions for the extent and the effect of ignited gas clouds. The analysis has shown that hydrogen release from the storage vessels with subsequent explosion dominates the still very small environmental risk. All sequences have been grouped into four categories with a similar explosive potential, as listed in Table 8-8.

The individual risk expressing the probability for a fatality as a consequence of an event was determined to be 10^{-5}/yr restricted to the immediate neighborhood of the building. The unusually large volume of the building is of advantage in case of small leak accidents. The H_2 storage in 18 interconnected bottles increases the leak frequency, however, reduces the consequences [18].

Peculiarities of the PHOEBUS plant such as type, size, venting concept, storage concept do not allow the results of this study to be transferable to future photovoltaic systems [18].

8.7.2.3. Liquefaction Plant

Some results from a safety analysis for the French liquefaction plant near Lille with an LH_2 production rate of 10 t/d have been reported showing that in a design basis accident represented by an LH_2 pipe rupture, the maximum escape rate is 1.9 kg/s. Assuming a wind velocity of 2 m/s, a hydrogen-air mixture cloud will evolve with a predicted maximum extension of approx. 200 m within the flammability limits. A safety distance of 238 m around the LH_2 facilities for the plant was considered sufficient to protect offsite residential areas [5].

8.8. ENVIRONMENTAL ISSUES

In principle, a significant reduction in the energy related impact on the environment is being achieved, if non-fossil hydrogen be substituting conventional fuels. There are no emissions of carbon oxides, hydrocarbons, dust or ash, heavy metals, lead compounds, or SO_2. Some environmental risks are left concerning, e.g., gas emission during combustion or the establishment of the infrastructure.

8.8.1. Water Vapor

Water vapor is the most climate-relevant atmospheric gas contributing a portion of 65 % to the overall greenhouse effect. The (anthropogenic) effect of the tremendous amounts of water vapor expected to be released into the atmosphere within a large-scale hydrogen technology is disputed among climate researchers. Critical voices estimate the liberation of latent heat upon condensation to contribute much stronger to global warming than carbon dioxide, so that any further water vapor sources should be avoided [63].

Others expect water vapor emissions in a hydrogen energy economy (assumption is that half of the present energy supply is covered by hydrogen) to be reducible down to the respective level presently given by the fossil and nuclear economy which is a 0.005 % share of the total atmospheric water cycle. In order to reach the above reduction factor, hydrogen losses need to be decreased from currently estimated 10 % over the whole chain to 2 - 3 %. Today's world energy economy emits around $20*10^{12}$ kg of water per year [134].

The primary product of hydrogen combustion is water which is ejected as water vapor and may form **condensation trails** (= contrails) which are ice clouds. Comparing the greenhouse effects of kerosene and hydrogen at varying cruising levels for mid-latitude atmospheric conditions, it can be stated that for mid-latitude atmospheric conditions below an altitude of 10 km, i.e., in the troposphere, the contribution of water vapor is negligible, the greenhouse effect is almost zero. Above 10 km, the emitted water vapor behaves like a greenhouse gas exceeding the effect of kerosene at altitudes > 12 km (cruising altitudes of today's aircraft, however, usually are not higher than 12 km [92]. On the other hand, water has a residence time in the order of one year for typical cruising levels which is short compared with CO_2 with 100 years residence time in the atmosphere independent of height.

Water vapor is a concern for the lower stratosphere. Its contents is $1.3*10^{12}$ kg of H_2O with an average lifetime of one year. The contribution by today's high-altitude air transportation which is 20 % of the total aviation, is $0.04*10^{12}$ kg of H_2O per year. A complete conversion to H_2-fueled aircraft would result in an emission of as much as $500*10^{12}$ kg of H_2O per year. Therefore it is mandatory to lower the cruising height below the tropopause [134].

The formation of contrails is dependent on ambient temperature and humidity. It prevails in the warm sectors of low-pressure areas. An LH_2 aircraft needs to fly at a 1 km lower cruising level to account for the same amount of evolved contrails as a kerosene-driven aircraft. The formation of contrails is avoided at lower cruising altitudes, however, at the expense of higher fuel consumption. The greenhouse effect of contrails is still unclear [92]. NASA scientists have found indications for a warming of the air below contrails, in particular in areas with high aircraft traffic, e.g., New York [51].

Within the CEC funded project **MOZAIC** ("Measurements of Ozone by Airbus In-Service Aircraft"), continuous measurements of water vapor (and ozone) in the upper troposphere are being made during commercial airbus flights. At 40° - 60° N latitude over the North Atlantic, contents of water vapor were found to range between 0.07 and 0.12 g/kg depending on the seasonal large-scale circulation and jet stream pattern [107].

8.8.2. Nitrogen Oxides

The only pollutants of concern in combustion processes of hydrogen-air mixtures are **nitrogen oxides** (NOX). Emissions of NOX which are generated as a function of temperature, pressure, and time, however, are small compared with conventional fuels and even negligible at temperatures < 200 °C. The generation and emission of NOX peaks at excess air ratios of about 1, but is steeply reduced by applying a lean H_2, low-temperature burning process (see Fig. 8-18) at high combustion rates and using a homogeneous fuel-air mixture to suppress local hot spots. In experimental tests with hydrogen combustors in aircraft engines starting in 1991 within the Euro-Quebec project, a reduction of the NOX level by 70 - 80 % compared with kerosene combustors was achieved (see Fig. 8-19) [78, 92]. Although connected with a power output loss of up to 30 %, the specific emissions per power unit are still smaller. In car engines, the NOX reduction achieved in practice is 30 to 60 % [124].

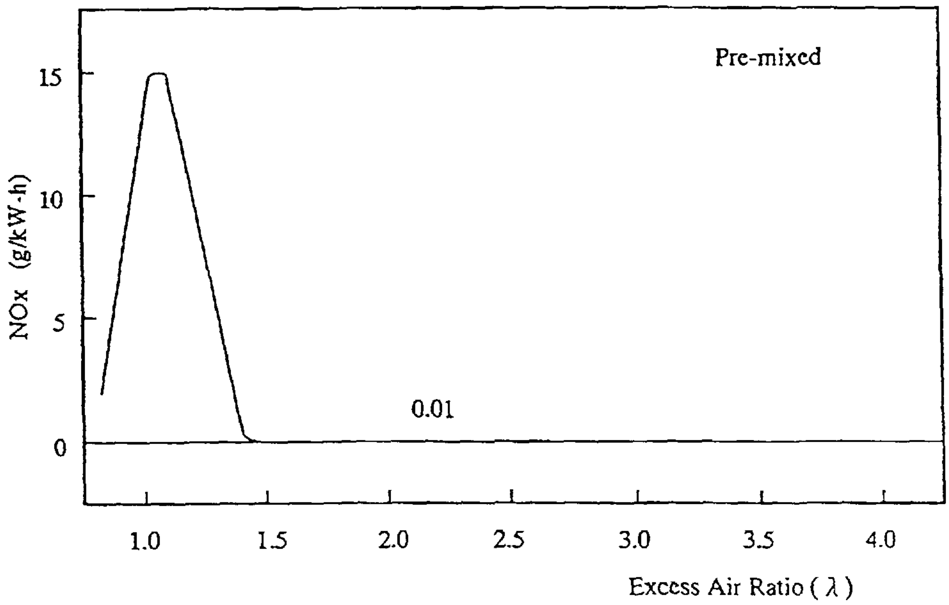


Fig. 8-18: NOX emissions in H_2 combustion processes in a rotary engine, from [78]

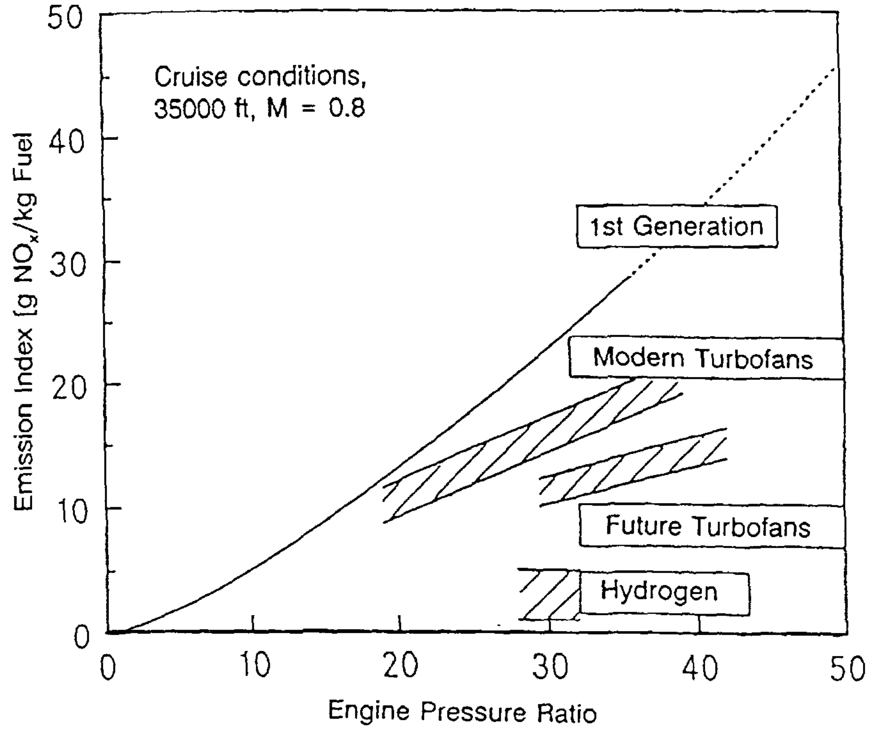


Fig. 8-19: NOX emissions for different combustion technologies, from [92]

Experimental data with hydrogen powered ICE cars have shown that if optimized to low NOX levels by using ultra-lean mixtures, the former US standard of 0.6 g/km could be met without catalyst [69].

8.8.3. Hydrogen

The present concentration of hydrogen in the atmosphere is 510 ppb which translates into a total mass of approx. 200 million tons, and the annual increase rate is 3 ppb. The average lifetime is two years before chemically bound or lost into space. The H_2 emissions from the industrial use are with < 1 million t/yr small compared with other natural and anthropogenic sources. In case of the hydrogen economy based on a 80 % CO_2 reduction scenario, H_2 emissions are predicted to be 1.1 - 1,4 million t/yr [108].

Hydrogen, and to a much higher extent, methane take part in a whole variety of chemical reactions in the atmosphere responsible for ozone depletion [108].

The ecological consequences of an accidental (liquid) hydrogen release are harmless due to its untoxic character compared with an uncontroled spill of fossil fuels [108].

8.8.4. Others

Emissions of other pollutants, hydrocarbons or CO, from hydrogen combustion in ICE become significant, if the engine burns excess lubricating oil. These emissions can be minimized by regular inspection and maintenance [69].

8.8.5. Modeling

An analytical NOX chemical kinetic model has been developed by the DLR to investigate the influence of various parameters on the formation of pollutants. It has been coupled with an eddy breakup model for the combustion process [133].

The NASA Goddard Space Flight Center has developed a "Residual Circulation Model" which uses emission and representative flight profile data to estimate the amount of stratospheric ozone depletion. Applied to the respective design data for the hypersonic X-30 engine based on a total of 150 flights within five years, the maximum local ozone depletion was predicted to be 0.006 % [127].

A respective study for the German SÄNGER spacecraft design estimates that in the lower and medium stratosphere accumulation of water vapor and trace gases would occur due to low vertical air exchange enhancing the greenhouse effect. It is only the planned low number of flights (24/yr) that makes this disturbance of the stratosphere negligible [108].

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Chapter 9

PAST AND PRESENT ACTIVITIES ON HYDROGEN IN THE WORLD

A whole variety of hydrogen energy applications of a demonstration character have been started or are projected worldwide encompassing autonomous or partial power systems on different scales as well as vehicle research projects. A selection is presented in the following sections.

9.1. GENERAL OVERVIEW

National hydrogen associations have been founded in many countries over the last two decades: Argentina, Canada, China, France, Germany, Italy, Japan, Norway, Russian Federation, South Korea, Sweden, Switzerland, USA. Their principal goals are to foster the introduction of hydrogen as an energy carrier, to stimulate information exchange among interested parties (experts, companies, scientists), and to activate public interest in this field.

It appears impossible to describe or even mention all on-going international efforts in the field of the application of hydrogen as an energy carrier. In the following, just examples are given which indicate the directions of present research.

The **IEA** is an autonomous body within the framework of the OECD with the basic aims to promote international cooperation for the development of a stable world energy market and to support information exchange. An IEA hydrogen program was initiated in 1977 which has dealt so far with all aspects of hydrogen technology. The current tasks (1995 - 1998) chosen for joint international research are [93]:

- photoproduction of hydrogen (as a long-term application)
- hydrogen storage in metal hydrides (as a medium-term application)
- integrated systems (as a short-term application)

A general overview of R&D activities on hydrogen in the different **European** countries is given in Table 9-1. European fuel cell research is sponsored within the different EC programs ("Altenes", "Joule", "Brite-Euram", "Thermie"). It is said, however, to be still 3 - 4 years behind respective activities in Japan and the USA [10]. According to the general strategy, focus is laid upon low-temperature fuel cell systems in the power range of 200 to 300 kW. The aim is the establishment of a grid of fuel cell power plants where the hydrogen fuel is centrally produced and then distributed via pipelines [32]. A part of the European activities is explained in more detail in the following sections.

In **Germany**, R&D activities sponsored by the Federal Government were the advanced alkaline water electrolysis, and the testing of components of a future hydrogen economy in projects such as HYSOLAR (see section 9.2.5.). However, the significant CO_2 reduction potential is presently not seen in the use of hydrogen as a vehicular fuel, but in a reduction of conventional fuel consumption. Funding is now concentrating on fuel cells while support of other hydrogen activities has significantly decreased since its high in 1990/91. As of February 1998, nine 200 kW(e) PAFC power plants are being operated in Germany. The

Table 9-1: European hydrogen research and development activities, from [51]

COUNTRIES	B	CH	D	DK	E	F	GB	I	IRL	N	NL	S	SF
RESEARCH AREAS													
PRODUCTION													
Advanced Electrolyis	#	#	#		#			#		#		#	
H_2 from PV		#	#		#			#					#
H_2 from Wind			#	#			#						
H_2 from Biomass			#						#				
H_2 via Photoprocess		#	#							#		#	
H_2 from Natural Gas										#			
H_2 from Concentr Solar		#			#								
STORAGE AND TRANSPORT													
Metal Hydrides		#		#	#					#		#	
Compressed Hydrogen			#			#							
Liquid Hydrogen			#			#	#			#			
Liquid Organic Hydrides		#							#				
Cryo Adsorption						#							
Seasonal Storage of H_2		#											
UTILIZATION SYSTEMS													
Intern. Combust Engine	#	#	#					#					
ICE Vehicles	#	#	#					#					
FC Vehicles/Boats	#		#				#	#					
H_2 Combust. Turbine											#		
H_2 Sensors												#	#
Embrittlement			#	#									
Solar H_2 House		#	#									#	
Integrated RE H_2 System	#		#		#			#					#
FUEL CELLS													
AFC	#		#		#							#	
PEMFC		#	#	#	#		#	#			#	#	
PAFC					#			#				#	
MCFC			#	#			#	#		#	#		
SOFC		#	#	#			#	#		#			
DMFC			#										

fuel cell lines currently under research and development are the SOFC and the MCFC in the high temperature range as well as the low-temperature PEFC [94]. The market for fuel cell power plants in Germany is predicted to be 300 - 800 MW per year at the turn of the century [66]. Projects currently sponsored by the German utilities are concentrating on renewable energies solar, wind, hydro, biomass. Hydrogen is merely present with just one project out of 265 current projects [53].

General goal of the present National Hydrogen Program in the **USA** as expressed in the "Hydrogen Future Act" of 1995, is to fund R&D activities in hydrogen production, storage, and use to ensure that the technologies are available for industrial considerations. The program also uses methods to evaluate and compare hydrogen technologies and integral systems for industrial, residential, transportation and utility applications. DOE hydrogen-related funding in the 5-years period of 1992 - 1996 included [91]:

- coal gasification, improved reforming processes, separation of hydrogen from gas stream impurities
- high-efficiency, low-cost stationary fuel cell systems operating with coal and coal / natural gas fuel for electricity and heat cogeneration
- technologies for broad use of hydrogen as an energy carrier and fuel
- thermochemical gasification of biomass, anaerobic digestion of solid wastes
- understanding of chemical, photochemical, photosynthesis, and photobiological reactions
- PEM fuel cells for vehicular power sources

The Ontario Ministry of Energy in **Canada** uses its EnerSearch program to promote the development of innovative energy technologies [52]. One project involves simulation and experimental work on the direct coupling of an electrolyzer with a photovoltaic power source and its installation and testing as a long-term field experiment in sunny and less sunny areas. Another project has the goal to use scrap aluminum where in the presence of an alkali hydrogen is generated. Experimental work resulted in the operation of a benchmark-scale prototype with a capacity of 5 l hydrogen per minute. A fuel cell project serves the purpose to demonstrate that an SPFC could be used to convert waste hydrogen from a chloralkali plant to electric power for re-use in the plant.

9.2. LARGE-SCALE HYDROGEN ENERGY SYSTEMS

Energy conversion always takes place in a system with many components, where the weakest one controls the whole performance. Therefore it is necessary to also consider complete autonomous systems. Other smaller-scale projects, many based on solar energy as the primary energy carrier, have been or are still being conducted to test parts of a future hydrogen energy economy and numerous more are still in the design stage.

9.2.1. WE-NET Project

Japan has shown a tremendous economic growth in the post-war period and is now one of the world's leading industrial countries. It has mainly resulted from private industry's rigorous efforts to invest in R&D exceeding those levels found in the USA and European countries. In 1971, the concept of "Industry-Ecology" was initiated to study the global environment.

In 1974, short after the first energy crisis, the Agency of Industrial Science and Technology (AIST) in MITI[21] of the Japanese government has initiated the **Sunshine project** to develop new energy technologies and four years later the **Moonlight project** to focus on energy conversion technologies. Both projects promoted energy R&D in close

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[21] MITI - Ministry of International Trade and Industry

cooperation between industry, government, and academic organizations. Due to the strong interrelations between new energies, energy conversion, and environmental technology, the **New Sunshine project** was started in 1993 to contribute to an international system based on environmentally friendly energy technologies with the goals of [46]

1. innovative technology development
   to implement the Global Warming Prevention Action,
2. international large-scale collaborative research
   to implement the Earth Regeneration Program "New Earth 21",
3. collaborative R&D on appropriate technologies
   to assist neighboring developing countries to promote technologies that suit the partner countries.

One important project pursued under item 2. is the **"International Clean Energy Network Using Hydrogen Conversion (WE-NET)"**, directly managed by NEDO[22] and currently representing the most ambitious hydrogen energy research program in the world. Its ultimate goal is the establishment of a worldwide energy system based on hydrogen. WE-NET is projected to run over 28 years, 1993 - 2020, in three distinct phases. Phase I (1993 - 1998) deals with surveys on key technologies and elemental research and system studies under 9 subtasks [76]:

Subtask 1: Investigation and Study for Evaluation and R&D Review
coordination of subtasks, evaluation of results
Subtask 2: Investigation and Study for Promoting International Cooperation
international information exchange
Subtask 3: Conceptual Design of the Total System
including power generation, hydrogen production, storage & transportation, safety
Subtask 4: Development of Hydrogen Production Technologies
electrolysis focusing on the alkaline water and the solid polymer electrolyte membrane water electrolysis
Subtask 5: Development of Hydrogen Transportation and Storage Technology
liquid hydrogen, liquefaction plant, tank ship, large-scale storage
Subtask 6: Development of Cryogenic Materials technology
behavior of structural materials at LH_2 temperatures
Subtask 7: Feasibility Study on Utilization of Hydrogen Energy
use of hydrogen in cryogenic power generation, motor power generation, automobile technology, fuel cells
Subtask 8: Development of a Hydrogen Combustion Turbine
evaluation of optimal design, combustion control, turbine components, design and construction of pilot plant
Subtask 9: Study on Innovative and Leading Technology

In Phase 2 (1999 - 2005), prototype systems in the order of 50 MW will be developed, while in Phase 3, the technology is to be demonstrated in sub and full systems.

According to the concept of the WE-NET system, primary energy sources considered are the renewables hydro, wind, solar, to be used for electrolytic hydrogen production.

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[22] NEDO (New Energy and Industrial Technology Development Organization) established in 1980 is an implementing agency of the Japanese government to promote the development of technologies related to new energy sources.

Table 9-2: Targets of Phase I and final targets in the WE-NET project, from [47]

Items Items	Phase I target	Final target
1. Production (SPEWE)	Electrode area: 6,000 cm^2 Current density: 1-3 A/cm^2 Efficiency: 80-90 %	Electrode area: 30,000 cm^2 Current density: 3 A/cm^2 Efficiency: > 90 %
2.1 Transportation & storage	Development of elemental technology for large-scale liquefaction plant, LH_2 tanker, LH_2 storage	Establishment of technology required for 300 t/d liquefaction plant, 20,000 m^3 tanker, 50,000 m^3 storage tank
2.2 Metal hydride alloys for distributed storage and transportation	Development of hydrogen absorbing alloys for - automobiles - compact stationary storage tank - large-scale storage system	Development of alloys for commercial use
3. Cryogenic Materials	Establishment of methods for materials evaluation	Development of structural materials for cryogenic tanker and storage plants
4. Utilization	Investigation and review of utilization technologies	Establishment of technologies for hydrogen-fueled automobiles, households, etc.
5. Hydrogen combustion turbine	Development of basic technology for design and construction of pilot plant	Pilot system on the basis of a 500 MW level commercial system inlet temperature of turbine: 1500 - 1700 °C Efficiency: 60 %
6. Ultrahigh temperature materials	Selection of candidates of promising materials, establishment of methods for materials evaluation	Development of ultrahigh temperature materials (2000 °C level)

Nuclear is excluded as an option in the first phase. Transmission system of choice for long-distance sea-borne transportation is LH_2 (Fig. 9-1), which is advantageous because of Japan's geographic location, and in second place liquid hydrides including the methanol variant. On the demand side, hydrogen is utilized as a fuel in the transportation sector, in fuel cell plants, in combustion turbines, in households as well as chemical feedstock.

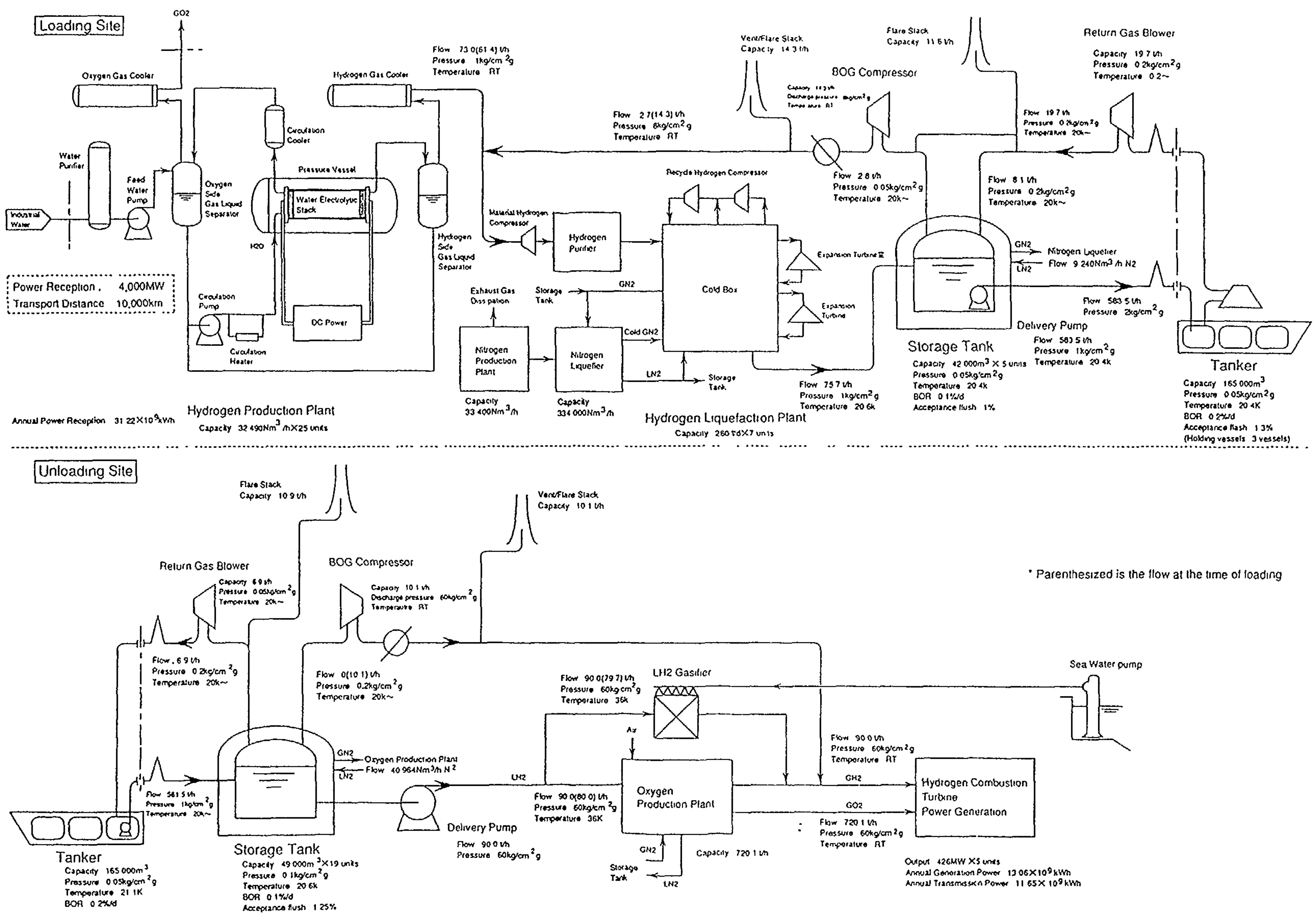

Fig. 9-1: Diagram of system flow (liquid hydrogen) in the International Clean Energy Network Using Hydrogen Conversion, from [77]

Table 9-2 summarizes the targets of Phase I (1993 - 1998) and the final targets (1999 - 2020). Investigation and research in the field of safety is the establishment of a comprehensive "System Safety Design" for WE-NET including a concept of safety measures for prevention of accidental LH_2 release or the mitigation of accident consequences. This will be done by an analysis of the risk of either WE-NET subsystem and by review and systematization of existing safety standards [34]. The main targets are an efficient 500 MW hydrogen combustion turbine, efficient membrane electrolysis including SPEWE, PEFC power plants in the 0.2 - 5 MW range, large-scale (300 t/d) H_2 liquefaction with a target efficiency of 40 %, LH_2 tank ship, large-scale LH_2 storage, metal hydrides, materials for low and high temperatures [33].

The Japanese cities Toyohashi (population 350,000) and Soga (population 170,000) have been selected as model cities in WE-NET to investigate the feasibility of a hydrogen supply system in a hydrogen-oriented society [78].

9.2.2. Euro-Quebec Hydro-Hydrogen Pilot Project

A study for the concept of a clean energy system based on hydrogen as a transportable energy medium was presented in 1987 as a result of the cooperation of more than 20 companies and institutions [39]. This study was the first definition phase of a larger project, the "Hydrogen Pilot Project – Canada", HPPC. The follow-on feasibility study as the phase II completed in 1990 contained the details of what was then called the "**Euro-Quebec Hydro-Hydrogen Pilot Project (EQHHPP)**" [4]. The idea of this project is to take 100 MW electricity from hydropower in Canada for hydrogen production via electrolysis which would be a technically feasible and representative size. The gaseous hydrogen is then liquefied (which requires another 30 MW of electricity input) and shipped in 3000 m^3 cylindrical barges on a barge carrier ship to Hamburg, Germany, where the barges are brought on shore for further distribution of the hydrogen to a variety of consumers (Fig. 9-2). The annual transportation of 14,600 tons of LH_2 corresponds to an estimated equivalent power output of 74 MW(e) plus some 7 MW "cold" energy recovery as shown in the energy balance in Fig. 9-3. The prime goal of the Euro-Quebec project is the demonstration of the possibilities of safe transport, storage, and distribution in a future hydrogen economy [4].

The EQHHPP has been designed as a "local" hydrogen energy economy with demonstrating character. One of the driving forces is to provide the basis for utilization of still unexploited hydro power (or any other low-cost non-fossil surplus primary energy) which are far away from the centers of high energy consumption. A very important near-term aspect of the Euro-Quebec project is the environmental concern about local pollution in cities.

Originally three options for the seaborne transport of hydrogen were investigated: (i) ammonia, (ii) methylcyclohexane (MCH)/ toluene, and (iii) liquid hydrogen. The LH_2 option was finally deemed the best alternative. The maritime transportation of the liquid hydrogen is done in barge-mounted mobile tanks (see chapter 5) which can also be used for on-shore storage. This concept avoids additional transfers which are always connected with vaporization losses. For completeness, the idea of LH_2 aircraft transportation was also studied, but soon considered an option with an unacceptably high energy requirement (see section 6.2.2.4.) [39].

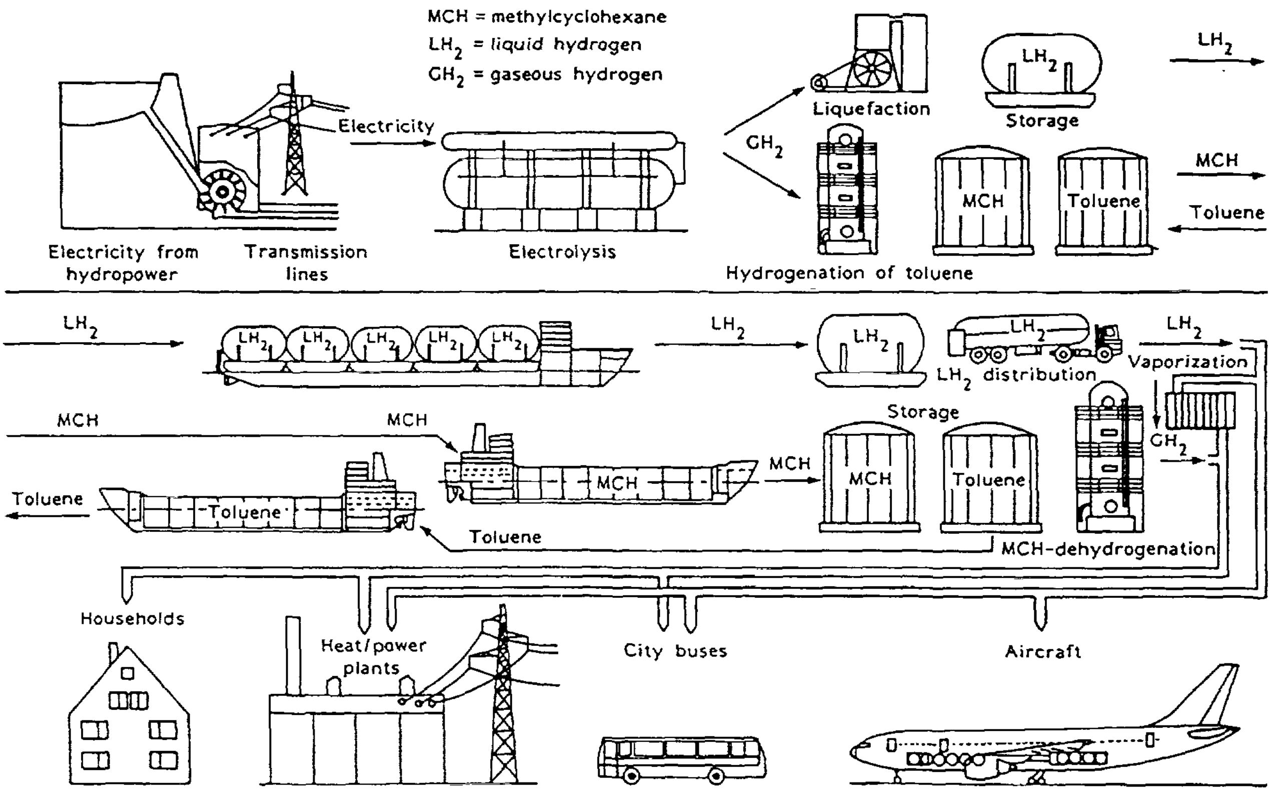

Fig. 9-2: Concept of the Euro-Quebec Hydro-Hydrogen Pilot Project, from [49]

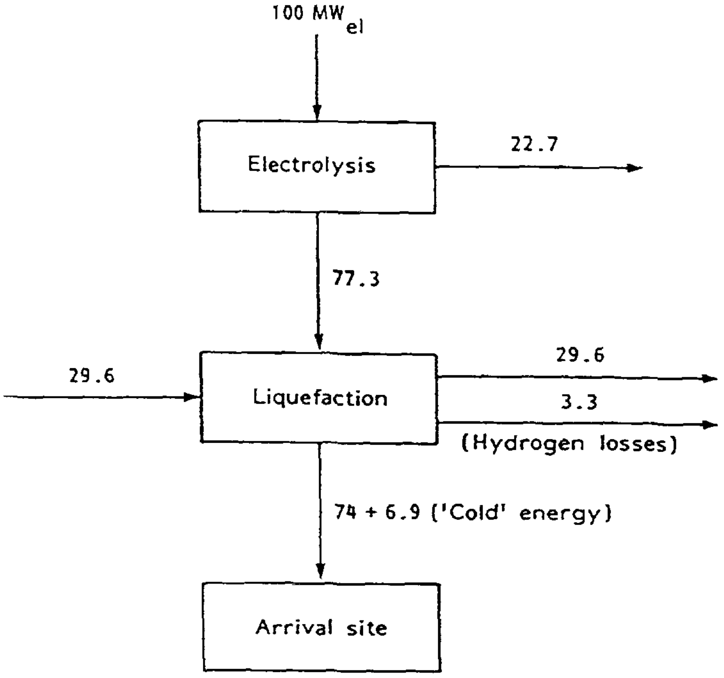

Fig. 9-3: Energy balance for the Euro-Quebec Hydro-Hydrogen project (in MW(e)), from [49]

The LH_2 terminal proposed comprises the port for loading and unloading operations of the barge-mounted tanks, a lifting platform to transfer the tanks after being floated out of the barge carrier ship to the shore, and the on-shore storage and distribution devices. The further distribution of the LH_2 is done in semi-trailers by tank trucks. Two reference LH_2 consumers were selected: a 5 MW(e) hydrogen fuel cell plant with an 80 m^3 stationary LH_2 vessel and an urban transit bus transportation system including a hydrogen filling station with an estimated consumption of 65 m^3 of LH_2 per day [104].

Other possibilities of hydrogen consumption investigated are, e.g., the operation of an LH_2 driven aircraft, heating power plant with gas turbine, the continuous supply of a steam power plant via a 1 km pipeline, and the leftover hydrogen to blend with natural gas to feed into the local gas distribution grid.

All safety considerations performed in the framework of the EQHHPP have shown that the anticipated hydrogen systems do not pose an unacceptable risk on people and the environment. This safety analysis resulted also in a compilation of all existing regulations to be followed in Germany if the project were existing [92].

With the start of Phase III (1992 - 1998) of the EQHHPP, pre-approval activities and a hydrogen demonstration program have been started. Its most important features are:

- city bus projects with internal combustion engine or fuel cell and LH_2 storage in Belgium, Canada, Germany, and Italy;
- fuel cell powered passenger boat in Italy;
- development, manufacture, testing and commercialization of advanced super-insulated transport containers for LH_2;
- safety tests for LH_2 vehicle tank and model tank for maritime transportation;
- emission testing on sectors of LH_2 adapted combustors for Airbus jet engines;
- utilization of hydrogen in the direct reduction of iron ore in a plasma arc furnace in Ireland;
- power plants in CHP mode with piston engine or PAFC;
- study on rules and regulations, safety, and acceptability of hydrogen;
- study on social economic effects of vehicle and aircraft emissions compared with emissions from hydrogen propulsion for the city areas of Los Angeles, London, and Munich.

Fact is that many single components exist already, so that no decisive technological breakthrough is necessary. However, further research efforts are required for the development of new components and their modification to enhanced application to hydrogen and for the introduction and demonstration of pilot plants [104].

9.2.3. NHEG Project

Norway is gaining its energy exclusively from hydro power and was able up to now to to refrain from using oil, gas, coal, or nuclear power. Large-scale production of electrolytic hydrogen is made since 1949 with a peak capacity peaking at 100,000 Nm^3/h (which corresponds to 450 MW of hydro power). It has been discontinued, however, since it could not compete with the hydrogen produced from hydrocarbons.

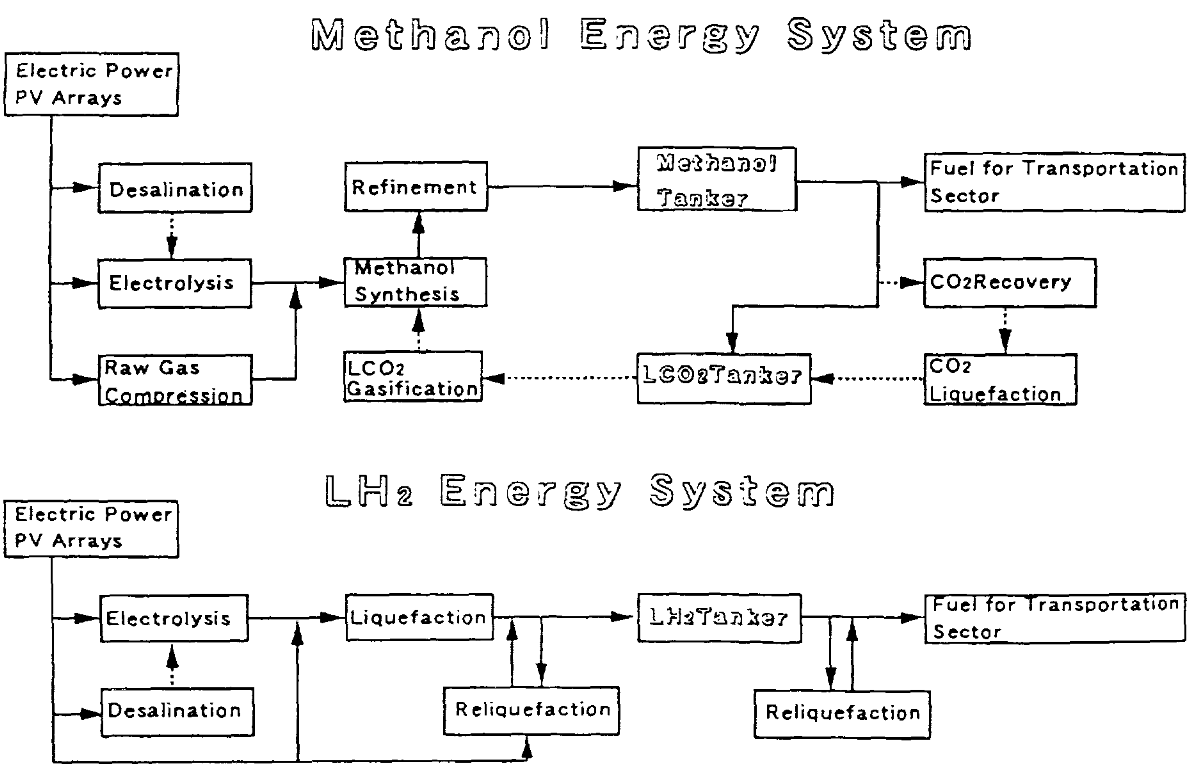

Fig. 9-4: Methanol and LH_2 solar energy system, from [56]

Very similar to the Euro-Quebec project, a joint German/Norwegian study, "**Norwegian Hydro Energy in Germany**", NHEG, has been conducted to investigate the technical and economic feasibility of a demonstration project on the generation of liquid hydrogen by Norwegian hydro power and its subsequent transportation and distribution to various cities in Germany. Similar to the Euro-Quebec project, the reference case is based on a power of 100 MW; two more cases investigated are related to 20 MW total power. Maritime transportation is considered to be done in ships with a capacity of 5700 m^3 of LH_2 per loading and 44 trips per year. The overall efficiency is calculated to be 54 %. The cost of the imported LH_2 has been estimated to be approximately the same as if the electricity were transmitted and used in Germany for H_2 liquefaction [3].

9.2.4. PORSHE Project

A solar hydrogen energy system has been proposed within the PORSHE ("Plan of Ocean Raft System for Hydrogen Economy") to substitute oil by hydrogen as a fuel in the Japanese transportation sector for the purpose of saving oil resources and reducing CO_2 emission. The concept is based on photovoltaic cells with a total surface area of 12,000 km^2 deployed on 12,000 overseas ocean rafts located in the South Pacific Ocean for electrolytic hydrogen production. Liquefied hydrogen at an amount of 25 million t/yr (which is $\approx$ 1700 times the LH_2 amount in the Euro-Quebec project) is then shipped in 270 tank ships with a capacity of 125,000 m^3 each to 20 import bases (capacity 120,000 m^3 each) for further distribution to 22 domestic bases (capacity 5,000 m^3 each) and LH_2 stations (capacity 10 m^3 each), respectively [55]. Also the option of an overseas methanol production has been investigated (Fig. 9-4) which is superior to LH_2 in terms of storage and transportation. The

CO_2 required is shipped in liquid form from the site of consumption back to the production site. The LCO_2 and the methanol ships are designed to have a tank capacity of 130,900 m^3 and 314,000 m^3, respectively [56].

9.2.5. HYSOLAR Project

In a joint German-Saudi research, development, and demonstration project, **HYSOLAR**, starting in 1986, solar hydrogen production and its utilization has been investigated. Three photovoltaic test facilities with powers of 350, 10, and 2 kW, respectively, were used for the production of electrolytic hydrogen. The 350 kW plant installed near Riyadh, Saudi Arabia, included the first prototype of an advanced type alkaline solarized pressurized electrolyzer, which was not designed for continuous H_2 production. Its operation time was two years. The produced H_2 was stored as a compressed gas up to a bottling pressure of 15 MPa. Two 10 kW(e) and one 2 kW(e) electrolyzers were deployed in Stuttgart for the purpose of systems development for advanced hydrogen equipment. Another 2 kW(e) electrolyzer in Jeddah served as an experimental setup. Hydrogen consumption units were realized in two different types of a catalytic burner for heating purposes, in several PAFC stacks with powers varying between 100 and 1000 W, and in three internal combustion engines with 6, 8, and 13.5 kW power [82]. System studies with the energetical and economic analysis of decentralized hydrogen systems were conducted with the time step simulation model INSEL-NETZ. The HYSOLAR project could demonstrate that solar hydrogen production is feasible with a reasonable efficiency.

9.2.6. Solar-Wasserstoff-Bayern Project

A solar hydrogen demonstration plant project on an industrial scale has been implemented since 1985 by the **Solar-Wasserstoff-Bayern GmbH** (SWB) in Neunburg vorm Wald, Germany, to test important subsystems of a future hydrogen energy economy on a long-term basis. Diverse components of novel or advanced design have been occasionally added to replace older ones or to complete the existing facility. Fig. 9-5 outlines a diagram with all subsystems of SWB:

- Eight photovoltaic fields with a total of 4200 m^2 of modules with a total peak power of 360 kW provide electricity from solar power.
- Two advanced types of electrolyzers of the 100 kW category have been tested for generation of hydrogen demonstrating an 80 % efficiency and a capacity of 80,000 m^3 per year. However, their further development was abandoned, since no market chances were seen. Now the testing of a pressure-type electrolyzer which works under 3.2 MPa pressure and at 150 °C has started avoiding the necessity of compressors for storage. Two H_2 storage tanks hold a volume of 5000 Nm^3, another oxygen tank has a capacity of 500 Nm^3.
- Two different fuel cell power plants have been tested. The alkaline type demonstrated good performance during its trouble-free operation, but due to repeated repair work, it was later stopped. Since 1993, a PAFC power plant of 79 kW(e) is in operation which also allows cogeneration of 180 °C heat. It is fueled with either hydrogen or natural gas to be converted to hydrogen in an upstream steam reformer. A 10 kW PEM fuel cell is operating a standard electric fork lift truck

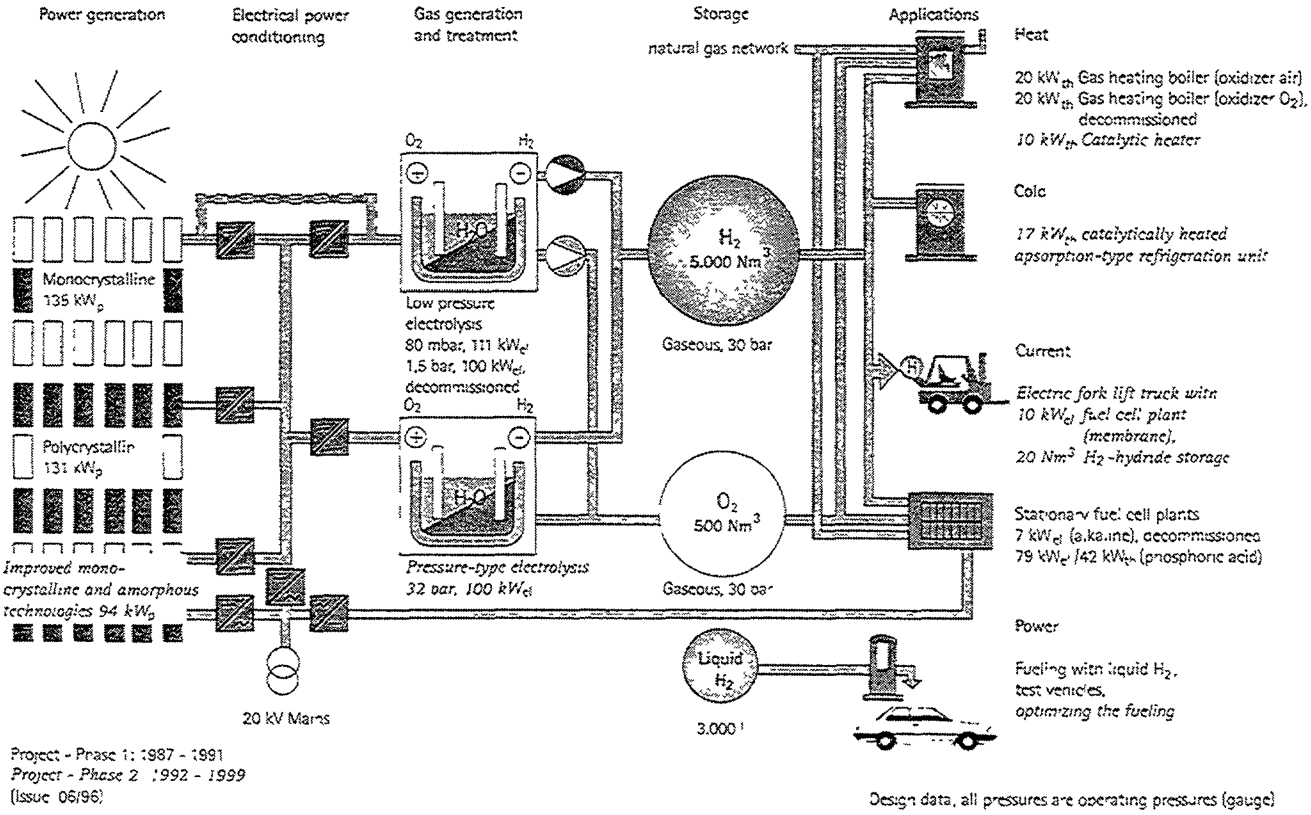

Fig. 9-5: Schematic of SWB subsystems, from [97]

with a 300 kg Ti-based hydride battery with a capacity of 23 Nm^3 of H_2 sufficient for 8 hours of operation.

- The calorific-value gas-fired heating boiler of 20 kW(th) is a standard unit modified to also allow for hydrogen fuel and mixtures of both H_2 and CH_4.
- A 10 kW(th) catalytic burner to be fueled with either natural gas or its mixture with up to 50 % hydrogen has been developed at the Research Center Jülich. The fuel gas is routed through a porous ceramic body, whose surfaces are covered with Pd and Pt as catalysts. NOX emissions were measured to be less than 20 mg/kWh.
- Tests were conducted in cooperation with BMW with an LH_2 refueling station for passenger cars. Refueling procedure with 130 l of LH_2 started with 1 hour duration and a 30 % loss: it has improved in the meantime to about 5 min duration and a loss of less than 5 %.

Despite the fact that not all of the systems installed worked satisfactorily, the overall impression is positive and the results are promising [98]. The SWB project is scheduled to be terminated by 1999.

9.2.7. PHOEBUS Project

A **Photovoltaic Hydrogen Fuel Cell Demonstration facility, PHOEBUS,** has been erected and is currently operated at the Research Center Jülich encompassing all components for a decentralized autonomous, all-year electricity supply from solar energy using hydrogen as the energy storage medium. Four process steps are being investigated:

1. Conversion of solar energy into electricity
2. Decomposition of water into hydrogen and oxygen by electrolysis
3. Storage of hydrogen and oxygen under high pressure
4. Electricity production in a fuel cell

The characteristic components of PHOEBUS are:

- Photovoltaic modules
  with 312 m^2 effective surface area.
- Pressure electrolyzer
  consisting of 21 cells in bipolar arrangement, using a 30 % KOH electrolyte and operating at 80 °C temperature and 0.7 MPa pressure. The hydrogen production rate is 6.5 Nm^3/h, the oxygen production rate is 3.25 Nm^3/h.
- Fuel cell
  on alkaline basis (AFC) with an electric power of 6.5 kW composed of 60 cells and operating at 80 °C temperature and 0.23 MPa pressure. The hydrogen consumption is 3.5 Nm^3/h. It is projected for 1998 to move over to two 5 kW PEM-FC stacks.
- Short-term storage
  in the form of a lead battery with a capacity of 300 kWh.
- Long-term storage
  in the form of pressure vessels. For hydrogen, 18 interconnected high-pressure bottles with a total volume of 27 m^3 and a capacity of 3000 Nm^3 of hydrogen at 15 MPa are used. The oxygen is stored in one pressure vessel with 20 m^3 volume and a capacity of 1500 Nm^3 of oxygen at 7 MPa.
- Energy management system.

The operation of the plant serves the purpose of a grid-independent electricity supply of the central library of the research center. Surplus solar energy in the summer season is stored as hydrogen gas and is re-converted into electricity in the wintertime. The daily balance of demand and supply is realized with the short-term storage battery with allows an operation for three days. The plant can be operated without personnel [27]. All plant components (electrolyzer, gas purification system, fuel cell, etc.) except the storage pressure tanks are located within a large experimental building (total volume = 20,000 m^3) on a 7 m x 18 m area with a distance to the roof of 17 m.

Fig. 9-6 presents the plant structure containing the figures from a simulated 1995 scenario. Based on an insolation of 282 MWh/yr, the PHOEBUS solar cells generate 29.0 MWh/yr and 26.3 MWh/yr D.C. electricity, respectively. Two thirds are being directly consumed or short-term stored in batteries. The remaining third enters the path with the production of hydrogen in an electrolyzer to be later consumed in a fuel cell. Conversion losses allow an energy output no higher than 3.2 MWh/yr. The overall energy consumption is assumed to be 17.4 MWh/yr corresponding to an efficiency of 59 % [27].

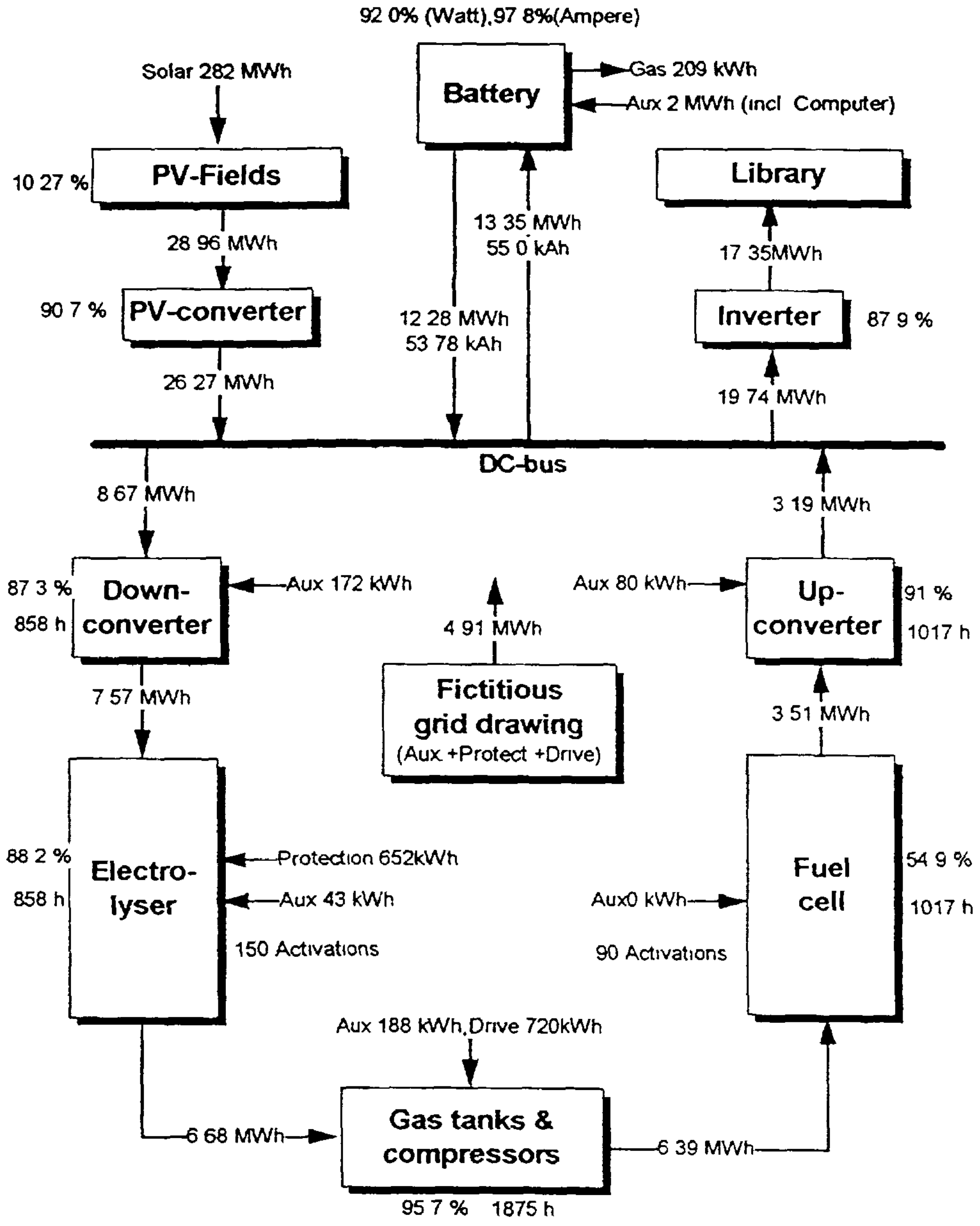

Fig. 9-6: Simulated 1995 scenario for PHOEBUS system, from [27]

In an advanced plant concept for the low-power range, PHOEBUS 2, high-pressure electrolysis is employed to avoid the compression step. Other new components are an air-driven PEM fuel cell and optionally metal hydride as an alternative storage concept. The goal is a simplification of the whole system.

A system extension is proposed in the PHOEBUS 3 design by including the combined heat and power concept and wind power as an additional renewable energy source. The CHP mode is represented by a heat pump to provide thermal energy drawn from the environment. A simulation of PHOEBUS 3 has shown a more regular annual energy production, an increase in efficiency, and a reduction of both energy losses and costs.

9.2.8. HYPASSE Project

Key goal of the Swiss-German **Hydrogen-Powered Applications Using Seasonal and Weekly Surplus Electricity, HYPASSE,** project starting in 1991 as a part of the European EUREKA program is the establishment of a seasonal energy storage system based on organic hydrides. Surplus electricity in weak-load periods including nuclear off-peak (estimated 3200 h/yr, 500 kW(e) electrolyzer) is used for hydrogen production via electrolysis which is stored as a compressed gas or chemically as MCH to be later used in a public bus transportation system to operate two MCH buses and one CGH_2 bus (13 pressure bottles with 147 Nl at 30 MPa) or for re-electrification. A hydrogen-powered city bus is being developed. The basis is a Mercedes Benz diesel engine modified to a H_2-fueled ICE with internal mixture formation. In the first phase focus was laid upon the improvement of the MCH/Toluene cycle efficiency [96]. Originally planned to run until 1999, the HYPASSE project has been terminated by the end of 1996, after the Daimler-Benz company has withdrawn its support with the argument that the technology to operate H_2 buses is mature and developed [28].

9.2.9. LH_2 Airport

Aviation is of high economic significance for developed countries. The environmental impact by aviation is much smaller compared with earth-bound traffic in absolute values. However, the specific emission per passenger and mile in aviation is very high plus it is the dominant source of anthropogenic pollution at high altitude affecting sensitive layers of the atmosphere. Pollution in the vicinity of airports is also not negligible.

High-purity hydrogen is required for the aircraft engines. It will be liquefied in the immediate vicinity of the airport since delivery by truck or pipeline is precluded for economic reasons. Conceivable designs for the hydrogen gas supply is either delivery to the airport via pipeline or electrolysis at the airport for on-site hydrogen generation. For one third of the LH_2 production plus reserves, buffer storage capacity needs to be available [38].

A number of conversion proposals for airports to service LH_2 fueled aircraft have been made. These are considered purely theoretical analyses and conceptual design studies. Investigations have been made for the airports San Francisco [65], Chicago [29], and Zurich [1] in terms of installations and investment required.

A preliminary assessment of the technical, operational, and economic impact on air terminals and airline ground operations, if LH_2 were used as a fuel for commercial air transport, was made taking **O'Hare International Airport in Chicago** as a basis [29]. The assumption was to replace the current fleet by 400 passenger, 10,186 km design range LH_2 aircraft operating present[23] routes at present frequencies, which was 112 airplanes per day and a simultaneous service required for up to 12 airplanes. The fuel capacity assumed for one airplane was 28 (metric) tons of LH_2 ($\approx$ 395 m^3). Due to efficient airline operation, preference was given to a baseline concept that permits both conventional jet fuel and LH_2 powered aircraft to operate from the same gates.

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[23] This study was published in 1976!

According to the baseline concept, the delivery of gaseous hydrogen to the airport is done via 0.36 m diameter pipelines at 4.5 MPa pressure into an underground buffer storage. The hydrogen gas is then routed to a liquefaction plant consisting of three modules with a liquefaction capacity of 726 t/d including 625 t/d for aircraft, 19 t/d ground system losses and the remainder of 82 t/d demand variation. The LH_2 is stored in four spherical tanks with a total capacity of 1450 tons or a two-days production. Two tanks serve as active tanks for distribution to the refueling stations. Defueling of the airplanes is done into tank trucks which transfer the LH_2 to the storage tanks. As a safety distance, 305 m between runway and LH_2 storage and liquefaction facilities was considered an adequate spacing.

Recovery and reliquefaction of all (boiled off) gaseous H_2 was considered simple and cost effective. LH_2 distribution to aircraft refueling devices is done via a vacuum-jacketed pipeline system. In order to meet redundancy requirements, a three-line system was selected in which normally one is filled with liquid and the other two are used for vent hydrogen where one vent line could be switched to LH_2 supply. The LH_2 supply line with 0.4 m diameter allows a flow rate of 227 t/h at 0.3 MPa pressure. The refueling flow rate is < 14.3 t/h to keep the airplane fuel pipe inner diameter below 0.18 m.

The low ignition energy of hydrogen requires that hydrogen can be vented or leaked only to controlled areas. The potential for ignition after leakage is always present, the elimination of ignition sources is not practical. The necessity to minimize leakage and to avoid any hazard from leak fire is successfully met by the chemical industries. It has to be assured that H_2-air mixtures cannot be formed or remain undetected in a closed area and that venting outside the building in a safe disposal system is possible.

The process of cooling down a system usually evolves a two-phase flow causing flow and pressure oscillations and different cooling rates and thus imposes excessive stresses on the piping. If venting is necessary, hydrogen can easily be burnt or flared at low venting rates (< 0.3 kg/s), whereas flare stacks or burn ponds in remote areas should be used for high flow rates. Experience is available for disposal rates up to 135 kg/s [42].

Safety considerations are

- separation of LH_2 facilities from roads, buildings, runways,
- ventilation for enclosed areas,
- preclusion of air ingress into LH_2 systems,
- automated system shutdown in case of malfunction,
- confinement and control of large LH_2 spills in critical areas,
- use of non-sparking electric devices.

A first approach of a fault tree analysis has been made as far as information was available. The analysis included the initiating events loss of fuel supply for one or both aircraft engines, failure of disconnecting the aircraft from the refueling station, leakage of loop piping for fuel supply for several aircraft, leakage of ground storage tank. Leakages are usually announced by a loss of insulation, which leads to high reliability of the LH_2 lines, since this is detectable and respective measurement devices could be sufficiently often checked. Many more data from operational experience are required to conduct a quantitative analysis including human reliability. But despite lack of information, the qualitative analysis has shown that no major problems with the existing design may be expected.

A comprehensive safety and risk analysis cannot be made yet due to the still incomplete design. From a first-stage analysis conducted by the BAM, it was concluded that a LH_2 powered airplane as well as the respective infrastructure is feasible from the safety point of view. New aspects, however, arise with the significantly increasing size of the components compared with existing technologies [23].

Numerous LH_2 refueling processes increase the possibility of a potential accumulation of impurities, solid N_2 or O_2, which enhance the risk of fuel system component damage and explosion, respectively. The conventional warmup to vaporize impurities is not practicable for frequently used tanks.

9.2.10. CRYOPLANE Project

Aviation could take over the leading position of introducing hydrogen on a larger scale, because [38]

- its oil consumption is currently only 3 %, which is easier to be substituted by hydrogen than the oil in other traffic branches,
- it is concentrated to a relatively small number of airports,
- it is handled by trained personnel, and
- it capitalizes on the weight-related energy density of LH_2.

In a joint German-Russian cooperation starting in 1990, a study has been worked out about the feasibility of an aircraft propelled by cryogenic fuels [38]. The goal of this "**CRYOPLANE**" project is to check whether the use of liquefied natural gas or liquified hydrogen as an aircraft fuel is technically possible and reasonable in terms of ecology and economy. While the German side is fully concentrating on LH_2, the Russians are pursuing also the LNG option because of its huge natural gas resources as an intermediate step. The CRYOPLANE project is coordinated by the German "Deutsche Aerospace Airbus".

Topics covered by the project are scenarios for the transition to an alternative fuel, infrastructure, aircraft design, fuel system layout, engine modifications, and ecological issues. A plausible scenario for the introduction of an alternative aircraft fuel is to start the transition for short / medium range aircraft serving routes in or between leading industrial nations with strong environmental concern, e.g., Europe, USA, Japan. The phases leading up to commercial LH_2 aviation will be the development of the appropriate infrastructure and the operation of a demonstrator airplane. The first generation of LH_2 aviation is foreseen to require a fleet of 400 - 500 airplanes with about 70 European airports to be equipped with an LH_2 infrastructure. The consumption of fuel is predicted to be two million t/yr of LH_2.

A technological development program for the fuel system components has been started in 1993 comprising materials for tanks and piping, control system and sensors for hydrogen leak detection, fuel pumps, LH_2 gasifier, combustion chamber. The aero engine running on H_2 requires a good mixture homogeneity to avoid high-temperature flame pockets. In contrast to kerosene, the hydrogen combustion process can be realized at lean mixtures (low temperatures) thus offering a much wider control range plus reducing the NOX

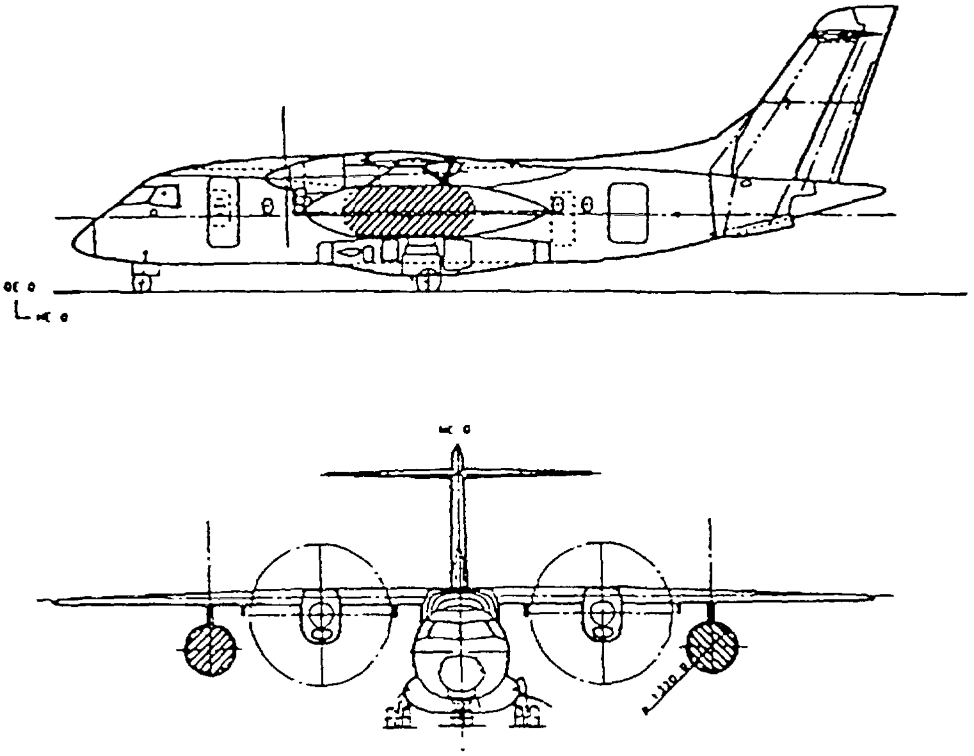

Fig. 9-7: General arrangement of the Do-328 Demonstrator. Shaded areas indicate the LH_2 fuel system, from [88]

emissions [87]. The most advanced low NOX concept is the lean premix combustion [106]. Experiments at the Fachhochschule Aachen on an ancillary gas turbine of the Airbus A320 converted to hydrogen have shown a 65 % reduction of NOX emissions. Research is now focusing on cryo pumps [11].

In the first stage, an **Airbus A310-300** was selected as the baseline aircraft. Its conversion into an LH_2-fueled aircraft required a new fuel tank concept dropping the conventional wing tank design. The most favorable design was deemed to be the top-mounted tank configuration with four tanks, two actives of 40 m^3 each for either engine and two passive tanks of 80 m^3 each (which refill the active ones). The total fuel weight is 15,600 kg of LH_2 compared with 27,000 kg of kerosene for the same flight range.

The former intention to have an Airbus-310 serve as the LH_2 demonstrator has been deferred in the meantime. Because of financial reasons, a 30 passenger regional airplane of type **Fairchild-Dornier 328** has been chosen now for modification into an LH_2-driven aircraft (Fig. 9-7). The advantages of this intermediate step are the availability of the hydrogen engine, the lower investment in infrastructure, and the earlier introduction of a series aircraft. Flight test of the DO-328 will start with one of the two engines converted to hydrogen with the other one to follow after demonstrating reliable operation. The fuel capacity is 420 kg (= 6 m^3) of LH_2 stored in two cylindrical tanks underneath the wings plus 1150 kg of kerosene for the second engine [88]. The ambitious goal is to demonstrate its flight performance by the year 2002.

9.2.11. Biohydrogen Production System

With the support of NEDO, a project for biological hydrogen production has been initiated in 1991 by the Research Institute of Innovative Technology for the Earth (RITE) to run over 8 years [70]. R&D activities comprise the areas

- breeding improvement for photosynthetic microorganisms
  genetic engineering and manipulation to enhance stability and improve efficiency,
- large-scale cultivation techniques,
- byproduct recovery techniques
  acquisition of useful materials such as enzymes, bacterial protein, pigments, nucleic acids,
- development of totally integrated system (see Fig. 9-8)

A computer model was used to analyze unintended impacts on climate, human health, and environment for a hypothetical biohydrogen production system. The figures given in Table 9-3 are based on a biohydrogen production capacity equivalent to 542 PJ/yr (≈ 17 GW). Emissions have been roughly estimated assuming a certain set of technical data for a hypothetical production plant some place in Southern Europe or North Africa [67].

A biohydrogen system is presently being designed for a small town in Germany. The demonstrating project whose realization is expected to start in 1996 includes the hydrogen production by biomass gasification to be used in a fuel cell cogeneration power plant, as a process gas in a metal industrial company, and in a later stage as a fuel for a fleet of vehicles [100].

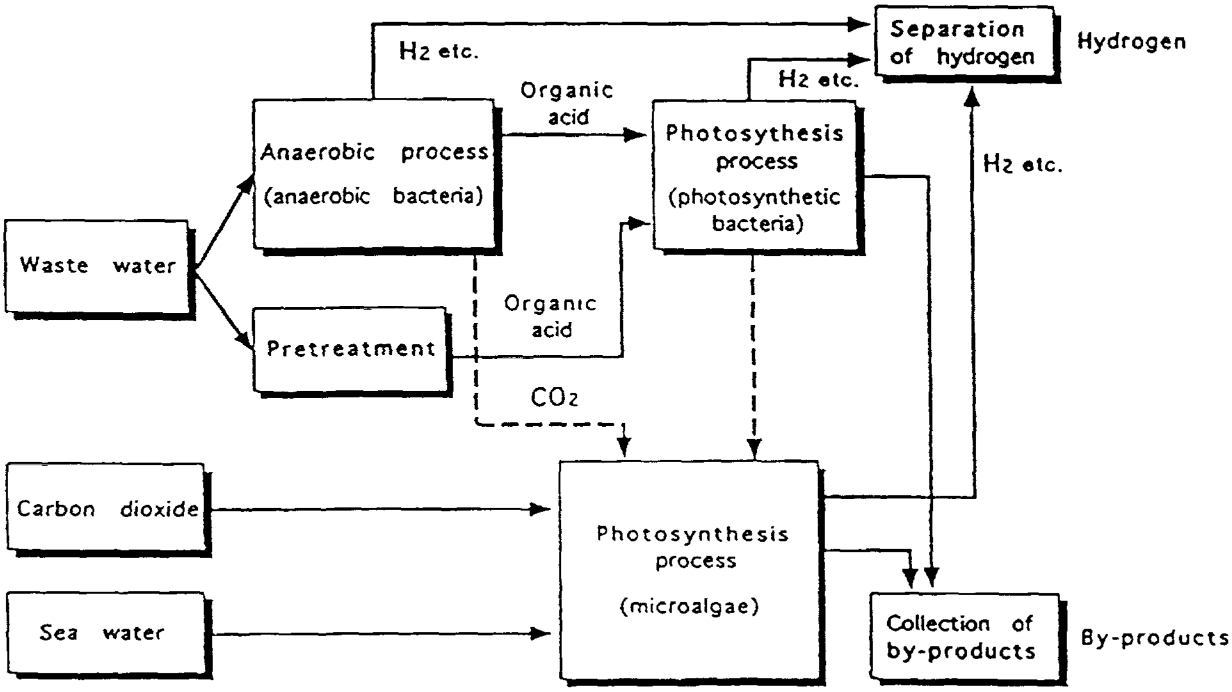

Fig. 9-8: Integrated system for hydrogen production from biomass, from [70]

Table 9-3: Area and freshwater demand and emissions of biohydrogen production equivalent to 542 PJ/yr, from [67]

		Equivalent to
H_2 production	542 PJ/yr	8 % of the estimated annual energy consumption in Germany in 2040
Area demand of production facilities	2,431 km^2	0.02 % of Sahara desert
Freshwater demand (90 % recycling)	$1.7*10^9$ m^3/yr	10 % of River Nile during dry season
Freshwater loss from production plant	$1.1*10^8$ m^3/yr	ground water used for agricultural irrigation in Germany
Excess biomass production	$3.7*10^6$ t/yr of dry mass	Sewage sludge production in Germany
Production-related emission of greenhouse gases	CO_2: $< 48.5*10^6$ t/yr CH_4: $< 1.2*10^5$ t/yr H_2O: $20\text{-}75*10^6$ t/yr due to losses from production plant H_2O: $33*10^6$ t/yr due to H_2 burning	CO_2: 7 % of emissions in Germany in 1987 CH_4: 3 % of emissions in Germany

9.3. LOCAL HYDROGEN SYSTEMS

Iceland possesses abundant renewable energy resources, but today's production is not more than 4500 GWh for domestic consumption. Energy sources are hydro (500 MW), geothermal (500 MW), corresponding to only 15 % and 2 %, respectively, of their estimated potentials, plus the import of 630,000 t of refined oil products. Iceland has been producing electrolytic hydrogen for 35 years at a rate of about 2000 t/yr consumed in fertilizer production. Plans are currently being made to better exploit the **Iceland natural energy sources for hydrogen production** (high-temperature electrolysis), export of electrolytic hydrogen to the European market, and consumption in energy-intensive industries. One alternative considered is the gasification of domestic peat (or imported coal) by means of geothermal steam for methanol production and, combined with electrolytic hydrogen, and subsequent hydrocarbon fuel synthesis [99]. Studies have been conducted where the use of geothermal energy in the form of 250 - 270 °C steam is considered to support hydrogen production in a Hot Elly type electrolysis and to operate turbines for the compression steps during hydrogen liquefaction. LH_2 production cost is estimated to be lower by 11 % compared with the conventional methods. Since the domestic fishing fleet is consuming a significant part of the imported oil, consideration is given to H_2-fueled ships for which 10 production plants along the coast line are foreseen with capacities ranging between 20 and 70 MW. On-board storage of the hydrogen is assumed as a metal hydride [22]. Within the WEIT project soon to start, vans will be fueled with hydrogen from renewable energy in Iceland (see section 9.5.2.2.).

A hydrogen project considered within the "**Hydrogen Initiative Bavaria**", WIBA, and partly funded by the state government deals with Munich airport aiming at ground-based traffic as H_2-fueled cars. On-site pressure electrolysis is used for the generation of hydrogen (32.5 Nm^3/h) to operate three buses and one passenger car plus the respective robot refueling station. In addition, LH_2 deliveries are planned to be taken as a backup fuel and to operate another passenger car including a robot refueling station. The project was started in September 1997. Vehicle operation is intended to begin in fall 1998 [9].

Arcosanti is an experimental town in the desert of Arizona for 7000 people in the final stage. It is based on the concept of "arcology", architecture + ecology, with efficient circulation of people and resources, multi-use buildings, and solar energy. The American Hydrogen Association has proposed an energy complex consisting of 40 genset dish units to convert sunlight into electricity and to use excess electricity for hydrogen production, and of a biomass conversion plant to convert organic matter and garbage into hydrogen and carbon material [8].

A "**Wind-Hydrogen-Energy Demonstration Plant**" has been initiated in Argentina. The initial primary power will be 1 MW, with half of it to be used for hydrogen production in an alkaline electrolyzer at a rate of 100 Nm^3/h. The storage is designed to be both as a compressed gas and as a hydride. Hydrogen utilization is planned to be done in 10 kW fuel cells, in an internal combustion engine, and in a catalytic burner. In a later stage, hydrogen serves to fuel five cars and two buses [30].

In 1990, ENEA has started the **Photovoltaic Hydrogen Cycle** project, a small-scale demonstration system including a KOH water electrolyzer, metal hydride storage for up to 18 Nm^3 of hydrogen and a 3 kW SPFC [48].

In the "**Clean Air Now (CAN) Solar Hydrogen Project**" near Los Angeles, a stand-alone electrolyzer is powered by photovoltaic cells with 48 kW total power. The produced hydrogen stored as a compressed gas (up to 34 MPa) is used to fuel three Ford Ranger trucks which are in commercial operation meeting the ULEV standard [89].

An energetically self-sufficient **solar house** has been investigated in Freiburg, Germany. Pertinent components are a seasonal storage of solar energy by means of a hydrogen system with electrolyzer for H_2 generation, storage vessel, catalytic burner for high-temperature heat generation, and a fuel cell for electricity generation. Important subject of research is the central technique for optimizing the system efficiency [73].

Canadian water electrolysis technology has been successfully marketed. The EI-250 technology with a 3 t/d capacity corresponding to approx. 7 MW as a part of a state-of-the-art **hydrogen liquefaction** plant in Quebec is being demonstrated since 1987. A similar plant with twice the capacity is being developed in Brazil [54]. Brazil has still a huge potential of hydro power which is not used yet. Especially with respect to the hydro potential available in the northeast of the country far from the industrialized areas in the south, hydrogen is considered the energy carrier of choice with the option to export surplus amounts as LH_2 [35].

In the city of Karlsruhe, various companies are planning a **Public Transportation Project** where city buses are powered by electrolytic hydrogen. The electrolyzer installed close by the refueling station is at the same time part of the idea of a rational energy utilization by a more economic operation of the electricity generating baseload power plants and a more efficient utilization of primary energy.

A **Renewable Hydrogen Transportation System** project is currently developed for the city of Palm Desert. Its goal is to operate a fleet of eight PEM fuel cell powered vehicles, a refueling infrastructure including a photovoltaic hydrogen generation, and a fuel cell service and diagnostic center [74].

An experimental program is carried out in Spain on **solar hydrogen** production using photovoltaic cells with a peak power output of 8.5 kW and operating a 7 kW(e) alkaline electrolyzer. R&D work is done on PAFC [51].

The Hydrogen Project of the Aare-Tessin AG (**Atel**) starting in 1989 is a demonstration project comprising the construction and operation of a 90 kW H_2 production plant (SPEWE) at a rate of 20 Nm^3/h and the hydrogen consumption in 3 kW SPFCs [44].

A **nickel hydride hydrogen rechargeable battery** (NHHRB) which is similar to a Ni-Cd battery has been developed in China for renewable electricity storage purposes. More than 10 tons of hydride have been taken so far to produce 1.4 million sets of high-quality NHHRBs [25]. The first NHHRB factory has opened in June 1997 with a production goal of 30 million batteries and a 300 tons of battery materials consumption per year.

9.4. POWER GENERATION

Fuel cell research and development is being carried out for more than 35 years in **Japan**, representing a typical example of the country's interest in demonstrating all technology before commercialization, whether commercially practical or not [20]. During the 1980s, major activity was on demonstrating the 1 MW class. Similar to the US ONSI system, Japan has developed its own manufacture of PC25 type units. Over 50 PAFC power plant units in the range of 50 - 500 kW are being operated in field tests since the beginning of the 1990s. Some have reached an operational time of almost 40,000 h, which represents already about the required stack lifetime for commercial application. Test operation of the large-scale PAFC power plant units with 11 MW, 5 MW, and 1 MW were terminated in 1997. Total capacity of PAFC plants operating in March 1995 was 24.75 MW with more than 1.1 million cumulative hours [20]. A PEFC development program has started in Japan relatively late in 1992. The operation of units in the kW range has been demonstrated; the next step will be a 30 kW unit. Focus is also laid upon fuel processing, e.g., of natural gas; the completion of a respective 2 - 3 kW unit is expected for 2000. Within the WE-NET project, a feasibility study for a 5 MW PEFC with an expected efficiency of more than 50 % fueled by LH_2 is being conducted as well as for a 200 kW precursor unit [81]. Operation tests of 100 kW MCFC stacks with external reforming have been completed to be the basis for the construction of a 1 MW pilot plant (4 x 250 kW stacks) powered by natural gas at 650 °C. Target efficiency is > 45 %, operation time > 5000 h. NEDO is supporting SOFC projects including fundamental studies on material science and reaction kinetics and on stack and system development with the goal of operating modules of several 10 kW power with steam reforming of natural gas until 1999 [21].

Development of **fuel cell technology** has existed in the **USA** for about 30 years starting with the US TARGET programm (1967 - 1976). Funding by DOE supported R&D for stationary power generation with PAFC and MCFC. The technology has advanced to near commercialization. In a Los Alamos project on "Fuel Cells for Stationary Power Generation from Hydrogen", PEM fuel cell stack hardware has been developed and tested in 1000 hours of continuous testing of a 100 cm^2 call with a stable performance, and an energy conversion efficiency of 60 % was achieved [50]. Combined cycles of advanced fuel cell systems with gas turbines are high on the US priority list [21]. A 50 W methanol fuel cell operated with a mixture of 3 % methanol and 97 % water is under development in California using ruthenium as a catalyst on the membrane which allows the utilization of up to 45 % of the potential energy in the methanol. Advantages are no need for the fuel processor, humidification, thermal management system and the use of methanol as both a fuel and coolant. Prototype models have been operated intermittently for 3000 h and an efficiency of 34 % was achieved [58].

The pilot project of a "**Fuel Cell CHP Plant**" is presently realized by the German utility HEW in a residential area in Hamburg within the Euro-Quebec project. The practical demonstration is done in two steps. Step 1 is the operation of a 200 kW(e) natural gas fueled PAFC (ONSI) which is being operated since 1995 to meet district heat demand. In step 2, the plant was completed by a 200 kW(e) hydrogen-fueled PAFC (ONSI). As the first-in-the-world H_2-based energy system in a municipal housing area, it has started its operation in August 1997. The hydrogen fuel will be stored as LH_2 in a 60 m^3 tank to be refilled every 2 - 3 weeks by a tank truck [79, 101]. The overall efficiency is 85 %. The operation requires legal permission procedures which may set standards in Germany.

The **Ansaldo** company in Italy is studying **H_2 fueled PAFC** power plants conceived as 850 kW standard modules for applications in the chemical industries, e.g., chloralkali plants, ammonia plants, petrochemical plants. The fuel consumption will be 750 Nm^3/h of hydrogen per MW electric power. Operation in the CHP mode would yield cogenerated heat at 140 °C in the amount of 0.7 MW per MW electric power [14].

Within the frame of the project "Fuel Cells" established at the Research Center Jülich in cooperation with industrial companies, focus is laid upon R&D work for **SOFC for stationary applications** and **PEM-FC for mobile applications** [68]. The main goals are the improvement of system and understanding by solving basic problems of process engineering as well as the environmental impact by analyzing the material streams. For the SOFC, the so-called substrate concept has been developed which allows the production of larger electrolyte sheets of up to 250 by 250 mm^2 as a 20 μm thick layer upon the anode as a 2000 μm thick support. The thin electrolyte allowed a lowering of the operation temperature down to 800 °C (the goal is 700 °C). The construction and operation of more than 400 single cells of 100 by 100 mm^2 and more than 30 single cells of 250 by 250 mm^2 were realized by the end of 1995. Operating temperatures were from 950 °C down to 850 °C. The next step will be the operation of a 1 kW natural gas fueled SOFC unit based on internal reforming with an operating temperature of 700 - 800 °C [75]. Assistance is given by numerical modeling (micro model, stack model) and the establishment of the necessary experimental data base. The PEM-FC activities at the FZJ include the overall balancing of energy conversion chains for different vehicle propulsion concepts. Favorable figures in terms of energy consumption and CO_2 emission were found to be achievable in fuel cell cars with methanol as fuel. One goal is the design, construction, and operation of a 25 kW stationary PEM-FC system including a compact methanol reformer, catalytic burner, and gas purification.

Based on the MCFC, the German companies MTU and Daimler-Benz have developed the "**Hot Module**" concept of a decentralized power plant, which can be fueled with natural gas, coke furnace gas, or biomass gas. Efficiencies of up to 65 % are expected to be achievable. A demonstration plant in Dorsten, Germany, with an electric power of 300 kW working with pipeline natural gas is being connected to the electricity grid since August 1997 [37]. In addition, process heat at a temperature of 400 - 450 °C can be utilized; the efficiency is about 50 %.

The German industry is pursuing the design of a **natural gas fueled SOFC** with a self-supporting structure of an electrolyte of 100 μm thickness and an area of 50 by 50 mm^2. Developmental steps of SOFC in the Siemens company have started with a 50 W unit in 1993, passed 370 W, 1.8 kW, 10.8 kW, and eventually reached 20 kW in 1996. The design specifications of a SOFC combined heat power plant (see Fig. 7-5) are an efficiency of > 50 %, a fuel utilization of > 90 %, a thermal cyclability of > 100 cycles, and an operational lifetime of > 40,000 hours. A 20 % pre-reforming of the natural gas fuel is required. Its construction is expected within the next 2 - 3 years [40].

A self-supporting SOFC-based power plant system, **HEXIS** (Heat Exchanger Integrated Stack), using circular planar elements has been developed by the Sulzer company in Switzerland for natural gas as a fuel and a power of up to 7 kW [26]. Field tests have started in summer 1997; commercialization is planned for the year 2002. The development goal is the construction of small-size systems in the power range of 1 - 200 kW.

Goal of a joint Dutch/Danish project is the installation and operation of a **100 kW SOFC power plant** to be connected to the electricity grid in The Netherlands. Based on the Westinghouse tubular design, the stack consists of 1152 fuel cell tubes which have a length of 1.5 m and a diameter of 2.2 cm. Testing of this SOFC unit was successfully done over 300 hours. It was put into operation at the end of 1997. The efficiency is expected to approach 47 % at 100 kW(e). If in addition the waste heat of 150 kW could be utilized in a gas turbine, the overall efficiency could be raised to 70 % [15].

The **Norsk Hydro** company is developing an environmentally benign concept of electricity production by burning hydrogen in a steam turbine. Natural gas is taken as primary energy source and converted in a steam reformer with the generated CO_2 utilized as injection gas in oil fields for oil recovery enhancement.

The **cracking of propane** is a subject of research at the Duisburg University, Germany. Since the crack product carbon black is deposited on the catalyst surface resulting in a decrease of the H_2 production, it has to be removed in a purification step. A small-scale arrangement of two chambers alternatingly used for cracking and purification has been erected providing a continuous H_2 flow of about 130 Nl/h (corresponding to approx. 0.5 kW) appropriate for being used in a fuel cell [19].

In a cooperative effort between the DLR and various other German companies, the project of a **hydrogen and oxygen fueled steam generator** was pursued which allowed the instantaneous provision of steam of any desired quality. Startup times of the steam generator are in the order of 1 - 2 s with a combustion efficiency of > 99 %. In a first step, a steam generator prototype was operated in 1991/92 in totally 285 combustion tests with a power output range between 25 and 70 MW. The second step was the installation of the demonstration facility for H_2/O_2 instant reserve, HYDROSS, consisting of a modified H_2/O_2 steam generator plus storage and supply system within a container [72].

Major tasks of the hydrogen energy program in the Russian Federation in which about 20 scientific organisations are involved include research on fuel cells and electrolyzers both with solid polymer electrolyte, on H_2 / O_2 steam generator (experiments with 20 - 100 kW and 10 - 20 MW thermal power), and on catalytic combustion [83].

9.5. ACTIVITIES ON HYDROGEN AS A FUEL IN TRANSPORTATION

9.5.1. Aviation

An early **rocket development** in the USA was based on both nuclear and hydrogen propulsion. A high-temperature graphite reactor was to vaporize and heat up liquid hydrogen. A prototype operated successfully for a limited time. This technology was said to be available if large-scale space propulsion for inter-planetary travel were needed [86]. The first rocket that used a hydrogen / oxygen engine was a NASA Centaur launched in 1963 with a thrust of 0.07 MN per engine. The Saturn-V rocket in the Apollo project was equipped with a 2nd and 3rd stage H_2 / O_2 rocket engines which reached a thrust of 1 MN (with a lifetime of one hour under normal operating conditions). Due to its work on the nuclear powered rocket using LH_2 as a propellant (project ROVER), the Los Alamos National Laboratory has gained since the 1960s comprehensive experience in large-scale handling of gaseous and liquid H_2 characterized by an excellent safety record [42, 41].

Also for the **Space Shuttle** main engine, an LH_2-LOX fuel system was selected which is installed in the External Tank. The LOX tank has a volume of 550 m^3, the LH_2 tank has a volume of 1575 m^3 both consisting of aluminum with a 2.5 m foam insulation [80]. The three high-pressure engines for the Space Shuttle reach a thrust of 2.1 MN each [84].

NASA has designed various concepts of **LH_2-fueled aircraft** distinguished mainly by the tank configuration. The first successful in-flight test of an experimental hydrogen-propelled aircraft, a twin-jet B57-Canberra with one engine modified for H_2 operation, took place in 1955/56. Also the unmanned U2 reconnaissance aircraft was fueled with LH_2. In 1988, a four seater Grumman Cheetah converted to hydrogen with an LH_2-fueled internal combustion engine became the first and only, so far, airplane to take off, cruise, and land by means of hydrogen power only [84].

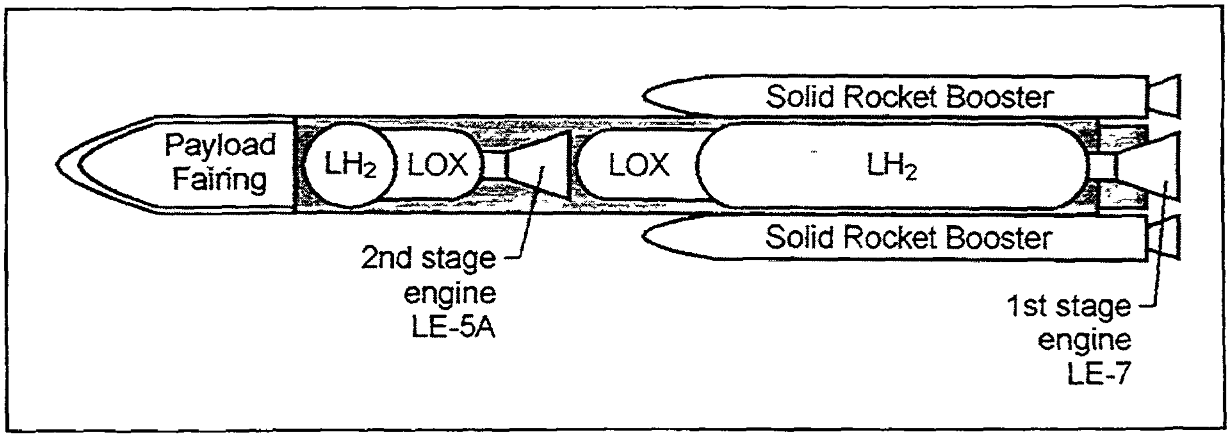

Fig. 9-9: Configuration of the Japanese H-II two-stage launch vehicle, from [7]

The **X-30 National Aerospace Plane** (**NASP**) was designed as a liquid hydrogen propelled vehicle that could go into the orbit as well as travel over intercontinental ranges at hypersonic speeds up to Mach 25 (= velocity needed to reach the orbit). Among other technologies identified which were considered critical to its success was the air-breathing supersonic combustion ramjet (= scramjet) propulsion system, where LH_2 is injected into the combustion chamber and ignited by hot compressed air. Slush hydrogen was considered as a fuel in the higher Mach flights. What eventually did skyrocket was not the X-30, but the estimated total cost of 17 billion US $ for flight testing. The high technical risk made earlier supporters loose their interests, so proponents were unable to save the project from termination which finally happened in 1995 [43]. New designs have since been pursued, e.g., with the Mach 15 X-33 reentry vehicle, its smaller and lighter successor, the Mach 8 X-34, whose development has started in summer 1996, or the HYPER-X with its first Mach 7 flight scheduled for 1999.

The National Space Development Agency of Japan, **NASDA**, has demonstrated the first successful launching of the **two-stage launch vehicle, H-II**, with LH_2 / LOX propulsion system in 1994 (Fig. 9-9). Advanced technology was required for the LE-7 main engine. The LH_2 and LOX cylindrical tanks have a diameter of approx. 4 m and a length of 17 m/4 m and 4 m/2.3 m, respectively, for the first/second stage engine [7]. A new and more powerful H_2 rocket was successfully launched in November 1997. Since 1991, the use of slush hydrogen as a fuel for rockets or future aircraft is currently being investigated. A concept study has been made on a civilian oriented reusable spaceplane, SSTO (Single Stage To Orbit), Hope-X-Prototype[24], based on an air-breathing propulsion system and scramjet engine which allows a speed of > Mach 15. The plane of 94 m length will have a 10 passenger capacity. The fuel is slush hydrogen; the oxidizer is liquid air [69].

The development of **China**'s space industry was initiated in the 1950s. Successful launching of the first domestically manufactured carrier rocket was in 1964. The Long March No. 3 three-stage large carrier rocket is propelled by a liquid hydrogen fueled combustion engine [5]. A small LH_2 production plant is being operated near Beijing for aerospace purposes.

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[24] The "Hope-X-Prototype" project was recently reported cancelled due to space research budget cuts in 1997 [17].

Experience in **Germany** with hydrogen as an aviation fuel has been gained already in the early 20th century. Rigid airships containing huge hydrogen gas bags served for freight and passenger transportation over more than 25 years until the "Hindenburg" accident 1937 in Lakehurst has immediately stopped these activities [84]. The German DLR operates the P8 test facility for research and technology studies on high-pressure (up to 30 MPa) LOX / GH_2 rocket engine fuel combustion as used in the **ARIANE** transportation system [71]. Basic research is conducted on chemical and physical processes during high-pressure H_2-O_2 combustion as well as material characterization. Experimental work is accompanied by intensive computer modeling efforts to simulate transient and stationary flow phenomena. In Munich, a **"Hydrogen Technology Centre"** is operated by the space division of Daimler-Benz Aerospace (DASA) covering not only space-related hydrogen aspects. The activities comprise conceptual studies as well as development, production, and testing of hydrogen systems and components. Experimental work included NOX emission measurements on an hydrogen combustion aero-engine.

Although many space rocket engine systems in **Russia** relied on kerosene as an inexpensive fuel, the interest in H_2 fueled scramjet engines started as early as 1954 with the Mach 3 Burya project which was flight-tested in 1957. In 1991, a scramjet SSTO was launched and operated over 130 seconds having probably achieved a speed of Mach 8 [13]. The Russian company ANTK-Tupolev is operating the **"Flying Laboratory" Tu-155** since 1988, which is a hybrid version of the Tu-154 airplane. One of the three engines can be fueled with either hydrogen or natural gas. Operating experience with LH_2 is 10 hours. Efforts, however, are concentrating on LNG because of the enormous domestic natural gas resources. Design development has begun in two directions: (i) a freight aircraft TU-156LNG, which is a two-engine version of a TU-154M with a kerosene/LNG hybrid propulsion and allows a payload of 14 t and a cruising range of 3600 km, and (ii) a passenger aircraft TU-204LNG for a payload of 21 t and a cruising range of 4300 km. Experience gained on cryogenic and engine component operation, infrastructure at airports, training of personnel, and effects of emissions on the atmosphere is being introduced into the joint German-Russian CRYOPLANE project [38].

The aviation company Aerospatiale in **France** has tested for several seconds the operation of a slush hydrogen fueled scramjet engine. Ignition in the combustion chamber called statoreactor (there are no moving parts) is to provide the thrust to reach Mach 6 speed [103].

9.5.2. Ground-based Vehicles

9.5.2.1. Urban and City Bus Projects

Clean energy systems have been realized such as the first "**zero emission fuel (ZEV) cell powered bus** developed by **Ballard Power Systems** Inc., Canada. The company has designed in phase 1 (1991 - 1993) a 20 passenger transit bus driven by 24 PEFC stacks with 5 kW each. The bus was the world's first ZEV vehicle and has met its performance targets. Phase 2 of Ballard's ZEV Fuel Cell Bus finished in 1995 was based on a 60 passenger commercial prototype bus with a power of 260 kW. In a subsequent phase 3, small fleets of buses are to provide the basic data for a full commercial production [64]. Within this phase, the city of Chicago has started in early 1997 a 3-years bus fleet testing program. A Ballard production of fuel cells for buses on a commercial base as a phase 4 is expected to start after successful testing. Projects involving Canadian participation within international programs include an urban bus transportation system using a mixture of 20 % H_2 and 80 % CH_4 = "**Hythane**" as a fuel. This bus with four roof-mounted aluminum tanks is a modified version of a natural gas driven bus. A demonstration phase with two buses has started in 1994. Ballard has announced in 1997 the intention to also invest into the manufacture of 250 kW stationary SPFC power plants.

Within the **Euro-Quebec project**, several city bus projects are being designed and demonstrated. The world's first full-size city bus with an internal combustion engine has been tested in **Belgium** since 1994. The H_2 fuel is supplied from a 125 l LH_2 tank, substituted by two 200 l LH_2 tanks in a later phase. A **MAN** city bus is the third generation bus promoted within the frame of the Euro-Quebec project. It is operated with a dual-fuel (LH_2, gasoline) 170 kW internal combustion engine. The storage of 570 l LH_2 is in three bottom-mounted tanks at 0.35 MPa. Boiloff loss is 3 % per day. Cruising range is 250 km for LH_2 and 450 km for gasoline. It has been operated in Erlangen, FRG, starting in April 1996, and is running since spring 1997 in Munich. The **DE NORA** and **ANSALDO** LH_2 Hybrid City Bus Demonstrator, sponsored within the Euro-Quebec project, is a Fiat Iveco bus equipped with a PEFC fueled by gasified LH_2 with 600 l in three top-mounted cylindrical tanks providing a constant power of 45 kW.

The first step towards an introduction of hydrogen as a fuel in **Norway** will be made with the operation of four city buses using LH_2 fuel in an internal combustion engine. The 600 l tanks allow a cruising range of 250 km.

The **Georgetown Fuel Cell Transit Bus Program** aims at the development and demonstration of a PAFC/battery propulsion system in urban transit buses [102]. The fuel is methanol stored in a standard fuel tank and converted in an on-board reformer to hydrogen to operate the fuel cell. A battery provides additional power necessary during acceleration and fluctuating power demand, since the PAFC system is not suitable for rapid changes in power level. The program encompassed the development of two 25 kW combined fuel cell/battery systems in Phase I (completed in 1991), and in Phase II the fabrication of three test bed buses, the first fuel cell powered vehicles to run on liquid fuel (the first delivered in 1994). Vehicle testing and evaluation is subject of Phase III. In the next step as a part of a commercialization effort, two buses will be powered by a 110 kW PAFC plus a 60 kW battery; their completion is scheduled for 1998.

A city bus, **NEBUS**, powered by 10 PEFC stacks with 25 kW gross each has been introduced in May 1997 as the third fuel cell prototype no-emission vehicle by Daimler-Benz. Seven H_2 tanks with 150 Nl at 30 MPa each allow cruising range of 250 km. Development goal is its commercial production in 2004.

In the project **Fuel Cell Bus**, sponsored by the state of Bavaria, a consortium of German industrial companies is planning to realize a zero-emission low-floor bus by the year 1999 [18]. The basis is an MAN bus whose conventional diesel engine will be replaced by four PEM fuel cell modules with a rated output of 120 kW (Fig. 9-10). The hydrogen fuel will be stored as compressed gas at 25 MPa in nine pressure bottles on the roof, sufficient for a 250 km cruising range.

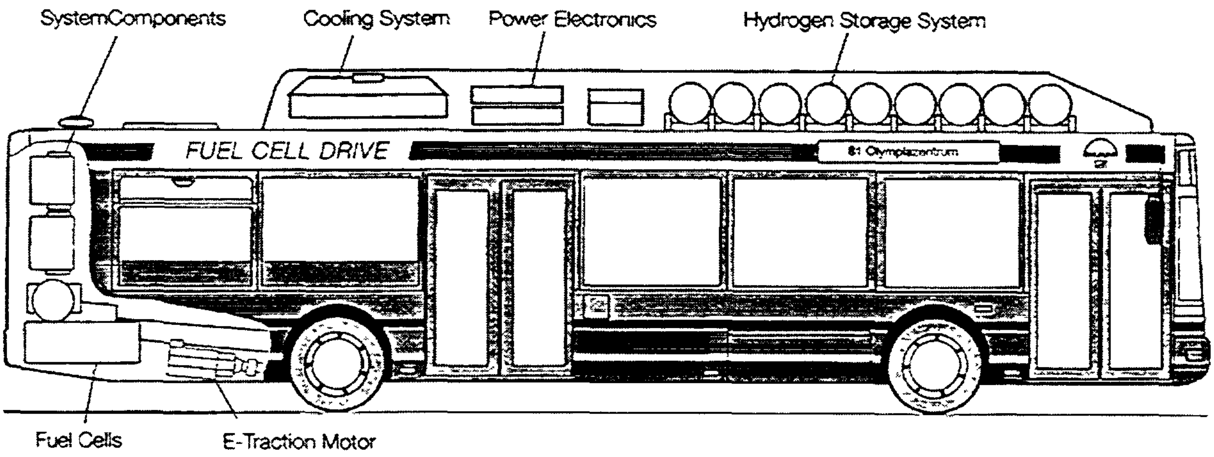

Fig. 9-10: Schematic of an MAN low-floor bus converted to a PEM fuel cell drive within the German project "Fuel Cell Bus"

The **Chula Vista** Hydrogen Bus Project is to demonstrate zero-emission bus transportation. The buses are equipped with Ballard PEM fuel cells and fueled by compressed hydrogen with a range of 250 miles [24].

9.5.2.2. Cars

R&D activities on hydrogen energy in **China** have started in the 1970s. The project of a gasoline / hydrogen hybrid automobile with hydride storage and internal combustion engine was pursued in the early 1980s and demonstrated a 10 - 15 % energy saving and a much lower pollution emission, however, it did not pass beyong research stage [25]. In the fuel cell area, China has studied the hydrogen-air PEFC and the direct methanol fuel cell. A double reactor for hydrogen production at a low-energy consumption level, 2.7 - 2.9 kWh per Nm^3 hydrogen, is later to operate on a pilot plant scale [25]. Current research is focusing also on the indirect methanol fuel cell for vehicles (cars and city buses).

A **BMW 745i test vehicle** designed in 1983/84 in cooperation with the DLR was the first in Europe licensed for LH_2 operation [85]. In a modified vehicle of the 735i type fueled with liquid hydrogen, the tank has an inner volume of 93 l, the maximum pressure allowed is 0.5 MPa. The cruising range is up to 300 km [90] (see also section 7.2.3.1.). The refueling procedure tested within the SWB project (see section 9.2.6) requires less than 20 minutes. The fourth generation test car (1995) operates at 80 kW with 130 l LH_2 tank providing a cruising range of 400 km. A CNG / gasoline driven hybrid BMW as an intermediate step to LH_2 has recently gone into series production.

The **Musashi** Institute of Technology in Japan has presented in 1975 its first test vehicle fueled with cryogenic hydrogen. A more recent development, the Musashi No. 8 car presented in 1993, applies direct injection using a high-pressure LH_2 pump. Musashi No. 9 is a 4-ton refrigerator van which makes use of the low temperature of the LH_2 to keep the goods at a temperature of 0 °C. The tank capacity is 360 l of LH_2. The operation of the truck has been successfully demonstrated [105].

Mazda has developed a rotary engine converted to hydrogen operation and employed in two prototypes, HR-X1 and HR-X2, presented in 1991 and 1993, respectively. The HR-X2 engine has a power of 96 kW fueled from a 280 kg metal hydride tank with a capacity of 43 Nm^3 of H_2 allowing a cruising range of 230 km. Within the WE-NET project, the Mazda Motor Corp. is testing the driving performance of a third hydrogen powered car based on the MX-5 Miata design also with a metal hydride storage system and with a 400 kg heavier weight than the standard car. Its acceptance as a ZEV is expected [78].

In 1991, the American Academy of Science has presented the first fuel cell car. A Ford Fiesta was modified to a hydrogen-fueled PEM-FC drive, the **LASERCEL1** prototype. The hydride storage with 2.3 kg of H_2 capacity is refueled within 5 min and allows a cruising range of 300 km [2].

From 1984 to 1988, **Daimler-Benz** has tested a fleet of 10 vehicles (5 passenger cars running on a H_2-gasoline mixture, 5 vans running on pure H_2) in the period 1984 - 1988 based on low-temperature hydride storage. The total operation range was more than 750,000 km. In the project, the hydrogen powered vehicles were operated by "normal" customers, the safety level was comparable with that of conventional cars.

In 1994, Daimler-Benz has introduced the New Electric Car, **NECAR I**, as the first generation fuel cell vehicle, an MB 100 van in which 12 PEFC stacks with a total power of 50 kW were deployed. A second generation, NECAR II, has been presented in 1996. It is a 6-seat V-class van operated by two 25 kW Ballard PEFC stacks with 65 % efficiency and fueled by compressed hydrogen in two 140 l tanks under 25 MPa pressure. Cruising range is 250 km. The mass-power ratio is 6 kg/kW compared with 21 kg/kW in NECAR I [57]. The overall efficiency for this protype vehicle was measured to be 29 % so far with a projected 40 - 45 % to be reached by 2003 [45]. In May 1998, Daimler-Benz has successfully test-operated its latest fuel cell vehicle, NECAR 3, an A-class passenger car powered by a 50 kW fuel cell system with an onboard conversion of methanol to hydrogen by a miniaturized steam reforming system. A 40 l methanol tank will allow a cruising range of about 400 km [36]. In cooperation with the Canadian Ballard Power Systems, Daimler is willing to invest into the world's first commercial fuel cell engine.

Within the project **ELBA** (Elektro-Auto mit Brennstoffzellen-Antrieb = Electric Car with Fuel Cell Propulsion) at the Research Center Jülich, the mobile application of fuel cells is currently being demonstrated. A Fiat Ducato van with electric drive and lead battery has been extended by a fuel cell system consisting of two PEFC with 2.5 kW power each, a hydrogen pressure bottle to store 4 Nm^3 at 20 MPa, 12 air pressure bottles to store 24.4 Nm^3 of air (O_2) at 30 MPa, two venting systems for reaction heat removal with 750 Nm^3/h capacity. The fuel consumption is 4 Nm^3/h. In the first test phase, the two 2.5 kW fuel cells are utilized to charge the battery during operation. In the second phase, a more powerful fuel cell (30 - 40 kW) could replace the battery. A comprehensive safety and risk analysis for ELBA has been conducted which revealed no significant individual risk (10^{-6}/yr) [31].

Within the **WEIT** (Hydrogen Energy Iceland Transfer) project, six delivery vans powered by renewable gaseous hydrogen will soon be operated in Hamburg, Germany. The project also includes the first ever publically accessible H_2 refueling station; its construction started in 1997. The H_2 fuel will be provided by the gas industry in the first phase and later imported from Iceland generated by renewable energies. The vans are conventional cars converted to H_2 propulsion. About 345 Nm^3 of hydrogen in pressure bottles (20 MPa) will allow a cruising range of 150 km [16, 62].

A project has started in 1996 to develop and install a 12 - 15 kW SPFC into a **Peugeot** minivan equipped with a special tank to store hydrogen at 70 MPa [12]. In the project FEVER (Fuel Cell Electric Vehicle for Efficiency and Range), **Renault** pursues a car design with a 30 kW PEM fuel cell and a 120 l LH_2 tank to allow a 500 km cruising range [59]. In both projects, the goal is to start test operation in 1997.

In 1996, **Toyota** has presented a fuel cell car, RAV4, which is fueled by methanol with on-board conversion to hydrogen. The car employs a battery buffer storage for additional power provision beyond 25 kW. Hydrogen is stored as a hydride in a rare earth based alloy in three small tanks. The cruising range is estimated to be 50 % larger compared with an ICE car running on methanol. Based on the same type of car, Toyota has unveiled the RAV4L electric vehicle in September 1997 as its latest fuel cell car [60].

Production methods, utilization, and environmental impact of **methanol** or other energy alcohols as synthetic liquid secondary energy carriers have been subjected to theoretical and experimental investigation at the Research Center Jülich. The new production methods allow a carbon conversion of > 90 % [63]. In the Center for Solar Energy and Hydrogen Research in Stuttgart, FRG, methanol is being investigated to be produced in a CO_2-neutral manner. The hydrogen is taken from an electrolysis process while CO_2 is recovered from the atmosphere by applying a KOH scrubbing solution to form a carbonate which is then electrolytically decomposed by using sulfuric acid [95]. In particular, Japanese studies treat the option to retain CO_2 generated during the combustion of methanol, to liquefy it and then to return it by maritime transportation back to the hydrogen / methanol plants. Drawback is the additional technology needed connected with a 20 % efficiency reduction [96].

The **Chrysler** company has designed a hydrogen fuel cell car, where in a multi-step process hydrogen is extracted from gasoline to be used in an automotive PEFC [6]. A 50 kW gasoline processor coupled to an SPFC stack has been presented in 1997. A proof-of-concept car is to be unveiled in 1999 [61]. The approach appears reasonable, because it converts gasoline (or methanol or ethanol) by reducing drastically the emission of pollutants and, at the same time, utilizes the existing gasoline distribution infrastructure. It thus represents an intermediate step on the way to a renewable hydrogen base. The single steps are:

- gasoline is heated until it is vaporized to a gas;
- a partial oxidation process is applied to the gasified gasoline for production of hydrogen and carbon monoxide;
- steam is introduced to convert the CO in a water gas shift reaction into CO_2 and to produce more hydrogen;
- the residue of 1 % CO, which is still way too much for a PEFC, is converted to CO_2 by adding air and using a Pt catalyst. CO is reduced to the required level of < 10 ppm;
- the clean hydrogen is then cooled in a heat exchanger down to the ≈ 80 °C operating temperature.

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Chapter 10

TRANSITION TO A FUTURE HYDROGEN ENERGY ECONOMY

10.1. TRANSITION FROM FOSSIL TO NON-FOSSIL ENERGY

Energy is fundamental to social and economic development. Three main features characterize an energy economy:

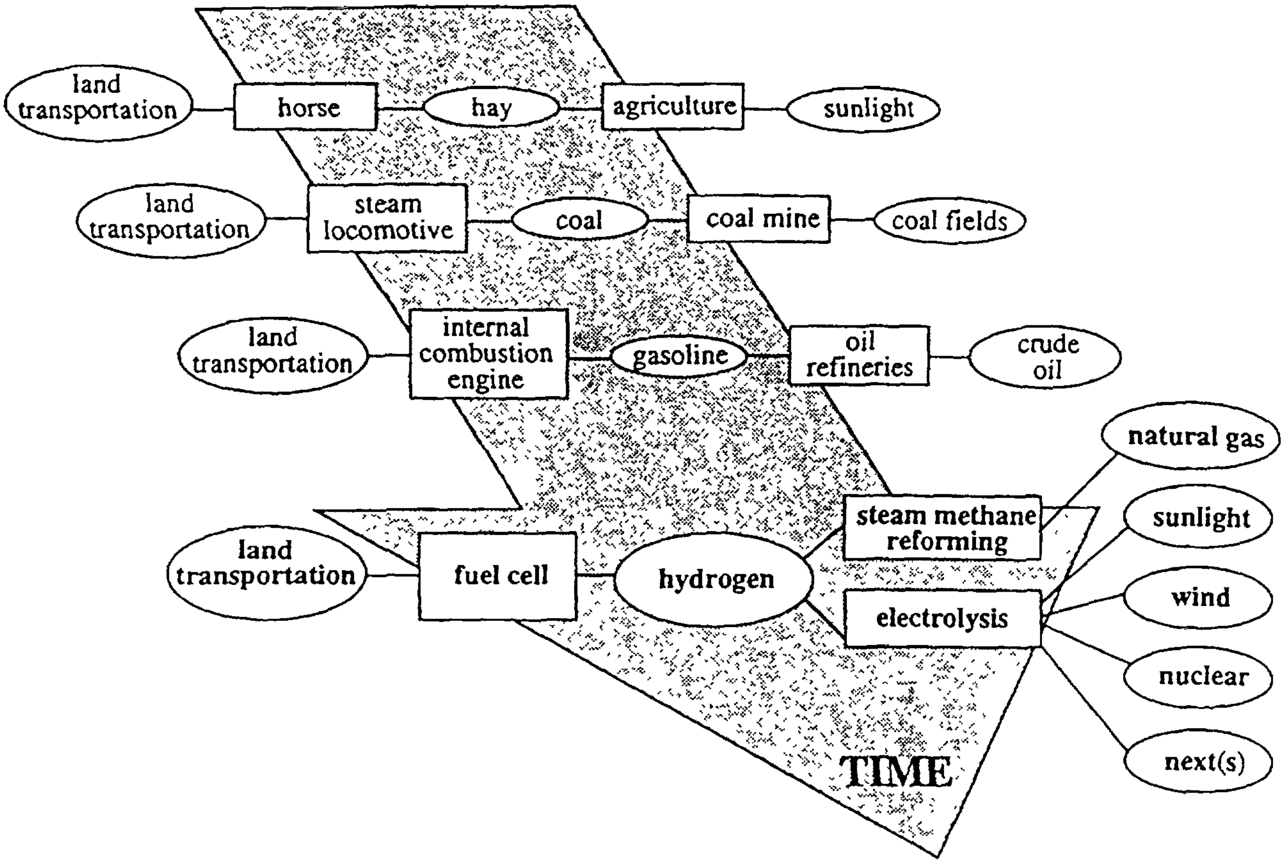
(i) the choice of the appropriate primary energy,
(ii) the selection of the appropriate conversion technology, and
(iii) the need to find the proper methods of storage and transportation for the new type of energy.

Increasing impacts on the environment with energy-related pollutants such as greenhouse gases urgently require appropriate countermeasures. It is necessary to drastically reduce the consumption of fossil fuels as the main source of anthropogenic CO_2 emissions.

In a future hydrogen energy economy, the hydrogen will ultimately come from non-fossil primary energies. Surplus energy from renewables with their limited energy density and strong fluctuations could be consumed in the production of hydrogen as an energy carrier. Hydrogen has a strong appeal from a pollution point of view and also from energy security by reducing dependence on conventional fuels, although fossil fuels will provide a long-term transitional resource. The main argument for a possible future hydrogen economy besides the environmental issue is the possibility of seasonal storage and transport of electric energy in large quantities and over long distances. A transitional production method for hydrogen on the way to non-fossil H_2 uses fossil raw material and energy for the reforming reaction from non-fossil sources representing a resource-saving (30 - 40 %), low-emission method.

The transition to a hydrogen/electricity energy economy is dependent on whether the electric grid is capable of serving the peak demand for electricity. For Europe, it is estimated that energy storage in the form of hydrogen is necessary, if the fluctuating portion in electricity generation exceeds 20 - 30 % [18]. Starting on the basis of the existing electricity grid, local and regional structures of renewable energies should be extended and integrated. In the future, hydrogen will take over the jobs that electricity alone is merely able to do: vehicle fuel, seasonal and strategic energy storage, raw material in the chemical and iron industry. Utilities generate and supply electrolytic hydrogen as their third main product besides electricity and heat. Electrolysis can be used at the same time to meet demand fluctuations. Electricity and hydrogen are interconvertible using electrolysis and fuel cells.

A restructuring of the existing energy system requires several decades and massive capital investment meaning that only really striking arguments will be able to initiate the change and it should start as early as possible. Motivation for the introduction of the hydrogen economy is continuously increasing traffic in the future and the need for a local reduction of emissions of high-density traffic in the cities. In the future, new zero-emission concepts for aviation in the sensitive ecosystem of the atmosphere are required. Hydrogen



Source: IESVic

Fig. 10-1: Evolution of the energy system for land transportation, from [2]

technologies must undergo a significant technological improvement and cost reduction and must advance beyond the proof-of-concept stage before significant investments will be made in infrastructure changes. Technical and cost issues may prevent its widespread use unless a framework of scientific principles, technical expertise, and analytical evaluation and assessment is developed. With the present energy policy, there is no need for a rapid introduction into the market, therefore efforts should be focused on the optimization of existing technologies.

A conceivable intermediate step for the transition to a comprehensive hydrogen economy is the concentration on a low-energy economy with minimum CO_2 emissions into the atmosphere using local excess potentials of electricity, e.g., renewables hydro, wind or cheap off-peak electricity in the day/night, working day/weekend, or winter/summer cycles. Where the available potential of primary energy does not (yet) suit the demand structure, i.e., far from energy consumption sites, storage systems must be used. Any additional hydrogen required could, e.g., be imported from the solar belts or from fossil fuels with solidification of CO_2 for disposal. The transition, however, i.e., the gradual reduction of the primary fossil fuel and substitution by non-fossils, requires "investment" energy.

A significant portion of the energy for transportation and other applications can be provided by hydrogen. The main problem in introducing hydrogen is not of a technical nature, it is the large investment in new infrastructure. The change of an existing system needs to be done in small steps. The time dependence of an emerging hydrogen economy for the example of land transportation is visualized in Fig. 10-1. A first step could be taken by the use of hythane (mixture of natural gas + hydrogen) thus minimizing infrastructure cost. Hythane allows a gradual transition from natural gas to ultraclean hydrogen. Starting with small proportions of H_2, the existing pipeline structure could be used. Continuous air quality improvement can be realized by increasing the hydrogen content with a safe fall-back position at every step along the way. "Smart" delivery systems could supply hydrogen to fuel cells while delivering hythane to cookers. Hythane with only 5 % hydrogen shows a disproportionately large reduction in the emission of pollutants. The first hythane evaluation project is underway in Denver.

One of the main areas appropriate for conversion to hydrogen is the transportation sector with immediate environmental benefits to urban areas. Commercially produced H_2-fueled cars based on either the internal combustion engine or on a fuel cell should be available at a reasonable price, have good performance and adequate range, as well as widespread availability of the fuel. Natural gas is expected to play a significant role as preceding technology. Also methanol has often been cited as a good compromise in terms of the desired characteristics of economics, environmental impact, supply logistics, and vehicle technology. Its synthesis could be realized by renewable hydrogen plus carbon-containing resources (e.g., biomass, CO_2) and its infrastructure would already be available. The conversion of air transportation to hydrogen would be an example on a larger scale.

In the longer term, hydrogen as a motor fuel may have a role to play in reducing oil consumption while addressing problems of urban air pollution and also global warming. A vehicle using a fuel cell and electrolytic hydrogen produced from renewable or nuclear energy would represent a true zero-emission fuel/vehicle system at any point from fuel production to end use. The problem of infrastructure for LH_2 vehicles is that 3 - 4 times as many tank trucks required for distribution would be on the road. Very few changes to consumer behavior are required to switch from gasoline or diesel to methanol.

Stationary off-grid applications such as gas turbine, fuel cell power plant, or internal combustion engines operated in the CHP mode are appropriate for decentralized energy provision. In particular high temperature fuel cells are applicable in households because of their need for both electricity and heat.

The duration of the transition period will depend on the so-called **harvest factor** of the new energy conversion plants, which is the ratio of the energy produced during its lifetime to the energy invested for its construction. A harvest factor of 10 means that a complete transition could be realized within a century; a harvest factor of less than 5, however, would prevent complete transition since the new system will not be self-sustainable. According to estimates published in 1993, photovoltaic power plants have a harvest factor of optimistically 1 - 3 with a forecast 3 - 6 range if the lifetime of the solar cells can be extended to as much as 30 years. An optimistic nuclear energy scenario based on the predicted figures of a PWR-1400 would result in a harvest factor of 14, provided a 40 y lifetime, a well functioning complete nuclear cycle, and, of course, public acceptance can be ensured [15].

10.2. DESIGN OF A HYDROGEN ENERGY ECONOMY

The first concepts of a "hydrogen economy" were developed in the 1960s representing integrated energy systems with the fuel hydrogen based on nuclear or solar primary energy. The diagram in Fig. 10-2 depicts the first concrete concept of a future electricity supply by solar hydrogen as was proposed in 1964 [8]: seawater is fed into pressure electrolyzers powered by solar electricity, with the produced hydrogen and oxygen gases to be introduced into a 5 MPa pipeline grid and with heavy water, D_2O, as a byproduct. The gases would be utilized in households and industries or for electricity production by means of magneto-hydrodynamic generators (MHD) or fuel cells (FC).

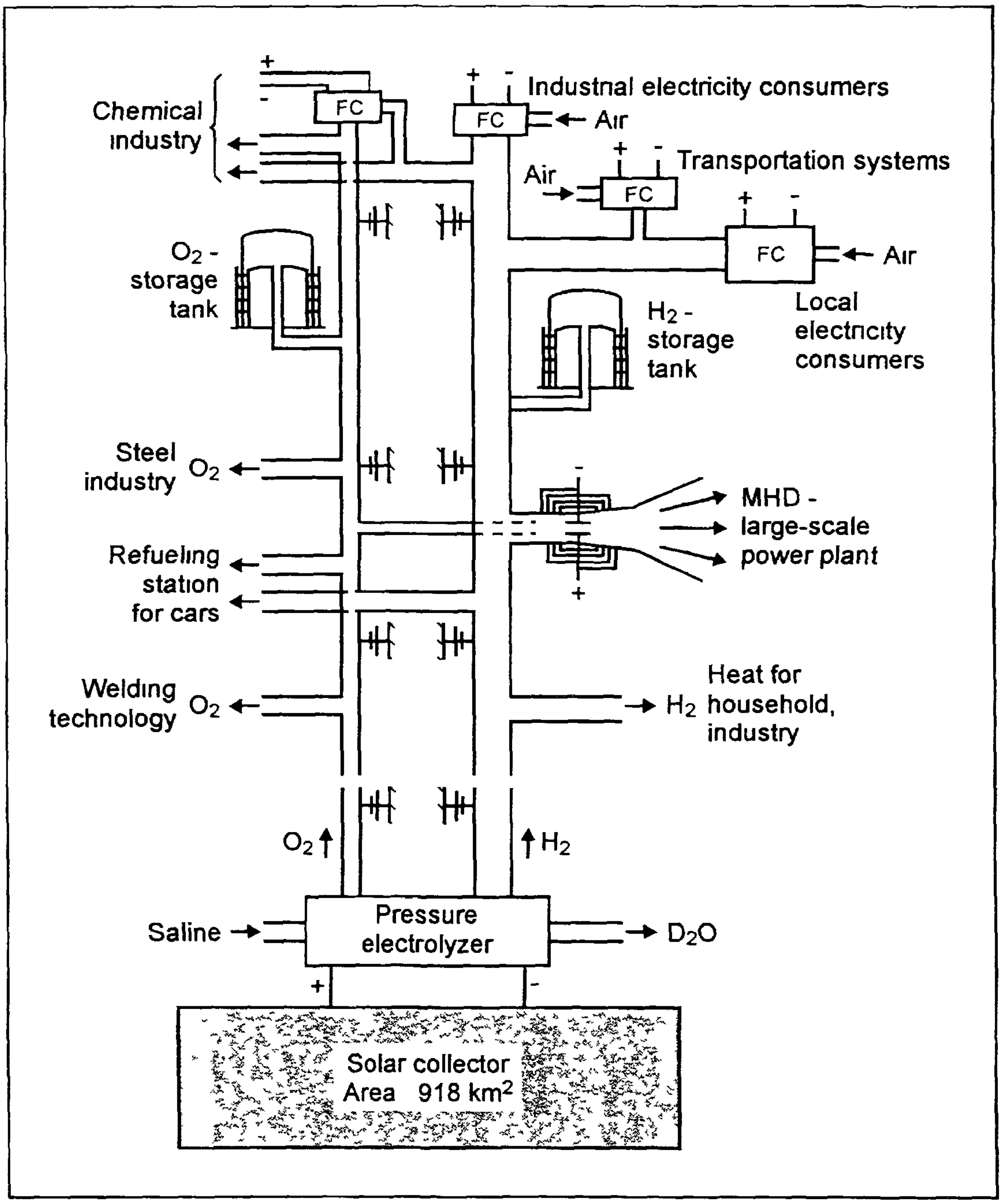


Fig. 10-2: Concept of a solar hydrogen economy from 1964, from [8]

In the concept of a prospective "**Novel Horizontally Integrated Energy System (NHIES)**" with zero emission as outlined in [5], the principal problem is not seen in the amount of fossil fuels consumed, but in the need to maintain cleanness during consumption, i.e., the treatment of emissions. This concept is based on (see Fig. 10-3)

- decomposition of coal, oil, gas and cleaning
- stoichiometric relation
- synthesis and conversion.

Unlike the conventional vertically integrated system, primary energy inputs comprising the entire spectrum, including nuclear, are decomposed and cleaned prior to combustion resulting in streams of CO and H_2, while O_2 is extracted from air. The demand for final energy in the form of electricity, H_2, CH_4, and CH_3OH is then met by taking CO, H_2, O_2 out of the grid (the so-called 2nd grid) in the respective stoichiometric mixture. It is a zero emission system in terms of NOX and SO_2. A later elimination of the CO grid represents the complete transition to a carbon-free hydrogen economy. For flow and cost assessment, the MARNES linear programming model was used as an analytical tool, which includes the concept of stoichiometric allocation and the conduct of streams of non-energetic materials such as NOX or CO_2, and which predicts NHIES to be macroeconomically cost-competitive with existing non-integrated systems [5].

The idea of a hydrogen economy as described in [11] is to transform the conventional infrastructure of cities consisting of energy, water sewerage, electricity, garbage control, and transportation to a hydrogen system based on the existing pipeline grids for town gas, clean water, and sewerage. Hydrogen is used for the cogeneration of heat for pyrolysis of biowastes and vaporization of the sewerage and of electricity for end use, e.g., charging hybrid vehicles. Electrolysis of polluted water could be used for hydrogen production and

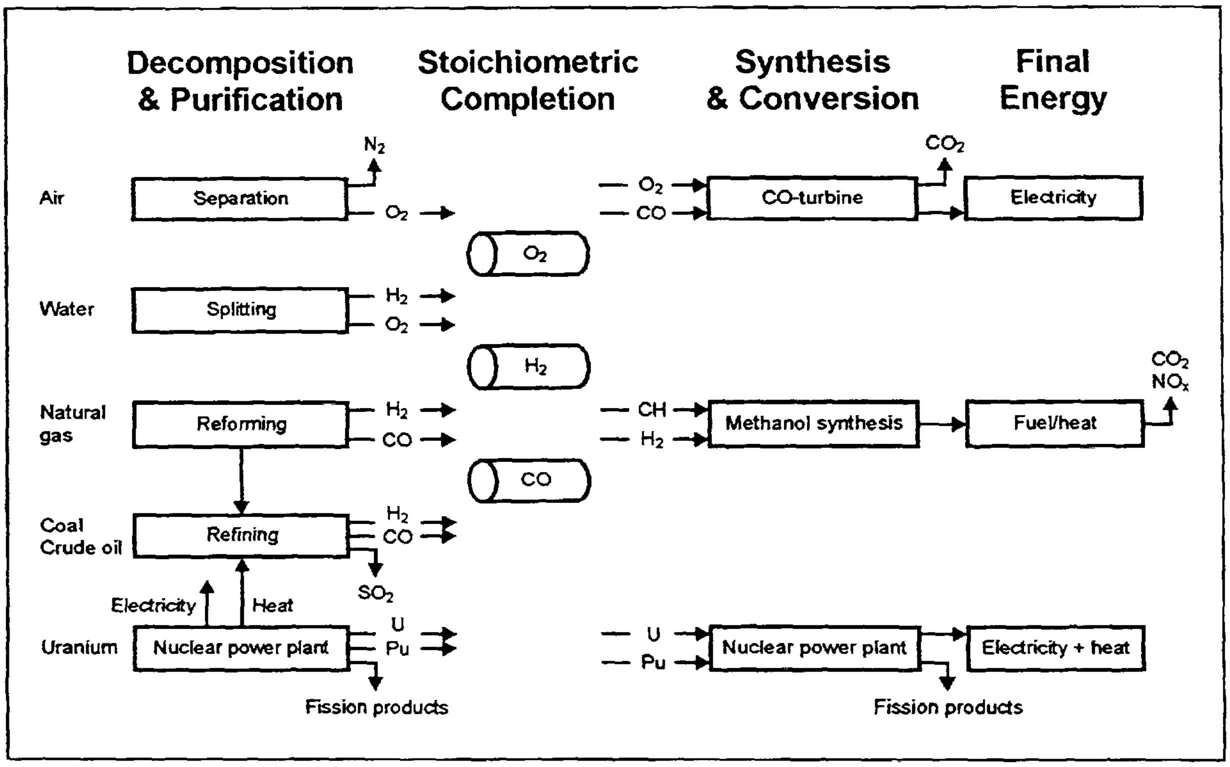


Fig. 10-3: The "Novel Horizontally Integrated Energy System (NHIES)", from [5]

water recycling. The transformation is seen by [11] to be feasible with an estimated billion dollars per 100,000 population and the technology required is "low tech with a few high tech whistles and bells".

Various technical and economic assessments of hydrogen energy systems have suggested that hydrogen could become competitive for use in efficient, low-polluting CO_2-neutral systems in the near future. The near-term option allowing for a smooth transition is to start with new, small-scale local infrastructures. For H_2-powered vehicles, the following scenarios are possible [12]:

- central H_2 production by steam reforming and delivery by either trucks or gas pipeline to refueling station
- withdrawal of excess H_2 from industrial plants and delivery via gas pipeline to refueling station
- decentralized H_2 production by small-scale steam reforming or electrolysis units on-site refueling station

A set of coherent programmatic pathways is applied in a project dealing with an integrated analysis of how hydrogen-powered vehicles can enter the market in substantial quantities. Each pathway investigated includes computer modeling comprising vehicle technology, refueling infrastructure, market scenarios, government actions. The latter is the key input of the models permitting the assessment of the effects of making government investments [19].

A reasonable approach to a gradual introduction of hydrogen is small-scale residential energy system modules comprising electrolyzer, metal hydride (or pressure vessel) as a buffer system, and CHP fuel cell components, ideal for applications far away from the grid. Roundtrip efficiencies of 30 % have already been demonstrated, 40 % are expected to be possible in the near future [20].

In principle, the operation of a fleet of LH_2 powered vehicles, e.g. city buses, is more appropriate than individual traffic. The infrastructure can be limited to a few refueling stations. Also boiloff losses can be avoided in fleet vehicles; for a private car the estimated loss seen over a whole year is between 30 and 60 % of the total fuel [16]. The daily hydrogen demand for a typical refueling station is estimated to be 3000 - 54,000 Nm^3/d [12] possibly provided by small reformer units, e.g., working off an existing natural gas pipeline.

The establishment of **strategies** is an indigenous task of policy. A whole variety of measures are conceivable for tackling the problem of environmental damage caused by the continuous contribution of the combustion of fossil fuels: direct legislative regulations and rules, investments, tax system, research funding. Industry may contribute to utilizing hydrogen technology by long-term investments, research activities and cooperation [3]. The "ultra-low emission vehicle" (ULEV), the "super ultra-low emission vehicle" (SULEV), and the "zero-emission vehicle" (ZEV) mandate in California[25] makes this state appear a good candidate for the introduction of hydrogen vehicles in a close cooperative effort between

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[25] According to the "Clean Air Act" (1990) in California, the percentage of total vehicles sold must be 2 % in 1998, 5 % in 2000, and 10 % in 2003.

fuel cell manufacturer, automobile industry, and academic groups. Legislative measures as taken in the USA are described in [6].

10.3. CONCEPT OF A NUCLEAR HYDROGEN ECONOMY

Fig. 10-4 describes the possibility of a chemical industrial complex where the energy required is provided by nuclear power based on small-sized modular HTGRs [7]. One option (upper part of the figure) employs a direct cycle gas turbine HTGR for efficient electricity production to be used in a water splitting process for hydrogen production, which is eventually consumed in H_2-driven turbines or fuel cell power plants. In the other option (lower part of the figure), cogeneration of electricity and process heat/steam is performed for the purpose of methanol and hydrogen production by means of steam reforming of natural gas and/or thermochemical cycles.

The concept of a nuclear hydrogen economy as shown in Fig. 10-5 is based upon hydrogen generation using nuclear power, the transport of energy stored in the hydrogen, and its consumption. The production facility consists of an HTGR combined with a thermochemical plant where the high-temperature heat is converted directly into chemical

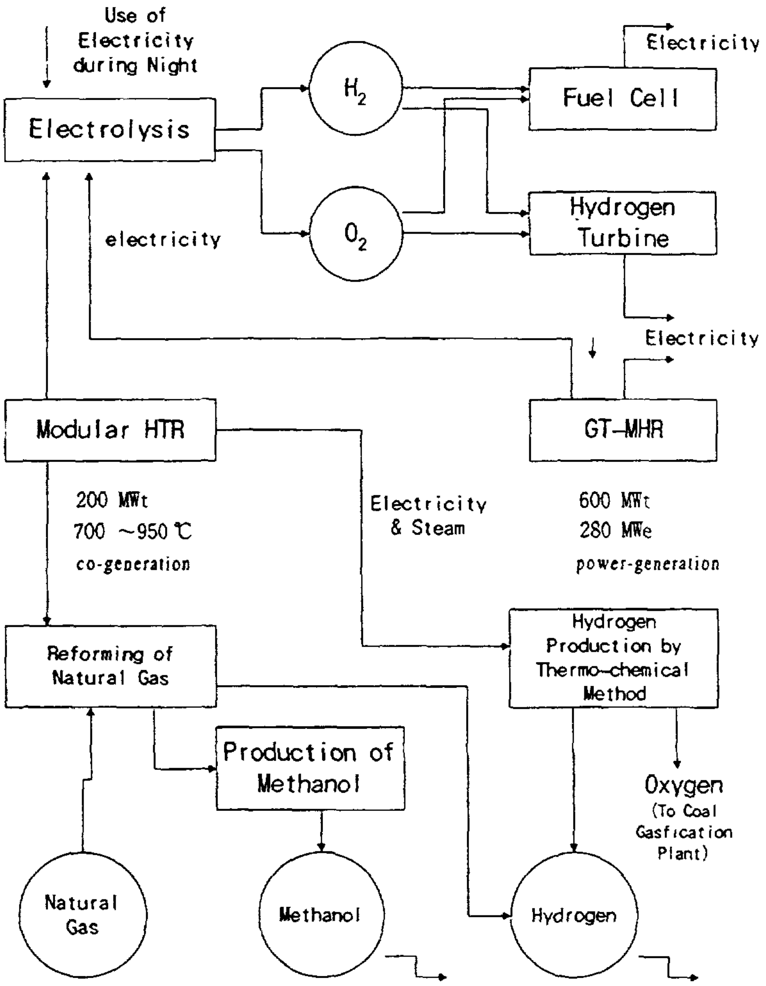

Fig. 10-4: Flow chart of a chemical industrial complex based on modular HTGRs as the energy source, from [7]

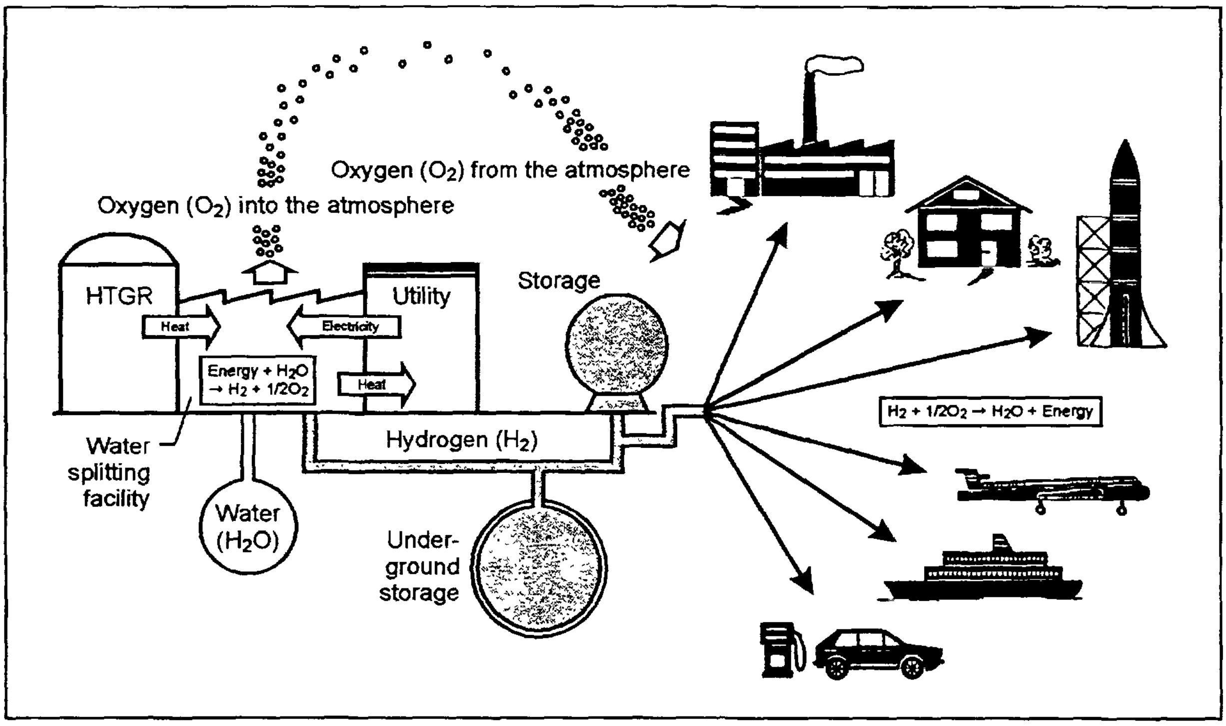

Fig. 10-5: Hydrogen energy economy on the basis of nuclear power and water splitting, from [17]

energy. Its basic product is hydrogen. Transport and distribution are provided by a pipeline grid. Small-scale and large-scale storage tanks serve the purpose of short-term and long-term energy demand balancing. Areas of consumption of hydrogen as an energy carrier are given as raw material in the chemical and steel industry, as a fuel for vehicles, for heating and cooking in households, and for electricity and long-distance heating provided by the utilities.

Sources of renewable energies (wind, water, sun) are deemed sufficient to more than replace all fossil fuel. Barriers to significant solar hydrogen utilization are the lack of high efficiency photoconverters, high stability and long lifetime, and cost-effective materials and systems. Environmental effects of energy use and the world's growing need for electricity are reasons for a renewed emphasis on nuclear power, at least it could serve as a transition facilitator. A transition period ranging from decades to more than a century is expected. The aspect of energy independence represents an argument in favor of the transition to hydrogen [13].

Nuclear energy may gain greatest importance in helping to get the hydrogen economy started. On a mid-term basis, overcapacities in countries with a high percentage of nuclear power (e.g., France) and reserve capacities, which exist in all larger distributed grids, could be used in electrolysis plants to be immediately disconnected again if needed, e.g., at peak load times. On a longer-term basis, nuclear power could be installed for hydrogen production if economically competitive with fossil primary energies.

10.4. SOME INTERESTING ASSESSMENTS

The following contains some interesting ballpark estimates which necessarily arise when discussing the world energy situation, in particular in connection with a future large-scale hydrogen energy economy:

- Anthropogenic CO_2 emissions guide back into the past with respect to CO_2 concentration in the atmosphere when the formation of the fossil fuels started. The speed at which the CO_2 concentration is currently changed, is roughly estimated to be 180,000 years per year of continued emissions [9].
- About 2000 km^2 of forest is necessary to bind the carbon dioxide emitted from a 300 MW coal power plant.
- In the European Community, the nuclear share of 33 % in electricity production allows the saving of CO_2 emissions to the amount of 700 million t/yr. This corresponds to the estimated CO_2 emissions of all passenger cars (more than 200 million) in Western Europe in the same time [1].
- The world hydrogen production today is $500*10^9$ Nm^3/yr with 97 % from fossil fuels. If this amount were to be produced by electricity (4.5 kWh/Nm^3 H_2) from power plants operated for 8000 h/yr, the installed power required would be 280 GW. This corresponds to more than 80 % of the currently available nuclear power in the world.
- The projection of a complete introduction of LH_2 aviation in the future implies for Europe the replacement of 45 million t/yr of kerosene (today: 30 million) by 16 million t/yr of hydrogen or 45,000 t/d; the present liquefaction capacity in Europe is 20 t/d. The German share of LH_2 aviation fuel is estimated to be 2.5 million t/yr LH_2 or 7,000 t/d with 60 % of this for Frankfurt airport alone. Liquefaction plants are expected to be established in units with 60 t/d capacity corresponding to the maximum available size today. Frankfurt airport is predicted to operate 65 of those liquefaction modules in the final stage.
  The German figure of 2.5 million t/yr of LH_2 translates into an electricity need of $1.6*10^{11}$ kWh/yr for H_2 production and liquefaction (based on 4.5 kWh/yr production and 10 kWh/kg liquefaction). This corresponds to 15 large LWRs or 250 modular HTGRs (German reference design) or to almost 3000 km^2 of PV area (PHOEBUS data).
- The Euro-Quebec project is designed to deliver 14,600 tons of liquid hydrogen per year to Hamburg, FRG. One barge carrier of the reference design is able to transport 1065 tons of LH_2, which translates into 13.7 shipments per year. The amount of LH_2 arriving in Hamburg corresponds to a power of 74 MW or $6.48*10^8$ kWh per year. A large-scale hydrogen economy would definitely require the employment of larger tank ships such as the SWATH ship with a transport capacity of 8150 t of LH_2. Primary energy consumption in Germany in 1996 was 350 million TOE or approx. $4.1*10^{12}$ kWh. The assumption that 1 % of this is provided by hydrogen means 111 loaded LH_2 SWATH ships per year arriving at Hamburg harbor.
- In 1992, energy consumption in Germany was 2515 TWh with 2084 TWh used in the form of fuel and 431 TWh used as electricity. If these amounts were to be provided by electrolytic hydrogen and assuming efficiencies of 85 % for water electrolysis, 90 % for transport and distribution, and 45 % for re-conversion

into electricity, the net electricity required would be 2724 TWh and 1252 TWh, respectively, i.e., almost 4000 TWh per year. In relation to the H_2 net heat of combustion, this energy is contained in $1.4*10^{12}$ Nm^3 or almost three times the present world hydrogen production. Water consumption on the basis of a specific value of 805 g of H_2O/m^3 of H_2 is then $1.2*10^9$ m^3 (without the cooling water needed, which for alkaline electrolysis is usually in the range of 25 - 30 % of the water to be split) corresponding to about 0.5 % of the mean precipitation in Germany [14].

- If car traffic in the city of Munich with 500,000 vehicles per day were converted to hydrogen-fueled traffic and assuming a 20 km cruising range per day and 1 kWh/km energy consumption, water vapor emissions would amount to about 1 million t/yr or 2 kg/(m^2 yr) in the city area. This is about 0.1 % of the mean annual precipitation. A 1000 MW water-cooled power plant emits about 14 million t/yr of water vapor assuming 7000 operation hours [4].
- If all light-duty vehicles in the US in 2010 were hydrogen fuel cell vehicles and if the hydrogen were produced by renewables, land use would be 3 % of the total US land in the case of biomass, 2 % for wind and 0.1 % for photovoltaics. Concerning the lower efficiency of ICE, land use would at least double for hydrogen ICE vehicles compared with fuel cell vehicles [10].
- Assuming the whole fuel demand of Germany's traffic sector to be supplied by methanol, about $220*10^9$ Nm^3 of hydrogen is required, which is eleven times the present annual H_2 production in Germany.

10.5. FURTHER WORK

Beyond the further development and improvement of hydrogen technologies and cost reduction as prerequisites for the introduction of H_2 as an energy carrier on a larger scale, it is the perceived safety risk that demands further efforts in parallel with the technological development. More information about the safety aspects of hydrogen would be helpful in reducing uncertainty ranges for more realistic safety and risk assessments of (nuclear) heat utilization plants and in increasing confidence in a safe operation of hydrogen systems. Better knowledge required for more detailed risk and safety assessments of the various H_2 production, storage, and transportation processes is seen in different areas:

- investigation of the evolution of the H_2 gas cloud and its mixing with and influence on the local atmosphere in terms of spilled amounts and release rates conceivable in large-scale accidents as well as the validation of respective calculation models;
- improvement of understanding of the turbulent processes in the flame zone, overpressures under various confinement conditions, pressure piling dependence on geometric boundary conditions, thermal radiation; quantification of the various parameters influencing flame acceleration and its influence on the initiation of a detonation;
- research on the combined effects of mechanisms that contribute to boiloff in LH_2 storage, in particular, moving storage systems (ortho-para conversion, heat leak, sloshing, flashing, thermal stratification);
- evolution and development of better hydrogen release detection devices;

- examination of air in-leakage into LH_2 (and SLH_2), solid air effects, and the influence on combustion behavior, oxygen detection;
- continued atmospheric research on the impact of aviation on stratosphere and enhanced water vapor emissions on troposphere;
- development of unified consistent standards for design, construction, operation, maintenance and their international acceptance;
- human factors engineering for industrial plants in a systematic manner.

Concentrating on nuclear power in connection with hydrogen production, further safety-related work is necessary on

- tritium and hydrogen transportation in the process heat system;
- process gas cloud explosion hazards inside/outside the reactor building, response of containment structures, and substitute liquid energy carriers (energy alcohols) on a natural gas and biomass basis;
- improvement of material and structural design by examination of long-term creep behavior and high-temperature corrosion properties of reference materials and the new superalloys including tests in a sulfur oxide atmosphere;
- passive cooling steam generator as an innovative safety concept which would not necessarily require a reactor shutdown in the case of a disturbance in the process heat system.

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Chapter 11

FINAL REMARKS

In principle, two different and independent areas have been covered in this report: on the one side hydrogen as an energy carrier and its application in a future large-scale hydrogen energy economy., and on the other side: nuclear power which represents an important option for providing primary energy for hydrogen production. The combination of both nuclear and hydrogen is not necessarily required but it represents a reasonable and a feasible option to facilitate the emergence of a hydrogen economy. Both areas will help to reduce global impact on the atmosphere. Hydrogen faces economic problems and possibly *public acceptance problems. Nuclear faces public acceptance problems.*

Many research activities still need to be done in both areas in terms of an economic breakthrough of hydrogen and its link to nuclear process heat. Since hydrogen is merely used today as an energy carrier, research is ongoing in all subsections encompassing technological development of components (storage, infrastructure, etc), safety-related investigations, and regulations. Nuclear power is used for hydrogen production by providing electricity for use, e.g., in electrolysis and by providing process heat, e.g., for conversion and upgrading fossil fuels. The former, electricity production, is a mature technology well established worldwide. The latter, however, process heat provision, for which the HTGR represents the ideal option, requires further research on plant components, material problems, as well as safety of the system permitting risk assessment for a whole industrial nuclear process heat complex, in particular, with a view to a large-scale hydrogen economy.

The limited efforts on the further development of a new energy technology as has been observed over the past decade is due to the fact that the price level for conventional energies is currently relatively low with even falling tendency, also the energy reserve situation is no concern, and no change is expected for the next years.

On the other hand, upheavals in the international political and economic scenery - collapse of the socialistic world, economic rise of the Asian countries, beginning crisis of the world economy - have occurred at the expenses of enhanced activities in the protection of environment and climate. Furthermore an accelerated international entanglement (globalization) has taken place which leaves national systems in a structural and efficiency crisis. Within the tight international competition, energy costs have become an increasingly more important issue reducing the chance for new technologies with benefits in the long run. Environmental and climate aspects seem to lose societal attention lowering the pressure on the political actors by a worried population; a climate change is too far away to be perceived as a threat. The present goal of energy politics is the achievement of a high level of congruence between supply security, economy, and environmental compatibility meaning an optimized, not necessarily minimized, energy consumption.

After the Kyoto summit in 1997, the reduction of greenhouse gas emission is considered just one among several strategies. There is hope that by means of the new political instruments (tradeable emission certificates, joint projects between industrial and developing countries, and others) of the climate protocoll, the political actors will proceed slowly, but steadily to take internationally sound actions and direct the powerful transnational economy and finance markets towards a low-emission economy and acquire acceptance and the readiness of accepting the expenses by those who are concerned.

The keywords that characterize the strategy for a transition into the world's future energy economy are: conservation, substitution, and diversification strategy, necessary to reduce the burning of fossil fuels and to improve efficiencies, to replace them by environmentally benign energy carriers, and to avoid new and too strong dependencies.

Of course, hydrogen as an energy carrier will be just one contender on the energy market competing with others, e.g., electricity, and at the present stage facing economic problems. The key issues, however, that are able to promote an innovative energy technology based on hydrogen are its environmental benefit in a world with still increasing demand for energy, its safety compared with other fuels, and, in the long run, its potential of mitigating the jeopardy by a critical energy supply situation in future. Also nuclear power represents but one contender among the non-fossil energy carriers, although providing an environmentally benign primary energy source which could be used for hydrogen production. Its major problem is its lack of public acceptance.

Various activities on a larger scale have been described in the report representing important steps in the process of solving the world's energy problem. Highly ambitious projects are currently being pursued with the "World Energy Network" in terms of hydrogen as the future principal energy carrier and with the process heat concept of the HTTR reactor in terms of nuclear as a primary energy provider.

The overall aim of all activities is an exchange of information among all interested parties. The goal could be achieved by establishing international working groups to cover the critical aspects:

- Introduction of "advanced systems", e.g., fuel cells in the conventional field and HTGRs in the nuclear field;
- Definition of a sound safety and risk assessment methodology of non-nuclear technologies including experiments on hydrogen safety;
- Feasibility of the combination of nuclear power plant / chemical plant;
- Analysis of the nuclear hydrogen production potential;
- Definition of fall-back positions with established systems.

Some of these activities are already underway, e.g., in an IAEA Co-ordinated Research Program on Design and Evaluation of Heat Utilization Systems for the HTTR (CRP-4), which is scheduled from 1994 to 1999. International support of these activities is essential.

Chapter 12

SUMMARY

In 1996, the world consumption of primary energy amounted to 8380 million TOE, where 90 % originated from fossil fuels and the remainder from nuclear power and renewable energies. Currently hydro (20 %) and nuclear (17 %) are the only significant non-fossil contributors to electricity production. Burning hydrocarbons means liberation of carbon oxide gases with undesirable side effects: CO_2 is currently labeled as one of the primary causes of the greenhouse effect. After the meetings of the world climate convention in Toronto (1988) and Rio de Janeiro (1992), the third world summit in Kyoto (1997) resulted in a commitment by all industrialized countries to reduce their overall emissions of greenhouse gases by 5.2 % compared with 1990 and 1995 by the year 2008/2012, respectively, an agreement which is for the first time obligatory according to international law.

The second aspect of hydrocarbons is their limited supply on earth. The future energy supply mix will depend on the magnitude of demand growth, changing objectives and social priorities, and the technologies to meet them. A strong demand for more energy (plus 1.6 %/yr) is anticipated. A balanced and stable program without pursuing extreme policies has the best prospects of achieving the lowest long-term social cost, therefore the future should be faced with an array of options and flexible strategies.

Limited stocks of fossil energy resources and pending environmental issues are likely to increase the significance of non-fossil energy forms – water, nuclear, solar, wind, geothermal – in the long run. Nuclear power is considered by many to be the most promising CO_2-free energy technology which has helped to save a significant additional CO_2 impact on the atmosphere. Principally used as base load power plants, nuclear off-peak electricity could be used for hydrogen production. Nuclear power in the "Combined Heat and Power" (CHP) mode can help raise energy conversion efficiencies. Hydrogen as an additional secondary energy carrier for the non-electric market is the driving force for its introduction as future energy carrier. The generation of hydrogen using nuclear energy contributes to fundamental objectives of energy policy: energy security, saving of resources, and protection of the environment. In a future low-emission energy economy, the energy carrier hydrogen could become a strong contender using its advantages compared with other alternatives.

NUCLEAR POWER AND ITS POTENTIAL FOR HYDROGEN GENERATION

More than half of the world primary energy consumption is used as hot water, steam and space heat. Unlike fossil energy carriers, nuclear power is almost exclusively used for commercial electricity production. Clearly nuclear heat production could play a major and important role in the non-electric sector. Nuclear growth depends on the future public perception of the comparative benefits, cost, and risks of alternatives. Based on the comparative evaluation of tangible risks to public health, safety, and environment, nuclear power appears to be a better choice than fossil fuels.

Potential of Nuclear Energy for Combined Heat and Power Production

With respect to a large-scale hydrogen production, nuclear power can play a significant role if used as a provider of electricity in the electrolysis process or as a provider of high-temperature heat in fossil fuel conversion or in thermochemical cycles. An introductory option would be the use of cheap surplus or offpeak electricity. For the introduction of nuclear process heat into the energy market, the estimation of present and future industrial demand for process steam needs to be made first, as well as establishing how nuclear power fits into the energy needs profile. Temperature requirements range from low level (e.g., hot water, district heating, desalination) to a high level of up to 1000 °C (e.g., petrochemical industry, water splitting).

With regard to the heat market, a light-water reactor (LWR) of the 1200 - 1400 MW(e) class has the potential to provide 10,000 GJ/h of low-temperature heat ($\approx$ 320 °C) in the CHP mode. Since hot water and process steam cannot be transported directly over long distances, nuclear power can be economically used only in areas with large heat consumption density like chemical industrial complexes, or in long-distance heating systems where some of the candidate chemical energy transmission systems can be operated at lower temperatures.

The concept of the high-temperature gas-cooled reactor (HTGR) has the important features of high-temperature heat, low-temperature heat, and electricity. Cogeneration applications are estimated to allow efficiencies in the range of 80 - 90 %. Steam applications include the generation of electricity in the steam cycle, the production of process heat in cogeneration with electricity, and the production of district heat. Using energy generating systems in the CHP mode, steam and electricity production in an HTGR or a conventional plant can be accomplished consecutively by routing the steam first through a turbine and then to the steam application system. Steam on a higher temperature level offers the chance to open up new markets for process steam applications in the chemical and petrochemical industries or for enhanced oil recovery. In heat applications, heat is delivered from the helium coolant with an outlet temperature at the high end of 750 - 950 °C, for the conversion of solid and liquid fossil fuels into "clean" gaseous and liquid fuels such as synthesis gas, hydrogen, or methanol.

The HTGR allows the nuclear heat to be utilized for methane reforming and at the same time for steam generation. According to the selected design, the shares of synthetic gas and electricity production are variable over a wide range adjusted by the steam generator inlet temperature. Unlike conventional fossil-fueled reformer tubes, the helium-heated reforming plant connected to an HTGR has to meet the much more stringent requirements of a "nuclear" component in terms of construction, quality assurance, and scheduled checking. In process heat reactor designs with no intermediate heat exchangers, the reforming tube placed in the primary circuit has the function of forming a radioactivity barrier between the primary helium and the process gas. Another major difference between nuclear and conventional steam reforming is the manner of heat input, which is convection transport with the helium in the nuclear version and radiation in the conventional version. The aim of reaching a heat flux density similar to that of the conventional method can be achieved by employing a helium-heated counterflow heat exchanger. Helium under pressure shows excellent heat transfer properties.

Since heat input for the coal gasification process is a significant cost factor, nuclear process heat provided by an HTGR was considered as a substitute for conventional firing. Another important advantage of nuclear coal gasification is its environmental effect since no coal is fired to provide the reaction heat. The main problem, however, is the need to transfer the heat via heat exchangers to the coal gasification process. In pilot facilities, both steam-coal gasification and hydro-gasification have been demonstrated to work successfully under "nuclear" conditions.

The process of hydrogen or methanol production by using a raw iron producing blast furnace also for stack gas utilization, can be realized with a process heat HTGR. A concept for the "non-integrated" employment of an HTGR in the iron and steel industry has been proposed. The nuclear reactor would be sited at a location favorable for the reduction gas generation from which the gas is delivered via a pipeline to the iron and steel industrial sites. A process for the conversion of biomass into methanol has been proposed, where wood is gasified by superheated steam. Electrolytic hydrogen is added to the product gas and then converted to methanol or methane. Both heat and electricity could be provided by an HTGR.

Also the high-temperature heat from HTGRs could be used in the water splitting processes to convert heat energy directly into chemical energy. Three processes are appropriate for application: high-temperature electrolysis, thermochemical cycle, and thermochemical-electric hybrid cycle. The basic design for nuclear power for thermochemical-electric hybrid processes is based on an HTGR to cogenerate low-temperature energy to be used in the steam generator and high-temperature energy to be used in the steam reformer. The heat required for this reaction is taken either from the steam generator or from the previous exothermal reaction.

Chemical energy transmission systems could be most effectively utilized when integrated with a parallel electric transmission system, taking the high-end temperature range for driving the heat pipe and the low-end for generating electricity.

Nuclear Components

Nuclear reformer tube heating with a high-temperature reactor is performed with helium, typically at 950 °C, as the heat source. A counterflow scheme allows the use of internal return pipes for the product gas. Experience in construction and operation was gained with the EVA-I and EVA-II facilities at the Research Center Jülich. The perceived disadvantages of a nuclear steam reformer with its comparatively low heat transfer and its high system pressure can be overcome by design optimization to increase heat input into the process gas and its conversion rate.

An intermediate heat exchanger (IHX) circuit separates the nuclear from the chemical system. It thus minimizes contamination of the process heat exchanger and allows it to be placed outside the reactor containment, prevents water and process gas ingress into the nuclear core in case of a tube rupture, and reduces hydrogen permeation from the process gas into the primary helium as well as tritium permeation in the reverse direction. Drawbacks of an IHX are its technical problems due to the higher temperature compared with the reformer, its additional electricity demand of 50 MW(e) in a 3000 MW(th) process heat HTGR, and the fact that it presents an additional component which may fail. The construction of the IHX for the Japanese HTTR was successfully finished and installed in the reactor building in 1995.

SAFETY CONSIDERATIONS CONCERNING NUCLEAR POWER FOR PROCESS HEAT AND/OR HYDROGEN PRODUCTION

Safety Design of Nuclear Heat Utilization Systems

After the severe accidents at the Three Mile Island and Chernobyl nuclear power stations, new designs with improved safety features have been proposed focusing on more intensive consideration of passive safety characteristics. A much more far-reaching demand for the introduction of innovative nuclear power plants in the future is made on a design such that fission product release is made impossible or, at least, restricted to the plant itself.

One possibility of assuring the restriction of radioactivity to the primary circuit is the deployment of an intermediate loop as an additional safety barrier to the system. In such an arrangement, all heat consuming components are physically separated from the primary circuit by means of an intermediate heat exchanger. In the case of heat consuming components to be arranged in the primary circuit, they have to act themselves as a safety barrier.

The deposition of fission products on primary circuit surfaces and, in particular, on the reformer tube walls causes difficulties during maintenance and catalyst refilling procedures. Cesium and silver isotopes are of major concern. Numerous experimental and theoretical efforts have been made to examine the plateout distribution of fission products in the primary circuit both under normal operating and accident conditions. Experimental data obtained from in-pile and out-of-pile deposition loops as well as from operating HTGRs were taken to derive plateout parameters and to validate the corresponding calculation models.

In nuclear process heat plants, hydrogen and tritium exhibit high mobility at 950 °C causing permeation through the walls of the heat exchanging components. Tritium produced in the primary circuit could permeate into the product gas and cause a radiation problem to the consumer. In the opposite direction, hydrogen from the secondary circuit could diffuse into the primary circuit to cause corrosion of the fuel elements and of the graphite liner in the core with the formation of methane. Possibilities of reducing the permeation streams are the formation of oxide layers or, as active measures, an improved design of the gas purification system or the construction of an intermediate circuit between the primary and secondary circuit to serve as a sink for both hydrogen and tritium.

Tests in the EVA-II plant have shown that its operation at the same load is possible even if up to 30 % of the reforming tubes were blocked, meaning that isolation of single tubes would not disturb the operation thus increasing the plant's flexibility. Analytical studies have been conducted at JAERI to investigate the steam generator as a passive heat sink in case of a failure of the heat removal system of the reformer to ensure its coolability.

The system pressure in the gasifier is designed to be somewhat higher compared with the pressure in the primary circuit, meaning that in case of a ruptured helium line no radioactivity could escape from the primary system, but product gas and steam as well as coal particles could enter the primary helium circuit. Leakage will be detected by humidity sensors, helium lines shut off from the process gas circuit. The basic consequences of the steam entrainment of a steam producing HTGR are equivalent to those of a water ingress accident into the core.

Gas Explosion Research

Any process heat plant design implies piping through the containment to connect the reactor vessel with the chemical plant. The fracture of a pipe could result in the accumulation of a flammable gas mixture in the containment. Precautions must be taken to minimize the risk of a fire or gas explosion such as avoidance of explosive gas ingress, proper detection devices, sufficient safety distances, inerting, appropriate layout of secondary coolant boundary, explosion-proofed wall, plant isolation valve.

The most important hydrogen source in an LWR core meltdown accident is the fuel element cladding/water reaction at temperatures > 1000 °C. Steam and hydrogen will be released simultaneously from the reactor vessel into the containment. The most likely mode of H_2 combustion in the containment is a deflagration as was observed in the TMI accident. Intercell flow distribution and local steam condensation rates have a significant influence on the local gas fractions in each compartment. A rapid condensation if possible may convert an inert atmosphere into a detonatable mixture, which would threaten the containment integrity and the survival of safety equipment. Assuming a 75 % cladding/water reaction, the potential of DDT is practically present in all nuclear containments. A radiological problem arises with the possible extensive formation of aerosols carrying CsI which decomposes during H_2 combustion and liberates volatile iodine.

Hydrogen-air-steam combustion experiments have been conducted to simulate local detonations in a nuclear containment and to validate the respective numerical detonation codes. Experimental facilities used were the Battelle model containment and the containment of the decommissioned HDR in Germany as well as one-compartment vessels at Hanford and Nevada Test Site in the USA or the RUT facility in Russia. Many codes have been developed to simulate the transport, convective mixing, and combustion of hydrogen in a containment building. State-of-the-art are CFD models or lumped parameter models with successful reproduction of, e.g., thermal stratification phenomena.

Research programs on gas explosions outside the nuclear containment have been initiated in various countries focusing on specific aspects of the offsite explosion and the consequences of flammable gas clouds, in particular, the impact of the pressure wave on the nuclear containment building. Evaluation of the status of knowledge on hydrogen's and other fuels' combustion behavior within the German LWR safety program has shown that existing safety margins of modern nuclear containments guarantee a safe enclosure.

A variety of methods can be employed as hydrogen mitigation systems. Mixing devices and venting systems can prevent locally high H_2 concentrations in the containment atmosphere. Inerting, which is widely applied, limits the supply of oxygen. Recombiners allow an immediate and continuous H_2 removal with no power supply required. The deliberate ignition of lean mixtures appears simple and easy, but it represents some challenge to building and equipment because of the difficulty of anticipating the consequences. In any case, the strategy applied should depend on the actual state of the building during and after the accident.

The PNP gas cloud safety program focused on the formation and explosion of clouds of the process gases H_2, CO, air and other representative combustible gases such as acetylene, ethylene, propane, methane, and the damage caused by the blast wave to simple structural elements (window pane, brick wall) after fast deflagration and detonation.

The release of product or feed gas into the environment and the formation of a flammable gas cloud could result in heat radiation and blast wave impact from fire / explosion. For the German PNP design, it was proposed to ensure that the gas be routed through inerted channels away from the gasifier and flared at a safe spot. The safety concept of the Japanese HTTR includes the appropriate blast wave resistance design of building structures, gas leak detection device, fire extinguishing system, emergency shutoff valve, safety distance which could be reduced by fireproof walls.

WORLD ACTIVITIES ON NUCLEAR POWER AND ITS POTENTIAL USE FOR HYDROGEN PRODUCTION

Two decades of enormous economic growth in the People's Republic of China have led to a significant need for energy and electricity, and the demand for more is greatly increasing. Chinese primary energy consumption is dominated by coal, but nuclear power is expected to gain more importance for base load electricity, for district heating, and for the process heat industries. Presently there are 23 hydrogen production units in operation with a total capacity of 582,600 Nm^3/h.

The HTR-10, under construction at Tsinghua University since 1995, is designed as a test reactor for multipurpose research. In a first phase, the HTR-10 is planned to be operated in connection with a steam turbine which works in a cogeneration mode to provide electricity and heat. In a second phase, the coolant outlet temperature will be raised to 900 °C to operate the HTR-10 in a gas turbine cycle. A long-term test program for nuclear process heat applications has been proposed in different phases including simulation experiments for nuclear coal gasification on a laboratory scale and in a pilot facility in connection with the HTR-10. A concept was proposed exploiting very heavy oil fields with an estimated total amount of 90 million t in the north-east of China by the use of nuclear process steam. HTGR designs with 1000 MW(th) were shown to be able to provide steam with the required parameters to open up these resources.

Primary energy consumption in Germany totaled 340 million TOE in 1995 with significant contributions from oil (40 %), coal (27 %), gas (20 %), and nuclear (10 %). The consumption of primary energy has been stagnant since the 1980s due to energy saving and industrial restructuring while gross internal production as well as electricity consumption have still been growing. Growth of the latter, however, has been observed to be getting slower.

The 46 MW(th) high-temperature gas-cooled AVR reactor in Jülich as a first-of-its-kind has been in operation for 21 years with a high availability demonstrating that nuclear power can be converted into high-temperature heat. For more than 10 years, the reactor was operated with an average outlet temperature of 950 °C. The reactor allowed successful testing of a large amount of high quality HTGR fuel elements. The follow-up pebble bed reactor THTR-300 has demonstrated the expected large-scale applicability of HTGR technology. The present German HTGR reference design for electricity production is the 200 MW(th) HTR-MODUL with a large number of inherent safety features; a variant with 170 MW(th) has been designed for process heat applications.

The "Prototype Plant Nuclear Process Heat" (PNP) project was founded in 1972 with the goals of developing HTGRs for high gas outlet temperatures of 950 °C as a source of process heat to test components for heat transfer to the process plant, and to demonstrate processes and experimental facilities for coal gasification. The technical feasibility of a nuclear process heat reactor for the refinement of coal has been established, main components developed, and its basic licensing capability confirmed. Studies on the technical feasibility and economic competitiveness of the processes for nuclear coal refinement were completed in 1987.

The steam reforming process of methane was experimentally investigated in the "Nuclear Long-Distance Energy" (NFE) project. Two different bundles of steam reformer tubes were tested. Convective helium heating was verified for both designs. The complete experimental chemical energy transmission system based on steam reforming of methane, "EVA / ADAM", was operated for more than 10,000 hours including steady state conditions at both full and partial load, transient procedures, and also special test situations such as tube blockage. From 1976 to 1984, catalytic and non-catalytic steam-coal gasification was established and successfully tested in a 1.2 MW semi-technical scale experimental facility. The maximum capacity was 230 kg/h of hard coal. The process of hydro-gasification of lignite as an alternative was successfully verified in a pilot plant with a throughput of 9.6 t/h of lignite corresponding to a power of 50 MW.

Starting in 1972, the project of a closed-cycle "High-Temperature Reactor with Helium Turbine of Large Power", HHT, had the main goals of obtaining a higher efficiency and reducing the number of components. But it was also considered to have a broad variety of utilizations, in particular, in the lower process temperature range. Research activities included a materials research program to investigate the lifetime of the turbine, hot gas duct, and insulation materials in a helium atmosphere, the development and testing of the hot gas duct and insulation, and the investigation of fission product behavior in the primary helium circuit.

Research work has been done on the application of thermochemical (hybrid) cycle processes for the production of hydrogen by proposing an HTGR for the cogeneration of high-temperature energy for process heat and low-temperature energy for electricity production.

Indonesia is an oil and gas producing country with an increasing domestic consumption rate. In the 1970s, several giant natural gas fields such as Natuna were discovered making gas a major export commodity. Minimizing the emission of carbon dioxide into the atmosphere has suggested the nuclear option in exploiting the Natuna gas field. Several alternatives have been identified as being feasible and economically competitive, distinguished by the desired fuel product and by the consumption of CO_2 which is an unwanted component in the Natuna gas. A feasibility study has been initiated by the IAEA to investigate the application of the HTGR for cogeneration purposes of CO_2 conversion, desalination, and H_2 production in terms of economy and technology.

The significant growth of Japan's economy in the 1960s was based on cheap petroleum imports which, however, ceased with the first oil crisis. The largest share in Japan's electricity production of $907*10^9$ kWh (1993) is provided by nuclear power with 34 %; others are natural gas, oil, hydro, and coal. Japan depends heavily on imported energy; therefore intensive research efforts are being conducted on new energy carriers. The economics of the many different designs for future reactors currently being pursued are considered promising and are expected to form Japan's next generation of reactors.

Starting in 1991, the 30 MW(th) High-Temperature Engineering Test Reactor, HTTR, is being constructed in Oarai and is expected to start its operation in summer 1998. The helium-cooled reactor will have an outlet temperature of 850 °C in the first stage and will be the first of its kind with an outlet temperature of 950 °C to be later connected to a high-temperature process heat utilization system; its demonstration is planned for the second core. Top candidate to be tested by JAERI in connection with the HTTR is steam reforming of natural gas for hydrogen and methanol coproduction including carbon dioxide recycling. The goal is the production of 1390 Nm^3/h of hydrogen plus 1930 kg/h of methanol, while the input is 950 kg/h of natural gas plus 10 MW process heat, which is introduced via the He-He intermediate heat exchanger.

A bench-scale test facility for hydrogen production using the thermochemical iodine-sulfur process has been established at JAERI. Its feasibility was successfully demonstrated in a lab-scale apparatus. Further demonstration steps are the employment of a metallic reactor for hydrogen production and a scale-up process to a 100 Nm^3/h rate. The bromine-calcium-iron or UT-3 process is considered in Japan to be superior to many other thermochemical cycles. One aspect of the main ongoing research efforts is its combination with an HTGR for hydrogen and electricity cogeneration. Another candidate for nuclear process heat application is hydrogen production by means of high-temperature electrolysis of steam. This has been tested by JAERI in a bench-scale arrangement of 12 tubular-type cells at a temperature of 850 °C. The construction of a prototype system is planned with a capacity of 10 and later 100 Nm^3/h.

The FAPIG organized a working group to study how to use heat from HTGRs to mitigate environmental and resource problems, to stabilize supply, and to promote effective use of energy. Three types of heat utilization plants have been modeled, for each of which system outline, basic plant layout, social effects, and technical issues were studied: a cogeneration plant for a typical chemical plant with an estimated overall efficiency of 74 %, a coal gasification plant to produce 1700 t/d of product gas, and a hydrogen production plant.

In the Russian Federation, about 20 different technologies have been studied in various industrial sectors with the possible use of an HTGR including the production of hydrogen, synthetic fuel, or methanol, and the reprocessing of oil. The conceptual design of a 200 MW(th) modular high-temperature gas-cooled reactor, VGM, has been developed and is intended to be used for process heat applications. To assure a high level of safety, the system is designed to have a helium-to-helium IHX and a helium-to-silicon oil process heat exchanger (PHX).

Within the United States HTGR program, a reference conceptual design of an 1170 MW(th) HTGR plant has been developed based on a prismatic core for steam / electricity cogeneration, which is readily adaptable to various applications such as a "Sensible Energy Storage" system based on a molten salt circuit for thermal energy storage and transport, a gas turbine cogeneration system, or a process heat system employing the chemical reforming process with synthetic fuel or chemical feedstock as the principal output.

A direct-cycle, modular variant, MHTGR-GT, has been designed as a second generation meltdown-proof nuclear power plant combining the experience of both gas-cooled reactor technology and industrial gas-turbine technology. The thermal reactor power is 450 MW with a projected efficiency of 46 %. A characteristic feature of the closed-loop Brayton cycle is its potential, besides electricity generation, for efficiently utilizing waste heat, e.g., for desalination, district heating, or steam generation.

CONVENTIONAL AND ADVANCED HYDROGEN PRODUCTION METHODS

Decomposition of Fossil Fuels

An easy and the most widely used method of hydrogen generation is steam reforming of natural gas, which is clean and available in large amounts. During the process, natural gas is mixed with steam to react at high temperatures, typically > 500 °C, and relatively low pressures in the presence of a nickel catalyst. In the homogeneous water-gas shift reaction, the equilibrium is moved towards more CO_2 in order to achieve a higher H_2 yield and to preclude carbon deposition due to the Boudouard reaction. The yield of the reforming process is a mixture of H_2, CO, CO_2, plus residual steam and methane. The mixture of H_2 and CO left after purification is called synthesis gas.

If the steam is completely or partly replaced by carbon dioxide, the H_2 to CO ratio is shifted towards more CO. This involves an environmental benefit, because two greenhouse gases (CH_4 and CO_2) are combined, resulting in a product gas which might be more favorable for certain applications, e.g., methanol. However, currently no industrial technology for the CO_2 reforming of methane is established. The reasons for this are the rapid deactivation of conventional catalysts if used without the presence of steam, and the relatively high soot formation.

Partial oxidation is able to convert methane and other hydrocarbons, catalyzed or non-catalyzed, at temperatures between 1100 and 1500 °C. Despite its lower efficiency compared with steam reforming, partial oxidation provides, on the other hand, exothermicity and a greater selectivity for synthesis gas production as well as advantages for certain applications such as compactness, rapid startup or load change, lower overall cost. If steam is added to the fuel and the oxidant, it is possible to heat balance the exothermal partial oxidation reaction with the endothermal reforming reaction, meaning that no external heat source (autothermal) is required.

An alternative to the steam reforming of methane is single-step thermocatalytic decomposition or thermal cracking. Methane (and other hydrocarbons) decompose at temperatures between 700 and 980 °C and if no air is present to form hydrogen and carbon. Cracking was studied for various catalysts in both continuous flow and pulse catalytic reactors. Variations in the operational parameters were found to produce CH_4-H_2 mixtures with a wide range of hydrogen concentrations, from 30 to 98 vol%.

Conventional steam reforming is a mature and well-established technology practiced on an industrial scale and currently representing the least expensive H_2 production method. Today's reformer plants for hydrogen production vary in size, from typically around 100 Nm^3/h capacity up to the largest currently existing with a maximum H_2 production rate of 140,000 Nm^3/h. Recent reformer improvement developments have focused on high efficiency, good load changing capability, and low cost through use of cheaper materials and production methods. Hydrogen purity is up to 99.99 %. Small size and suitability on a small scale makes them beneficial for integration into a fuel cell power plant. Fuel cell manufacturers are developing advanced miniaturized designs for vehicle or household applications which allow the reforming process to take place inside the fuel cell stack. A future high-temperature fuel cell application could be the production of hydrogen, where more H_2 is generated in the internal reforming step than is converted into electricity.

The conversion of coal to both liquid and gaseous hydrocarbons has been commercially deployed worldwide. Gas production from coal is realized by means of a gasification medium which reacts with the coal at temperatures > 800 °C. All organic constituents of the coal will be converted with sufficiently long reaction times. If air or oxygen is injected into the gasifier, part of the coal is burnt directly leading to an autothermal reaction.

For the steam-coal gasification process, steam of 600 - 1000 °C is needed to convert the organic solid in the heterogeneous water gas reaction. The production of hydrogen and carbon monoxide is optimal at high temperatures and low pressures. The heat of the hot gas is recuperated for use in the production of high-pressure steam. Coal gasification with oxygen and steam is conventional chemical engineering and is employed to generate about 15 % of the world hydrogen production and primarily used for ammonia synthesis in the fertilizer industry. Different types of autothermal coal gasification used on a large scale are represented by the Lurgi, Winkler, Koppers-Totzek processes or modifications of them. There is also the option of implementing the steam-coal gasification process in an Integrated Gasification Combined Cycle (IGCC) power system, which is currently considered the cleanest and most efficient (34 → 38 %) coal-fueled technique so far.

In hydro-gasification, coal is converted to synthetic natural gas in a fluidized bed at temperatures of around 800 °C in an exothermal reaction. Parallel reactions are the steam reforming and the water-gas shift reactions. In order to obtain a high conversion rate of coal, the methane fraction in the product gas of the reforming step (which will then be the feed gas for the hydro-gasification) should be no higher than 5 %, which requires a low-temperature separation step. The advantage of hydro-gasification compared with steam-coal gasification is its 200 K lower pre-heating temperature which reduces potential corrosive attack. A major drawback, however, is the relatively large amount of residual coke of up to 40 %. Standardized reformer equipment for power industries is available.

Other sources of hydrogen are provided by the conversion of oil or other feedstocks such as municipal solid waste and biomass, decomposition of hydrogen sulfide, or recovery from refinery offgases.

Splitting of Water

The electrolysis of water is usually applied if cheap electricity is available or high-purity hydrogen is required. The electrolytic decomposition of water requires electric energy which is dependent on the reaction enthalpy and the temperature. Typical cell voltages are about 1.8 to 2.0 V, which translate into efficiencies of 60 - 70 %. The electrolysis of steam at higher temperatures (900 - 1000 °C) reduces the electric energy required and lowers the activation barriers at the electrolyte surfaces resulting in higher efficiencies.

Alkaline water electrolysis is the only large-scale method to be commercialized, where the H_2 is actually a byproduct of chlorine production. Solid polymer electrolyte water electrolysis is considered to be a promising method because it can operate at high current densities and has the advantages of cell compactness, simplicity in design and operation as well as lack of corrosion problems. At the high end, 800 - 1000 °C, zirconia-based ceramic membranes are used, which show a high conductivity for oxygen ions at operating temperatures. The electricity demand at 1000 °C is 30 % lower compared with that of room temperature. The high-temperature technology is able to create so-called regenerative cells which can work either in the electrolyzer mode or in the fuel cell mode.

In the thermochemical method, the splitting process is subdivided into different partial reactions, each running on a lower temperature level. A large number of possible cycles has been tested and checked in terms of appropriate reaction temperatures and velocities and in the economic respect. Major problems arise due to the large material flows and the introduction of impurities. The main problem is to achieve satisfactory overall energy efficiencies which are no higher than around 40 % and, in connection with severe materials and equipment design difficulties, do not allow large-scale thermochemical process applications so far. Systems investigated include metal-halide, bromine-calcium-iron (UT-3), sulfuric acid methanol process, and iron-chlorine processes. One of the thermochemical cycles with the most considerable potential is the iodine-sulfur (IS) process developed by General Atomics, which has demonstrated its feasibility for many years and is now being pursued at JAERI.

Thermochemical hybrid cycles offer the possibility of running low-temperature reactions on electricity. The expectations for realization of hybrid processes are similar to those for purely thermochemical processes. Various hybrid processes are energetically possible, but not always practicable. Important criteria are the minimum voltage for the electrolysis step, realizability, efficiency. The sulfuric acid hybrid or Westinghouse process is expected to reduce material streams as compared with the IS process. The electric energy demand here is a factor of 7 (in reality 3 - 4) lower than in the electrolytic water splitting process. Technological improvements are still possible.

Photolytic processes use light energy to promote the water splitting reaction. It is of great interest because solar energy can provide an unlimited energy source for hydrogen production. In photoelectrochemical systems, inorganic materials are being used for direct conversion of (sun) light into hydrogen at a semiconductor electrode. In photobiological systems, hydrogen is produced as a result of the way certain biological organisms use sunlight. Some photosynthetic algae and bacteria absorb energy from sunlight and use it for water splitting in the process of generating plant tissue or creating heavier hydrocarbons or oxygen for assimilation. The commercialization of the photosynthetic processes requires a drastic increase of the conversion efficiency as well as an improvement and upgrading of the microorganisms. Anaerobic bacteria could be used for pre-treatment of waste water to degrade organic substances that the photosynthetic bacteria are not able to handle.

If hydrogen production processes are compared, the interdependence of efficiency, capital investment and value of the byproduct has to be taken into account. Reforming of natural gas and partial oxidation of heavy oils are presently the least expensive and most frequently applied methods of hydrogen production. Electrolytic hydrogen has a small, but stable market; it is preferred if there is a fluctuating demand, a need for small amounts or the requirement for high-purity hydrogen. Since coal is abundantly available in the world, R&D efforts should concentrate on coal-based processes; the advanced processes of methane cracking and coal cracking (HYDROCARB) have a huge economic potential.

Liquefaction of Hydrogen

The minimum (theoretical) work required for the liquefaction of hydrogen is 3.92 kWh/kg; a realistic value is about 10 kWh/kg or approx. 30 % of the H_2 net heat of combustion. In contrast to the gases in air, the production and liquefaction of hydrogen is conducted in two separate energy-intensive steps. Conventional processes used are the Linde-Hampson process and the Claude process. The magnetic refrigeration method looks promising, because it offers a compact cooling system with an extremely long lifetime, lower capital investment and it promises higher efficiencies. The liquefaction plants in the world presently produce liquid hydrogen (LH_2) with a total capacity of 265 t/d but not more than 19 t/d in Europe. Based on current experience, the construction of plants with a capacity of up to 250 t/d is expected to be feasible, the goal in Japan's WE-NET project is even 600 t/d.

STORAGE AND TRANSPORT OF HYDROGEN

The commercial provision of energy worldwide has turned into a very complex structure, not limited by national boundaries. Hydrogen storage and transport technologies have to be developed to fit these structures. Relevant issues and R&D activities are summarized below.

Storage of Hydrogen

Gaseous hydrogen at ambient temperature can be compressed in high pressure tanks which are easy to handle. Pressures range from < 1 MPa to around 30 MPa. Pressure vessels must be periodically tested and inspected to ensure their safety. A classical storage type is no-vessel underground mass storage used in seasonal peak consumption periods. Geological formations with porous permeable layers underneath a dense layer are chosen, which can be either an aquifer or a depleted natural gas resource or a specifically formed cavern in a salt mine. Typical ratios of the capacities of a 100 km high-pressure pipeline section to cavern storage to porous storage are 70 to 1300 to 20,000.

Liquid hydrogen must be stored in a superinsulated tank and even then depending on the insulation quality and the surface-to-volume ratio a certain fraction is an unavoidable boiloff to keep the rest cold. A supporting structure and interconnections between the fluid container and the outer vessel have to assure that the inner shell can freely undergo contraction / expansion. A multilayer insulation and a vacuum jacket inside help minimize the transport of heat into the cryogen. The largest LH_2 tank constructed so far is the NASA 3407 m^3 vacuum perlite-insulated spherical storage tank used in the US space shuttle program. The tank has a boiloff rate of 0.03 % per day. Improved concepts of insulations have been developed for future large-size LH_2 storage tanks with a volume of about 24,400 m^3. Projected tanks for large-scale LH_2 storage within the WE-NET project have a storage capacity of 50,000 m^3. Target boiloff is 0.1 % per day.

The safety of LH_2 storage tanks has been investigated in extensive experiments. Passenger car tanks have been exposed to deformation and perforation, as well as fire and burst testing to check the performance in conceivable traffic accidents. Tests with a 61 m^3 container representative of maritime transportation were conducted, the first with an LH_2 tank of that size, to investigate the thermodynamic behavior of the LH_2 in the tank.

Metal hydride is an intermetallic compound that traps hydrogen at moderate pressures. It stores large amounts of hydrogen in an exothermal diffusional process. Some drawbacks are its cost and its heavy weight, and its requirement for very pure hydrogen. Metal hydride advantages include convenience, compactness, stable storage, and intrinsic safety.

New classes of hydrogen storage are nanocrystalline metal hydrides, which are polycrystals with a typical grain size < 20 nm, or high-strength glass microspheres with 25 - 500 μm in diameter and with 1 μm wall thickness, which are loaded in a high pressure bath of hydrogen. After cooling the hydrogen is trapped. Engineered microspheres could make storage and transport of large amounts of hydrogen much more efficient. A qualitative step forward appears to be the discovery of graphite fibers which were reported to store 30 l of H_2 per gram; it would allow a cruising range of 8000 km for a H_2 fueled car. The tremendous storage capability, however, is still unexplained and needs further verification.

Transport of Hydrogen

In most countries, pipeline systems for natural gas serve both transportation and distribution purposes. The transport of hydrogen in the same energy quantity would require a 3.3 times higher compression because of its lower heat of combustion per unit volume. Transport of gaseous hydrogen in a pipeline system is a technology which has long been applied. More than 750 km of hydrogen pipelines (1990) have been put in place worldwide. Transportation cost is expected to be in the same order as natural gas for regional distribution and to be higher for large-scale transportation.

Vehicle-bound distribution systems for both gaseous and liquid hydrogen encompass trucks, rail cars and ships. A tank ship transport of LH_2 is reasonable if transported over long distances. The comparatively low volumetric energy density of LH_2, however, requires very large tank ships and a much higher fraction of the hydrogen transported is needed for the transport itself.

Chemical Energy Transmission Systems

The key components of a chemical energy transmission system or a chemical heat pipe are a primary energy source to provide heat, an input catalyst reactor where in an endothermal reaction energy is stored in newly created products, and an output catalyst converter, where the reverse exothermal chemical reaction helps to extract the stored heat for further consumption.

The energy transport system by steam reforming / methanation, also known as EVA/ADAM, was theoretically and experimentally investigated on a representative scale and demonstrated its technical performance and efficiency as a thermochemical pipeline system. A complete EVA/ADAM system was successfully operated in Germany under the realistic conditions of an industrial application with a transported power of 5.4 MW. Hydrogen evolution from cyclohexanes at the demand site and the reverse reaction at the supply site offers the advantages of safe and commonly used transport at ambient temperature in chemical tank ships or trucks and mild reaction conditions. The advantage of ammonia dissociation is the complete absence of any side reactions. The fact that ammonia condenses at around room temperature and separates from the reactant mixture allows storage of feedstock for both endothermal and exothermal reaction in the same vessel.

Chemical heat pump systems are important if the utilization of low-quality heats ($\approx$ 80 °C), e.g., solar or geothermal or nuclear heat, waste heat in factories, is considered for heat storage and temperature upgrading.

APPLICATIONS OF HYDROGEN

Hydrogen has many and versatile uses: It plays a significant role as a chemical feedstock for industrial and petrochemical processes, e.g., in the conversion of coal into clean synthetic fuels or in the generation of process heat. Furthermore it possesses a huge potential as a direct fuel for producing mechanical energy, heat, or electricity for a future large-scale use.

Hydrogen as Raw Material

About 40 % of the hydrogen produced worldwide is consumed in ammonia synthesis. Feed gas for the steam reformer is methane or gasoline. Adding air in a secondary reformer leads to partial oxidation of the residual methane and of the CO. After separation of the CO_2, the product gas is a mixture of nitrogen and hydrogen whose ratio (desired 1:3) is adjusted by the operating conditions. NH_3 production on an industrial scale allows a daily output of 1000 - 2000 t consuming 80,000 - 160,000 Nm^3/h of H_2.

In the conventional method for the generation of methanol from synthesis gas, a mixture of CO, CO_2, and H_2 is compressed and introduced into a fixed-bed catalytic reactor. The reactions are exothermal and volume-reducing, thus low temperatures and high overpressures are desirable. A catalyst is required to maximize methanol output. Methanol production generates a surplus of hydrogen which can, by adding CO_2, be utilized to increase the methanol yield. Methanol is basically used in the chemical industry as intermediate product. It is gaining further attention as secondary energy carrier with less CO_2 emission, e.g., as a vehicle fuel.

Steady utilization of hydrogen in refineries commenced more than 50 years ago. It is mainly used for hydro-cracking and hydro-treating in upgrading processes. In the catalytic hydrogenation process, hydrogen is used to convert coal to gasoline and to remove sulfur, oxygen, and nitrogen. Rigid specifications concerning the contents of the catalyst poison CO have to be met. A purity of 98 % hydrogen is desirable. The Fischer-Tropsch synthesis is the catalytic hydrogenation of CO to form hydrocarbons to be used as raw material in the petrochemical industry. The high purity of vaporized LH_2 is utilized in the semiconductor industry.

Hydrogen as a Fuel

Liquid hydrogen was early recognized to be an important rocket and aircraft fuel. Air-breathing engines with supersonic combustion, scramjet, offer an excellent thrust potential. With its high combustion heat per mass unit, fast ignition and high heat sink capacity, hydrogen is a perfect candidate, in particular, for supersonic applications. In addition, it avoids all pollutants of fossil fuels except for NOX. The main penalty is the storage volume of the hydrogen tanks which is larger than kerosene by a factor of about four. Hydrogen in space transportation is being used by the USA, Russia, Europe, China, Japan, and India.

Internal combustion engines that run on hydrogen are very efficient, because they take advantage of the fast-burn and far-lean combustion characteristics of hydrogen. Since the 1970s, many automobile companies have designed and operated prototypes of cars or trucks. It was shown that the most practicable solution for onboard H_2 storage is liquid hydrogen.

Catalytic combustion of hydrogen exhibits many advantages in comparison with flame combustion. It occurs at low temperatures, is safe and leads to a very high conversion of the burning gas (99.9 %). The NOX formation as present in conventional combustion at temperatures of about 1700 K is almost completely suppressed.

The fuel cell is an energy conversion device that works in reverse of electrolysis. In the cell, the energy of a fuel is directly converted in an electrochemical reaction into D.C. electricity with an approx. 60 - 70 % efficiency. The principal advantages of a fuel cell in comparison with the indirect energy conversion (which goes via heat first) are its cleanness and its high efficiency, which is nearly constant independent of size and operating range. Thus configurations of power plants could range from kilowatts to hundreds of megawatts. Heat from the electrochemical reaction is available for cogeneration application.

The low-temperature polymer electrolyte and alkaline fuel cells are an efficient, compact, robust, and quiet method of generating electricity. They have the highest power density of all cell types, good load change behavior and good efficiency at partial load, thus being ideally appropriate for mobile applications. The indirect methanol fuel cell operates on liquid or gaseous methanol combined with a reforming process and offers a good storage capability in mobile systems. Most practical experience has been gained in the operation of phosporic acid fuel cells (PAFC). The molten carbonate fuel cell (MCFC) can be operated with hydrogen, methanol, methane or coal gas with external or with partial or full internal reformation. The solid oxide fuel cell (SOFC) is attractive because of its very high temperature which allows fast chemical reactions, but on the other hand implies stringent requirements for materials development and construction. SOFC converts gaseous hydrocarbons either directly or after internal reforming with a very low emission level. Stationary applications of fuel cells embrace large-scale central power generation, distributed generation, and cogeneration. The potential of fuel cell power plants is strongly related to the global demand for new power and heat capacity. A cogeneration system with waste heat recovery can achieve efficiencies of up to 80 %. PAFC, MCFC, and SOFC are currently the strongest contenders for commercial stationary power generation.

Hydrogen is an ideal fuel for gas turbines. Due to its rapid mixing with air, a smaller combustion chamber is sufficient and the efficiency is higher compared with conventional fuels. Gas turbines modified for liquid hydrogen operation yield an up to 10 % higher thermal efficiency and output compared with fossil-fueled turbines. For systems with advanced heat exchange, efficiencies of more than 50 % are estimated to be achievable. The combustion is stable, largely free of pollutants, and favorable for lifetime and maintenance. Of disadvantage is NOX production at high flame temperatures. The H_2-O_2 steam generator as a novel power plant component is able to provide instantaneously spinning reserve capacity upon demand. Combustion heat is used to vaporize feed water where the steam is routed to the intermediate pressure steam turbine.

SAFETY RISKS OF A LARGE-SCALE HYDROGEN APPLICATION

Hydrogen gas is colorless, odorless, tasteless, non-toxic, and undetectable for human senses. If released in a confined area, hydrogen can cause suffocation by dilution of the oxygen content. Mixtures of hydrogen with air are flammable over a wide range of concentrations. Explosion of the mixture can occur with very low impact. The hydrogen flame is nonluminous, comparatively hot, but hardly radiates any heat. The investigation of the combustion behavior of hydrogen connected with the pressure development under accident conditions is the basis of all safety-related considerations.

The broad introduction of hydrogen as an energy carrier requires a concomitant and prognostic evaluation of its safety and risk. The inadvertant release of hydrogen caused by a leak or spillage and its mixing with air creates explosion hazards making mandatory the assessment of conceivable risks and its hazard potential after an inadvertant release. Systematic prognosis procedures are applied in probabilistic safety and risk analyses. The tools for the deterministic analysis are calculation models to simulate all the steps of an accident scenario as realistically as possible. Model validation is based on the evaluation of experiments and postexamination of previous accidents.

NASA experience with hydrogen began in the 1950s, when hydrogen was considered the principal liquid rocket fuel. Safety engineering soon started to address hydrogen hazards and to develop procedures for the safe operation of equipment and facilities. The large-scale industrial application of hydrogen has led to a safety concept with a scale of safety measures aimed at minimizing risks by preventive safety measures and by mitigation measures.

Hydrogen has long been recognized to have a deleterious effect on metals by changing their physical properties. Depending on the type of appearance of this phenomenon, named embrittlement, a distinction is made between hydrogen reaction embrittlement, internal hydrogen embrittlement, and environmental hydrogen embrittlement. The effect is strongly connected with locally high hydrogen concentrations which can be caused by stress-enhanced diffusion rates to lattice defects and reaction sites to initiate cracks. Despite of the fact that some metals can become brittle due to hydrogen or hydrogen compounds, there is a good safety record which is explained by possibly conservative assumptions for the design stress and a scheduled retesting of the vessels.

The evaluation of reports and statistics of accidents with hydrogen has revealed a number of accidents in the order of a few cases per year. The Hindenburg accident in 1937 at Lakehurst is very familiar to the public. However, the airship did not explode, it tragically caught fire due to a highly combustible skin coating used at that time. The accident with the Challenger Space Shuttle was presumably caused by so-called "phantom" fires resulting from undetected small cryogenic hydrogen leakages from the external tank and their early ignition by the anomalous plume from the rocket booster. The spectacular accident in Hanau in 1991 demonstrated the consequences to be expected from the catastrophic failure of a tank with pressurized hydrogen. The explosion resulted from a fatigue rupture near a longitudinal welding seam.

Although hydrogen has a reputation as a particularly dangerous fuel, the overall statement was made that the technology of handling hydrogen as a high-pressure gas or as a liquid is successful and safe, primarily based on the existence of well-trained personnel and extreme concern about system reliability. Measures for accident prevention are the appropriate choice of materials, coatings, adsorption layers, the deployment of stainless steel liners in composite vessels and piping, and proper welding procedures.

Liquid Hydrogen Pool Spreading and Atmospheric Dispersion of Hydrogen Gas Clouds

Starting from large-scale liquid fuel (LNG, LPG) maritime transportation and application in the 1970s, interest increased in the assessment of the consequences of cryogen spill accidents. If hydrogen is released in its liquid form, it can accumulate and form a cryogenic pool on the ground and immediately starts to vaporize. A cutoff of the mass input results in a breakup of the pool from the central release point creating an inner pool front. The ring-shaped pool then recedes from both sides until it has completely died away. LH_2 vaporization is determined by heat transport into the pool. Of all contributions, heat transfer by conduction from the "hot" ground plays the dominant role. The most detailed investigation of LH_2 pool spreading so far was conducted by the Research Center Jülich during a series of LH_2 spill experiments in 1994, where the LH_2 pool size on water and on a solid ground was measured as a function of time and location.

State-of-the-art modeling of cryogenic pool spreading and vaporization is based on the solution of the so-called shallow-layer differential equations. This allows the tracking of the dynamic behavior of pool growth and recession and calculates pool height and velocity as a function of time and location. Respective calculation models with successful performance have been implemented in the British GASP code and in the German LAUV code.

The accidental release of (gaseous or liquid) hydrogen leads to the evolution and dispersion of a gas cloud whose shape is influenced by type and rate of release and by the atmospheric conditions as well as topography. The dilution with ambient air makes the hydrogen cloud pass through the whole broad flammable range from high to low concentrations. Condensation of the always available humidity in the ambient air, which makes the hydrogen cloud visible, reduces the cloud density and liberates latent heat, both effects supporting the positive buoyancy. Release types are distinguished according to vaporization of a liquid hydrogen pool on the ground, where the hydrogen escapes upwards, away from the site of release, a jet stream released through a small opening in a pressurized system, where the cryogen is widely sprayed in a multi-phase mixture, and the catastrophic failure of a pressure vessel with the explosion-like expansion of the stored gas.

Little experimental work has been conducted in the past to study the atmospheric dispersion behavior of a hydrogen gas cloud. The NASA series of seven LH_2 spill tests demonstrated that the evolving H_2 cloud was existent for a couple of 100 m downwind, especially if the ground was able to cool sufficiently. Also the completely different dispersion behavior of the "light" hydrogen and the "heavy" propane was shown.

Only a few theoretical efforts have been made to simulate the dispersion of hydrogen gas since there is scanty experimental data. The specification of the source term is of particular importance for the accurate modeling of gas cloud evolution and dispersion. State-of-the-art modeling of the transient behavior of gases with positive or negative buoyancy in the atmosphere is provided by computer fluid dynamics (CFD) models which simulate complex flow processes by solving the Navier-Stokes equations. Besides their need for immense computer time and storage capacity, which can only be realized by the most advanced computer generation, these models require a detailed input of initial and boundary conditions for the calculation grid. In the two-equation k-ϵ turbulence model, special partial differential equations are solved to describe the transport of turbulence as well as its generation and dissipation. Of all the approaches, the k-ϵ model offers the highest relative independence of empirical relations. K-ϵ modeling has been realized in a variety of computer codes. Representatives of this category of codes are the German BASSIM, the JRC-Ispra code ADREA-HF, or the commercially available British CFX code.

Combustion Behavior of Hydrogen

If liquid hydrogen is released in ambient air with a high humidity content, the flammable fraction of the gas cloud is generally enclosed in the visible cloud, while under conditions of a dry atmosphere, flammable fractions could also exist outside the visible cloud. The ignition of a gas cloud always requires an ignition source. Under normal circumstances, a spreading cloud is always ignited at its perimeter. According to accident statistics, the most probable reasons for the ignition of hydrogen gas clouds are autoignition on hot surfaces, an electric spark, or an electric discharge. But only a small portion of the energy of a hydrogen cloud is expected to be liberated in an open air explosion; it is estimated to be in the range of 0.1 - 10 %, mostly < 1 %.

The "Unconfined Vapor Cloud Explosion" is the explosive type of deflagration where about 60 % of the combustion energy is expressed as kinetic energy in the form of pressure waves. Heat transport by conduction and diffusion from the reaction zone into the preheating zone enables the propagation of the flame. A near-ground deflagration results in a hemispherical fireball. Depleting fuel terminates the radial spreading and the buoyant forces allow for a liftoff of the fireball resulting in the typical mushroom shape. A "Boiling Liquid Expanding Vapor Explosion", BLEVE, characterizes the failure mechanism of a liquid gas container where the major part of the contents is released by flash vaporization and explodes while the rest forms a pool which burns down. This type of explosion is caused if a storage tank is exposed to a heat source from outside.

In contrast to a deflagration, the chemical reaction in a detonation is faster by several orders of magnitude where the reaction front propagates at a supersonic speed of several km/s. The shock wave passing through the flammable mixture results in its instantaneous compression, heating, and spontaneous ignition; the release of the chemical energy keeps the shock wave going. The damage potential is much stronger than in a deflagration. The shock front possesses a 3D cellular structure characteristic of the fuel-air mixture. The decisive criterion for flame acceleration up to the deflagration-to-detonation transition (DDT) is the state of turbulence in the gas cloud. The explosion of an unconfined hydrogen gas cloud in the presence of a weak ignition source was never observed to have turned into a detonation. The ignition energy required for a direct detonation can only be provided by either an intensive turbulent hot gas jet or by an explosive.

Numerous large-scale and small-scale test facilities have been used to investigate flame acceleration and DDT. The most dangerous configurations were, as expected, those with (partial) confinement and obstruction. Large-scale tests were conducted in the USA in the FLAME apparatus. In Germany, a series of balloon tests of different geometries with mixtures of hydrogen and other hydrocarbon fuels with air at volumes between 7.5 and 2100 m^3 were conducted with ignition by an explosive to cause a detonation. In the Russian RUT facility, one of the key results was the observation of a 12.5 vol% H_2 lower detonability limit, demonstrating that larger-scale facilities seem to extend the detonability range of a flammable gas mixture.

Although the mechanisms of DDT and flame acceleration are qualitatively understood, there are still difficulties in fully describing them on a quantitative basis. The most advanced approaches are the CFD models, which are similar to the dispersion models, based on the Navier-Stokes equations with a k-ϵ approach to deal with turbulence. They need, however, to be adapted to high-speed flows of explosions and short time steps characteristic of chemical reactions. Numerical simulation methods are applied to study turbulent combustion, flame acceleration processes, and (re-initiation of) detonations. Today's modeling and simulation show a good agreement with a variety of fast combustion phenomena. Examples of codes are, e.g., the Dutch REAGAS or a 2D development by the German DLR or again the BASSIM and CFX codes.

In a deflagration, the volume expansion of the burnt products reacts like a piston pushing the unburnt gas mixture aside. The static pressure loading in slow deflagration processes is conservatively described by the adiabatic, isochoric, complete combustion pressure representing an upper bound in a closed volume. Pressure and density decrease in the wave direction. In contrast, a detonation generates a compression wave. Its pressure-time behavior is characterized by a distinct rapid increase and a subsequent exponential decay. In the far distance, deflagration and detonation show about the same pressure shape. In a first approximation, it is possible to deduce the strength of the destroying pressure waves from the evaluation of damage. Charts with characteristic destruction lines give peak overpressure of a damage-equivalent pressure wave as a function of the distance. "Experimental" data were derived from explosives and nuclear weapon explosions, which are, however, only partially applicable to a deflagration. A simplification of the load-damage analysis has led to the development of the "Pressure-Impulse" methodology as a computer simulation technique for quick and easy predictions.

Safety distances can be fixed according to physically defined criteria, e.g., the dose of thermal radiation or peak overpressure, to have reached a certain threshold value. A basic prerequisite is knowledge of the source term which is dependent on leak size and thermodynamic conditions of the leaking material. Different relations illustrate the variation in conservativism of different institutions that generate safety criteria. The safety distances are distinguished for people and for less demanding equipment, e.g., adjacent storage tanks, working buildings, or distinguished with respect to fireballs, shrapnel, structural response or physiological effects.

Environmental Issues

Water vapor is the most climate-relevant atmospheric gas contributing a portion of 65 % to the overall greenhouse effect. The (anthropogenic) effect of water vapor released into the atmosphere within a large-scale hydrogen technology is disputed among climate researchers. With respect to the greenhouse effect caused by hydrogen fueled aircraft, it can be stated that for mid-latitude atmospheric conditions at an altitude below 10 km, the contribution of water vapor is negligible. Above 10 km, the emitted water vapor behaves like a greenhouse gas exceeding the effect of kerosene at altitudes > 12 km. The formation of contrails is avoided at lower cruising altitudes, however, at the expense of higher fuel consumption.

Nitrogen oxides (NOX) are generated in combustion processes as a function of temperature, pressure, and time. Emissions are small compared with conventional fuels. The generation and emission of NOX peaks at excess air ratios of about 1, but is steeply reduced by applying a lean H_2, low-temperature burning process.

CURRENT ACTIVITIES ON HYDROGEN IN THE WORLD

A variety of hydrogen energy applications of a demonstration character have been started or are projected worldwide encompassing autonomous or partial power systems on different scales as well as vehicle research projects. Some examples of large-scale H_2 systems are presented in the following.

The most ambitious hydrogen energy R&D program in the world is currently being conducted in Japan where private industry is demonstrating rigorous investment efforts exceeding those levels found in the USA and European countries. The "International Clean Energy Network Using Hydrogen Conversion", WE-NET, pursued under the New Sunshine project, has the ultimate goal of establishing a worldwide energy system based on (liquid) hydrogen. WE-NET is projected to run over 28 years, 1993 - 2020. Phase I (1993 - 1998) deals with surveys on key technologies and elemental research. Main targets are an efficient membrane electrolysis, large-scale liquefaction and storage, LH_2 ship transportation, and the development of a hydrogen combustion turbine.

The "Euro-Quebec Hydro-Hydrogen Pilot Project", the concept of a clean energy system based on hydrogen, was presented in 1990. The idea of this project is to take 100 MW electricity from hydropower in Canada for electrolytic hydrogen production. Liquid hydrogen is then shipped by barge carriers to Hamburg, where it is distributed to a variety of consumers. The Euro-Quebec project is designed as a local hydrogen energy economy. Its prime goal is the demonstration of the possibilities of safe transport, storage, and distribution of (liquid) hydrogen. Since 1992 with the start of phase III, pre-approval activities and a demonstration program have been started, the most important include various city bus projects, development and testing of advanced LH_2 maritime transport containers, emission testing on sectors of LH_2 adapted combustors for aircraft engines, power plants in CHP mode, and last but not least, a study on rules and regulations, safety, and acceptability of hydrogen.

A solar hydrogen demonstration plant project on an industrial scale has been implemented since 1985 by Solar-Wasserstoff-Bayern in Germany and is scheduled to run until 1999. It aims at testing important subsystems of a future hydrogen energy economy on a long-term basis. Components tested are photovoltaic fields, advanced-type electrolyzers of the 100 kW category, AFC and PAFC power plants, gas-fired heating boilers, an LH_2 refueling station, and recently also a PEFC powered fork lift truck. Despite the fact that not all of the systems installed worked satisfactorily, the overall impression is positive and the results are promising. A new project was started in 1997 in Germany by the "Hydrogen Initiative Bavaria", WIBA, to demonstrate H_2-fueled ground-based traffic at Munich airport.

A Photovoltaic Hydrogen Fuel Cell Demonstration facility, PHOEBUS, has been erected and is currently operated at the Research Center Jülich encompassing all components for a decentralized autonomous, all-year electricity supply from solar energy using hydrogen as the energy storage medium. The characteristic components of PHOEBUS are 312 m^2 photovoltaic modules, a pressure electrolyzer, an alkaline fuel cell, a battery for short-term storage of electricity, pressure vessels for long-term storage of hydrogen and oxygen, as well as an energy management system. A third of the PV electricity is used to produce hydrogen in an electrolyzer to be later consumed in a fuel cell. The overall energy consumption is assumed to be 17.4 MWh/yr corresponding to an efficiency of 59 %.

In a joint German-Russian cooperation, the "Cryoplane" project started in 1990 to investigate the feasibility of an aircraft propelled by LNG or LH_2. Topics covered by the project are scenarios for the transition to an alternative fuel, infrastructure, aircraft design, fuel system layout, engine modifications, and ecological issues. Precursor phases of commercial LH_2 aviation will be the development of the appropriate infrastructure and the operation of a demonstrator. The Cryoplane project is currently in a phase of developing and testing the fundamental technologies of single components such as the fuel tank, cryogenic pump and hydrogen combustor. A regional airplane of Dornier-328 type has been selected to serve as a demonstrator and is projected to fly by the year 2000.

TRANSITION TO A FUTURE HYDROGEN ENERGY ECONOMY

In a future hydrogen energy economy, the hydrogen will ultimately come from non-fossil fuel, although fossil fuels will provide a long-term transitional resource. Sources of renewable energies (wind, water, sun) are deemed sufficient to more than replace all fossil fuel. In the concept of a nuclear hydrogen economy, the production facility would consist of an HTGR combined with a thermochemical plant where the high-temperature heat is directly converted into chemical energy. The aspect of energy independence represents an argument in favor of promoting the transition to hydrogen.

Nuclear energy may gain its greatest importance in helping to get the hydrogen economy started and to facilitate the transition. On a mid-term basis, overcapacities in countries with a high percentage of nuclear power (e.g., France) and reserve capacities, which exist in all large distributed grids, could be used in electrolysis plants to be immediately disconnected again if needed, e.g., at peak load times. On a longer-term basis, nuclear power could be installed for hydrogen production if economically competitive with fossil primary energies.

The duration of the transition period will depend on the so-called harvest factor of the new energy conversion plants, which is the ratio of the energy produced during its lifetime to the energy invested for its construction. A harvest factor of 10 means that a complete transition could be realized within a century; a harvest factor of less than 5, however, would even prevent complete transition since the new system will not be self-sustainable. Photovoltaic power plants, as estimated in 1993, have harvest factors of optimistically 1 - 3 with a forecast 3 - 6 range if the lifetime of the solar cells can be extended to as much as 30 years. An optimistic nuclear energy scenario could result in a harvest factor of 14, provided there is a well functioning complete nuclear cycle, and, of course, public acceptance. A transition period ranging from decades to over a century is expected.

A conceivable intermediate step for the transition to a comprehensive hydrogen economy is the concentration on a low-energy economy with minimum CO_2 emissions into the atmosphere using local excess potentials of electricity, e.g., renewables such as hydro, and wind or cheap off-peak electricity in the day/night, working day/weekend, or winter/summer cycles.

A change of the existing system for the introduction of hydrogen as an energy carrier for use in efficient, low-polluting systems in the near future needs to be done in small steps. Examples in the traffic area are city bus projects or LH_2 aviation in the longer run. Furthermore small-scale energy storage systems comprising electrolyzer, metal hydride, and fuel cell components, ideal for applications far away from the grid will be a reasonable approach. Natural gas is expected to play a significant role as the preceding technology.

The problem is not the amount of fossil fuels consumed, it is the need to maintain cleanness during consumption, i.e., the treatment of emissions. Häfele has envisioned the concept of a "New Horizontally Integrated Energy System", NHIES, with zero emission, underlying the ideas of decomposition of coal, oil, gas and cleaning, stoichiometric relation, and synthesis and conversion. The NHIES has to compete with the presently existing vertically integrated energy systems. The "ultra-low emission vehicle" (ULEV) and the "zero-emission vehicle" (ZEV) mandate in California makes this state appear to be a good candidate for the introduction of hydrogen vehicles in a close cooperative effort between fuel cell manufacturer, automobile industry, and academic groups.

The establishment of strategies is an indigenous task of policy. A variety of measures is conceivable for tackling the problem of environmental damage caused by the continuous contribution of the combustion of fossil fuels: direct legislative regulations and rules, investments, tax system, research funding. Industry may contribute by long-term investments, research activities and cooperation for utilizing hydrogen technology.

FINAL REMARKS

In principle, two different and independent areas have been covered in this report: on the one side hydrogen as an energy carrier and its application in a future large-scale hydrogen energy economy, and on the other side nuclear power which represents an important option for providing primary energy for hydrogen production. The combination of both nuclear and hydrogen is not necessarily required but it represents a feasible option to facilitate the transition. Both areas will help reduce global impact on the atmosphere. Hydrogen faces economic problems and possibly public acceptance difficulties. Nuclear power faces public acceptance problems.

The limited efforts on the further development of a new promising energy technology as has been observed over the past decade are due to currently low conventional energy prices with even falling tendency, also the energy reserve situation is no concern, and no change is expected for the next years. Current goals of energy policy include the achievement of a high level of congruence between supply security, economy, and environmental compatibility meaning an optimized, not necessarily minimized, energy consumption.

After the Kyoto summit in 1997, the reduction of greenhouse gas emission is considered just one among several strategies. There is hope that by means of the new policy instruments (tradeable emission certificates, joint projects between industrial and developing countries, and others) of the climate protocol, the policy actors will proceed slowly, but steadily to take internationally sound actions and direct the powerful transnational economy and finance markets towards a low-emission economy and acquire acceptance and the readiness of accepting the expenses by those who are concerned.

The keywords that characterize the strategy for a transition into the world's future energy economy are: conservation, substitution, and diversification strategy, necessary to reduce the burning of fossil fuels and to improve efficiencies, to replace them by environmentally benign energy carriers, and to avoid new and too strong dependencies.

Of course, hydrogen as an energy carrier will be just one contender on the energy market competing with others, e.g., electricity, and is currently facing economic problems. The key issues, however, that are able to promote an innovative energy technology based on hydrogen are its environmental benefit in a world with still increasing demand for energy, its safety compared with other fuels, and, in the long run, its potential of mitigating the jeopardy by a critical energy supply situation in future. Also nuclear power represents but one contender among the non-fossil energy carriers, although providing an environmentally benign primary energy source which could be used for hydrogen production. Its major problem is its lack of public acceptance.

Many research activities still need to be done in both areas aiming at an economic breakthrough of hydrogen and its link to nuclear process heat. The necessary concomitant efforts concern safety considerations for a large-scale hydrogen economy. This could be promoted by enhanced information exchange among all interested parties, e.g., by establishing international working groups to cover critical aspects, including:

- Introduction of "advanced systems", e.g., fuel cells in the conventional field and HTGRs in the nuclear field;
- Definition of a sound safety and risk assessment methodology of non-nuclear technologies including experiments on hydrogen safety;
- Feasibility of the combination nuclear power plant / chemical plant;
- Analysis of the "nuclear" hydrogen production potential;
- Definition of fall-back position with established systems.

This would be useful to promote confidence in the technologies and implementation of steps towards a hydrogen economy.

Appendix A

THERMOCHEMICAL CYCLES FOR HYDROGEN PRODUCTION

A.1. PRINCIPLE

Since a direct thermolysis of water, which requires temperatures of > 2500 °C, is not practicable under normal circumstances, the splitting process is subdivided into different partial reactions, either one running on a lower temperature level. The principle is given by the following cycle:

$$
\begin{array}{rcll}
2\ AB + 2\ H_2O & \rightarrow & 2\ AH + 2\ BOH & +\ \text{heat at } T_1 \\
2\ BOH & \rightarrow & 2\ B + 1/2\ O_2 + H_2O & -\ \text{heat at } T_2 \\
2\ AH & \rightarrow & 2\ A + H_2 & -\ \text{heat at } T_3 \\
2\ A + 2\ B & \rightarrow & 2\ AB & +\ \text{heat at } T_4
\end{array}
$$

After the first cycle (vanadium - chlorine) was proposed in 1964, some 2000 - 3000 potential thermochemical cycles have been tested and checked in terms of appropriate reaction temperatures and velocities and in economic respect. Thermochemical cycles are Carnot cycle-limited meaning that high temperatures could improve the conversion efficiency. Major problems arise by the large material flows, by the introduction of impurities, and by the potential creation of toxic and environmentally unacceptable species. The main goal is to achieve satisfactory overall energy efficiencies which are currently not higher than around 40 % and, in connection with separation steps and severe materials and equipment design difficulties, do not allow, so far, large-scale thermochemical process applications [11]. Studies are focusing on reaction kinetics, thermodynamics, reactant separation, material stability, flow sheeting, and cost analysis.

Thermochemical multistage cycles are usually classified in families according to the chemicals involved. Cycles can consist of up to 8 equations, usually 3 - 6, with up to 5 elements others than H_2 and O_2 involved [5].

A.2. THERMOCHEMICAL CYCLES

A.2.1. Oxide System

The most simple water splitting process is the two-step cycle with metal oxides (MeO) as the redox system

$$
\begin{array}{lrcl}
(1) & 3\ MeO + H_2O & \rightarrow & Me_3O_4 + H_2 \\
(2) & Me_3O_4 & \rightarrow & 3\ MeO + 1/2\ O_2\ -\ \text{heat}
\end{array}
$$

where Me = Mn, Fe, Co

The High-Temperature Solar Chemistry Section of the PSI in Switzerland has realized a sunlight-concentrating device based on the metal iron (Me=Fe) with a power of 60 kW to provide the required temperatures of 2200 °C (for step (2)). Efficiency is expected to be 20 % [13].

In other cases of water splitting reactions, the metal reacts exothermally with water at a temperature < 800 K [13]

$$x\ \mathrm{Me} + y\ \mathrm{H_2O} \quad \longleftrightarrow \quad \mathrm{Me_xO_y} + y\ \mathrm{H_2} + \text{heat}$$

For the electrothermal dissociation of metal oxides into their elements, high temperatures are needed which can be lowered by using chemical reducing agents. The combination with CH_4 as a reducing agent in a reforming process results in the coproduction of metals and synthesis gas:

$$\mathrm{Me_xO_y} + y\ \mathrm{CH_4} \quad \longleftrightarrow \quad x\ \mathrm{Me} + y\ (2\ \mathrm{H_2} + \mathrm{CO})$$

Due to its molar ratio, the synthesis gas mixture is particularly suitable for methanol production. The iron system, Me = Fe, has been extensively studied in laboratory electric furnaces [13]. The other two systems have a very low hydrogen yield only [9].

A.2.2. Halide Family Processes

In the **metal-halide system**, the hydrogen producing reaction is written as [9]

$$3\ \mathrm{MeX_2} + 4\ \mathrm{H_2O} \quad \rightarrow \quad \mathrm{Me_3O_4} + 6\ \mathrm{HX} + \mathrm{H_2}$$

where Me = Mn, Fe
X = Cl, Br, I

The Mn system is insignificant due to negligible yield of hydrogen. For the oxygen producing reaction, three main reaction paths have been proposed. In one of them, the oxidizing reaction of H_2O is conducted in two steps through the addition of an oxide phase which reacts to give the corresponding halide [9]:

$$\begin{aligned} \mathrm{Fe_3O_4} + 8\ \mathrm{HX} &\rightarrow 3\ \mathrm{FeX_2} + 4\ \mathrm{H_2O} + \mathrm{X_2} \\ \mathrm{AO} + \mathrm{X_2} &\rightarrow \mathrm{AX_2} + 1/2\ \mathrm{O_2} \\ \mathrm{AX_2} + \mathrm{H_2O} &\rightarrow \mathrm{AO} + 2\ \mathrm{HX} \end{aligned}$$

where A = Mn, Ca
X = Cl, Br

The **bromine-calcium-iron process** based on the combination A = Ca and X = Br is also named "**UT-3**" (University of Tokyo-3) process:

(1) $CaBr_2 + H_2O \rightarrow CaO + 2\,HBr$ 700 - 750 °C

(2) $CaO + Br_2 \rightarrow CaBr_2 + 1/2\,O_2$ 500 - 600 °C

(3) $Fe_3O_4 + 8\,HBr \rightarrow 3\,FeBr_2 + 4\,H_2O + Br_2$ 200 - 300 °C

(4) $3\,FeBr_2 + 4\,H_2O \rightarrow Fe_3O_4 + 6\,HBr + H_2$ 550 - 600 °C

Stages (1) and (3) produce reactants for the stages (2) and (4). All reactions in the UT-3 cycle are solid-gas reactions with the net result of a steam decomposition into H_2 and O_2 [16]. Therefore it is easy to separate gas from solid products. The process has four reactors connected in series in a loop. After one cycle, the reactors are switched and the direction of the cycle is reversed. Solid reactants are given in the form of spherical pellets. Heat exchangers are used to regulate reaction temperatures. Conversion rates for some reactions are small meaning that gas flow and thus reactor size is relatively large.

Another promising thermochemical cycle is based on the **"iron-chlorine compound"** (or "Mark 9") [4, 8]:

(1a) $3\,FeCl_2 + 3\,H_2O \rightarrow 3\,FeO + 6\,HCl$ 1100 °C

(1b) $3\,FeO + H_2O \rightarrow Fe_3O_4 + H_2$ 650 °C

(2) $Fe_3O_4 + 8\,HCl \rightarrow FeCl_2 + 2\,FeCl_3 + 4\,H_2O$ 100 - 300 °C

(3) $2\,FeCl_3 \rightarrow 2\,FeCl_2 + Cl_2$ 420 °C

(4) $Cl_2 + H_2O \rightarrow 2\,HCl_2 + 1/2\,O_2$ - heat 700 - 1000 °C

investigated in Germany, Italy, Japan, and the USA. Its theoretical efficiency is 44 %, in practice, however, no higher than 30 % due to difficulties given by material problems, the coupling to the process heat source, and the separation of the gaseous phases. Subjects of investigation at the Research Center Jülich were the "modified AGNES" process with the reaction (4), the reverse Deacon process, conducted in two steps:

(4a) $Cl_2 + 2\,Mg(OH)Cl \rightarrow 2\,MgCl_2 + H_2O + 1/2\,O_2$

(4b) $2\,MgCl_2 + 2\,H_2O \rightarrow 2\,HCl + 2\,Mg(OH)Cl$

A.2.3. Sulfur Family Processes

Three surviving thermochemical cycles are based on the sulfur family processes which all have in common the thermal decomposition of sulfuric acid at high temperatures. A typical representant is the four steps process:

(1) $3/2\,SO_2 + H_2O \rightarrow H_2SO_4 + 1/2\,S$

(2) $H_2SO_4 \rightarrow H_2O + SO_2 + 1/2\,O_2$ - heat 850 °C

(3) $3/2\,S + H_2O \rightarrow H_2S + 1/2\,SO_2$

(4) $H_2S \rightarrow H_2 + S$ - heat

The most considerable potential has the **iodine-sulfur (IS) process** which has been first investigated at General Atomics, San Diego, USA, for many years demonstrating its feasibility and evaluating first chemical engineering flow sheets. The IS process as pursued at JAERI consists of the following three steps:

$$\begin{array}{llcll}
(1) & I_2 + SO_2 + 2\,H_2O & \longleftrightarrow & 2\,HI_x + H_2SO_4 & < 100\ ^\circ C \\
(2) & 2\,HI & \longleftrightarrow & H_2 + I_2 & 700\ ^\circ C \\
(3) & H_2SO_4 & \longleftrightarrow & H_2O + SO_2 + 1/2\,O_2 & 850\ ^\circ C
\end{array}$$

comprising the exothermal water consuming Bunsen reaction, the endothermal decomposition of hydrogen iodide in an electrodialysis cell as the hydrogen producing reaction, and the thermal decomposition of sulfuric acid as the oxygen producing reaction [12]. The decomposition of H_2SO_4 and HI was found to be an expending procedure causing severe corrosion problems. According to analytical studies, an efficiency of 40 - 50 % under optimal operating conditions can be expected [10]. General Atomics gives a figure of 47 % [15]. The IS process was originally designed to be coupled with a high-temperature reactor or a fusion reactor and more recently also with a solar thermal plant. The cycle has been verified on a laboratory scale (1 - 10 Nl of H_2 per hour) in Japan and is intended to be later connected to HTTR process heat for demonstration (see also chapter 8).

The **sulfuric acid-methanol process** is given by

$$\begin{array}{rcll}
H_2SO_4 & \rightarrow & H_2O + SO_2 + 1/2\,O_2 - \text{heat} & 700 - 1000\ ^\circ C \\
CH_4 + H_2O & \rightarrow & CO + 3\,H_2 & 700 - 1000\ ^\circ C \\
CO + 2\,H_2 & \rightarrow & CH_3OH & 300\ ^\circ C \\
CH_3OH + H_2O + SO_2 & \rightarrow & CH_4 + H_2SO_4 & \approx 100\ ^\circ C
\end{array}$$

with the goals to design and optimize the processing steps and to demonstrate its feasibility on an industrial scale [2].

In the "sulfate" process by

$$\begin{array}{rcll}
4\,FeSO_4 & \rightarrow & 2\,Fe_2O_3 + 3\,SO_2 + SO_3 + 1/2\,O_2 & \text{HT} \\
Fe_2O_3 + 3\,SO_2 + SO_3 + H_2O & \rightarrow & 4\,FeSO_4 + H_2 & \text{LT}
\end{array}$$

the high-temperature (HT) step is easily selected at > 980 K, whereas the low-temperature (LT) step results in H_2S and FeS_2 formation rather than H_2. This brought up the idea to substitute the LT step by an electrolysis step.

A.3. THERMOCHEMICAL HYBRID CYCLES

The **thermochemical hybrid process** is a combined cycle process with both thermochemical and electrolytic reactions of water splitting. The hybrid process offers the possibility to run low-temperature reactions on electricity. The expectations for realization of hybrid processes are similar to those for purely thermochemical processes [3]. Various hybrid processes are energetically possible, however, not always feasible. Important criteria are the minimum voltage for the electrolysis step, realizability, efficiency.

A.3.1. Sulfuric Acid Bromine Hybrid Process

The **sulfuric acid-bromine hybrid process** (or "Mark 13") which has been tested at the JRC Ispra, Italy, consists of the reactions:

(1a) $H_2SO_4 \longleftrightarrow H_2O + SO_3$ 700 - 1000 °C

(1b) $SO_3 \longleftrightarrow SO_2 + 1/2\ O_2$ 700 - 1000 °C

(2) $SO_2 + Br_2 + 2\ H_2O \longleftrightarrow 2\ HBr + H_2SO_4$ 20 - 100 °C

(3) $2\ HBr \longleftrightarrow H_2 + Br_2$ - electricity 80 - 200 °C

with reaction (3) as the electrochemical step. This cycle using only liquid or gaseous species operated successfully in 1978 in a laboratory scale plant with a hydrogen production rate of 100 l/h over 150 h. An efficient way was found to remove SO_2 by reaction with bromine which was the basis for creating a new flue gas desulfurization process [14]. The efficiency is given as 37 % [15].

A new innovative system is being developed to apply solar energy for the step of HBr production. Concentrated solar radiation is absorbed by bromine vapor to produce bromine atoms which then react with steam at temperatures between 600 and 1000 °C to form HBr and oxygen. A 1 kW solar system was constructed and tested. HBr conversion rates were observed to be 70 % of the theoretical maximum [6].

A.3.2. Sulfuric Acid Hybrid Process

The **sulfuric acid hybrid cycle** (Westinghouse process) is given by the reaction equations

(1a) $H_2SO_4 \rightarrow H_2O + SO_3$ > 450 °C

(1b) $SO_3 \longleftrightarrow SO_2 + 1/2\ O_2$ > 800 °C

(2) $2\ H_2O + SO_2 \longleftrightarrow H_2SO_4 + H_2$ - electricity 80 °C

Optimum efficiency is reached with a 65 % concentration of sulfuric acid in water. The weak point is again the decomposition of the sulfuric acid introducing significant corrosion problems. The cycle efficiency is 40 % which has the potential to be increased to 46 % if the electrolysis is conducted in several stages.

The cycle, developed by Westinghouse in 1975, has been experimentally investigated at the Research Center Jülich in close cooperation with JRC Ispra. It has eventually led to a three-compartment electrolysis cell with a hydrogen production rate of 10 Nl/h successfully operated in a 600 h test run. Cell conditions were 80 °C at 1.5 MPa [15]. Tube materials selected have shown an excellent corrosion resistance. The possibility to use direct sunlight for the SO_3 decomposition step was also demonstrated.

The two-step sulfuric acid hybrid process is using in the thermal (≈ 900 °C) oxygen-producing step the decomposition of sulfuric acid and sulfonic acid in the electrochemical hydrogen-producing step:

$$\begin{aligned} H_2SO_4 \quad &\longleftrightarrow \quad H_2O + SO_2 + 1/2\ O_2 \\ H_2O + H_2SO_3 \quad &\longleftrightarrow \quad H_2SO_4 + H_2 \end{aligned}$$

The hybrid process with just two steps is expected to reduce material streams as compared with the above described IS process. The electric energy demand here is a factor of 7 (in reality 3 - 4) lower than in the electrolytic water splitting process.

A.3.3. Hydrocarbon Hybrid Process

Hydrocarbon hybrid processes are promising thermochemical cycles. The hydrogen producing step is typically done by methane splitting connected with the formation of CO.

In the **methane-methanol-methanal process**, the major steps are methane splitting, methanol synthesis, methanal synthesis, and methanal electrolysis, for which the chemical reactions are [1]:

(1)	$H_2O + CH_4$	$\rightarrow$	$CO + 3\ H_2$	- 250 kJ/mol	700 - 950 °C
(2)	$2\ H_2 + CO$	$\rightarrow$	CH_3OH	+ 90 kJ/mol	250 - 300 °C
(3)	CH_3OH	$\rightarrow$	$CH_2O + H_2$	- 83 kJ/mol	400 - 500 °C
(4)	$CH_2O + H_2$	$\rightarrow$	$CH_4 + 1/2\ O_2$	- 0.4 V	50 - 300 °C

The main energy input is in the steam reforming step (1), which is a well developed and frequently applied technology as is the step (2) of methanol synthesis. Secondary products such as methane and higher hydrocarbons created during the methanol synthesis are considered not significant. The cycle is characterized by a selectively working catalyst and a high reaction rate. The methanal (= formaldehyd) is generally applied on a large-scale in an autothermal operation at about 600 °C by combining exothermal oxidation (methanol + oxygen → methanal + water) with endothermal dehydration (methanol → methanal + water). The electric energy required in the methanal electrolysis in step (4) is about a third of that needed in the direct electrolysis of water. In contrast to the previous steps, this process step (4) is not well known and needs further development work. Advantages of the cycle are that all reaction partners are in either liquid or gaseous state and neither one is exotic nor poisonous. Recuperation, i.e. the reuse of released heat energy, is significant for an economic process. Anticipating design improvements, the above process is expected to achieve an efficiency of 51 % [1].

The cycle processes "methane-methanol" and "methanal-methanol" based on only three and two, respectively, main reactions require a larger electricity input. The process "sulfonic acid-sulfuric acid" consumes the least electricity, but is probably plagued by severe material problems. Other processes such as "aceton-propane-propylen" and "chinon-hydrochinon" need more instrumental effort [1].

The **methane production**, reactions (3) and (4), could also be made by means of methanol plus iodine

$$2\,CH_3OH + I_2 \rightarrow 2\,CH_3I + H_2O + 1/2\,O_2$$

$$2\,CH_3I + H_2O \rightarrow CH_3OH + I_2 + CH_4$$

with a conversion rate achieved in experiments of up to 50 % of methane [15].

Production of methanol is made in the following hybrid cycle

(1) $CO_2 + 3\,CH_4 + 2\,H_2O \longleftrightarrow 4\,CO + 8\,H_2$

(2) $4\,CO + 8\,H_2 \longleftrightarrow 4\,CH_3OH$

(3) $3\,CH_3OH \rightarrow 3\,CH_4 + 3/2\,O_2$ - electricity

(4) $CO_2 + 2\,H_2O \rightarrow CH_3OH + 3/2\,O_2$

The carbon source CO_2 could be taken from the waste gas of coal power plants. This cycle represents a good candidate for the production of a liquid energy carrier with nuclear heat as well [15].

A combined procedure for the **co-production of hydrogen and electricity** from water splitting and coal has been proposed with the following reaction system

(1) $C + 2\,H_2SO_4 \longleftrightarrow CO_2 + H_2O + 2\,SO_2$ - heat 250 - 300 °C

(2) $2\,SO_2 + 4\,H_2O \longleftrightarrow 2\,H_2 + 2\,H_2SO_4$

(3) $C + 2\,H_2O \rightarrow CO_2 + 2\,H_2$

The fuel coal, represented by "C", is oxidized with chemically bound oxygen. The heated combustion gases are routed to a gas turbine to run the electrolysis step. The SO_2 and H_2O are applied in a Westinghouse cycle. An optimum efficiency is seen at 57 % [15].

A.3.4. Metal-Metal Hydride Hybrid Process

In the metal-metal hydride system, the following reactions occur with "Me" representing an alkali metal [15]

(1) $H_2O + 2\,Me \rightarrow 2\,MeH + 1/2\,O_2$ - electricity 250 - 400 °C

(2) $2\,MeH \rightarrow 2\,Me + H_2$ - heat 700 - 900 °C

where Me = Li, Na, K or mixtures

Oxygen gas is developed while the hydrogen is bound into the metal. A few tests were conducted with the **lithium hybrid process**, which has been developed at the RWTH Aachen, Germany. Out of some 40 candidate materials for the cell membrane, TiNi alloys were shown to be corrosion resistant for more than 500 h under electrolysis conditions. A thermodynamic analysis indicates an efficiency of 45 %, if hydrogen at a pressure of 4 MPa is provided [15].

Using experience with sodium from the breeder technology, the RWTH Aachen has investigated the **sodium cycle**, Me=Na, in 1988/89 with a promising > 50 % overall efficiency. The high-temperature step was operated continuously on a laboratory scale. Cathodic membrane material problems were encountered in the electrochemical step [7].

The Me/MeH hybrid cycle offers an interesting possibility of hydrogen production in connection with a high-temperature gas-cooled reactor.

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Appendix B

CHEMICAL ENERGY TRANSMISSION SYSTEMS

B.1. STEAM REFORMING SYSTEM (EVA/ADAM)

Within the project "Nukleare Fernenergie" (NFE) (= "Nuclear Long-Distance Energy"), the energy transport system by **natural gas steam reforming / methanation** was theoretically and experimentally investigated at the Research Center Jülich in Germany. Its goal was to demonstrate the operation of a complete helium-heated system for steam reforming of methane on a representative scale and to demonstrate the technical performance and efficiency of a thermochemical pipeline system [5]. Fig. B-1 shows a schematic of this long-distance energy transportation system. The heat source was an electric heater simulating HTGR conditions.

In 1972, the first experimental setup, the so-called **EVA** ("Einzelspaltrohr-Versuchs-Anlage" = "Single Tube Test Facility") was established to account for the endothermal reforming reactions:

$$CH_4 + H_2O \longleftrightarrow CO + 3\ H_2 - 206\ \text{kJ/mol}$$
$$CH_4 + 2\ H_2O \longleftrightarrow CO_2 + 4\ H_2 - 165\ \text{kJ/mol}$$

The tube with a variable length of 10 - 15 m and a variable inner diameter of 100 - 150 mm was entered at the bottom by helium of 950 °C which flowed upwards in an annulus at the outside providing heat to the reformer tube inside. The feed gas methane was heated up in a counter current flow and reached a temperature of 825 °C at the tube bottom. The resulting product gas was then cooled down by flowing upwards again through return pipes inside the reformer tube (internal pigtails). The temperature profiles in the EVA system are shown in Fig. B-2, left hand side.

The construction of a follow-up reformer test stand, **EVA-II**, was started in 1980. EVA-II consisted of a bundle of 30 reforming tubes based on the baffle plate design with an inner/outer diameter of 100/120 mm and a length of 11.4 m. Helium throughput was 4 kg/s. The other components of this helium loop besides the 10 MW electric heater were a hot gas duct, steam generator, and helium circulator. Methane input was 0.6 kg/s. The product gas was generated at a rate of 4400 kg/h.

The reverse process of methanation was realized in 1979 in the test facility **ADAM** ("Anlage mit drei adiabaten Methanisierungsreaktoren" = "Facility with three adiabatic methanation reactors"). A three-stage methanation reaction including a dilution of the product gas by feedback of already retransformed gas was chosen to mitigate the large heat release, to minimize soot formation, and to maximize CH_4 output. The feed gas was synthesis gas at a rate of 600 Nm^3/h in ADAM-I and 9600 Nm^3/h in ADAM-II [6].

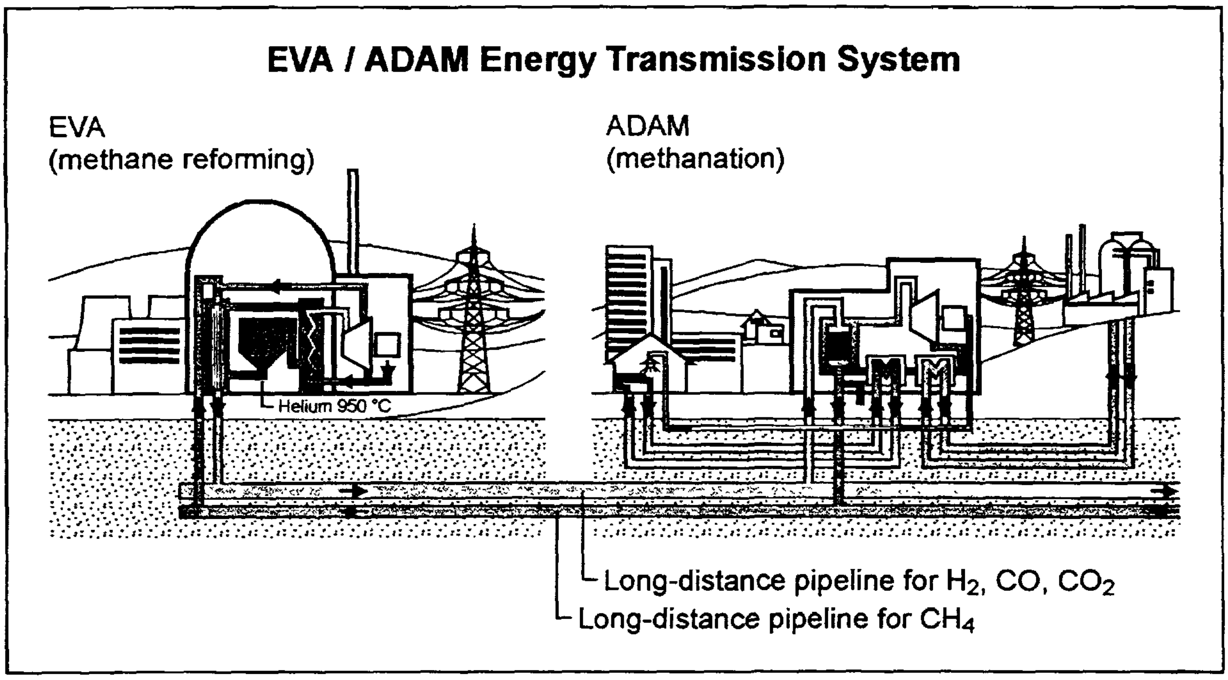

Fig. B-1: Schematic of long-distance energy transportation in the EVA/ADAM facility, from [1]

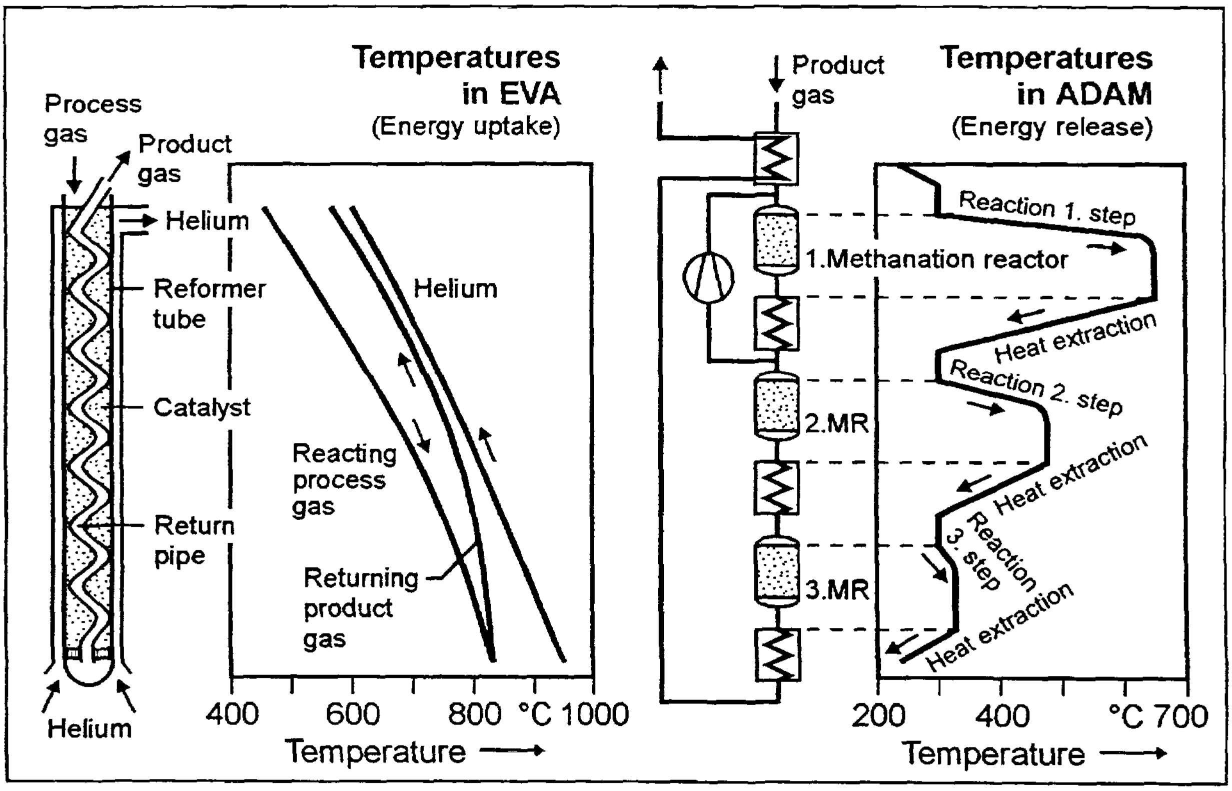

Fig. B-2: Temperature behavior in the methane reformer EVA (left) and in the methanation system ADAM (right), from [1]

The two significant features of the ADAM plant were the complete reconversion to methane, thus releasing the complete reaction enthalpy again and the realization of a 650 °C gas mixture after the first methanation step which allowed for the generation of superheated high-pressure steam for further use (here added to the heating system of the Research Center Jülich). The temperature profiles in the ADAM system are shown in Fig. B-2, right hand side [1].

The complete EVA-II / ADAM-II system was operated in Jülich for a total time of 10,150 hours. It has demonstrated for the first time the chemical cycle process under the realistic conditions of industrial application with a transported power of 300 kW (EVA / ADAM) and of 5.4 MW (EVA-II / ADAM-II), respectively. The test facilities, however, were not operated for the sake of maximizing the energy efficiency, they were rather used to examine the components' behavior under various load conditions including fast transients [1, 5, 6].

The CH_4 - H_2O system needs a second return pipe from ADAM to EVA for the liquid water, if a cleanup of the water and the loss of unconverted hydrocarbons are to be avoided [4].

The EVA / ADAM system has been established, besides in Germany, also in the USA and the Russian Federation [9].

B.2. CO_2 REFORMING SYSTEM

The CO_2 reforming process of methane

$$CH_4 + CO_2 \quad \longleftrightarrow \quad 2\,CO + 2\,H_2 - 247\text{ kJ/mol}$$

has been studied as a chemical heat pipe system since 1980 as an alternative in order to overcome some of the potential difficulties. In contrast to the CH_4 - H_2O system, a third pipe is not required since it is not necessary to clean the water. Thus an open cycle system could be adopted [4].

At the Weizmann Institute in Israel, the closed-cycle CO_2 reforming process of natural gas has been adapted and modified to solar energy as the primary heat input. The use of gaseous CO_2 eases the daily startup / shutdown cycles. A lab-scale facility with 5 - 10 kW power was successfully operated. A scale-up plant designed for 480 kW heat input to the reforming reaction and 250 kW heat output in the methanation step is being tested since 1994. Catalysts are rhodium and ruthenium. So far 150 cycles have been completed [3]. The solar power absorbed was 97 kW, a methane conversion rate of 70 % maximum was achieved. A computer code has been developed for loop design and optimization purposes [9].

B.3. METHANOL SYSTEM

The production of energy alcohol on the basis of biomass plus CO_2-free primary energy features a CO_2-neutral system since the CO_2 release upon combustion of methanol has been formerly extracted from the atmosphere for the biomass production.

The methanol-carbon dioxide system is described by

$$CH_3OH + H_2O \longleftrightarrow CO_2 + 3\ H_2 - 131\ \text{kJ/mol}$$

The heat released during the methanol synthesis corresponds to not more than 15 % of the energy stored in the hydrogen. If, however, this heat can be fed into the reforming process, a high storage efficiency could be gained. No additional CO_2 is emitted, if atmospheric CO_2 is used as the carbon source.

The nuclear variant of using CH_3OH as the energy carrier taking the HTGR as the primary source for the required process heat is being described in section 4.3.2.3. Congenial systems are the methanol-carbon monoxide system

$$CH_3OH \longleftrightarrow CO + 2\ H_2$$

and the methanol-methyl formate (= formic acid salt) system:

$$2\ CH_3OH + H_2O \longleftrightarrow HCOOCH_3 + 2\ H_2$$

B.4. METHYLCYCLOHEXANE - TOLUENE SYSTEM

Among the many candidates of hydrogen transportation or seasonal storage methods, the H_2 evolution from cyclohexanes at the demand site and the reverse reaction, the hydrogenation of benzene, at the supply site offers the advantages of safe and commonly used transport at ambient temperature in chemical tank ships or trucks and mild reaction conditions. Cyclohexanes have a hydrogen density and content comparable with metal hydrides [8]. Methylcyclohexane is the choice of preference, since unlike benzene, toluene is not carcinogenic.

The **methylcyclohexane (MCH) cycle** is described by:

$$C_7H_{14} \longleftrightarrow C_7H_8 + 3\ H_2 - 215\ \text{kJ/mol}$$

The hydrogen storage capacity of MCH is 6.2 wt%. Dehydrogenation at 1 MPa is an endothermal catalytic reforming step with a high yield of toluene (98 %) at elevated temperatures (> 400 °C). A critical point is the initial conditioning and regeneration of the catalyst. The process conditions of the hydrogenation of the toluene are 2 MPa at 220 °C achieving a yield of 99 % [2]. A comparison of the MCH vector with the LH_2 vector has been made within the frame of the Euro-Quebec project. Characteristics of the LH_2 and the MCH vectors are listed in Table B-1.

Table B-1: Characteristics of the two vectors investigated in the EQHHPP, from [10]

Liquid Hydrogen	**Methylcyclohexane / Toluene**
No hydrocarbons involved during production and utilization	Hydrocarbons involved due to conversion limitations
Low environmental impact upon inadvertant release	High environmental impact upon inadvertant release
Use as liquid or gaseous fuel	Use as gaseous fuel only
Sophisticated transport technology not yet commercially available	Conventional transport in chemical tank ships
Limited storage period	Unlimited storage period
Part of liquefaction energy can be recovered	Energy needed for dehydrogenation

Long-term storage of energy by means of MCH is reasonable in cases where the energy structure results in a large cost difference of seasonal electricity production (e.g., hydro, solar).

B.5. NH_3 SYSTEM

The ammonia dissociation reaction as a closed-cycle liquid hydride energy storage system has been investigated primarily by Australian researchers in connection with solar primary energy [7]:

$$2\ NH_3 \quad \longleftrightarrow \quad N_2 + 3\ H_2 - 59\ \text{kJ/mol}$$

The advantage of the above process is the complete absence of any side reactions. The relatively low exothermal reaction rates can be raised, if higher pressures are applied. The fact that ammonia condenses at around room temperature and separates from the reactant mixture allows storage of feedstock for both endothermal and exothermal reaction in the same vessel. Experience with a pilot plant operating at pressures up to 16 MPa and temperatures up to 720 °C indicate a 1 kW closed-loop system to be feasible [7].

A hydrogen storage system using formates seems to be promising. The reversible catalytic reaction with sodium formate to decompose to bicarbonate and hydrogen is

$$NaCOOH + H_2O \quad \longleftrightarrow \quad NaHCO_3 + H_2$$

The hydrogen capacity is 2.9 wt%. Its advantages are cheap raw materials and the potential of storing H_2 in solid form [11].

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Appendix C

CHEMICAL HEAT PUMP SYSTEMS

C.1. 2-PROPANOL - ACETONE SYSTEM

A key process is the dehydrogenation catalysis of 2-propanol under mild reaction conditions converting low-quality heat into chemical energy and recovering high-temperature heat or hydrogen gas at the energy demand site.

$$(CH_3)_2CHOH \quad \longleftrightarrow \quad (CH_3)_2CO + H_2 \text{ - 55 kJ/mol}$$

The 2-propanol / acetone / hydrogen chemical heat pump is operated in three steps:

1. 2-propanol dehydrogenation
   is an endothermal reaction at low temperatures (≈ 80 °C) assisted by a catalyst.
2. Acetone hydrogenation
   is the reverse exothermal reaction at higher temperatures (150 - 200 °C).
3. Separation
   of the 2-propanol from acetone and hydrogen by condensation in a fractional distillation column at ambient temperatures.

High thermal efficiencies can be achieved with properly designed catalysts. A pilot plant for this chemical heat pump system was constructed in Oarai, Japan, and successfully tested in 1994. A pilot plant driven by solar energy was realized at the Florida Solar Energy Center demonstrating an average yield of 180 ml/h of hydrogen (over several days).

C.2. CYCLOHEXANE - BENZENE SYSTEM

The reaction couple consists of cyclohexane dehydrogenation at 200 °C under normal atmospheric pressure and benzene hydrogenation at 350 °C.

$$C_6H_{12} \quad \longleftrightarrow \quad C_6H_6 + 3\ H_2 \text{ - 206 kJ/mol}$$

This system can be realized in a tube wall type reactor.

The use of a membrane reactor with a hydrogen-permeable palladium alloy membrane inside a catalyst-packed bed allowed a shifting of the chemical equilibrium to efficiently drive the dehydrogenation process at lower temperatures, e.g., waste heat. It thus serves as a chemical heat pump system.

C.3. HYDRIDE SYSTEM

A closed-loop heat pump system based on hydrides, a **metal hydride super heat pump (MHSHP)** system, has been investigated at JAERI with the purpose not only to amplify nuclear waste heat, but also to mass store hydrogen for transportation purposes. The L reactor contains an MHX alloy where hydrogen is stored. A medium-temperature heat source liberates the hydrogen. After transfer to the H reactor, the hydrogen is absorbed in the Ca alloy and upon reaction liberates high-temperature heat which can be decoupled from the system by a helium heat exchanger. Candidate MHX materials are currently subject to further research. In a test facility, heat conversion from 500 to 900 °C was achieved. The MHSHP system is considered to be connected to the UT-3 hydrogen production cycle.

C.4. SPONGE IRON

The use of sponge iron resulting from the direct iron ore reduction as a hydrogen storage system has been found to be practicable although with the penalties of a heavy weight, its solid state as a fuel, and not too high an amount of energy to be stored. Applications might be seen in heavy transportation systems, e.g., fuel cell powered locomotives.

ABBREVIATIONS

ADAM	Facility with Three Adiabatic Methanation Reactors (Anlage mit drei adiabaten Methanisierungsreaktoren)
AFC	Alkaline Fuel Cell
AICC	Adiabatic Isochoric Complete Combustion
ALWR	Advanced Light-Water Reactor
BMC	Battelle Model Containment
BWR	Boiling Water Reactor
CETS	Chemical Energy Transmission System
CFD	Computer Fluid Dynamics
CHP	Combined Heat and Power
CNG	Compressed Natural Gas
DDT	Deflagration-to-Detonation Transition
DLR	Deutsche Forschungsanstalt für Luft- und Raumfahrt
DMFC	Direct Methanol Fuel Cell
EC	European Community
EPR	European Pressurized Water Reactor
EPRI	Electric Power Research Institute
EQHHPP	Euro-Quebec Hydro-Hydrogen Pilot Project
ET	External Tank
EVA	Single Tube Test Facility (Einzelspaltrohr-Versuchsanlage)
FAPIG	First Atomic Power Industry Group
FZJ	Forschungszentrum Jülich GmbH
FZK	Forschungszentrum Karlsruhe GmbH
GRS	Gesellschaft für Anlagen- und Reaktorsicherheit mbH
HDR	Superheated Steam Reactor (Heißdampfreaktor)
HHT	High-Temperature Reactor with Helium Turbine of Large Power (Hochtemperaturreaktor mit Heliumturbine großer Leistung)
HTGR	High-Temperature Gas-Cooled Reactor
HTTR	High-Temperature Engineering Test Reactor
IAEA	International Atomic Energy Agency
ICE	Internal Combustion Engine
ICT	Institut für Chemische Technologie der Fraunhofer Gesellschaft
IEA	International Energy Agency
IGCC	Integrated Gasification Combined Cycle

IGFC	Integrated Gasification Fuel Cell
IHX	Intermediate Heat Exchanger
IMFC	Indirect Methanol Fuel Cell
INET	Institute for Nuclear Energy Technology, Beijing
IS	Iodine - Sulfur (Thermochemical Cycle)
JAERI	Japan Atomic Energy Research Institute
JCT	Japan - China - Taiwan
KVK	Component Experimental Loop (Komponenten-Versuchskreislauf)
LH_2	Liquid Hydrogen
LMFBR	Liquid Metal Fast Breeder Reactor
LNG	Liquid Natural Gas
LOX	Liquid Oxygen
LPG	Liquid Petroleum Gas
LWR	Light Water Reactor
MCFC	Molten Carbonate Fuel Cell
MCH	Methylcyclohexane
MHR	Modular Helium Reactor
MHTGR	Modular High-Temperature Gas-Cooled Reactor
NASA	National Aeronautics and Space Administration
NASDA	National Space Development Agency of Japan
NBP	Normal Boiling Point
NFE	Nuclear Long-Distance Energy (Nukleare Fernenergie)
NHIES	Novel Horizontally Integrated Energy System
NOX	Nitrogen Oxides
NRC	US Nuclear Regulatory Commission
NTS	Nevada Test Site
OECD	Organization for Economic Cooperation and Development
PAFC	Phosphoric Acid Fuel Cell
PEFC	Polymer Electrolyte Fuel Cell
PEM-FC	Proton Exchange Membrane Fuel Cell
PHWR	Pressurized Heavy Water Reactor
PNP	Prototype Plant Nuclear Process Heat (Prototypanlage Nukleare Prozeßwärme)
PRA	Probabilistic Risk Assessment
PSA	Probabilistic Safety Assessment
PV	Photovoltaics

PWC	Pressurized Water Cooler
PWR	Pressurized Water Reactor
RE H_2	Hydrogen from Renewable Energies
RT	Room Temperature
RUT	Rocket Shock Tube
RWTH	Rheinisch-Westfälische Technische Hochschule, Aachen
SLH_2	Slush Liquid Hydrogen
SNG	Synthetic Natural Gas
SOFC	Solid Oxide Fuel Cell
SPEWE	Solid Polymer Electrolyte Water Electrolysis
SPFC	Solid Polymer Fuel Cell
STP	Standard Temperature and Pressure
SULEV	Super Ultra-Low Emission Vehicle
SWATH	Small Waterplane Area Twin Hull
TMI	Three Mile Island
TNO	Netherlands Organization for Applied Scientific Research
TNT	Trinitrotoluene
TOE	Tons of Oil Equivalent
ULEV	Ultra-Low Emission Vehicle
WE-NET	International Clean Energy Network Using Hydrogen Conversion (World Energy Network)
ZEV	Zero Emission Vehicle

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