J. Webster (ed.), *Wiley Encyclopedia of Electrical and Electronics Engineering*

HYDROGEN ENERGY SYSTEMS

Utilization of fossil fuels appears to be causing global problems such as the greenhouse effect, ozone layer depletion, and acid rain and pollution, which are posing great danger to our environment and eventually to life on our planet. Many engineers and scientists agree that a solution to all these global problems would be to replace the existing fossil fuel system with the hydrogen energy system. Hydrogen is a very efficient and clean fuel. Its combustion produces no greenhouse gases, no ozone layer-depleting chemicals, little or no acid rain ingredients, and no pollution. Hydrogen, produced from renewable (solar) energy sources, would provide a permanent energy system, which we may never have to change.

However, other energy systems have been proposed for the postpetroleum era such as the synthetic fossil fuel system. In this system, synthetic gasoline and synthetic natural gas are to be produced using the abundant deposits of coal. In a way, this could ensure the continuation of the present fossil fuel system.

The two possible energy systems for the postfossil fuel era (solar hydrogen energy system and synthetic fossil fuel system) are compared with the present fossil fuel system by taking into consideration production costs, environmental damage, and utilization efficiencies. Results indicate that the solar hydrogen energy system is the best energy system to guarantee a sustainable future.

Under normal conditions, hydrogen is a gas, and for many applications it will be used in gaseous form, just like natural gas. Wherever space considerations are important, such as in aerospace applications, hydrogen is used in liquid form. If space saving becomes the number one priority, as in the case with the earth-to-stationery orbit single-stage transport, then slush hydrogen could be the best answer.

Fossil Fuels

After the invention of the steam engine in the 1860s, when advances brought about by the Industrial Revolution started to replace humans' and beasts' toil with nature's energy sources, a bright future seemed to be certain for humankind. More and more of nature's energy, initially in the form of wood and coal and later as oil and natural gas, was being harnessed for the benefit of humans. This resulted in mass production of goods with a corresponding reduction in prices, thus raising living standards. Communities asked for factories, railroads, highways, seaports, and airports. This meant more jobs, more income, more goods, and more services. The world's standard of living was rising. When the Industrial Revolution started, the annual gross world product per capita was in some tens of dollars; today, it is about $6600 and rising exponentially.

Fossil fuels, which fed this amazing economic growth, were the medicine to cure deprivation, but it was an untested medicine. As humans consumed more and more fossil fuels, two important predicaments started to emerge: (1) fossil fuels would be depleted in a foreseeable future, and (2) fossil fuels and their combustion products were causing global environmental problems.

Depletion. The demand for energy continues to rise for two main reasons: (a) the continuing increase in world population and (b) the growing demand by the developing countries in order to improve their living standards. At the present time, a large portion (about 70%) of the world energy demand is met by fluid fossil

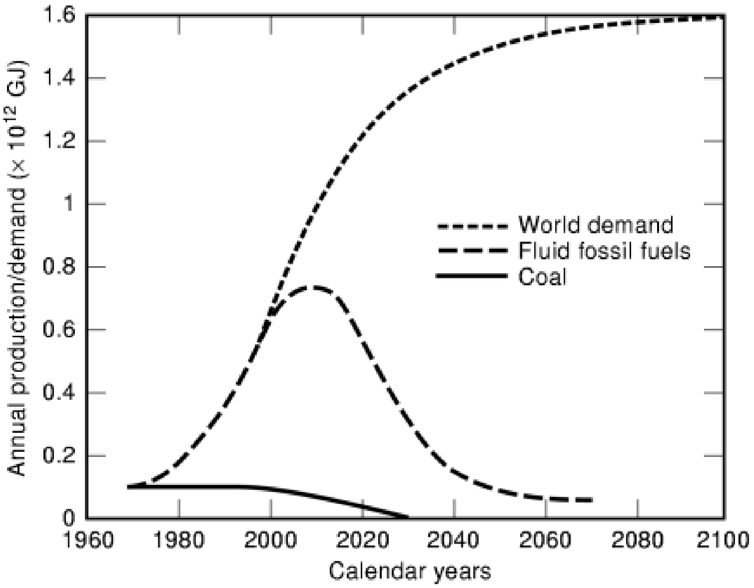

Fig. 1. Estimates of world fossil fuel production.

fuels (petroleum and natural gas) because of the availability of these resources and their convenience of use. However, it is expected that the world fluid fossil fuel production will soon peak and thereafter begin to decrease (1,2,3,4). Figure 1 shows estimates of the production rates of fossil fuels and the world demand. It can be seen that the fluid fossil fuel production worldwide will continue to rise for the next 15 years and then will start to decrease. The coal production—because of obvious environmental reasons—is expected to remain nearly constant for the next decade and then start to decrease.

Meanwhile, as a result of the growing world population and the desire of people to better their living standards, the world demand for fluid fuels is rising (Fig. 1). It is expected that the world population (which is 5.88 billion as of 1998 and rising at 1.5% per year) growth will slow down and reach about 10 to 12 billion by the end of the next century (5). Consequently, the world demand for fluid fuels will slow down and reach around 1.6 $\times 10^{12}$ GJ per year (1 GJ of energy is approximately equal to the energy contained in 3.4 gallons of petroleum). There will be a growing gap, starting within the next 10 years, between the demand and production of fluid fuels.

Environmental Damage. The second predicament involving fossil fuels is the environmental damage being caused by their combustion products. Technologies for fossil fuel extraction, transportation, processing, and particularly their end use (combustion) have harmful effects on the environment, which cause direct and indirect negative effects on the economy. Excavation of coal devastates the land, which has to be reclaimed and is out of use for several years. During the extraction, transportation, and storage of oil and gas, spills and leakages, which cause water and air pollution, occur. Refining processes also have an environmental impact. However, most of the fossil fuel environmental impact occurs during end use. End use of all fossil fuels is combustion, irrespective of the final purpose (heating, electricity production, or motive power for transportation). The main constituents of fossil fuels are carbon and hydrogen in addition to some other ingredients, which are originally in the fuel (sulfur) or are added during refining (lead, alcohols). Combustion of fossil fuels produces various gases (CO_x, SO_x, NO_x, CH), soot and ash, droplets of tar, and other organic compounds, which are all released into the atmosphere and cause air pollution. Air pollution may be defined as the presence of some gases and particulates that are not a natural constituent of the atmosphere, or the presence of natural constituents in an abnormal concentration. Air pollution causes damage to human health, animals, crops, and structures, in addition to reducing visibility, among other problems.

Once in the atmosphere, triggered by sunlight or by mixing with water and other atmospheric compounds, these primary pollutants may undergo chemical reactions, change their form, and become secondary pollutants, like ozone, aerosols, peroxyacyl nitrates, and various acids. Precipitation of sulfur and nitrogen oxides, which have dissolved in clouds and in rain droplets to form sulfuric and nitric acids is called acid rain, but also acid dew, acid fog, and acid snow have been recorded. Carbon dioxide in equilibrium with water produces weak carbonic acid. Acid deposition (wet or dry) causes soil and water acidification, resulting in damage to the aquatic and terrestrial ecosystems, affecting humans, animals, vegetation, and structures.

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

Using the studies by scores of environmental scientists, these stated damages have been calculated for the different types of fossil fuels listed (6). Table 1 presents the results for each type of damage (in 1998 US dollars). It can be seen that the environmental damage for coal is \$14.51/GJ of coal consumed, for petroleum is \$12.52/GJ of petroleum consumed, for natural gas \$8.26/GJ of natural gas consumed, and the weighted mean damage in the world is \$12.05/GJ of fossil fuel consumption. These damage costs are not included in the prices of fossil fuels, but they are paid for by the people directly or indirectly through taxes, health expenditures, insurance premiums, and a reduced quality of living. In other words, today's fossil fuels are heavily subsidized. If the respective environmental damages were included in the fossil fuel prices, it would force earlier introduction of cleaner fuels, such as hydrogen, with many benefits to the economy and the environment.

In order to see the worldwide dimensions of the fossil fuel environmental damage, Table 2 has been prepared. Note that 37% of the total damage is caused by coal, whereas the coal consumption is 31% of the total fossil fuel consumption. On the other hand, only 20% of the damage is caused by natural gas, which has a market share of 29%. It is clear that increasing the natural gas consumption at the expense of coal and petroleum will be environmentally beneficial. This would also pave the way for greater public acceptance of gaseous fuels, which may result in a smoother change to hydrogen, also a gaseous fuel.

Note also from Table 2 that the annual worldwide environmental damage caused by fossil fuels is \$4345 billion, or 11% of the gross world product. This is a very large figure. Conversion to a cleaner fuel, such as hydrogen, would enable the world to save this enormous sum and perhaps use it to improve the quality of life worldwide.

New Energy System

Because of the environmental problems fossil fuels are causing, energy researchers are looking at all possible sources of energy to replace these fuels. There are quite a number of primary energy sources, such as thermonuclear energy, nuclear breeders, solar energy, wind energy, hydropower, geothermal energy, ocean currents, tides, and waves, that are available. At the consumer end, about one-quarter of the primary energy is used as electricity and three-quarters is used as fuel. The primary energy sources already mentioned must therefore be converted to these energy carriers needed by the consumer. In contrast with fossil fuels, none of the new primary energy sources can directly be used as a fuel (e.g., for air and land transportation). Consequently, they must be used to manufacture a fuel or fuels as well as to generate electricity.

Comparison of Fuels. Because we need to manufacture a fuel for the post fossil fuel era, we are in a position to select the best possible fuel. There are many candidates, such as synthetic gasoline, synthetic natural gas (methane), methanol, ethanol, and hydrogen. The fuel of choice must satisfy the following conditions (7):

Table 1. Environmental Damage Caused by Fossil Fuels

	Environmental Damage 1998 ($/GJ)					
	Coal		Petroleum		Natural Gas	
Type of Damage (n)	Itemized Damage	Subtotals	Itemized Damage	Subtotals	Itemized Damage	Subtotals
Effect on Humans		5.16		4.19		3.09
Premature deaths	1.75		1.42		1.05	
Medical expenses	1.75		1.42		1.05	
Loss of working efficiency	1.66		1.35		0.99	
Effect on Animals		0.75		0.63		0.45
Loss of domestic live stock	0.25		0.21		0.15	
Loss of wildlife	0.50		0.42		0.30	
Effect on Plants and Forests		1.99		1.61		1.20
Crop yield reduction–ozone	0.25		0.21		0.15	
Crop yield reduction–acid rains	0.13		0.10		0.07	
Effect on wild flora (plants)	0.77		0.62		0.46	
Forests decline (economic value)	0.27		0.22		0.16	
Forest decline (effect on biological diversity)	0.53		0.43		0.33	
Loss of recreational value	0.04		0.03		0.03	
Effect on Aquatic Ecosystems		0.26		1.55		0.16
Oil spills	–		0.44		–	
Underwater tanks leakages	–		0.90		–	
Liming lakes	0.04		0.03		0.03	
Loss of fish population	0.04		0.03		0.03	
Effect on biological diversity	0.18		0.15		0.10	
Effect on Man-Made Structures		1.66		1.34		0.98
Historical buildings and monuments degradation	0.18		0.15		0.10	
Buildings and houses' detriment	0.37		0.30		0.22	
Steel constructions corrosion	0.99		0.80		0.59	
Soiling of clothes, cars, etc.	0.12		0.09		0.07	
Other Air Pollution Costs		1.45		1.16		0.88
Visibility reduction	0.30		0.23		0.18	
Air pollution abatement costs	1.15		0.93		0.70	
Effect of Strip Mining		0.73		–		–
Effect of Climactic Changes		2.04		1.66		1.22
Heat waves—effects on humans	0.27		0.22		0.16	
Droughts						
Agricultural losses	0.16		0.13		0.10	
Livestock losses	0.13		0.10		0.07	
Forests losses	0.16		0.13		0.10	
Wild flora and fauna losses	0.93		0.75		0.56	
Water shortage and power production problems	0.25		0.21		0.15	
Floods	0.07		0.06		0.04	
Storms, hurricanes, tornadoes	0.07		0.06		0.04	
Effect of Sea Level Rise		0.47		0.38		0.28
Totals		14.51		12.52		8.26

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

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

Table 2. Worldwide Fossil Fuel Consumption and Environmental Damage for 1998

Fossil Fuel Consumption	(10^{18} J/year)
World coal consumption	112
World petroleum consumption	148
World natural gas consumption	105
World fossil fuel consumption	365
Environmental Damage Estimate	(1998 billion $)
Damage due to coal	1,625
Damage due to petroleum	1,853
Damage due to natural gas	867
Total Damage	4,345
Demographic and Economic Data	
World population (in billions)	5.96
Damage per capita	$ 730
World GWP (billion $)	$39,340
GWP per capita	$ 6,600
Damage/GWP	0.11

Transportation Fuel. Surface vehicles and airplanes must carry their fuel for a certain distance before replenishing their fuel supply. In the case of space transportation, space vehicles must carry the fuel, as well as the oxidant, necessary for their scheduled range. Therefore, it is important that the transportation fuel be as light as possible and also take as little space as possible. We can combine these requirements in a dimensionless number, termed the motivity factor (8):

$$\varphi_{\mathrm{M}} = \frac{\left(\dfrac{E}{M}\right)\left(\dfrac{E}{V}\right)^{2/3}}{\left(\dfrac{E_{\mathrm{h}}}{M_{\mathrm{h}}}\right)\left(\dfrac{E_{\mathrm{h}}}{V_{\mathrm{h}}}\right)^{2/3}} \tag{1}$$

where E is the energy generated by the fuel, M is the mass of the fuel, V is the volume of the fuel, and the subscript h refers to hydrogen. The higher the motivity factor, the better the fuel for transportation. Table 3 lists the pertinent properties of some fuels, as well as the motivity factors calculated using Eq. (1). It can be seen that among the liquid fuels LH_2 has the best motivity factor, whereas methanol has the lowest motivity factor. Among the gaseous fuels, GH_2 has the best motivity factor.

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

Versatility. At the user's end, all fuels must be converted through a process (such as combustion) to other forms of energy (thermal, mechanical, or electrical energies). If a fuel can be converted through more than one process to various forms of energy at the user's end, it becomes more versatile and more convenient to use. Table 4 lists various fuels and processes by which they can be converted to other forms of energy at the user's end. It can be seen that most fossil fuels can be converted through one process only, that of combustion. In certain cases, natural gas could be used in catalytic combustion and in fuel cells, in addition to flame combustion. Hydrogen, however, can be converted to other forms of energy in five different ways; in addition to flame combustion, it can be converted directly to steam, converted to heat through catalytic combustion,

Table 3. Energy Densities (HHV) and Motivity Factors for Liquid and Gaseous Fuels

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

Table 4. Versatility (Convertibility) of Fuels

Conversion Process	Hydrogen	Fossil Fuels
Flame combustion	Yes	Yes
Direct steam production	Yes	No
Catalytic combustion	Yes	Yes*/No
Chemical conversion (hydriding)	Yes	No
Electrochemical conversion (fuel cells)	Yes	Yes*/No

be used as a heat source and/or heat sink through chemical reactions, and be converted directly to electricity through electrochemical processes (9). In other words, hydrogen is the most versatile fuel.

Utilization Efficiency. In comparing the fuels, it is important to take into account the utilization efficiencies at the user's end. For utilization by the user, fuels are converted to various energy forms, such as mechanical, electrical and thermal. Studies show that in almost every instance of utilization, hydrogen can be converted to the desired energy form more efficiently than other fuels. Table 5 presents the utilization efficiency factors, defined as the fossil fuel utilization efficiency divided by the hydrogen utilization efficiency for various applications. It can be seen that hydrogen is the most efficient fuel. This results in conservation of resources, in addition to conserving energy.

Safety. The safety aspects of fuels involve their toxicity on the one hand and the fire hazard properties on the other. In addition to the toxicity of their combustion products, the fuels themselves can be toxic.

Toxicity increases as the carbon-to-hydrogen ratio increases. Hydrogen and its main combustion product, water or water vapor, are not toxic. However, NO_x, which can be produced through the flame combustion of hydrogen (as well as through the combustion of fossil fuels) displays toxic effects.

Table 5. Utilization Efficiency Comparisons of Fossil Fuels and Hydrogen

Application	Utilization Efficiency Factor $\phi_U = \eta_F/\eta_H$
Thermal energy	
Flame combustion	1.00
Catalytic combustion	0.80
Steam generation	0.80
Electric power, fuel cells	0.54
Surface transportation	
Internal combustion engines	0.82
Fuel cells/electric motor	0.40
Subsonic jet transportation	0.84
Supersonic jet transportation	0.72
Weighted average	0.72
Hydrogen utilization efficiency factor	1.00
Fossil fuel utilization efficiency factor	0.72

Table 6. Characteristics Related to Fire Hazard of Fuels

Property	Gasoline	Methane	Hydrogen
Density[a]	4.40	0.65	0.084
Diffusion coefficient in air[a] (cm^2/sec)	0.05	0.16	0.610
Specific heat at constant pressure[a] (J/g K)	1.20	2.22	14.89
Ignition limits in air (vol %)	1.0–7.6	5.3–15.0	4.0–75.0
Ignition energy in air (mJ)	0.24	0.29	0.02
Ignition temperature (°C)	228–471	540	585
Flame temperature in air (°C)	2197	1875	2045
Explosion energy[b] (g TNT/kJ)	0.25	0.19	0.17
Flame emissivity (%)	34–43	25–33	17–25

[a] At normal temperature and pressure.

[b] Theoretical maximum; actual 10% of theoretical.

Table 6 lists the characteristics of fuels related to fire hazards. Lower density makes a fuel safer because it increases the buoyancy force for speedy dispersal of the fuel in case of a leak. For the same reason, higher diffusion coefficients are helpful. Higher specific heat causes a fuel to be safer because it slows down the temperature increases for a given heat input. Wider ignition limits, lower ignition energies, and lower ignition temperatures make the fuels less safe, as they increase the limits within which a fire could commence. Higher flame temperatures, explosion energy, and/or flame emissivity make a fuel less safe as well because its fire would be more damaging.

Table 7 compares the safety of fuels. For each of the toxic element and fire hazard characteristics, it ranks the fuels from 1 to 3, 1 being the safest and 3 the least safe. These rankings have been summed up for each fuel in order to arrive at an overall ranking. The total rankings have been prorated to obtain the *safety factors,* defined as the ratio of the total ranking for hydrogen to that of a given fuel. It can be seen that hydrogen becomes the safest fuel, whereas gasoline is the least safe, and methane is in between the two.

Table 7. Safety Ranking of Fuels

	Fuel Ranking[a]		
Characteristic	Gasoline	Methane	Hydrogen
Toxicity of fuel	3	2	1
Toxicity of combustion (CO, SO_x, NO_x, HC, PM)	3	2	1
Density	3	2	1
Diffusion coefficient	3	2	1
Specific heat	3	2	1
Ignition limit	1	2	3
Ignition energy	2	1	3
Ignition temperature	3	2	1
Flame temperature	3	1	2
Explosion energy	3	2	1
Flame emissivity	3	2	1
Totals	30	20	16
Safety factor ϕ_s	0.53	0.80	1.00

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

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

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

Figure 2 presents a schematic diagram of the proposed hydrogen energy system. In this system, hydrogen (and oxygen) is produced in large industrial plants where the primary energy source (solar, nuclear, and even fossil) and water (H_2O), the raw material, are available. For large-scale storage, hydrogen can be stored underground in ex-mines, caverns, and/or aquifers. Hydrogen is then transported, by means of pipelines or super tankers, to energy consumption centers. It is then used in electricity, transportation, and industrial, residential, and commercial sectors as a fuel and/or an energy carrier. The by-product is water or water vapor. If flame combustion of hydrogen is used, then some NO_x is also produced. Water and water vapor are recycled back, through rain, rivers, lakes and oceans, to make up for the water used in the first place to manufacture hydrogen.

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

It should be noted that in the hydrogen energy system, hydrogen is not a primary source of energy. It is an intermediary or secondary form of energy or an energy carrier. Hydrogen complements the primary energy sources and presents them to the consumer in a convenient form at the desired location and time.

Details of the hydrogen energy system, including production, storage, transportation, distribution, utilization, environmental impact, and economics, can be found in the proceedings of the THEME and the World Hydrogen Energy Conferences (10,11,12,13,14,15,16,17,18,19,20,21,22,23).

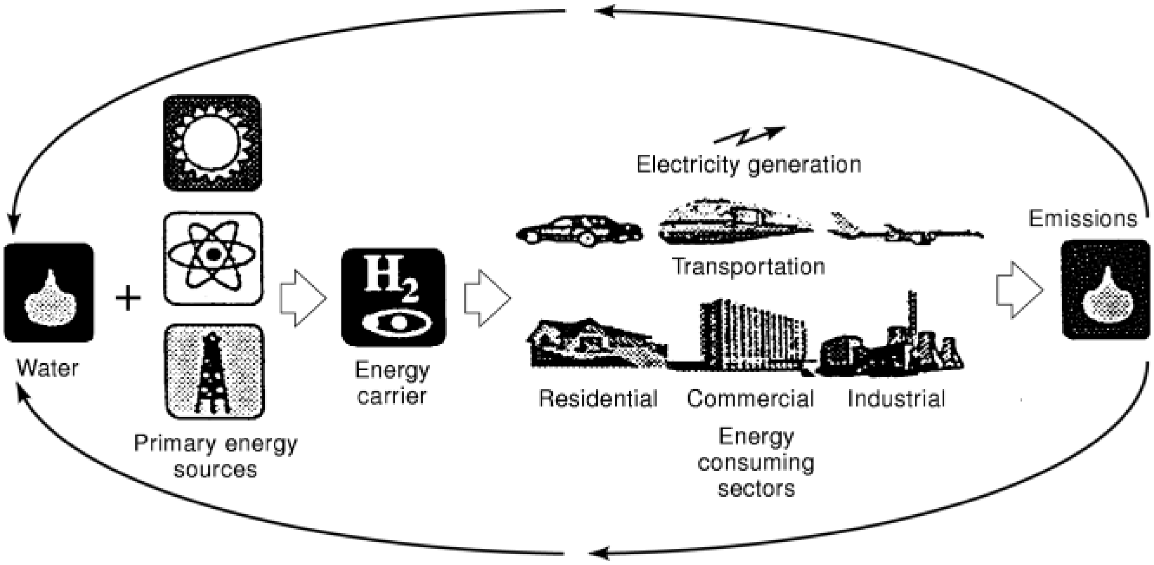

Fig. 2. A schematic diagram of the hydrogen energy system.

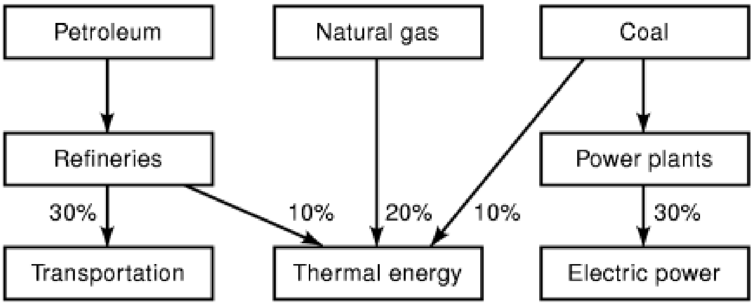

Fig. 3. Fossil fuel system.

Fossil Fuel System. A simplified version of today's energy system is shown in Fig. 3. Fossil fuels are used for transportation (mostly petroleum products); for heat generation in residential, commercial and industrial sectors; and for electric power generation. For transportation, mostly petroleum products are used (gasoline, diesel fuel, jet fuel, etc.). Heat generation includes space and domestic water heating, cooking, steam generation and direct heating, and/or drying in various industrial processes. All three forms of fossil fuels are used for these purposes. In electric power generation, coal is used mainly for the base load generation, and natural gas and heating oil are used for peak load. Part of the electric power is produced by hydro and nuclear powers.

In comparing with other energy systems, it can be assumed that 40% of the primary energy (in fossil fuel equivalent units) will be used for thermal energy generation, 30% for electric power generation, and 30% for transportation (2/3 for surface transportation and 1/3 for air transportation) (24). Energy supplied by hydro and nuclear power plants (mostly in the form of electric power) and by other nonfossil fuel sources do not need to be taken into account because it is assumed that it will be the same for all three considered systems. Actually, it is reasonable to expect that in the future even more electrical energy will be supplied by these sources.

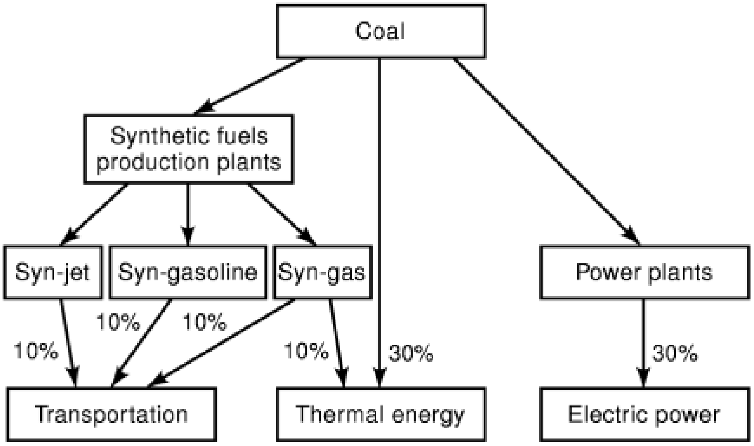

Fig. 4. Coal/synthetic fossil fuel system.

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

Coal/Synthetic Fossil Fuel System. Reserves of fossil fuels are finite, particularly those of oil and natural gas. Known reserves of oil and natural gas are about 8000 EJ (1 EJ = 10^{18} J), which would be enough for the next 40 years at the current consumption rate (25). If the exponential population growth and the demand for growth are taken into account, they would only last about 25 years. Even if the estimated additional undiscovered resources were added, that would satisfy energy needs for fluid fuels an additional 30 years or so. Coal reserves are much larger, known reserves are about 20,000 EJ, but estimated ultimately recoverable resources add up to 150,000 EJ. These large amounts of coal could eventually be used to produce synthetic liquid fuels, allowing society to continue employing the present energy system. Such a system is called the coal/synthetic fossil fuel system because coal is to be used to manufacture synthetic fossil fuels, as well as to be directly used for electricity generation.

In this case, it can be assumed that the present fossil fuel system will be continued by the substitution with synthetic fuels derived from coal wherever convenient and/or necessary. Patterns of energy consumption are also assumed to be unchanged (see Fig. 4). Coal will be used extensively for thermal as well as electric power generation because it is much cheaper than synthetic fuels. However, some end uses require fluid fuels. Therefore, it has been assumed that synthetic natural gas (*SNG*) will be used for some thermal energy generation (primarily in the residential sector) and also as fuel for surface transportation, where it will share the market with synthetic gasoline. Synthetic jet fuel will be used in air transportation.

Solar Hydrogen Energy System. If solar energy, in its direct and/or indirect forms (e.g., hydro, wind, etc.), is used to manufacture hydrogen, then the resulting system is called the solar hydrogen energy system. In this system, both the primary and secondary energy sources are renewable and environmentally compatible, resulting in a clean and permanent energy system. Figure 5 presents a schematic of the solar hydrogen energy system.

In this case, it is assumed that the conversion to hydrogen energy will take place, and one-third of the hydrogen needed will be produced from hydropower (and/or wind power) and two-thirds by direct and indirect (other than hydropower) from solar energy forms. The same percentage of energy demands sectors

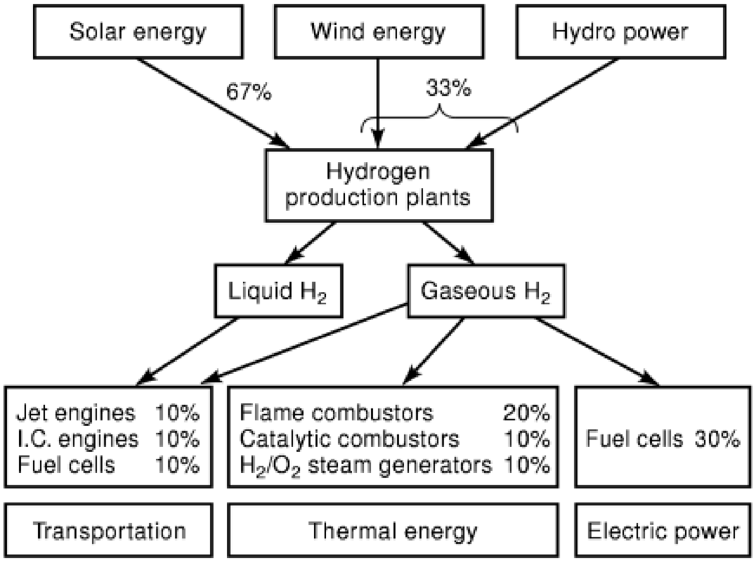

Fig. 5. Solar-hydrogen energy system.

as the above systems will be assumed. It will further be assumed that one-half of the thermal energy will be achieved by flame combustion, one-quarter by steam generation with hydrogen/oxygen steam generators, and the last quarter by catalytic combustion; electric power will be generated by fuel cells; one-half of the surface transportation will use gaseous hydrogen-burning internal combustion engines, and the other half will use fuel cells. In air transportation, both subsonic and supersonic, liquid hydrogen will be used.

Comparison of Energy Systems

These three energy systems will now be compared environmentally and economically.

Pollution. Table 8 lists the pollutants for the three energy systems described earlier. It can be seen that the coal/synthetic fossil system is the worst from the environmental point of view, whereas the solar hydrogen energy system is the best. The solar hydrogen system will not produce any CO_2, CO, SO_x, hydrocarbons, or particulates, except some NO_x. However, the solar-hydrogen-produced NO_x is much less than that produced by the other energy systems. This is due to the fact that in the solar hydrogen energy system only the flame combustion of hydrogen in air will generate NO_x. The other utilization processes (such as direct steam generation, use of hydrogen in fuel cells, hydriding processes, etc.) will not produce any NO_x.

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

Only the flame combustion of fuels in air or in oxygen will produce water vapor. In the case of hydrogen, those other processes mentioned earlier will not produce any water vapor. Consequently, contrary to popular belief, the solar hydrogen energy system will produce less water vapor than the other systems.

Global warming, which is caused by the utilization of fossil fuels, also causes an increase in water vapor generation. Assuming that Earth's mean temperature has increased by 0.5°C since the beginning of the Industrial Revolution (26), this additional water vapor generation and that produced by the combustion of fuels have been calculated. The results are presented in Table 9. It can be seen that (1) the two fossil fuel systems

Table 8. Pollutants Produced by the Three Energy Systems

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

[a] Particulate matter.

Table 9. Comparison of Vapor Generation by Three Energy Systems (for 1998 Energy Consumption)

Item	Unit	Fossil Fuel System	Coal Synthetic Fossil Fuel System	Solar Hydrogen System
Annual vapor generation by energy system	10^{12} kg	8.9	9.300	6.0
Annual vapor generation due to global warming	10^{12} kg	3900	3900.000	0
Total vapor generation due to energy system and global warming	10^{12} kg	3909	3909.000	6.0
Total vapor generation as fraction of that produced naturally	%	0.782	0.782	0.001

Note: Annual vapor generation caused by solar heating is 5×10^{17} kg.

generate much more additional (above natural) water vapor than the solar hydrogen energy system; (2) the additional water vapor generated by global warming is much greater than that produced by the combustion of fuels; (3) the amount of water vapor generated by fuels is minimal compared to that generated naturally; and (4) the solar hydrogen energy system causes the smallest increase in vapor generation. Again, when the additional vapor generation is considered, the solar hydrogen energy system becomes environmentally the most compatible system.

Environmental Damage. Table 10 presents the environmental damage per gigaJoule of the energy consumed for each of the three energy systems considered and also for their fuel components in 1998 US dollars, as well as the environmental compatibility factors, defined as the ratio of the environmental damage caused by the hydrogen energy system to that caused by a given energy system. The environmental damage for the solar hydrogen energy system is a result of the NO_x produced. It can be seen that the solar hydrogen energy system is environmentally the most compatible system.

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

Economics. An economical comparison between competing energy systems should be based on the effective costs of the services these fuels provide. The effective costs include the utilization efficiency, the cost

Table 10. Environmental Damage and Environmental Compatibility Factors

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

of the fuel, and the costs associated with fuel consumption but that are not included in its price (so-called external costs). External costs include the costs of the physical damage done to humans, fauna, flora, and the environment as a result of harmful emissions, oil spills and leaks, and coal strip mining, as well as governmental expenditures for pollution abatement and expenditures for military protection of oil supplies.

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

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

$$C_r = (C_i + C_e)\,\frac{\eta_{fk}}{\eta_{sk}} \qquad (2)$$

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

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

$$C_o = \sum_{n=1}^{n} \alpha_n C_{rn} \qquad (3)$$

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

$$\sum_{n=1}^{n} \alpha_n = 1 \qquad (4)$$

Table 11. Effective Cost of Fossil Fuel System

Application	Fuel	Energy Consumption Fraction	Effective Cost (1998 US $/GJ)
Thermal energy	Natural gas	0.20	17.46
	Petroleum fuels	0.10	27.56[a]
	Coal	0.10	17.75
Electric power	Coal	0.30	17.25
Surface transportation	Gasoline	0.20	31.61
Air transportation	Jet fuel	0.10	25.98
Total of fractions		1.00	
Overall effective cost			22.11

[a] Average for residential and industrial sector.

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

$$C_{\mathrm{o}} = \sum_{n=1}^{n} \alpha \left[(C_{\mathrm{i}} + C_{\mathrm{e}}) \frac{\eta_{\mathrm{fk}}}{\eta_{\mathrm{sk}}} \right]_n \tag{5}$$

Using Eqs. (2)–(5), Tables 11, 12, 13 have been prepared for the three energy scenarios (i.e., the fossil fuel system, the coal/synthetic fossil fuel system, and the solar hydrogen energy system) in 1998 US dollars. Comparing the results, it becomes clear that the solar hydrogen energy system is the most cost-effective energy system and results in the lowest overall effective cost to society.

Gaseous Hydrogen

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

Hydrogen is an odorless, colorless gas. With a molecular weight of 2.016, hydrogen is the lightest element. Its density is about 14 times less than air (0.08376 kg/m^3 at standard temperature and pressure). Hydrogen is liquid at temperatures below 20.3 K (at atmospheric pressure). Hydrogen has the highest energy content per

Table 12. Effective Cost of Coal/Synthetic Fuel System

Application	Fuel	Energy Consumption Factor	Effective Cost (1998 US $/GJ)
Thermal energy	Coal	0.30	17.75
	SNG	0.10	36.64
Electric power	Coal	0.30	17.25
Surface transportation	SNG	0.10	36.64
	Syn-gasoline	0.10	51.65
Air transportation	Syn-jet	0.10	45.45
Total of fractions		1.00	
Overall effective cost			27.55

unit mass of all fuels—higher heating value is 141.9 MJ/kg, almost three times higher than gasoline. Some important properties of hydrogen are compiled in Table 14.

Hydrogen Production. Hydrogen is the most plentiful element in the universe, making up about three-quarters of all matter. All the stars and many of the planets essentially consist of hydrogen. However, on Earth free hydrogen is scarce. The atmosphere contains trace amounts of it (0.07%), and it is usually found in small amounts mixed with natural gas in crustal reservoirs. A few wells, however, have been found to contain large amounts of hydrogen, such as some wells in Kansas that contain 40% hydrogen, 60% nitrogen and trace amounts of hydrocarbons (27). The Earth's surface contains about 0.14% hydrogen (the tenth most abundant element), most of which resides in a chemical combination with oxygen as water.

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

Except for the space program, hydrogen is not being used directly as a fuel or energy carrier. It is being used in refineries to upgrade crude oil (hydrotreating and hydrocracking), in the chemical industry to synthesize various chemical compounds (such as ammonia and methanol), and in metallurgical processes (as a reduction or protection gas). The total annual hydrogen production worldwide in 1996 was about 40 million tons (5.6 EJ) (28). Less than 10% of this was supplied by industrial gas companies; the rest is produced at consumer-owned and -operated plants (so-called captive production), such as refineries, and ammonia and methanol producers. Production of hydrogen as an energy carrier would require an increase in production rates by several orders of magnitude.

Hydrogen Production from Fossil Fuels.

Steam Reforming of Natural Gas. Steam reforming of hydrocarbons (mainly natural gas) has been the most efficient, economical, and widely used process for hydrogen production. A simplified basic flow diagram of a conventional steam reforming process is shown in Fig. 6 (29). The process basically consists of three main steps: (1) synthesis gas generation, (2) water–gas shift, and (3) gas purification. The feedstock (natural gas) is mixed with process steam and reacted over a nickel-based catalyst contained inside a system of alloyed steel tubes. To protect the catalyst, natural gas must be desulfurized before being fed to the reformer. The following

Table 13. Effective Cost of Solar Hydrogen Energy System

Application	Fuel[a]	Energy Consumption Factor	Effective Cost (1998 US \$/GJ)
Thermal energy			
Flame combustion	GH_2	0.20	26.04
Steam generation	GH_2	0.10	20.83
Catalytic combustion	GH_2	0.10	20.83
Electric power			
Fuel cells	GH_2	0.30	14.06
Surface transportation			
IC engines	GH_2	0.10	21.36
Fuel cells	GH_2	0.10	10.41
Air transportation			
Subsonic	LH_2	0.05	26.26
Supersonic	LH_2	0.05	22.51
Total of fractions		1.00	
Overall effective cost			19.23

[a] It has been assumed that 1/3 of hydrogen will be produced from hydropower and/or windpower, and 2/3 from solar.

reactions take place in the reformer:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{6}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{7}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{8}$$

The reforming reaction is strongly endothermic, and energy is supplied by combustion of natural gas or fuel oil. The metallurgy of the tubes usually limits the reaction temperature to 700° to 925°C. The synthesis gas leaving a catalytic reformer is typically a mixture of H_2, CO, CO_2, and CH_4. After the reformer, the gas mixture passes through a heat recovery step cooling it down to about 350°C and feeding it into a water–gas

Table 14. Properties of Hydrogen

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

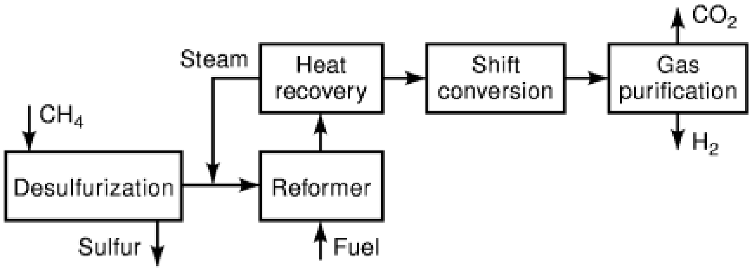

Fig. 6. Block diagram of hydrogen production by steam reforming of natural gas.

shift reactor to produce additional hydrogen. Next, the cold gas passes through gas purification units to remove the CO_2, the remaining CO, and other impurities in order to deliver purified hydrogen. Several commercial processes can be used for removing CO_2 (and CO), such as wet scrubbing, pressure swing adsorption, and, recently, membrane processes.

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

Partial Oxidation. Partial oxidation is used for converting hydrocarbons heavier than naphtha (for which steam reforming is not applicable). Most recently, partial oxidation reformers are being developed for on-board reforming of natural gas, ethanol, and even gasoline, to be coupled with fuel cells for automobile propulsion. A simplified basic flow diagram of an industrial partial oxidation process is shown in Fig. 7. There are three main steps: (1) synthesis gas generation, (2) water–gas shift reaction, and (3) gas purification. The partial oxidation reactions are typically as follows:

$$C_nH_m + n/2O_2 \rightarrow nCO + m/2H_2 + \text{heat} \qquad (9)$$

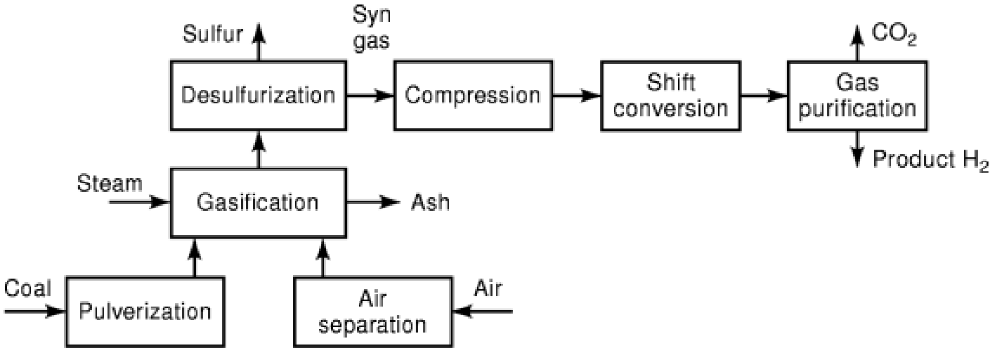

Fig. 7. Block diagram of hydrogen production by partial oxidation.

$$C_nH_m + n\,H_2O + \text{heat} \rightarrow n\,CO + (n + m/2)H_2 \qquad (10)$$

$$CO + H_2O \rightarrow CO_2 + H_2 + \text{heat} \qquad (11)$$

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

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

While the hydrocarbon–oxygen reaction is exothermic, additional energy required for the endothermic hydrocarbon–steam reaction, which is similar to steam reforming, is supplied by burning the additional fuel. Operating temperatures are rather high, 1150° to 1315°C, but with novel catalysts it is possible to accomplish the partial oxidation process at lower temperatures. The product steam (a very hot mixture of hydrogen, oxygen, CO, CO_2, steam, and a small amount of CH_4) is typically quenched with water as it exits the reactor to solidify the slag for downstream removal with cyclones or gas filtration or in a slurry. The sulfur contained in the feedstock is converted mainly to H_2S and only a small portion to COS. After sulfur removal, the gas is treated through the shift reaction and gas purification in the same way as the product gas from the steam-reforming process.

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

Recently, partial oxidation combined with steam reforming has started to be used for reforming lighter hydrocarbons and alcohols, such as gasoline, natural gas, propane, methanol, and ethanol. These reformers are being developed for small-scale reforming (50 kW and less) for both transportation and stationary power applications (30). They typically use air instead of pure oxygen, which results in a lower hydrogen content in the reformatted gas. The CO_2 removal process is not necessarily applied. With proper catalyst selection and thermal integration, those reformers can reach up to 80% efficiency.

Thermal Cracking of Natural Gas. The thermal decomposition of natural gas has been practiced for many years for the production of carbon black for rubber tire vulcanization, for pigment, and for the printing

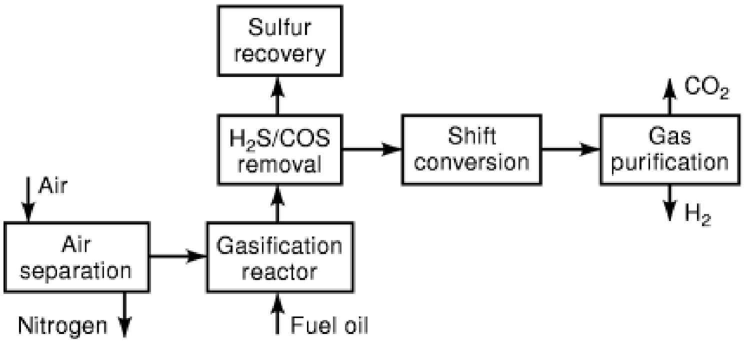

Fig. 8. Block diagram of hydrogen production by coal gasification process.

industry. A methane–air flame is used to heat up firebrick to temperatures in the order of 1400°C. The air is then turned off, and the methane alone decomposes on the hot firebrick until the temperature drops to about 800°C. The micron-size carbon particles are collected in the effluent gas stream in bag filters. The process is typically practiced batchwise in tandem furnaces: while one furnace is producing carbon black, the other is being heated up. Attempts have also been made to thermally crack natural gas in a continuous fixed bed reactor (31). With appropriate catalysts, it is possible to increase the rate of decomposition and accomplish an efficient continuous process (32). Another approach is to use high-temperature plasma for thermal cracking of natural gas or even heavier hydrocarbons (33).

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

Coal Gasification. In the coal gasification process (so called Koppers–Totzek process), the pulverized coal is rapidly partially oxidized with oxygen and steam at essentially atmospheric pressure. The raw gas is then cooled to recover waste heat, followed by quenching with water to remove entrained ash particles before going through the steps of compression, shift conversion, and gas purification (again by conventional wet scrubbing or pressure swing adsorption processes). The product is hydrogen at about 2.8 MPa with purity higher than 97.5%. The simplified block diagram is shown in Fig. 8.

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

The coal gasification process is complicated because of the necessity to handle solid fuel and to remove large amounts of ash. The solids-handling problem has a significant impact on costs. Generally, the lower cost of coal does not compensate for the higher capital cost of coal gasification systems (compared to steam reforming), and the cost of the produced hydrogen is about $12 to $14/GJ (29).

Hydrogen Production from Biomass. Hydrogen can be obtained from biomass by a pyrolysis/gasification process (34). The biomass preparation step involves heating of the biomass/water slurry to a high temperature under pressure in a reactor. This process decomposes and partially oxidizes the biomass, producing a gas product consisting of hydrogen, methane, CO_2, CO, and nitrogen. Mineral matter is removed from the bottom of the reactor. The gas stream goes to a high-temperature shift reactor where the hydrogen content is increased. A relatively high purity hydrogen is produced in the subsequent pressure swing adsorption unit. The whole system is very similar to a coal gasification plant, with the exception of the unit for pretreatment of the biomass and the design of the reactor. Because of the lower calorific value per unit mass of biomass as compared to coal, the processing facility is larger than that of comparably sized coal gasification plants.

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

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

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

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

$$\text{Cathode reaction:} \quad 2\mathrm{H_2O(l)} + 2e^- \rightarrow \mathrm{H_2(g)} + 2\mathrm{OH^-(aq)} \tag{12}$$

$$\text{Anode reaction:} \quad 2\mathrm{OH^-(aq)} \rightarrow \tfrac{1}{2}\mathrm{O_2(g)} + \mathrm{H_2O(l)} \tag{13}$$

$$\text{Overall cell reaction:} \quad \mathrm{H_2O(l)} \rightarrow \mathrm{H_2(g)} + \mathrm{O_2(g)} \tag{14}$$

The reversible decomposition potential ($E_{\text{rev}} = \text{DG}/nF$) of this reaction is 1.229 V at standard conditions. The total theoretical water decomposition potential is 1.480 V corresponding to hydrogen's enthalpy (because $\text{DH} = \text{DG} + \text{TDS}$). Because of irreversible processes occurring at the anode and cathode, including the electrical resistance of the cell, the actual potentials are always higher, typically between 1.75 V and 2.05 V. This corresponds to efficiencies of 72% to 82%, respectively.

Several advanced electrolyzer technologies are being developed. List includes the following:

- Advanced alkaline electrolysis, which employs new materials for membranes and electrodes that allow further improvement in efficiency—up to 90% (35,36).
- Solid polymer electrolytic (*SPE*) process, which employs a proton-conducting ion exchange membrane as electrolyte and as a membrane that separates the electrolysis cell. This type of electrolyzers can operate at very high current densities (up to 2 A/cm^2, which is about one order of magnitude higher than standard electrolyzers with alkaline liquid electrolyte). The water to be dissociated does not require dissolved electrolytes to increase its conductivity and is added solely to the anode side (36,37).
- High temperature steam electrolysis, which operates between 700° and 1000°C and which employs oxygen ion-conducting ceramics as electrolyte. Electrical energy consumption is reduced because part of the energy required for water dissociation is supplied in the form of heat. The water to be dissociated is entered on the cathode side as steam which forms a steam–hydrogen mixture during electrolytic dissociation. The O_2-ions are transported through the ceramic material to the anode, where they are discharged as oxygen (38).

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

Performance of photovoltaic–electrolyzer systems has been studied extensively both in theory and in practice (39,40,41,42). Several experimental PV-electrolysis plants are currently operating all over the world, such as

- Solar-Wasserstoff-Bayern pilot plant in Neunburg vorm Wald in Germany (43),
- HYSOLAR project in Saudi Arabia (44),
- Schatz Energy Center, Humboldt State University, Arcata, California (45),
- Helsinki University of Technology, Helsinki, Finland (46),
- INTA Energy Laboratory, Huelva, Spain (47).

Direct Thermal Decomposition of Water (Thermolysis). Water can be split thermally at temperatures above 2000 K. The overall thermal dissociation of water can be shown as (48):

$$H_2O\,\tfrac{3}{4} \rightarrow aH_2O + bOH + cH + dO + eH_2 + fO_2 \qquad (15)$$

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

Thermochemical Cycles. Thermochemical production of hydrogen involves the chemical splitting of water at temperatures lower than those needed for thermolysis, through a series of cyclical chemical reactions which ultimately release hydrogen. Since the mid-1960s, research has been performed to investigate a number of potential thermochemical cycles for the production of hydrogen, and some 2000 to 3000 cycles have been invented. After examining their practicability in terms of reaction and process technology, only 20 to 30 remained applicable for large-scale hydrogen production. Some of the more thoroughly investigated thermochemical process cycles follow (37,49,50):

sulfuric acid–iodine cycle,
hybrid sulfuric acid cycle,
hybrid sulfuric acid–hydrogen bromide cycle,
calcium bromide–iron oxide cycle (UT-3), and
iron chlorine cycle (Mark 9).

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

Photolysis. Photolysis, or direct extraction of hydrogen from water using only sunlight as an energy source, can be accomplished by photobiological systems, photochemical assemblies, or photoelectrochemical cells (51,52). Intensive research activities are opening new perspectives for photoconversion, where new redox catalysts, colloidal semiconductors, immobilized enzymes, and selected microorganisms could provide means of large-scale solar energy harvesting and conversion into hydrogen.

Table 15. Hydrogen Storage Types and Densities

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

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

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

(1) Stationary Large Storage Systems These are typically storage devices at the production site or at the start or end of pipelines and other transportation pathways.
(2) Stationary Small Storage Systems These can be found at the distribution or final user level, for example, a storage system to meet the demand of an industrial plant.
(3) Mobile Storage Systems for Transport and Distribution These include both large-capacity devices, such as a liquid hydrogen tanker–bulk carrier, and small systems, such as a gaseous or liquid hydrogen truck trailer.
(4) Vehicle Tanks These store hydrogen used as fuel for road vehicles.

Because of hydrogen's low density, its storage always requires relatively large volumes and is associated with either high pressures (thus requiring heavy vessels) or extremely low temperatures and/or a combination with other materials (much heavier than hydrogen itself). Table 15 shows achievable storage densities with different types of hydrogen storage. Some novel hydrogen storage method may achieve even higher storage densities, but it has yet to be proven in terms of practicality, cost, and safety.

Large Underground Hydrogen Storage. Future hydrogen supply systems will have a structure similar to today's natural gas supply systems. Underground storage of hydrogen in caverns, aquifers, depleted petroleum and natural gas fields, and human-made caverns resulting from mining and other activities is likely to be technologically and economically feasible (53). Hydrogen storage systems of the same type and energy content will be more expensive by approximately a factor of 3 than natural gas storage systems because of hydrogen's lower volumetric heating value. Technical problems, specifically for underground storage of hydrogen other

Table 16. Hydriding Substances as Hydrogen Storage Media

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

than expected losses of the working gas in the amount of 1% to 3% per year are not anticipated. The city of Kiel's public utility has been storing town gas with a hydrogen content of 60% to 65% in a gas cavern with a geometric volume of about 32,000 m^3 and a pressure of 80 to 160 bar at a depth of 1330 m since 1971 (54). Gaz de France, the French National Gas Company, has stored hydrogen-rich refinery by-product gases in an aquifer structure near Beynes, France. Imperial Chemical Industries of Great Britain stores its hydrogen in the salt mine caverns near Teeside in the United Kingdom (55).

Above-Ground Pressurized Gas Storage Systems. Pressurized gas storage systems are used today in natural gas businesses in various sizes and pressure ranges from standard pressure cylinders (0.05 m^3, 200 bar) to stationary high-pressure containers (over 200 bar) or low-pressure spherical containers ($>30{,}000$ m^3, 12 bar to 16 bar). This application range will be similar for hydrogen storage.

Vehicular Pressurized Hydrogen Tanks. Development of ultralight but strong new composite materials has enabled storage of hydrogen in automobiles. Pressure vessels that allow hydrogen storage at pressures >200 bar have been developed and used in automobiles (such as Daimler-Benz NECAR II). Storage density of higher than 0.05 kg H_2/kg of total weight is easily achievable (56).

Metal Hydride Storage. Hydrogen can form metal hydrides with some metals and alloys. During the formation of the metal hydride, hydrogen molecules are split, and hydrogen atoms are inserted in spaces inside the lattice of suitable metals and/or alloys. In such a way, an effective storage is created comparable to the density of liquid hydrogen. However, when the mass of the metal or alloy is taken into account, then the metal hydride gravimetric storage density is comparable to storage of pressurized hydrogen. The best achievable gravimetric storage density is about 0.07 kg H_2/kg of metal, for a high temperature hydride such as MgH_2 as shown in Table 16, which gives a comparison of some hydriding substances with liquid hydrogen, gaseous hydrogen, and gasoline (57).

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

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

Novel Hydrogen Storage Methods. Hydrogen can be physically adsorbed on activated carbon and be "packed" on the surface and inside the carbon structure more densely than if it has been just compressed. Amounts of up to 48 g H_2/kg of carbon have been reported at 6.0 MPa and 87 K (58). The adsorption capacity is a function of pressure and temperature; therefore, at higher pressures and/or lower temperatures even larger amounts of hydrogen can be adsorbed. For any practical use, relatively low temperatures are needed ($<$100 K). Because adsorption is a surface process, the adsorption capacity of hydrogen on activated carbon is largely the result of the high surface area of the activated carbon, although some other carbon properties affect the capability of activated carbon to adsorb hydrogen.

Researchers from Northeastern University in Boston, MA, have recently announced that they have developed a carbon storage material that can store as high as 75% of hydrogen by weight (59). This material, apparently some kind of carbon nanotubes or carbon whiskers, is currently being researched in several laboratories. The best results achieved with carbon nanotubes to date confirmed by the National Renewable Energy Laboratory is hydrogen storage density corresponding to about 10% of the nanotube weight (60).

Hydrogen can be stored in glass microspheres of approximately 50 mm diameter. The microspheres can be filled with hydrogen by heating them to increase the glass permeability to hydrogen. At room temperature, a pressure of approximately 25 MPa is achieved, resulting in a storage density of 14% mass fraction and 10 kg H_2/m^3 (61). At 62 MPa, a bed of glass microspheres can store 20 kg H_2/m^3. The release of hydrogen occurs by reheating the spheres to again increase the permeability.

Researchers at the University of Hawaii are investigating hydrogen storage via polyhydride complexes. Complexes that catalyze the reversible hydrogenation of unsaturated hydrocarbons have been found. This catalytic reaction could be the basis for a low-temperature hydrogen storage system with an available hydrogen density greater than 7% (62).

Hydrogen Transport and Distribution.

Interregional Hydrogen Transport. In the hydrogen energy system, it is envisaged that, from the production plants and/or storage, hydrogen will be transmitted to consumers by means of underground pipelines (gaseous hydrogen) and/or supertankers (liquid hydrogen). Presently, hydrogen transportation through pipelines is used either in links between nearby production and utilization sites (up to 10 km) or in more extensive networks (roughly 200 km). Table 17 lists the principal existing hydrogen pipelines (63). Future developments will certainly entail greater flow rates and distances. It would be possible to use the existing natural gas pipelines with some modifications. For hydrogen pipelines, it is necessary to use steels less prone to embrittlement by hydrogen under pressure [particularly for very pure hydrogen ($>$99.5% purity)]. Reciprocating compressors used for natural gas can be used for hydrogen without major design modifications. However, special attention must be given to sealing (to avoid hydrogen leaks) and to materials selection for the parts subject to fatigue stress. Use of centrifugal compressors for hydrogen creates more problems because of hydrogen's exceptional lightness.

As a rule, hydrogen transmission through pipelines requires larger diameter piping and more compression power than natural gas for the same energy throughput. However, because of lower pressure losses in the case of hydrogen, the recompression stations would need to be spaced twice as far apart. In economic terms, most of the studies found that the cost of large-scale transmission of hydrogen is about 1.5 to 1.8 times that of natural gas transmission. However, transportation of hydrogen over distances greater than 1000 km is more economical than transmission of electricity (64).

Table 17. Some Major Hydrogen Pipelines

Location	Years of Operation	Diameter (mm)	Length (km)	Pressure (MPa)	Purity (%)
AGEC, Alberta Canada	Since 1987	273	3.7	3.79	99.9
Air Liquide, France	Since 1966	Various	290	6.48–10	Pure and raw
Air Products, Houston, TX	Since 1969	114.324	100	0.35–5.5	Pure
Air Products, Louisiana	Since 1990	102–305	48	3.45	
Chemische Werke Huls	Since 1938	168–273	215	to 2.5	Raw gas
Cominco, B.C., Canada	Since 1964	5	0.6	>30	62–100
Gulf Petroleum Canada		168.3	16		93.5
Hawkeye Chemical, IA	Since 1987	152	3.2	2.75	
ICI Bilingham, UK			15	30	Pure
Philips Petroleum	Since 1986	203	20.9	12	

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

Hydrogen in the gas phase is generally transported in pressurized cylindrical vessels (typically at 200 bar) arranged in frames adapted to road transport. The unit capacity of these frames or skids can be as great as 3000 m^3. Hydrogen gas distribution companies also install such frames at the user's site to serve as stationary storage.

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

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

Hydrogen Combustion in Internal Combustion and Jet and Rocket Engines. Hydrogen is a very good fuel for internal combustion engines. Hydrogen-powered internal combustion engines are on average about 20% more efficient than comparable gasoline engines. The ideal thermal efficiency of an internal combustion engine is

$$\eta = 1 - \left(\frac{1}{r}\right)^{k-1} \tag{16}$$

where

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

Equation (16) shows that the thermal efficiency can be improved by increasing either the compression ratio or the specific heat ratio. In hydrogen engines, both ratios are higher than in a comparable gasoline engine because of hydrogen's lower self-ignition temperature and ability to burn in lean mixtures. However, the use of hydrogen in internal combustion engines results in the loss of power because of the lower energy content in a stoichiometric mixture in the engine's cylinder. A stoichiometric mixture of gasoline and air and gaseous hydrogen and air premixed externally occupy ∼2% and 30% of the cylinder volume, respectively. Under these conditions, the energy of the hydrogen mixture is only 85% of the gasoline mixture, thus resulting in about 15% reduction in power. Therefore, the same engine running on hydrogen will have ∼15% less power than when operated with gasoline. The power output of a hydrogen engine can be improved by using more advanced fuel injection techniques or liquid hydrogen. For example, if liquid hydrogen is premixed with air, the amount of hydrogen that can be introduced in the combustion cylinder can be increased by approximately one-third (65).

One of the most important advantages of hydrogen as a fuel for internal combustion engines is that hydrogen engines emit by far fewer pollutants than comparable gasoline engines. Basically, the only products of hydrogen combustion in air are water vapor and small amounts of nitrogen oxides. Hydrogen has a wide flammability range in air (5% to 75% vol.), therefore, high excess air can be utilized more effectively. The formation of nitrogen oxides in hydrogen/air combustion can be minimized with excess air. NO_x emissions can also be lowered by cooling the combustion environment using techniques such as water injection, exhaust gas recirculation, or using liquid hydrogen. The emissions of NO_x in hydrogen engines are typically one order of magnitude smaller than emissions from comparable gasoline engines. Small amounts of unburned hydrocarbons, CO_2, and CO have been detected in hydrogen engines due to lubrication oil (65).

The low-ignition energy and fast-flame propagation of hydrogen have led to problems of preignition and backfire. These problems have been overcome by adding hydrogen to the air mixture at the point where and when the conditions for preignition are less likely, such as delivering the fuel and air separately to the combustion chamber and/or injecting hydrogen under pressure into the combustion chamber before the piston is at the top dead center and after the intake air valve has been closed. Water injection and exhaust gas recirculation techniques are also used in hydrogen engines to help control premature ignition. Note that most of the research on hydrogen combustion in internal combustion engines has been conducted with modifications of existing engines designed to burn gasoline. Redesign of the combustion chamber and coolant systems to accommodate hydrogen's unique combustion properties could be the most effective method of solving the problems of preignition and knocking (65).

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

Steam Generation by Hydrogen/Oxygen Combustion. Hydrogen combusted with pure oxygen results in pure steam; that is,

$$2H_2 + O_2 \rightarrow 2H_2O \tag{17}$$

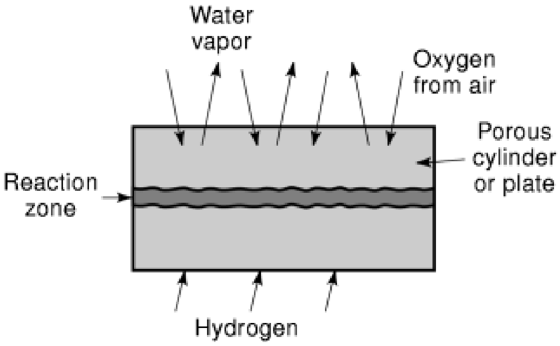

Fig. 9. Schematic representation of catalytic burner.

This reaction would develop temperatures in the flame zone above 3000°C; therefore, additional water has to be injected so that the steam temperature can be regulated at a desired level. Both saturated and superheated vapor can be produced.

The German Aerospace Research Establishment (*DLR*) has developed a compact hydrogen/oxygen steam generator (66). The steam generator consists of the ignition, combustion, and evaporation chambers. In the ignition chamber, a combustible mixture of hydrogen and oxygen at a low oxidant/fuel ratio is ignited by means of a spark plug. The rest of the oxygen is added in the combustion chamber to adjust the oxidant/fuel ratio exactly to the stoichiometric one. Water is also injected in the combustion chamber after it has passed through the double walls of the combustion chamber. The evaporation chamber serves to homogenize the steam. The steam temperature is monitored and controlled. Such a device is close to 100% efficient because there are no emissions other than steam and little or no thermal losses.

The hydrogen steam generator can be used to generate steam for spinning reserve in power plants, for peak load electricity generation, in industrial steam supply networks, and as a micro steam generator in medical technology and biotechnology applications (66).

Catalytic Combustion of Hydrogen. Hydrogen and oxygen in the presence of a suitable catalyst may be combined at temperatures significantly lower than flame combustion (from ambient to 500°C). This principle can be used to design catalytic burners and heaters. Catalytic burners require considerably more surface area than conventional flame burners. Therefore, the catalyst is typically dispersed in a porous structure. The reaction rate and resulting temperature are easily controlled by controlling the hydrogen flow rate. The reaction takes place in a reaction zone of the porous catalytic sintered metal cylinders or plates in which hydrogen and oxygen are mixed by diffusion from opposite sides. A combustible mixture is formed only in the reaction zone and assisted with a (platinum) catalyst to burn at low temperatures (Fig. 9). The only product of catalytic combustion of hydrogen is water vapor. Because of low temperatures, no nitrogen oxides are formed. The reaction cannot migrate into the hydrogen supply because no flame and hydrogen concentration is above the higher flammable limit (75%).

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

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

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

- Alkaline fuel cells (*AFC*) use concentrated (85 wt %) KOH as the electrolyte for high-temperature operation (250°C) and less concentrated (35 wt % to 50 wt %) for lower-temperature operation (<120°C). The

Table 18. Fuel Cell Reactions

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

electrolyte is retained in a matrix (usually asbestos), and a wide range of electrocatalysts can be used (such as Ni, Ag, metal oxides, and noble metals). This fuel cell is intolerant to CO_2 present in either the fuel or oxidant (67).

- Polymer electrolyte membrane or proton exchange membrane fuel cells (*PEMFC*) use a thin polymer membrane (such as perfluorosulfonated acid polymer) as the electrolyte. Membranes as thin as 12 μm to 20 μm have been developed; they are excellent proton conductors. The catalyst is typically platinum with loadings about 0.3 mg/cm^2, or, if the hydrogen feed contains minute amounts of CO, Pt–Ru alloys are used. Operating temperatures are usually below 100°C, more typically between 60° and 80°C.
- Phosphoric acid fuel cells (*PAFC*), use concentrated phosphoric acid (~100%) as the electrolyte. The matrix used to retain the acid is usually SiC, and the electrocatalyst in both the anode and cathode is Platinum black. Operating temperatures are typically between 150°C and 220°C (67,68).
- Molten carbonate fuel cells (*MCFC*) have the electrolyte composed of a combination of alkali (Li, Na, K) carbonates, which are retained in a ceramic matrix of $LiAlO_2$. Operating temperatures are between 600°C and 700°C where the carbonates form a highly conductive molten salt, with carbonate ions providing ionic conduction. At such high operating temperatures, noble metal catalysts are typically not required (67,68).
- Solid oxide fuel cells (*SOFC*) use a solid, nonporous metal oxide, usually Y_2O_3-stabilized ZrO_2 as the electrolyte. The cell operates at 900° to 1000°C where ionic conduction by oxygen ions takes place (67,68).

A typical fuel cell consists of the electrolyte in contact with porous electrodes on both sides. A schematic representation of a fuel cell with reactant and product gases, along with ions flow directions for the major types of fuel cells are shown in Fig. 10. The electrochemical reactions occur at the three-phase interface—porous electrode/electrolyte/reactants. The actual electrochemical reactions that occur in these types of fuel cells are different (as shown in Table 18), although the overall reaction is the same (i.e., $H_2 + 1/2O_2 \rightarrow H_2O$). Low-temperature fuel cells (AFC, PEMFC, PAFC) require noble electrocatalysts to achieve practical reaction rates at the anode and cathode. High-temperature fuel cells (MCFC and SOFC) can also utilize CO and CH_4 as fuels. The operating temperature is high enough so that CO and CH_4 can be converted into hydrogen through the water–gas shift and steam reforming reactions, respectively.

The electrolyte not only transports dissolved reactants to the electrode, but it also conducts ionic charge between the electrodes and thereby completes the cell electric circuit, as shown in Fig. 10.

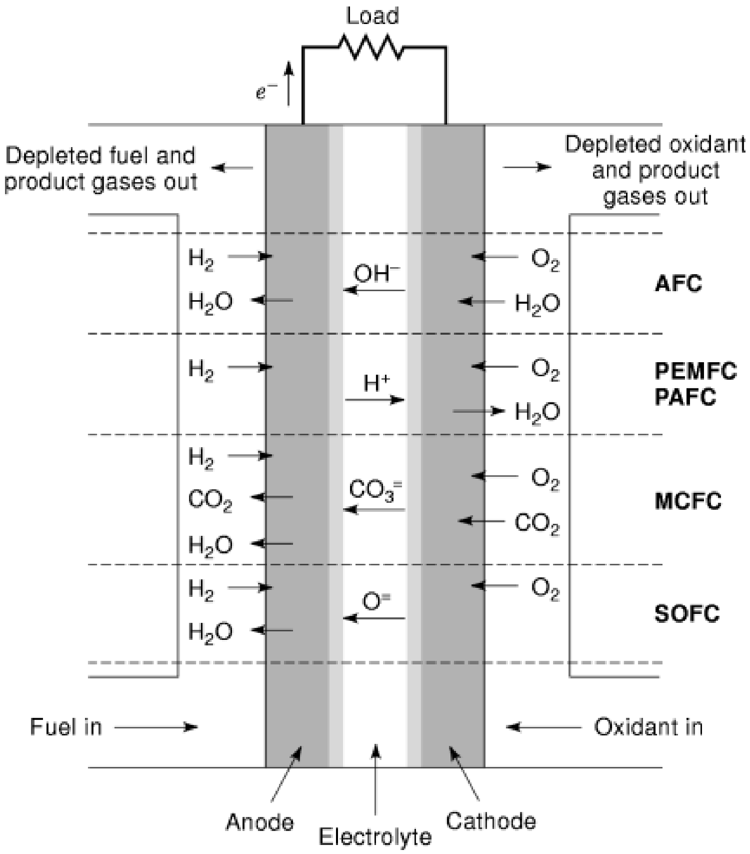

Fig. 10. Operating principle of various types of fuel cells.

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

$$\mathrm{DG}^0 = nFE^0 \qquad (18)$$

where

DG^0 = Gibbs free energy at 25°C and atmospheric pressure
n = number of electrons involved in the reaction
F = Faraday's constant
E^0 = reversible potential at 25°C and atmospheric pressure (V)

The reversible potential changes with temperature and pressure; in general, it is lower at higher temperatures (reaching ~1.0 V at 1000 K), and it is higher at higher pressures or higher concentrations of reactants. The actual voltage of an operational fuel cell is always lower than the reversible potential resulting from various irreversible losses, such as activation polarization, concentration polarization, and ohmic resistance. Even though ohmic resistance is directly proportional to the current, activation polarization is a logarithmic function of current, and thus more pronounced at very low current densities, and concentration polarization is an exponential function of current and thus becomes a limiting factor at high current densities. Figure 11

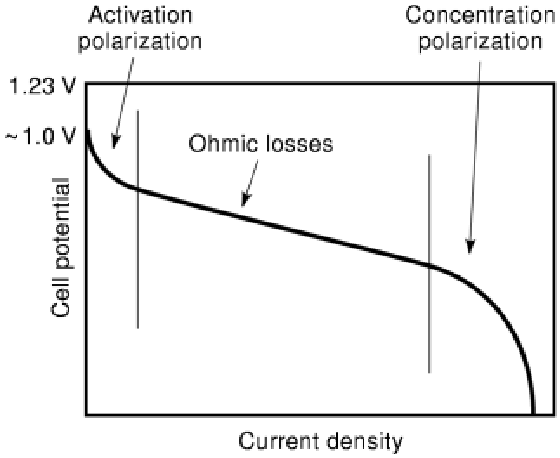

Fig. 11. Typical fuel cell polarization curve.

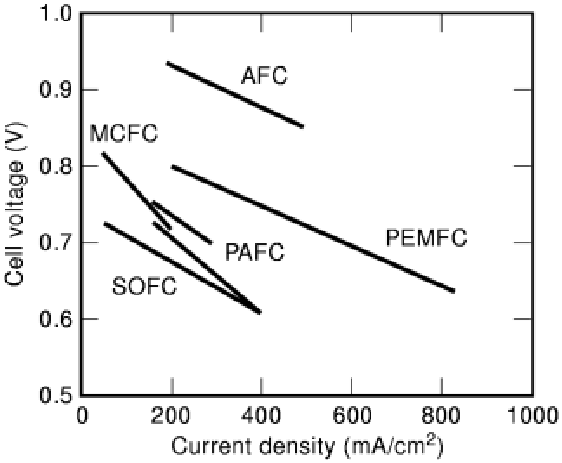

Fig. 12. Polarization curves of some representative fuel cells. AFC—United Technologies' fuel cell operating in Space Shuttle, with H_2 and O_2 at 80° to 90°C, 410 kPa. PEMFC—Ballard's 25 kW fuel cell operating in Daimler-Benz vehicle (NECAR II) with H_2 and air (1996). PAFC—IFC's fuel cell operating in ONSI PC25 200 kW power plant, operating on reformed natural gas and air at atmospheric pressure (1996) (dashed line in IFC's PC23 operating at 820 kPa). MCFC—ERC's atmospheric pressure fuel cell operating with natural gas (1994). SOFC—Westinghouse fuel cell operating at atmospheric pressure using natural gas (1991).

shows a typical fuel cell polarization curve with pronounced regions of predominant irreversible losses. Figure 12 shows actual polarization curves of some representative fuel cells. The fuel cells are typically operated in a range between 0.6 V and 0.8 V. The Space Shuttle fuel cell (alkaline) is designed to operate at 0.86 V and 410 mA/cm^2 (67). PEM fuel cells have the highest achievable current densities, between 1 and 2 mA/cm^2 at 0.6 V with pressurized hydrogen and air.

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

$$h_{FC} = \mathrm{DG/DH} \qquad (19)$$

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

$$h_{\mathrm{FC}} = h_{\mathrm{Th}} \cdot h_{\mathrm{v}} \cdot h_{\mathrm{F}} \cdot h_{\mathrm{U}} \qquad (20)$$

where

$h_{\mathrm{Th}} =$ thermal efficiency, which is the ratio between Gibbs free energy of the reaction and the heating value of the fuel, $\mathrm{DG}_r/\mathrm{DH}_{\mathrm{fuel}}$ (similar to internal combustion engines, the fuel cell efficiency is often expressed in terms of the lower heating value);

$h_{\mathrm{v}} =$ voltage efficiency, defined as a ratio between the actual voltage (V) and thermodynamic voltage (E) (i.e., V/E);

$h_{\mathrm{F}} =$ Faradaic efficiency, or the ratio between the actual current and the current corresponding to the rate at which the reactant species are consumed [I/nFm, where m is the rate (in moles/s) at which the reactants are consumed];

$h_{\mathrm{U}} =$ fuel utilization, or the ratio between the amount of fuel actually consumed in the electrochemical reaction and fuel supplied to the fuel cell.

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

In order to get usable voltages (i.e., tens or hundreds of volts), the cells are combined in a stack. The cells are physically separated from each other and electrically connected in series by a bipolar separator plate. Figure 13 shows a schematic representation of a typical fuel cell stack.

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

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

$$\text{Charging or absorption:} \qquad \mathrm{M} + x\mathrm{H}_2 \rightarrow \mathrm{MH}_{2x} + \text{heat} \qquad (21)$$

$$\text{Discharging or desorption:} \quad \mathrm{MH}_{2x} + \text{heat} \rightarrow \mathrm{M} + x\mathrm{H}_2 \qquad (22)$$

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

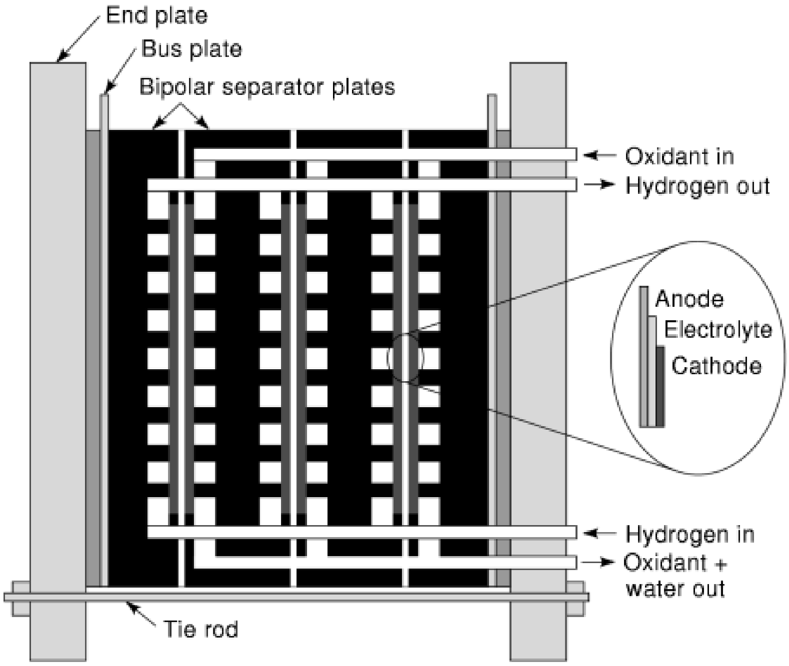

Fig. 13. Schematic representation of a typical fuel cell stack.

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

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

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

$$\text{Heat} + \text{Hydride}\,\tfrac{3}{4} \rightarrow \text{Hydriding substance} + \text{Hydrogen} \quad (23)$$

Whenever heat is needed, hydrogen released can be supplied back to the hydride, releasing the hydriding reaction heat; namely,

$$\text{Hydrogen} + \text{Hydriding substance}\,\tfrac{3}{4} \rightarrow \text{Hydride} + \text{Heat} \quad (24)$$

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

Electricity Storage. Hydriding substances can be used for electricity storage in two ways. In one of the methods, electricity (direct current) is used to electrolyze the water, and the hydrogen produced is stored in a hydriding substance. When electricity is needed, hydrogen is released from the hydriding substance by adding heat and using it in a fuel cell to produce direct current electricity. Heat from the fuel cell can be used to release hydrogen from the metal hydride. In the second method, one electrode is covered with a hydriding substance (e.g., titanium nickel alloy). During the electrolysis of water, hydrogen produced on the electrode surface is immediately absorbed by the hydriding substance covering the electrode. Then, when electricity is needed, the electrolyzer operates in a reverse mode as a fuel cell producing electricity using the hydrogen released from the metal hydride.

Heating/Cooling. Hydrogen together with hydriding substances can be used for heating or air-conditioning the buildings. Figure 14 shows how one of the proposed systems works. The system consists of four hydride tanks, a solar collector (or a heat source), and a number of heat exchangers. Hydride tank 1 is connected to hydride tank 3 with a hydrogen pipe in order to allow the movement of hydrogen from one tank to the other. Similarly, hydride tanks 2 and 4 are connected in the same fashion. Tanks 1 and 2 contain the same hydriding substance ($CaNi_5$), and tanks 3 and 4 contain another hydriding material ($LaNi_5$). Heat exchangers and the hydride tanks are connected by water-carrying pipe circuits or loops, equipped with a set of switches and valves, so that a hydride tank in a given water loop can be replaced by another hydride tank.

When the system works as a heater, the heat from a heat source (e.g., solar collector) is carried to tank 1 at about 100°C. The heat drives the hydrogen from tank 1 to tank 3, where hydrogen is absorbed forming a hydride, and heat is released at 40°C. The water loop carries this heat to the building heat exchangers and heats the air in the building. At the same time, water in the other loop absorbs heat from the ambient and carries it to tank 4. This heat drives off the hydrogen from tank 4 to tank 2 where hydride is formed and heat is generated at 40°C. The whole operation of driving hydrogen from tanks 1 and 4 to tanks 3 and 2 takes about 2 minutes. At the end of this cycle, the hydride tanks are switched from one loop to the other in cycle II (as shown in Fig. 14). Now, the solar and ambient heats are used to drive off the hydrogen in tanks 2 and 3 to tanks 4 and 1, respectively. The heat produced during the absorption processes in tanks 1 and 4 is used for heating the building. After this, the cycles are repeated.

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

Electricity Generation. If passed through a turbine or expansion engine, hydrogen moving from one hydride tank to another could produce mechanical and electrical energy, as shown in Fig. 15. The system is somewhat similar to the one proposed for heating and cooling. However, it consists of only three tanks containing the same kind of hydriding substance (in this case $LaNi_5$ alloy). During the first cycle, hydrogen driven off from the desorption tank (tank 1) by means of solar heat (or heat from any other source) passes through the expansion turbine producing mechanical energy and electricity and then at a lower pressure is absorbed by the hydriding substance in tank 2 producing heat at 40°C. In this case, the heat is produced at a lower temperature than the temperature of desorption because hydrogen is at a lower pressure after passing through the turbine. The heat produced in the absorption tank (tank 2) is rejected to the environment through the water cooling system. The same water cooling system is also used to cool down the cooling tank (tank 3) from 100° to 40°C because it has served as the desorption tank in the previous cycle. In the second cycle through a system of switches and valves, the tanks are displaced one step to the right in the diagram (i.e., the cooling tank becomes the absorption tank, the absorption tank becomes the desorption tank, and the desorption tank becomes the cooling tank). Then, the cycles are repeated. Using this method, low-quality heat could be converted to electricity.

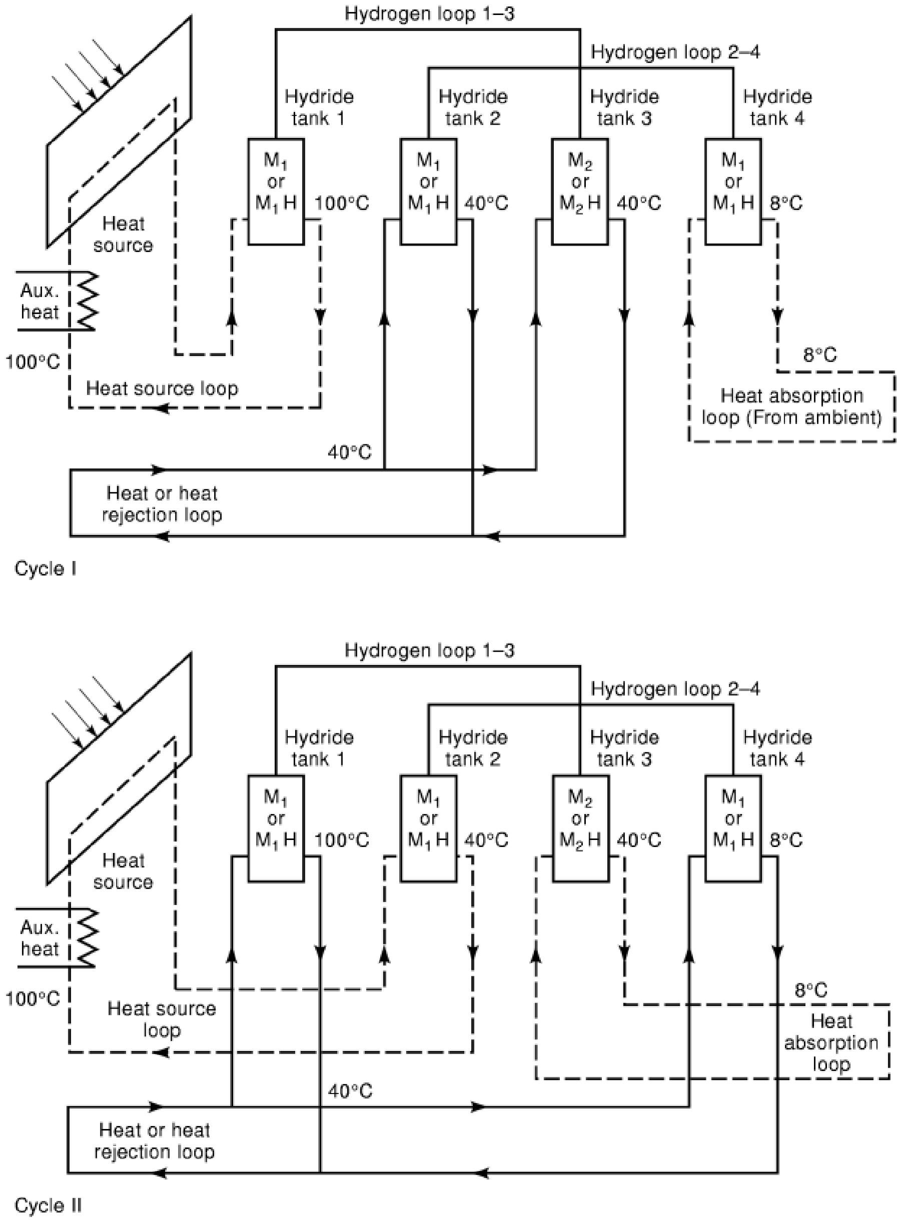

Fig. 14. Hydrogen/hydride heating–cooling system.

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

$$p = \exp\left(\frac{\Delta H}{RT} + S\right) \qquad (25)$$

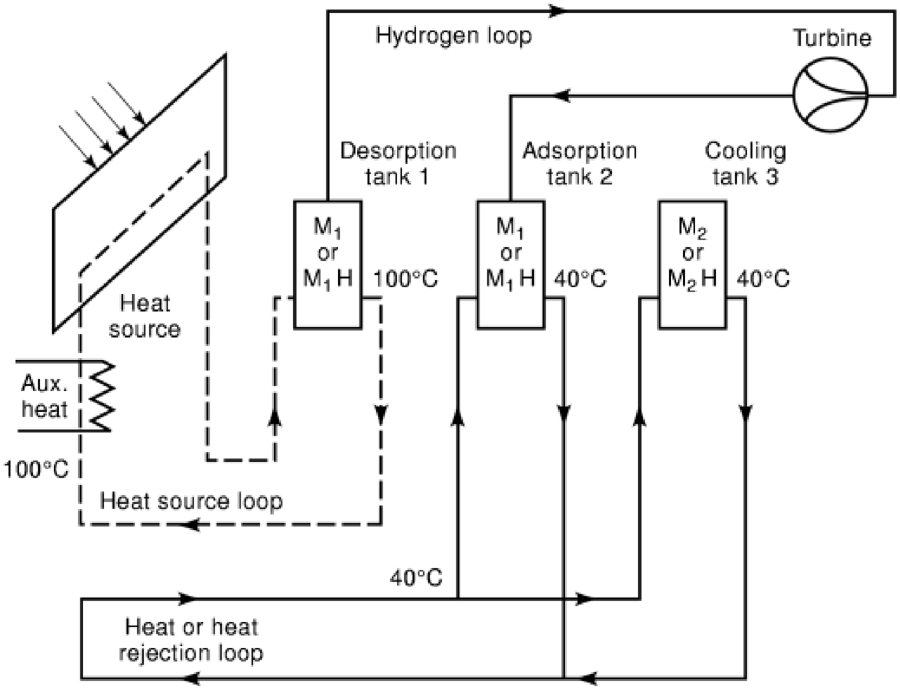

Fig. 15. Electricity generation via hydrogen and hydrides.

where the numerator in the exponent term is the hydriding reaction enthalpy, R is the gas constant, and S is a constant depending on the hydriding substance. If hysteresis is neglected, Eq. (25) would hold for both the absorption and desorption processes. By using heat, it would be possible to increase hydrogen pressure by a hundred or more times. The pressure ratio would be

$$\frac{p_{\mathrm{Hi}}}{p_{\mathrm{Lo}}} = \exp\left[\frac{\Delta H}{R}\left(\frac{1}{T_{\mathrm{Hi}}} - \frac{1}{T_{\mathrm{Lo}}}\right)\right] \tag{26}$$

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

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

Deuterium Separation. The property of hydrides used for hydrogen purification can also be used for deuterium separation. The system is similar to the hydrogen purification system. Deuterium is flushed from the hydriding tank, while hydrogen remains bonded in the metal hydride. Using titanium nickel alloy as the

Table 19. Properties and Leak Rates of Hydrogen and Natural Gas

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

hydriding substance, it is possible to obtain 85% pure deuterium after only two steps. With three and four steps, it is possible to obtain 99.9% and 99.999% pure deuterium, respectively.

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

Because hydrogen has the smallest molecule, it has a greater tendency to escape through small openings than other liquid or gaseous fuels. Based on properties of hydrogen such as density, viscosity, and diffusion coefficient in air, the propensity of hydrogen to leak through holes or joints of low-pressure fuel lines may be only 1.26 to 2.8 times faster than a natural gas leak through the same hole (and not 3.8 times faster as frequently assumed based solely on diffusion coefficients). Experiments have indicated that most leaks from residential natural gas lines are laminar (69). Because natural gas has over three times the energy density per unit volume, the natural gas leak would result in more energy release than a hydrogen leak.

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

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

If a leak should occur for whatever reason, hydrogen will disperse much faster than any other fuel, thus reducing the hazard levels. Hydrogen is both more buoyant and more diffusive than either gasoline, propane, or natural gas. Table 19 compares some properties and leak rates for hydrogen and natural gas.

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

Hydrogen has a very low ignition energy (0.02 mJ), about one order of magnitude lower than other fuels. The ignition energy is a function of fuel/air ratio, and for hydrogen it reaches a minimum at about 25% to 30%. At the lower flammability limit, hydrogen ignition energy is comparable with that of natural gas (70).

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

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

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

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

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

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

One of the most remembered accidents involving hydrogen is the Hindenburg dirigible disaster in 1937. However, hydrogen did not cause that accident, and hydrogen fire did not directly cause any casualties. The accident appears to have been caused by a static electricity discharge, and it was the balloon’s lining that caught fire first (71). Once hydrogen that the balloon was filled with for buoyancy (instead of helium as it was originally designed to be filled with) was ignited, it burned (as any fuel is supposed to). However, hydrogen fire went straight up, and it did not radiate heat so the people in the gondola underneath the balloon were not burned or suffocated. As a matter of fact, 56 survivors walked out of gondola when it landed and all the hydrogen and balloon structure burned out. Therefore, even in a worst case scenario accident, hydrogen proved to be a safe fuel.

Liquid Hydrogen

Hydrogen may be stored in gaseous, liquid, slush, and solid forms (metal hydrides). Every mode of storage has its advantages and disadvantages in terms of cost, stability, convenience of usage, and energy density. Liquid hydrogen has several advantages over other storage modes, especially in terms of energy density and convenience of utilization. However, several problems stand in the way of its large-scale production and long-term storage. This includes problems associated with energy consumed in liquefaction as well as boil-off losses during storage and handling. Boil-off losses occur because of a variety of mechanisms such as ortho–para conversion, thermal stratification and self pressurization, heat leaks, sloshing, and flashing. This section will review some of these problems and discuss some of the prospects of large-scale liquid hydrogen production and utilization.

Introduction. Liquid hydrogen has many different uses, and its usefulness in a number of areas has been demonstrated. Presently, liquid hydrogen is primarily used as a rocket fuel and is predestined for supersonic and hypersonic space vehicles primarily because it has the smallest boiling point density and the highest specific thrust of any known fuel. Its favorable characteristics include its high heating value per unit mass, its wide ignition range in hydrogen/oxygen or air mixtures, as well as its large flame speed and cooling capacity due to its high specific heat which permits very effective engine cooling and cooling the critical parts of the outer skin (72,73). Liquid hydrogen has some other important uses such as in high-energy nuclear physics and bubble chambers. The transport of hydrogen is vastly more economical when it is in liquid form, even though cryogenic refrigeration and special dewar vessels are required. Although liquid hydrogen can provide many advantages, its uses are restricted in part because liquefying hydrogen by existing conventional methods consumes a large amount of energy (around 30% of its heating value). Also, boil-off losses associated with the storage, transportation, and handling of liquid hydrogen can consume up to 40% of its available combustion energy. It is therefore important to search for ways that can improve the efficiency of the liquefiers and diminish the boil-off losses. Improving liquefier efficiency not only helps to recover some of the aforementioned 30% losses but can also contribute to reducing the other 40% losses caused by boil-off. This can be partially achieved by reliquefaction of the evaporated hydrogen. A significant improvement in the reliquefier efficiency is required, however, in order to provide an economical reliquefaction process.

Liquid Hydrogen Production. The production of liquid hydrogen requires the use of liquefiers that use different principles of cooling. In general, hydrogen liquefiers may be classified as conventional, magnetic, or hybrid. Many types of conventional liquefiers exist such as the Linde–Hampson liquefiers, the Linde dual-pressure liquefiers, the Claude liquefiers, the Kapitza liquefiers, the Heylandt liquefiers, and those liquefiers using the Collins cycle, just to name a few. Conventional liquefiers generally are made up of compressors, expanders, heat exchangers, and Joule–Thomson valves. Magnetic liquefiers, on the other hand, use the magnetocaloric effect. This effect is based on the principle that some magnetic materials experience a temperature increase upon the application of a magnetic field and a temperature drop upon lifting the magnetic field. The magnetic analog of several conventional liquefiers include the Brayton liquefiers, the Stirling liquefiers, and the active magnetic regenerative (*AMR*) liquefier. Additional information on liquid hydrogen production methods can be found in Sherif et al. (74).

Liquid Hydrogen Storage. As reported earlier, long-term storage of liquid hydrogen is associated with several problems primarily related to boil-off losses. Research on the mechanisms contributing to boil-off losses in cryogenic hydrogen storage systems exists to varying degrees of sophistication depending on the nature of the boil-off mechanism. These mechanisms are (1) ortho–para conversion; (2) heat leak (shape and size effect, thermal stratification, thermal overfill, insulation, conduction, radiation, cooldown), (3) sloshing, and (4) flashing. These mechanisms will be described in what follows.

Boil-Off Resulting from Ortho–Para Conversion. The hydrogen molecule is made up of two identical atoms, each of which is composed of a nucleus of one proton and one neutron and an electron orbiting around the nucleus. The rotational band in the vibration–rotation spectrum of hydrogen was early observed to show a weak–strong alteration in intensity. This led to the idea that two varieties of hydrogen exist. This idea was rationalized by Heisenberg and Hund in terms of the possible combinations of the nuclear spins in the hydrogen molecule (75).

At high temperatures, the equilibrium mixture consists of 75% ortho-hydrogen and 25% para-hydrogen. Hydrogen of this composition is termed normal and is in equilibrium at room temperature and above. At 0 K, on the other hand, all the molecules must be in a rotational ground state at equilibrium. Therefore, all the hydrogen molecules at equilibrium should be in the para state at absolute zero. Pure para-hydrogen may be prepared at equilibrium, but the maximum possible concentration of ortho-hydrogen is 75% under equilibrium conditions. Many of the thermophysical properties of normal and para-hydrogen are significantly different from each other. These differences have often been taken advantage of in analyses involving hydrogen. For instance, at 120 K to 190 K, the thermal conductivity of para-hydrogen is 50% more than that of ortho-hydrogen. The thermal conductivity can, therefore, be used to determine the ortho–para ratio of a hydrogen sample (76).

By cooling hydrogen gas from room temperature to the *nbp* (normal boiling point), the ortho-hydrogen converts to para-hydrogen spontaneously. The decrease of ortho concentration should be from 75% to 0.2%. Because the percentage of the ortho–para composition is temperature-dependent, and because, in the liquefaction process, the temperature continuously decreases, one of the questions that should arise pertains to the rate of conversion. The conversion of a nonequilibrium ortho–para composition to an equilibrium composition is a very slow process in the absence of a catalyst. This mode of conversion (i.e., in the absence of a catalyst) is called self-conversion.

The self-conversion rate is also a function of temperature. At the nbp of air, the half-life of conversion is greater than one year, whereas at 923 K and a 0.0067 MPa the half-life is on the order of 10 min. The half-life period is defined as the amount of time required to convert half of the excess ortho (or para) composition present at the starting time (76).

The conversion of ortho-hydrogen to para-hydrogen is an exothermic reaction. The heat of conversion is related to the change of momentum of the hydrogen nucleus when the direction of spin changes. The amount of heat given off in this conversion process is temperature-dependent. The heat of conversion is greater than the latent heat of vaporization of normal and para-hydrogen at the nbp. If the unconverted normal hydrogen is placed in a storage vessel, the heat of conversion will be released within the container, which leads to the evaporation of the liquid. Because of these peculiarities in the physical properties of hydrogen, the boil-off of the stored liquid will be considerably larger than what one would be able to determine from calculations based on ordinary heat leak to the storage tank.

In order to minimize the storage boil-off losses, the conversion rate of ortho-hydrogen to para-hydrogen should be accelerated with a catalyst that converts the hydrogen during the liquefaction process (77,78,79,80). In the presence of a catalyst that is well mixed with hydrogen, the reaction approaches a first-order one for the gas phase. If the catalyst is added to the liquid phase, the reaction becomes a zero-order one (81).

The transformation can be catalyzed by a number of surface active (or paramagnetic) species. A convenient way is to absorb normal-hydrogen on active charcoal cooled with liquid hydrogen and then pump off the equilibrium mixture. The conversion may take only a few minutes if a highly active form of charcoal is used (75), but the conversion effectiveness appears to depend on the presence of an absorbed layer of oxygen, which, for thoroughly purified hydrogen, may not be available (77). Other suitable ortho–para catalysts are metals such as tungsten or nickel, any paramagnetic oxides like chromium or gadolinium oxides, and other paramagnetic substances like NO_2, ferric hydroxide gel, and nickel silicate. These catalysts are capable of enabling almost complete conversion to be achieved in a few minutes. In paramagnetic fields during a homogeneous conversion process (using paramagnetic gases or by passing hydrogen through solutions containing paramagnetic ions), the nuclear spin is reversed without breaking the H—H bond. This suggests that strongly paramagnetic species such as Gd^{3+} are highly effective. It has been shown that paramagnetic catalysis conversion is accelerated by the action of an externally applied magnetic field. This effect tends to achieve saturation in a field of about 1000 Oersted (79577 A/m) (75). In a magnetocaloric liquefier, there is a good chance of taking advantage of this phenomenon primarily because both the magnetic ions and the external magnetic field are available, thus making a good design the only prerequisite for achieving a fast and economic conversion.

The use of a catalyst usually results in a larger refrigeration load and consequently in an efficiency penalty primarily because the heat of conversion must be removed. The time for which hydrogen is to be stored usually determines the optimum amount of conversion. For use within a few hours, no conversion is necessary. For example, large-scale use of liquid hydrogen as a fuel for jet aircraft is one of those cases where conversion is not necessary because utilization of the liquid is almost a continuous process and long-term storage is therefore not needed (80). For some other uses, a partial conversion might be required to create more favorable conditions. It should be noted that, for every initial ortho concentration, there exists a unique curve for boil-off of hydrogen with respect to time.

The heat of conversion at higher temperatures is small (at 300 K, the heat of conversion is 270 kJ/kg) and increases as the temperature decreases, where it reaches 519 kJ/kg at 77K, the nbp for liquid nitrogen. For temperatures lower than the nbp of nitrogen, the heat of conversion remains constant (523 kJ/kg). However, the equilibrium percentage of para-hydrogen at the nbp is 50%. Therefore, in order to produce equilibrium liquid hydrogen, 50% of hydrogen must be converted from ortho to para at temperatures lower than liquid nitrogen temperatures. Because the heat of conversion is almost constant for temperatures lower than those of liquid nitrogen, the refrigeration load required to remove the heat of conversion should be almost constant at different temperatures. Ideal refrigeration requires that the energy needed for the same amount of refrigeration load be temperature-dependent. This suggests that, in order to operate at an optimum power, it is necessary to have continuous conversion, especially for temperatures lower than those of liquid nitrogen. By continuous conversion, up to 15% energy saving may be achieved.

Boil-Off Resulting from Heat Leak.

Reservoir Shape and Size Effect. Hydrogen is usually transported in large quantities by truck tankers of 30 m^3 to 60 m^3 capacity, by rail tank cars of 115 m^3 capacity, and by barge containers of 950 m^3 capacity (82). Liquid hydrogen storage vessels are usually available in sizes ranging from one liter dewar flasks used in laboratory applications to large tanks of 5000 m^3 capacity. The National Aeronautics and Space Administration (*NASA*) typically uses large tanks of 3800 m^3 capacity (25 m in diameter) (83). The total boil-off rate from such dewars is approximately 600,000 *LPY* (liters per year), which is vented to a burn pond. The heat leakage losses are generally proportional to the ratio of surface area to the volume of the storage vessel (*S*/*V*). The most favorable shape is therefore spherical because it has the least surface to volume ratio. Spherical shape containers have another advantage. They have good mechanical strength because stresses and strains are distributed uniformly. In large sizes, spherical containers are expensive because of their manufacturing difficulty. They are often used for on-site large volume storage, however.

Storage vessels may also be constructed in other shapes such as cylindrical, conical, or any combination of these shapes. Cylindrical vessels are usually required for transportation of liquid hydrogen by trailers or railway cars because of limitations imposed on the maximum allowable diameter of the vessel. For normal highway transportation, the outside diameter of the vessel cannot exceed 2.44 m. From an economics standpoint, cylindrical vessels with either dish, elliptical, or hemispherical heads are very good, and their *S*/*V* ratios are only about 10% greater than that of the sphere (84).

Because boil-off losses resulting from heat leak are proportional to *S*/*V* as reported earlier, the evaporation rate will diminish drastically as the storage tank size is increased. For double-walled vacuum-insulated spherical dewars, boil-off losses are typically 0.3% to 0.5% per day for containers having a storage volume of 50 m^3, 0.2% for 103 m^3 tanks, and about 0.06% for 19,000 m^3 tanks (85). Obviously, the larger the size of the dewar, the smaller the cost per unit volume of storage. Interestingly enough, the rate of evaporation does not substantially decrease with increasing the size of the container for cylindrical vessels of constant diameter.

Thermal Stratification and Thermal Overfill. Stratification is the existence of a fluid at different temperatures within one vessel. Heat transfer from the sidewalls and bottom to a liquid hydrogen storage vessel will always result in an increase of the sensible enthalpy of the liquid. When the heat flux is small enough and the inside wall of the vessel is smooth, boiling is unlikely to occur (77). In this case, the added energy tends to get distributed nonuniformly because the imposed heat flux usually produces a free convective flow. The warm liquid hydrogen becomes buoyant and rises to the top. With the passage of time, the lower boundary of the stratified region moves toward the bottom of the vessel. Because the warm liquid rises to the surface, it is not uncommon to have the temperature at the top layers rise much more rapidly than that of the bulk liquid (84). As a consequence, the upper layers are more likely to experience a relatively large vapor pressure increase, whereas the lower layers experience little or no vapor pressure change. This thermal stratification creates a vessel pressure corresponding to a temperature greater than the average liquid temperature because the tank pressure is mostly determined by the vapor pressure of the free surface. This in turn greatly reduces the length of liquid storage time without having to vent the vapor. Naturally, this leads to a decrease in the lock-up time. The stratification in temperature is stable because the warmer liquid has the lower density, in addition to the fact that liquid hydrogen is a poor thermal conductor (84).

Thermal overfill is a phenomenon that occurs when one of the following conditions exists.

(1) The average specific enthalpy of the liquid is greater than that of the saturation temperature, in which case the liquid boil-off from the vented dewars is found to be nonuniform. This can be attributed to the unstable stratification which occurs in vented dewars as a result of a sudden lowering of atmospheric pressure (generally, the liquid becomes superheated in the lower region, while the surface temperature remains saturated, which leads to generating instant vapor of large quantities).
(2) The operating pressure of the tank is less than that corresponding to the saturation temperature of the feed liquid, in which case only the surface layer is able to respond to the new operating pressure. If the surface layer is distributed by some means, for instance by top-loading more liquid, the underlying liquid may be brought into rapid equilibrium, and that, in turn, would cause a rapid boil-off (77,86).

One way to decrease boil-off losses resulting from stratification and thermal overfill is by employing high-conductivity plates (conductors) installed vertically in the vessel. The plates produce heat paths of low resistance between the bottom and top of the vessel and can operate most satisfactorily in eliminating temperature gradients and excessive pressures. Another way is to pump the heat out and maintain the liquid at subcooled or saturated conditions. An ideal refrigeration system to perform this task can be an efficient magnetic refrigerator. The magnetic refrigerator is very suitable for this job because of its relatively higher efficiency, compactness, lower price, and reliability (87,88,89,90,91,92,93,94,95).

Barclay (88) proposed a magnetic refrigerator that can be used for the reliquefaction of the hydrogen vapor. This design can be modified and used for the preceding cases. In order to perform the refrigeration effectively, a thermal valve is needed to permit heat flow when there is superheat and to stop heat flow when there is no superheat (86).

Insulation and Conduction Through Supports. Liquid hydrogen containers are usually of three types: double-jacketed vessels with liquid nitrogen in the outer jacket, superinsulated vessels with either a reflecting powder or multilayer insulation, and containers with vapor-cooled shields employing super insulation. Although multilayer insulation (*MLI*) provides for a low boil-off rate, the addition of a vapor-cooled shield (*VCS*) will lower the boil-off losses even further. A VCS is a type of insulation that takes the vapor boil-off and passes it past the tank before being reliquified or vented. Published data indicate that a reduction of more than 50% in boil-off may be achieved for a 45,045 kg liquid hydrogen cryogenic facility with a VCS than without one. Brown (96) showed that locating the VCS at half the distance from the tank to the outer surface of a 10.16 cm MLI of a 45,045 kg facility would reduce the boil-off by 10%. A dual VCS system on the tank would improve the performance by 40% over a single VCS. Brown (96) also showed that the preferred locations for the inner and outer shields in a dual VCS system are 30% and 66% of the distance from the tank to the outer surface of the MLI.

Mechanical supports that connect the inner and outer vessel of double-walled vacuum tanks are an integral part of the insulation problem, primarily because of the heat influx that can be conducted to the inner vessel. One way to diminish these boil-off losses is to cool the support employing the produced hydrogen vapor continuously in a counterflow fashion.

In practice, the thermal conductivity of the support varies with temperature, and there exists difficulty in manufacturing a continuous heat exchange surface in the temperature range of interest. In this case, a succession of discrete cooling stations provides for a better design. Bejan (97,98,99) introduced an optimization method for finding the location and the temperature of the cooling stations, and he used that procedure in order to optimize helium boil-off losses.

Another optimization of boil-off losses can be considered by changing the value of the heat sink temperature from 20.4 K to 33 K (critical temperature) and examining the temperature at which the boil-off rate is minimum. This is primarily because, as the storage temperature increases, the amount of heat leak and, consequently, the boil-off losses decrease. On the other hand, the latent heat of vaporization decreases with decreasing storage temperature which contributes to increasing the boil-off. Thus, there should be an optimum storage temperature or pressure that balances the aforementioned effects. Employing this procedure, the optimum temperature and pressure of the hydrogen vessel may be determined.

Boil-Off Resulting from Sloshing. Another process that leads to boil-off during liquid hydrogen transportation by tankers is sloshing. Sloshing is the motion of liquid in a vessel caused by acceleration or deceleration. Because of different types of acceleration and deceleration, there exist different types of sloshing. Acceleration causes the liquid to move to one end and then reflect from that end, thus producing a hydraulic jump. The latter then travels to the other end, thus transforming some of its impact energy to thermal energy. The thermal energy dissipated eventually leads to an increase in the evaporation rate of the liquid (77,84). The insertion of traverse or antislosh baffles not only restrains the motion of the liquid, thus reducing the impact forces, but also increases the frequency above the natural frequency of the tanker (77,81).

Boil-Off Resulting from Flashing. Another source of boil-off is flashing. This problem occurs when liquid hydrogen, at a high pressure (2.4 to 2.7 atm), is transferred from trucks and rail cars to a low-pressure dewar (1.17 atm). This problem can be reduced if transportation of liquid hydrogen is carried out at atmospheric pressures. Furthermore, some of the low-pressure hydrogen can be captured and reliquefied. One of the best systems that can be selected for reliquefaction is one that employs a magnetic refrigerator as an external cycle. Another suitable cycle can be the Claude cycle with a saturated-vapor compressor and a wet expander. The system operates best if the sink is a liquid nitrogen bath.

One other method, which is proposed by NASA, is to capture some of this low-pressure hydrogen by metal hydrides and then reliquefy the hydrogen vapor. According to this scheme, a liquefier with a capacity of 40 tons per day (*TPD*) would be necessary to make up for the losses. This idea was considered expensive and was later rejected.

Concluding Remarks on Liquid Hydrogen. This section addressed the production, storage, and utilization of liquid hydrogen. More research is probably needed to address some of the fundamental issues that are relevant to the efficient utilization and storage of liquid hydrogen. Additional information on liquid hydrogen storage can be found in Gursu et al. (100,101).

Slush Hydrogen

Slush hydrogen is a mixture of liquid and frozen hydrogen in equilibrium with the gas at the triple point. Slush hydrogen is expected to be the primary propellant for the National Aero-Space Plane (*NASP*) because of its potential in reducing its physical size and significantly cutting the projected gross liftoff weight. This section provides an overview of slush hydrogen production methods and reviews the current state of knowledge regarding slush hydrogen utilization.

Introduction. Hydrogen has become an important rocket fuel despite the problems associated with its use. Some of these problems include its low density, temperature stratification, short holding time caused by its low latent heat, hazards associated with high vent rates, and unstable flight conditions caused by sloshing of the liquid in the fuel tank. Rapial and Daney (102) report that two techniques can completely eliminate some of these undesirable features and partially eliminate the others. One is the production of liquid–solid hydrogen mixtures “slush hydrogen” by further refrigeration of the liquid. The other is the gelation of liquid hydrogen by the addition of a fine particle gelling substance.

Slush hydrogen is a mixture of liquid and frozen hydrogen in equilibrium with the gas at the triple point, 13.8 K. The density of the icelike form is about 20% higher than that of the boiling liquid. To obtain the icelike form, one must remove the heat content of the liquid at 20.3 K until the triple point is reached and then remove the latent heat of fusion. The "cold content" of the icelike form of hydrogen is some 25% higher than that of the saturated vapor at 20.3 K. Justi (103) reports that in producing the slush hydrogen, in comparison with the icelike form, one loses part of the increase in density and cold storage, but in mixing the icelike form with liquid hydrogen, one obtains a medium that is transportable in pipelines. Slush hydrogen can be produced from liquid hydrogen with the help of a vacuum pump and expansion through a jet (103).

Baker and Matsch (104) gave a tabulated comparison among the properties of liquid and slush hydrogen. According to them, the smaller enthalpy of slush hydrogen reduces the evaporation losses during storage and transport and as a consequence permits longer storage without venting. The increased density permits ground transport equipment to carry 15% greater loads; for space vehicles, a given fuel load can be carried in tankage that is 13% smaller in volume.

Kandebo (105) reported that slush hydrogen is expected to be the primary propellant for the NASP. He mentioned that using slush instead of liquid hydrogen reduces the physical size of the NASP and cuts the projected gross liftoff weight by up to 30%. The freeze–thaw process, which is the most used slush production process, and the auger process, which is relatively new, were discussed and compared. One expensive alternative method to pressurize tanks was also mentioned. This alternative is to pressurize tanks with a combination of helium and hydrogen because helium does not condense at slush hydrogen storage temperatures and is not very dense.

Justi (103) reported that the slushlike form of hydrogen has the advantage of a greater "cold content" compared to liquid hydrogen. The disadvantage of slush hydrogen lies in the present state of the technology for its production, which is not yet well advanced, so that it is impractical to calculate a realistic price. Justi argues, however, that the production cost of slush hydrogen now and in the near future is greater than the liquefaction costs of hydrogen because of the larger energy use involved.

Sindt (106) studied the characteristics of slush hydrogen preparation, storage, transfer and instrumentation. In that study, slush preparation by intermittent vacuum pumping was discussed. Slush was aged 100 h, during which time the solid particle size and structure were observed. The solid particle structure was found to change dramatically during aging, even though the changes in the particle size were insignificant. Sindt also mentioned that slush with over 50% solid content could be transferred and pumped with losses similar to those in triple-point liquid hydrogen if the Reynolds numbers were high enough.

Voth (107) reported on a slush hydrogen production method with an auger rotating inside a brass tube refrigerated with liquid helium. The auger was reported to produce small particles from the cryogens on a continuous basis so that the resulting slush mixture could be transferred and stored. He also reported that the auger is capable of producing slush at pressures higher than the triple-point pressure of the cryogen.

Methods for determining the quality of liquid–solid hydrogen mixtures, along with relevant thermodynamic analyses were discussed by Daney and Mann (108) and Mann et al. (109). Properties of liquid and slush hydrogen and their applications were discussed by Smith (110) and Angus (111). The flow characteristics of slush hydrogen with different solid contents were examined by Sindt and Ludtke (112) and by Sindt et al. (113). The latter study reported on experimental results in which a second component was added to liquid hydrogen to determine the effect produced by the freeze–thaw process on the size of the solid particles. Perrel and Haase (114) developed a computer simulation method to describe the self-catalysis of ortho-hydrogen molecules. The simulations were performed on a small computer using Monte Carlo techniques. Roder (115) studied the phase transitions in solid hydrogen and suggested that, except for the lambda transition that occurs at low temperatures in solid hydrogen, and involves a change from hexagonal close-packed (*hcp*) to face-centered cubic (*fcc*), there may be an additional phase transition in solid hydrogen.

Although current interest in liquid–solid mixtures of hydrogen as a potential rocket propellant has lead to theoretical and experimental investigations of its characteristics, there is still a lot of potential for additional investigations. For example, the problem of transferring heat to slush hydrogen along with solid density stratification in large containers needs to be investigated more thoroughly.

Production of Slush Hydrogen. Several successful methods for producing solids from liquid–solid mixtures were reported in the literature. However, if the preparation method is to be usable, it must work in systems of all sizes and still meet certain basic criteria that create a process that is thermodynamically efficient and reproducible. The process should also be able to produce a mixture with enough fluidity to transfer through existing systems and with sufficient solid content so that the density and heat capacity are significantly greater than those for the normal boiling point liquid.

Freeze-Thaw Method. Sindt (106) summarized the basic principles of the freeze–thaw method and its feasibility. Two of the methods reported by Sindt involve the formation of solid particles by spraying precooled liquid into an environment well below the triple-point pressure and inducing solid formation by allowing precooled helium gas to flow through a triple-point temperature liquid. The spray technique produced a very low density solid particle, which had to be partially melted to form a liquid–solid mixture. The technique of allowing helium to flow through the liquid-produced solid by reducing the partial pressure of hydrogen below its triple-point pressure which resulted in a clear, rigid tube of solid forming around the helium bubble train. The solid was found not to be convertible to a mixture without further treatment such as crushing. Sindt found that a more desirable preparation method was to evacuate the ullage over the liquid, which created a solid layer at the liquid surface. The solid layer produced had a texture that was very dependent upon the rate of vacuum pumping. Low pumping rates produced a dense, nearly transparent layer of solid. Subsequent breaking of the solid left large rigid pieces that formed inhomogeneous mixtures even with vigorous mixing. Higher pumping rates produced a solid layer that was porous and consisted of agglomerates of loosely attached fine solid particles. The solid layer was found to be easily broken and mixed with the liquid to form a homogeneous liquid–solid mixture that could be defined as slush. Sindt discovered, however, that solids could not be continuously generated at the liquid surface without vigorous mixing.

Sindt (106) also reported on a continuous preparation method, which he developed, capable of forming solid layers in cycles by periodic vacuum pumping. During the pumping (pressure reduction) portion of the cycle, the solid layer formed as previously described. When the pumping was stopped, the solid layer melted and settled into the liquid, forming slush. Although mixing was not necessarily required, the preparation method was accelerated by some mechanical mixing which helped break the layer of solids. This technique has been called the freeze–thaw process.

In the same study, Sindt was able to determine the acceptable limits of vacuum pumping rates for freeze–thaw slush production. He found that low pumping rates were unacceptable because of the texture of the solid produced. Very high pumping rates were also found to be undesirable because liquid droplets were carried into the warm regions of the system by the velocity of the evolving gas. The evaporation of these droplets was, therefore, considered a loss to the preparation of solid. Sindt also determined the rate that produces solids that are easily transformable into slush by measuring the evolved gas during many cycles of freeze–thaw preparation. This rate was determined to be 0.9 m^3s^{-1}/m^2 of liquid surface area at vacuum pump inlet conditions of 300 K and 6.9 kNm^{-2}. This was also found to be the pumping rate during the evacuation phase of the freeze–thaw cycle. He concluded that the range of the vacuum pumping rate for satisfactory slush production was 0.8 m^3s^{-1}/m^2 to 1.2 m^3s^{-1}/m^2 of liquid surface area. Pumping rates in that range were found to result in an efficient exchange of energy between the evaporating and freezing liquids. The efficiency of this exchange of energy is best illustrated by the experimentally determined irreversibility reported by Daney and Mann (108), which was found to be less than 3.4%. Pumping rates within this range have been used to produce slush of solid fractions to 0.45 in vessels 10 cm to 76 cm in diameter.

According to Voth (107), although the freeze–thaw production method proved to be technically feasible and fully developed, it was shown to have disadvantages. These disadvantages include the fact that the freeze–thaw process is a batch process and that it operates at the triple-point pressure of the cryogen. For hydrogen, this pressure was estimated to be 0.07 bars absolute, a pressure capable of drawing air through inadvertent leaks in the system. The air could be thought of as presenting a potential safety problem in a hydrogen system. Voth also showed that the freeze–thaw process required either costly equipment to recover the generated triple-point vapor or the loss of approximately 16% of the normal boiling-point liquid hydrogen and approximately 24% of the normal boiling-point liquid oxygen if the vapor was discarded.

Auger Method. Voth (107) reported on a study for producing liquid–solid mixtures of oxygen or hydrogen using an auger. He described an auger used to scrape frozen solid from the inside of a refrigerated brass tube in order to produce slush hydrogen. He showed that slush hydrogen could be continuously produced by this method, and because it could be immersed in liquid, slush was produced at pressures above the triple-point pressure. Voth was also able to produce the increased pressure pneumatically or by generating a temperature stratification near the surface of the liquid. He observed that the auger system produced particles in the size realm of the particle produced by the freeze–thaw method so that, like the freeze–thaw-produced slush, the auger-produced slush could be readily transferred and stored.

According to Voth (107), the surface freezing occurring in the freeze–thaw production process is thermodynamically reversible. In contrast, the freezing process in the auger is irreversible because a temperature difference must exist between the refrigerant and the freezing cryogen, and the energy added to scrape the solid cryogen out of the brass tube must be removed by the refrigerant. Voth argued that in spite of these irreversibilities, the auger system was found to require less energy to produce slush hydrogen than a particle freeze–thaw system. He reported that the temperature difference required refrigeration temperatures below the triple-point temperature of hydrogen so that a gaseous or liquid helium refrigerator was required for the auger.

Although this method was determined to offer the advantage of operating above atmospheric pressures (an important consideration in lowering the possibility of oxygen intrusion into the slush), it was shown to have the disadvantage of using expensive helium coolant.

Quality Determination. A thermodynamic analysis of the freeze–thaw production process for forming mixtures of slush developed by Mann et al. (109) showed that the measurement of two quantities—(1) the mass fraction pumped during the production process, and (2) the heat leak per unit mass into the production dewar—were sufficient to determine the quality of the resulting mixture. Because irreversibilities were observed to exist in the freeze–thaw process, a comparison of the predicted quality with the qualities determined by the measurement of thermodynamic properties was found necessary.

According to Daney and Mann (108), in the freeze–thaw method of forming a triple-point mixture of hydrogen, the latter was partially evaporated under the reduced pressure obtained by a vacuum pump, while a refrigeration effect (approximately equal to the latent heat of vaporization) was experienced by the remaining liquid or liquid–solid mixture. They suggested, by specifying the initial state and the process or path to be followed, that the quality of the liquid–solid mixture could be predicted as a function of the mass of the vapor removed. According to them, therefore, the problem of quality prediction consisted of two parts. The first was the determination of when a specific initial state, triple-point liquid was reached, whereas the second was the prediction of the quality once this standard initial state was achieved. They also reported that the arrival at the triple-point liquid condition may be determined in several ways: (1) vapor pressure measurement, (2) visual observation of the formation of a few solid particles, and (3) prediction from the mass fraction of the vapor pumped off in the cooling-down process. Daney and Mann argued that the first two methods provided a more accurate means of determining the arrival at triple-point liquid conditions, and hence a more accurate quality determination could be realized. However, they also argued that it may be of interest to see what accuracy in quality determination could be expected by starting the mass accounting with a normal boiling-point liquid instead of a triple-point liquid.

Energy Requirements. A study to determine the energy requirements of the freeze–thaw and auger methods was reported by Voth (107) who mentioned that producing slush appears to be a reasonable way of increasing the density and heat capacity of cryogens. He observed that when large quantities of slush were produced, the energy required to produce them became significant. He therefore concluded that the production energy depended on both the thermodynamic reversible energy requirements to produce slush and the energy required to overcome irreversibilities in a practical system. He determined the energy required to produce slush with a 0.5 solid mass fraction for four practical slush-hydrogen-producing systems. Three of the systems employed the freeze–thaw production method, whereas the fourth used an auger and a helium refrigerator to produce slush from normal boiling-point liquid hydrogen.

According to Voth (107), the thermodynamic reversible energy required to produce slush hydrogen was equal to the thermodynamic availability of the slush. Also using normal hydrogen at a temperature of 300 K and a pressure of 1.013 bars as the base fluid, the reversible energy required to produce normal boiling-point para-hydrogen was 3971.4 W·h/kg, whereas the reversible energy required to produce slush with a solid mass fraction of 0.5 was 4372.8 W·h/kg. Voth explained that the energy required by practical systems was higher because of component inefficiencies. The calculated energies for the four cases were based on liquefier and refrigerator efficiencies of 40% of that of Carnot. He assumed that the vacuum pumps required by the freeze–thaw production had an efficiency of 50% of the isothermal efficiency. However, he did not include the increased production energy resulting from heat leak into the containers and transfer lines because it was difficult to estimate without a firm system definition and because the heat leak would have been nearly equal for all the systems studied. Because heat leak was not included, the calculated energies for the four cases were lower than those of an actual system, but the results did allow a comparison among the various slush production systems.

Voth also found that the auger method introduced additional irreversibilities because of the rotational power added to the slush generator and the temperature difference between the refrigerant and the freezing hydrogen. He concluded that a value of 1.05 for the ratio of total supplied refrigeration to the refrigeration available for the freezing hydrogen in the auger system was usually needed to determine the refrigeration required to produce slush with a solid fraction of 0.5. The input energy to the refrigerator connected to the auger was observed to depend on the refrigeration temperature; the lower the temperature, the higher the input energy. For the auger system, he assumed that the lowest refrigeration temperature was 10 K. Because a refrigerator was required to cool the normal boiling-point liquid to a triple-point liquid, the highest refrigeration temperature was assumed to be 19.76 K. He noted that these refrigeration temperatures were within the capabilities of a closed-cycle helium refrigerator. Voth also reported that even though the power required to produce slush hydrogen using the auger was relatively easy to calculate, the power required to produce slush hydrogen using the freeze–thaw production method was very system dependent.

Solid Particle Characteristics. Because applications of slush Hydrogen always include some storage, Mann et al. (109) observed the aging effects on solid particles in slush as solids aged as much as 100 hours. Particles of slush in freshly prepared solids were observed to be in the form of agglomerates of very small subparticles loosely attached. These agglomerates were remnants of the porous layer that forms during the pumping phase of preparation. They observed that as slush aged, the solid particle configuration changed dramatically and the loosely attached subparticles filled in with solids to form a more smoothly rounded particle of higher density. They asserted that the exact mechanism of the change was not completely understood but suggested that it involved a mass energy exchange that occurred in such a way as to assume a more stable spherical shape with less surface area. According to them, the major portion of the change occurred within the first 5 h. They remarked that accompanying the change in particle configuration was an increase in the density of slush that had settled to the bottom of the vessel. This tended to increase density partly from the increase in the bulk density of each particle and partly from a closer packing of particles because of their more rounded shape after aging. They thus concluded that the aging phenomenon of the particles and the accompanying increase in settled slush density were apparently a result of heat flow to the slush. Freshly prepared slush was concluded to have a maximum settled solid fraction of 0.35 to 0.45.

During the experimental study of Mann et al. (109), the slush particle size and particle settling velocity were measured using photo instrumentation. They noted that these characteristics of particles should be determined because they generally affect the fluid mechanics of liquid–solid mixtures. They also reported that particle size determines the minimum restrictions permissible in systems using the mixtures. They concluded that although particle configuration changed with age, particle size did not change significantly and that the distribution of particle size could be satisfactorily described by a modified logarithmic function. They reported that size ranged from 0.5 mm to 10 mm, with 2 mm being the most frequently occurring size. They also reported over 170 settling velocity measurements on both fresh and aged slush particles and concluded that the settling velocity of fresh particles was lower than that of aged particles and was extremely dependent on the shape of individual particles.

Sindt (106) reported that mixing of slush hydrogen to maintain homogeneity was required in most of the potential applications, and if mixers were to impart velocities to the fluid greater than the settling velocities, particles would have been carried along and mixing would have resulted. Sindt used several methods to mix the slush in a vessel. One method used a simple propeller with blades designed to impact velocity to the fluid with lift. Another method used high-velocity streams of fluid expelling from openings in a duct. According to him, both methods of mixing had been used to mix slush of a solid fraction as high as 0.6. Also, the solid content in slush could be maintained and even increased by transferring slush into the vessel and removing liquid through a screen with 0.6 mm openings. Sindt explained that by using this method the solid fraction could be increased until the solids protrude above the liquid–gas interface.

Transfer Characteristics. Most of the studies on transfer characteristics of slush hydrogen have been carried out at the Cryogenics Division of the National Institute of Standards and Technology (*NIST*). Experimental results pertaining to slush hydrogen fluidity will be reported in this section.

Slush Hydrogen Flow in Pipes. Sindt (106) reported that transfer and pumping characteristics of slush hydrogen should be similar to those of liquid hydrogen if slush is to be used in the existing liquid hydrogen system and if slush is to be handled as a fluid. During the experimental study of Sindt et al. (113), slush of solid fractions as high as 0.6 was transferred through vacuum-insulated pumps of 16.6 mm to 25 mm in diameter. Transfer pressure losses were determined in triple-point liquid and in slush of solid fractions up to 0.55 in a 16.6 mm diameter pipe. They estimated slush data to have an uncertainty occurring at the high solid fractions and the lowest flow rates. According to them, pressure loss data for flowing slush revealed that, at low flow rates, pressure losses in flowing slush were double those of triple-point liquid if solid fractions were high. The data also revealed that at high flow rates, pressure losses in flowing slush were less than the losses in triple-point liquid if the solid fraction was near 0.35. They also carried out a more complete analysis of the losses in flowing slush hydrogen by calculating a friction factor and plotting it versus the Reynolds number. In the calculations, they used triple-point liquid viscosity because the viscosity of slush hydrogen was generally unknown.

Sindt and Ludtke (112) observed that the characteristics of slush hydrogen flow losses at the higher Reynolds numbers were more evident when displayed in terms of the friction factors than if displayed as pressure losses. They reported that friction losses in flowing slush of solid fractions to 0.4 were as much as 10% less than in liquid and that the friction-loss curve for 0.5 solid fraction slush appeared to be following a slope such that it would be below triple-point liquid losses at high Reynolds numbers. They reported these data for a 16.6 mm diameter pipe and concluded that low losses in slush aged 10 hours were 4% to 10% higher than losses in 1-hour old slush.

The experiments of Sindt et al. (113) revealed that a gradient in the solid concentration may develop when the slush velocity is 0.5 ms^{-1}, whereas at a velocity of 0.15 ms^{-1}, the solids were likely to settle forming a sliding bed. Considering these observations, it was concluded that the critical velocity of slush in the pipe was about 0.5 m/s.

Slush Hydrogen Flow in Restrictions. Sindt et al. (113) experimentally determined flow losses in restrictions such as valves, orifices, and venturies using slush hydrogen of solid fractions to 0.5. They determined the losses in a 3/4 inch nominal copper globe valve with the valve fully opened and in cases when it was partially opened and expressed the losses as a resistance coefficient independent of the slush solid fraction. According to their study, with the valve partially opened, the losses seemed to be less with increasing the solid fraction, whereas with the valve fully opened, the trend was reversed. Also, the loss coefficients compared favorably with the typical valve coefficient for water.

Sindt and Ludtke (112) remarked that liquid–solid mixtures of hydrogen flow through orifices of 6.4 mm and 9.5 mm in diameter with no plugging and with a pressure drop of the same magnitude as that of the triple-point liquid. They observed that the slush mass flow rate was dependent on the pressure differential across the orifice as would have been expected for a nearly incompressible, Newtonian fluid and that when the minimum pressure in the orifice reached the triple-point pressure, cavitation with accompanying choking occurred. At that point, the mass flow became dependent on the upstream pressure and independent of the downstream pressure. Flow characteristics of slush flowing through a venturi have also been determined by Sindt et al. (113). According to them, flow losses through the venturi were not affected by the solid fraction of the slush.

Concluding Remarks on Slush Hydrogen. This section presented an overview of the state-of-the art of slush hydrogen production and utilization technologies. It is apparent that the use of slush hydrogen should be considered only for cases in which higher density and greater solid content are really needed. This is mainly because the production costs of slush hydrogen now and in the near future are greater than the liquefaction costs of hydrogen resulting from the larger energy use involved.

Conclusions

As a result of the aforementioned facts, it can be seen that hydrogen as a fuel and the Solar Hydrogen Energy System have unmatched advantages when compared with fossil fuels and the Fossil Fuel System, respectively.

Hydrogen. The advantages of hydrogen vis-à-vis fossil fuels can be summed up as follows:

(1) Liquid hydrogen is the best transportation fuel when compared with liquid fuels such as gasoline, jet fuel, and alcohols; and gaseous hydrogen is the best gaseous transportation fuel.
(2) Hydrogen can be converted to useful energy forms (thermal, mechanical, and electrical) at the user end through five different processes, whereas fossil fuels can be converted through only one process (i.e., flame combustion). In other words, hydrogen is the most versatile fuel.
(3) Hydrogen has the highest utilization efficiency when it comes to conversion to useful energy forms (thermal, mechanical, and electrical) at the user end. Overall, hydrogen is 39% more efficient than fossil fuels. In other words, hydrogen will save primary energy resources. It could also be termed as the most energy-conserving fuel.
(4) When fire hazards and toxicity are taken into account, hydrogen becomes the safest fuel.

Solar Hydrogen Energy System. The advantages of the Solar Hydrogen Energy System vis-à-vis the present Fossil Fuel System and the Synthetic Fossil Fuel System can be summed up as follows:

- 5.When the environmental impact is taken into consideration, the Solar Hydrogen Energy System becomes the most environmentally compatible energy system. It will not produce greenhouse gases, ozone-layer-damaging chemicals, oil spills, and climate change and will produce little or no acid rain ingredients and pollution. It will actually reverse the global warming and bring the Earth back to its normal temperatures by decreasing the CO_2 in the atmosphere to its level before the Industrial Revolution.
- 6.The Solar Hydrogen Energy System has the lowest effective cost when environmental damage and the higher utilization efficiency of hydrogen are taken into account. In other words, the Solar Hydrogen Energy System will cost society least when compared with the present Fossil Fuel System and the Synthetic Fossil Fuel System.

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