HYDROGEN ENERGY

1. Introduction

The world relies on energy to power industry, move people and products, and keep us safe and comfortable. Fossil fuels, including coal, natural gas, and petroleum, provide much of the energy we use today (1). However, their supply is inherently and geographically limited, and there are significant environmental impacts to the continued and increased conventional use of fossil fuels (2). To address social equity, global climate change, urban air pollution, energy security through diversity, and economic growth issues, new energy solutions are needed.

Scientists and engineers are pursuing many pathways to clean and sustain energy systems. One of the most promising solutions is a system using hydrogen and electricity as primary energy carriers (3–5).

The simplest element, hydrogen (H_2), has the potential to provide all of our energy services (heating and cooling, lighting, communication, mobility, and cooking) with little or no impact on the environment, both locally and globally. It can be made from domestic resources, offering opportunities for energy independence to all countries and regions. Hydrogen can be used in all applications that currently use more familiar hydrocarbon fuels.

Hydrogen is an energy carrier, in the same way that electricity is an energy carrier. Both can provide energy services to meet our needs. Like electricity, hydrogen can be produced from many different resources, including fossil fuels, renewable resources, and nuclear energy. Unlike electricity, hydrogen can be produced at one point in time and used at a later date, that is, it can be stored for long periods of time. This is an important characteristic, especially when we consider storing large amounts of intermittent renewable (wind or solar) energy (6), or distributing large quantities of energy from one region to another. In the future, when intermittent renewable energy resources provide more of our energy services, storage will be an increasingly important consideration. Hydrogen is an effective storage medium for large amounts of energy, particularly for more than a few days. This would reduce the supply side burden of covering fluctuations in demand, which is costly and inefficient in our current system. For example, utilities must purchase and maintain expensive stand-by generating capacity that is used only part time.

Hydrogen offers benefits as an on-board fuel for “zero-emission” transportation needs that can never be met with hydrocarbon fuels. However, significant advances in hydrogen storage capacities are needed to give hydrogen vehicles driving ranges comparable to conventional and hybrid gasoline-fueled vehicles. By comparison, current battery electric vehicles are unable to provide the needed range, although research advances are closing the gap (7).

2. Fundamentals of Hydrogen Energy Systems

Molecular hydrogen (H_2) is not found in substantial quantities in Nature: hydrogen atoms (H) are almost always associated with other elements, principally oxygen (ie, water, (H_2O)) and carbon (ie, methane, CH_4; coal and other fossil fuels; and organic matter). Therefore, energy must be used to produce hydrogen. This, of course, is also the case with electricity production. This energy can be thermal, photonic, or electrical energy, and can be provided by renewable, fossil, or nuclear resources. It is important to consider the process by which hydrogen is produced when evaluating the overall environmental, security, diversity, efficiency, and economic impacts of hydrogen systems (8,9).

Once produced, hydrogen needs to be stored. Although hydrogen has the highest energy density of common fuels on a weight basis, it has the lowest energy density on a volumetric basis, at standard conditions (see Table 1).

Table 1. **Properties of Selected Fuels**[a]

Property	Hydrogen, H_2	Methane, CH_4	Methanol, CH_3OH	Gasoline, $C_6–C_{12}$
boiling point, °C	–253	–162	65	wide range A[b]
physical state at 25°C	gas	gas	liquid	liquid
heating value—weight basis				
LHV, MJ/kg	120	48	20	42–44
HHV, MJ/kg	142	53	23	44–46
heating value-volume basis[c]				
LHV, MJ/Nm^3	11	35	15,700	~32,000
HHV, MJ/Nm^3	13	39	18,100	~33,000
flammability limits, vol% in air	4.1–74	5.3–15	6–36.5	1.4–7.6
explosive limits, vol% in air[d]	18.2–58.9	5.7–14	6.7–36	1.4–3
molecular diffusion coeff, cm^2/s in air	0.61	0.16	0.13	0.05
autoignition temperature in air, °C	571	632	470	220
liquid density, g/L	77	425	792	720–780
liquid specific gravity at 25°C, water = 1			0.79	0.72–0.78
vapor specific gravity at 25°C, air = 1	0.07	0.55	1.1	3.5–4.5

[a] See Refs. 10,11.

[b] Gasoline contains a wide range of constituents (ie, alkanes, cycloalkanes, aromatic hydrocarbons) that vaporize at temperatures as low as 25°C and as high as 225°C.

[c] Nm^3 of gas at atmospheric pressure, or m^3 of liquid.

[d] Flammability limits and explosive (detonation) limits are often (incorrectly) used interchangeably. For most hydrocarbon gases and vapors, the lower values (LFL and LEL) tend to be comparable at atmospheric pressures. This is not the case for hydrogen.

In order to store the same amount of energy in a given volume, significantly higher pressures are required for compressed hydrogen gas systems than for other gases. Another way of looking at this is that, for a given pressure, more or larger tanks would be required to provide the same amount of energy from hydrogen as compared to other hydrocarbon fuels. Liquid hydrogen has a higher volumetric energy density than compressed hydrogen, but hydrogen is liquid only at extremely low temperatures (20 K), and specialized containers are required (12). In order for hydrogen to be considered as a viable fuel for transportation needs, advanced storage systems must be developed.

Materials of construction, including materials used in valves and seals, must be carefully selected to account for the properties of hydrogen and its interactions. Hydrogen can absorb into metals, with detrimental effects on material properties. Embrittlement can occur when certain steels are subjected to temperature and/or pressure swings in the presence of pure hydrogen. Subsequent loss of tensile strength, ductility, and fracture toughness can result in failure. Material susceptibility to hydrogen embrittlement (13) is shown in Table 2. Susceptibility to embrittlement generally increases with increased tensile stress level and as the ultimate strength of the alloy increases. Embrittlement is also a function of the purity of the hydrogen to which the material is exposed (increasing with increasing hydrogen purity). The use of appropriate materials for valves

Table 2. **Hydrogen Susceptibility**[a]

Level of embrittlement	Negligible	Slight	Severe	Extreme
material				
	310 SS	304 ELC SS	Ti-6Al-4V	410 SS
	316 SS	305 SS	Ti-5Al-2.5Sn	1042 Steel
	1100 Al	Be-Cu Alloy 25	AlSl 1020	17-7 pH SS
	6061-T6 Al alloy	Titanium	430F	4140
	7075-T73 Al alloy		Nickel 270	440 C
	OFHC Copper		A515	Inconel 718
	A286			

[a] Not a comprehensive list.

and seals is also critical, since hydrogen can permeate a large number of materials due to its small molecular size and high diffusivity and permeability.

Using hydrogen to provide energy services (ie, lighting, heating, mobility, and communication) requires an electrochemical device (eg, a fuel cell) or a thermochemical device (eg, a combustion engine). In these devices, hydrogen combines with oxygen to form water as the main product, and to release useful energy:

$$\begin{array}{lll} H_2 + \frac{1}{2}\,O_2 = H_2O(g) & \Delta H = -242 \text{ kJ/mol } H_2 & \text{(lower heating value)} \\ H_2 + \frac{1}{2}\,O_2 = H_2O(l) & \Delta H = -286 \text{ kJ/mol } H_2 & \text{(higher heating value)} \end{array} \qquad (1)$$

Both electrical and thermal energy can be released via these reactions. High overall energy (thermal + electric) efficiencies are possible, depending on the design of the system (14).

The water cycle is an important aspect of hydrogen energy systems: that is, water is a feedstock for the production of hydrogen (even when using fossil fuels) and is also the principal product of the use of hydrogen. This characteristic is important in understanding the role of hydrogen in sustainable energy systems.

3. Hydrogen Production

Today, nearly 50 million tons/year of hydrogen are produced and used globally, almost exclusively as a chemical feedstock for the refining, chemical, metals, and electronics industries. If all of this hydrogen were diverted for use in energy systems, only 2% of the world energy demand would be met. Thus, for hydrogen to be considered as an energy carrier on par with electricity, we will need to significantly expand current production and develop a number of new production routes in order to provide sufficient hydrogen to meet energy service demands.

3.1. Commercial Hydrogen Production Processes. Today, hydrogen is produced primarily from fossil fuels (natural gas, petroleum, and coal) using well-known commercial processes. Worldwide, the predominant feed is natural gas (48%), followed by oil–petroleum (30%), coal (18%), and electricity

(4%). “Captive” hydrogen is produced at the consumer site where it is used in ammonia–fertilizer and methanol production and in petroleum refining. These represent the vast majority of hydrogen production and consumption (98.8%). “Merchant” hydrogen, sold by industrial gas companies to consumers in relatively smaller quantities, is either intentionally produced or recovered as a by-product from other industrial processes. The chloralkali process, in which hydrogen is a by-product, is a major contributor to the electrolytic hydrogen production numbers.

Steam Methane Reforming (SMR). Large-scale catalytic steam reformation of natural gas is a well-known, high energy efficiency, commercial process for the production of hydrogen (15). Natural gas is, on average, ~95% methane, with the balance being higher hydrocarbons (ethane, propane) and trace contaminants, such as H_2S and CO_2. [For simplicity, chemical equations will be presented herein for methane (CH_4); however, in a real SMR system, the appropriate composition of the natural gas must be considered in the design of the process units.]

SMR is widely used, especially in the United States, to provide high purity hydrogen to the chemical, petrochemical, and refining industries. This method is a multistep process: gas pretreatment; catalytic reforming; high temperature water–gas shift; low temperature water–gas shift; purification; and compression–liquefaction. A simplified block flow diagram is shown in Figure 1.

Gas pretreatment is generally required, since untreated natural gas nearly always contains sulfur compounds. Since the nickel-based reforming catalyst is poisoned by these compounds, desulfurization is carried out ahead of the reformer.

The catalytic steam reforming reaction

$$\mathrm{CH_4 + H_2O(g) \leftrightarrow CO + 3H_2} \qquad \Delta H = +206\ \mathrm{kJ/mol\ CH_4} \tag{2}$$

takes place at elevated pressure (3–25 bar) and high temperatures (650–900°C). The catalyst, typically nickel based, is packed into tubes and the heat needed for reaction 2 is provided externally by combustion of additional natural or purge gas (from the purification subsystem). To prevent side reactions, excess steam is provided. A steam/carbon ratio of 3 is typically used to prevent the production

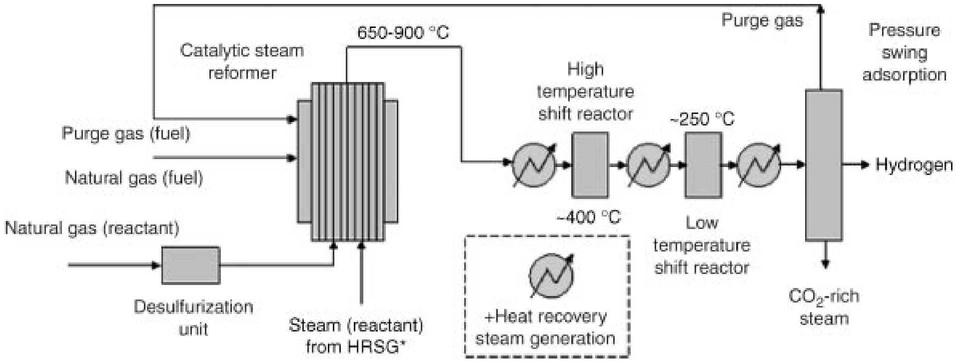

Fig. 1. Simplified block flow diagram of conventional steam methane reforming process.

of solid carbon or "coke," which can build up on the catalyst and plug the reactor tubes.

The synthesis gas mixture ("syngas"—a mixture of hydrogen and CO) is sent to the high and low temperature shift reactors, where additional hydrogen is produced via the water–gas shift reaction

$$CO + H_2O(g) \leftrightarrow CO_2 + H_2 \qquad \Delta H = -41 \mathrm{kJ/mol\ CO} \tag{3}$$

Hydrogen production via reaction 3 is favored at lower temperatures. To compensate for slower reaction kinetics at lower temperatures, a two-stage water–gas shift reaction is generally used, with the high temperature stage operating at ~400°C and the low temperature stage at ~250°C.

The exit gas, containing primarily H_2, and also CO_2, H_2O, and small amounts of CO, methane and higher hydrocarbons is then purified. Pressure swing adsorption (PSA) is the most common process used in large systems, where very high purity hydrogen (99.99+%) is the desired product. With adjustments to the PSA operation, one can also produce a high purity CO_2 stream for sequestration or for sale, in addition to the hydrogen stream (16).

Petroleum Refining. Within a petroleum refinery, hydrogen is produced in some sections and consumed in others, in large quantities. Hydrogen is used to remove sulfur and nitrogen from crude oil (ie, hydrodesulfurization), to reduce aromatic content, and to lower the molecular weight or "crack" hydrocarbon constituents. For most heavy crude oils, the hydrogen balance within the refinery is "negative," requiring hydrogen to be purchased or produced from other sources. When this is the case, SMR units within or near the refinery are commonly used to provide the remaining hydrogen requirement.

Hydrogen from Coal. The partial gasification of coal, associated with the production of coke for the steel industry, is an important source of hydrogen worldwide. Coke oven gas contains 40–55% hydrogen, which can be recovered for sale; however, hydrogen recovery from coke oven gas is not currently practiced on a wide scale. Conceptually, any type of coal gasification process that produces a syngas could be modified to produce high purity hydrogen (17,18).

Electrolysis. Electrolysis is another important process that can directly produce very high purity hydrogen. The source of the electricity used by the process can be fossil, renewable, or nuclear power.

Chloralkali Process. Caustic soda (sodium hydroxide, NaOH) is an important inorganic chemical produced by the electrolysis of brine (aqueous NaCl), with coproduction of hydrogen and chlorine (Cl_2):

$$2\,NaCl + 2\,H_2O \rightarrow 2\,NaOH + Cl_2 + H_2$$

Newer chloralkali technologies based on diaphragm and membrane systems predominate, with a general phasing out of the older mercury cell process. The half-reactions of interest for the diaphragm and membrane cells are

$$\text{Cathode } H_2O + e^- \rightarrow \tfrac{1}{2}\,H_2 + OH^-$$
$$\text{Anode } Cl^- \rightarrow \tfrac{1}{2}\,Cl_2 + e^-$$

Hydrogen purity is generally >98%, with some systems able to produce hydrogen at 99.9% purity.

Water Electrolysis. High purity hydrogen can be produced directly from water by two types of electrochemical systems, characterized by the movement of ions. In an alkaline electrolyzer, electrodes (a cathode and an anode) are immersed in a conducting aqueous electrolyte and electricity is applied across the cell. The two half-reactions are

$$\begin{aligned} \text{Cathode} \quad & 2\,H_2O + 2e^- \rightarrow H_2 + 2\,OH^- \\ \text{Anode} \quad & 2\,OH^- \rightarrow \tfrac{1}{2}O_2 + H_2O + 2e^- \end{aligned}$$

In a proton exchange membrane (PEM) electrolyzer, the electrolyte is a proton-conducting polymer membrane and mobile ion is a proton. The two half-reactions are

$$\begin{aligned} \text{Cathode} \quad & 2\,H^+ + 2e^- \rightarrow H_2 \\ \text{Anode} \quad & H_2O \rightarrow 2e^- + 2\,H^+ + \tfrac{1}{2}\,O_2 \end{aligned}$$

The overall reaction for both types is

$$\begin{aligned} H_2O(g) &\rightarrow H_2 + \tfrac{1}{2}O_2 \; \Delta H = +\,242 \text{ kJ/mol } H_2O(g) \text{ (lower heating value)} \\ H_2O(l) &\rightarrow H_2 + \tfrac{1}{2}O_2 \; \Delta H = +\,286 \text{ kJ/mol } H_2O(l) \text{ (higher heating value)} \end{aligned} \tag{4}$$

The theoretical voltage requirement for the dissociation of water is 1.23 V at 25°C. In practice, ~1.75 V is required, resulting in an energy efficiency of ~70% (lower heating value basis). To reduce the consumption of electricity, researchers are developing higher temperature electrolysis processes, in which some of the required enthalpy of reaction is provided by heat, rather than premium electric power, as illustrated in Figure 2.

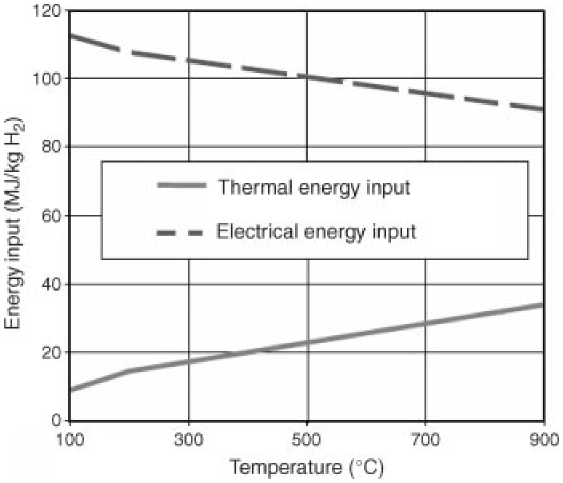

Fig. 2. Effect of temperature on electrical requirement for water electrolysis (19).

3.2. Future Hydrogen Production Processes. Research is being conducted to develop improved and innovative hydrogen production technologies. Although we may continue to rely on existing large-scale production processes (ie, SMR) to supply most of the hydrogen that will be needed in the early years of transition to a Hydrogen Economy, for the long term, there are technical, economic, and energy efficiency improvements required to make hydrogen a pervasive commodity fuel. For example, one approach is to produce hydrogen on a smaller scale in a production facility close to or at the point of consumption (20). Doing so will significantly reduce or eliminate the costs associated with delivering hydrogen, which can contribute, depending on the application, up to 75% or more of the cost of the delivered hydrogen (ie, if the plant-gate cost of hydrogen from large-scale SMR is \$6/GJ, the delivered product would be \$25–35/GJ or more) (21). Thus, many current research efforts are focused on small-scale, on-site production of hydrogen.

In addition to process innovations, nonconventional resources present opportunities and challenges for hydrogen production. Sources of methane-rich gas, such as landfill gas, volcanic offgas, and coalbed methane; and organic waste streams, such as municipal solid waste (MSW), paper, plastics, animal waste, and sewage sludge, represent important resource streams for hydrogen production.

Small-Scale (Fossil-Based) Production Processes. Small-scale steam methane reformers based on large commercial systems are available, although the footprint needed for these units is much larger than acceptable for most refueling applications. The high temperatures and pressures dictate the use of costly materials of construction. Redesign and reengineering, rather than “shrinking” existing unit operations, is an important and viable approach to efficient, on-site production of hydrogen (22). Several processes are being developed, including lower temperature and pressure processes using compact designs. These operating parameters permit the use of less expensive materials, and the compact designs can be factory-built. New processes being developed include partial oxidation, autothermal reforming, and sorbent-enhanced reforming processes.

Partial Oxidation (POX). Feed (in this example, CH_4) is oxidized by O_2 to produce a syngas:

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2\,H_2 \qquad \Delta H = -36\text{kJ/mol } CH_4$$

Additional hydrogen is produced by “shifting” the CO to CO_2 and H_2 (see reaction 3). The exothermic reaction does not require a catalyst, and the partial “burning” of the feed translates into quick response, a useful feature for inconsistent or variable hydrogen demand. Because of the higher temperature of the POX reaction compared to reforming, heat losses can be significant, especially if there is no use for the waste heat (likely to be the case for refueling station applications).

If air is used instead of O_2, the dilution of the hydrogen stream by nitrogen requires modification to the PSA purification process. This is because nitrogen behaves in a manner similar to hydrogen in the PSA system (ie, it is not adsorbed), and it is therefore hard to separate N_2 from the product stream without PSA process modification, or use of other purification processes.

Autothermal Reforming. Feed (in this example, CH_4) reacts with steam and O_2 to produce a syngas:

$$CH_4 + H_2O \leftrightarrow CO + 3\,H_2 \quad \Delta H = +206\ \text{kJ/mol}\ CH_4$$
$$CH_4 + \tfrac{1}{2}\,O_2 \rightarrow CO + 2\,H_2 \quad \Delta H = -36\ \text{kJ/mol}\ CH_4$$

Both the steam reforming and the partial oxidation reactions occur. With the appropriate mix of fuel, steam, and O_2, the overall heat of reaction can be provided without an external heat source or exchangers. As with the partial oxidation process, if air is used rather than oxygen, modification to the purification section is required to remove nitrogen.

Sorbent-Enhanced Reforming. The extent of the reforming reaction (reaction 2) can be shifted toward the production of hydrogen if CO_2 were removed as a product by a sorbent. This has the effect of allowing the process to be operated at a lower temperature and/or pressure, while still maintaining a high methane conversion. However, the regeneration of the sorbent is the area in need of research, as it is critical to the overall economics of the process that the sorbent be robust (ie, has to maintain its particle size, porosity, and activity through multiple cycles).

Advanced Coal Gasification Processes. The reserves of coal in the United States and around the world are enormous. Using these vast resources to produce hydrogen is very attractive, especially if the environmental impact of increased coal use can be mitigated. Hydrogen-from-coal production processes, integrated with reduced or near-zero CO_2 emissions, could make an important contribution to the Hydrogen Economy, and enable the use of abundant indigenous resources in developing countries (especially China and India) with the possibility of minimal impact on global climate and urban air quality.

Coal gasification, using partial oxidation or oxygen-blown gasifiers, produces a syngas that can be used to produce hydrogen and a stream of relatively high purity CO_2, with the addition of unit operations similar to other commercial hydrogen processes. Providing that the 90+% CO_2 stream can then be further concentrated to near 100% purity, it could then be sequestered to significantly reduce the impact of increased coal utilization on natural global systems. The U.S. Department of Energy's FutureGen Program includes research, development, and demonstration projects addressing the production of hydrogen from coal. Additional information on efforts to extend and improve existing technologies can be found at http://www.netl.doe.gov.

One concept, Zero Emission Coal and Carbon Technology, consists of two processes: hydrogasification of coal with power hydrogen production and mineral carbonization (23). This is a highly integrated process in which recycled hydrogen and steam are used to produce additional hydrogen (and/or electricity) and a "pure" stream of CO_2 that is ready for sequestration.

The hydrogasification of coal (see Fig. 3) produces a gas (mainly steam, CH_4, and H_2) that is then steam reformed in a bed of lime (CaO) to produce hydrogen and limestone ($CaCO_3$). About one-half of the hydrogen is recycled back to the gasifier and the remainder is sent to a solid oxide fuel cell (SOFC) to produce power, process steam, and heat. This heat is then transferred to the limestone, converting it back to lime and CO_2.

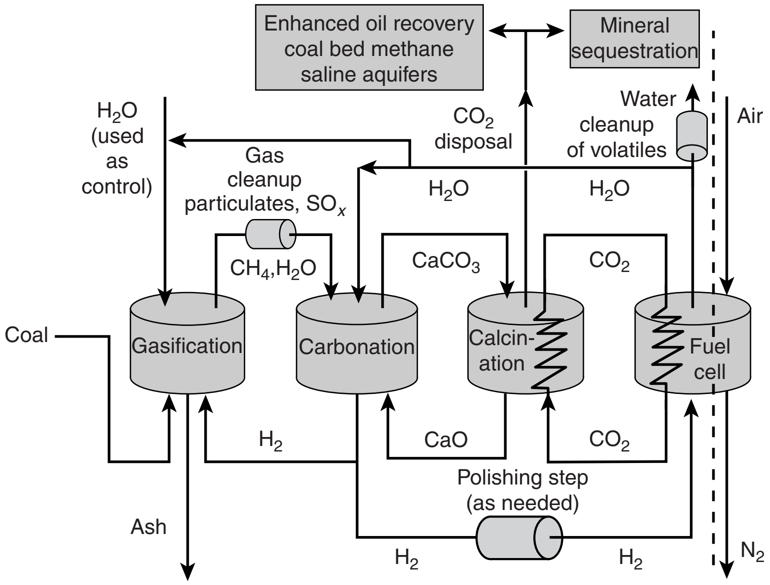

Fig. 3. Process schematic for zero emission coal (ZEC) technology concept (23).

The main advantage is that the CO_2 is essentially pure and at a high pressure, and in this state, it can readily be used for enhanced oil recovery, enhanced coal-bed methane production, or sequestered in deep saline aquifers. Ultimately, it may also be possible to react it with a magnesium silicate (serpentine or olivine) to form magnesium carbonate and silica, which are subsequently landfilled back in the serpentine mine. Because the magnesium carbonate is thermodynamically stable, it may represent a permanent CO_2 sequestration solution.

The overall efficiency of this process, estimated to be ~70%, is about double that of conventional pulverized coal-fired generators, and on a par with other advanced integrated gasification combined cycle (IGCC) process configurations. More information on technical and economic aspects of this concept can be found at http://www.zeca.org/.

Biomass-Based Production. Biomass, including agricultural residues, animal waste, forest thinnings, energy crops (biomass specifically grown for energy use), municipal solid waste, and urban wood waste, is an important resource for hydrogen production. Thermal processes, including pyrolysis and gasification, can be used to produce hydrogen. These processes are similar to existing commercial processes using fossil fuels, and could be used to produce hydrogen in regions of countries where agriculture and the forest products industry are prevalent. Even though these processes produce CO_2 as a by-product in the same way as the fossil-based processes, biomass-derived CO_2 is photosynthetically recycled by growing additional biomass to provide additional feedstock (24).

In addition to its potential for hydrogen production, biomass pyrolysis produces a liquid product (bio-oil) that, like crude oil, contains a wide spectrum

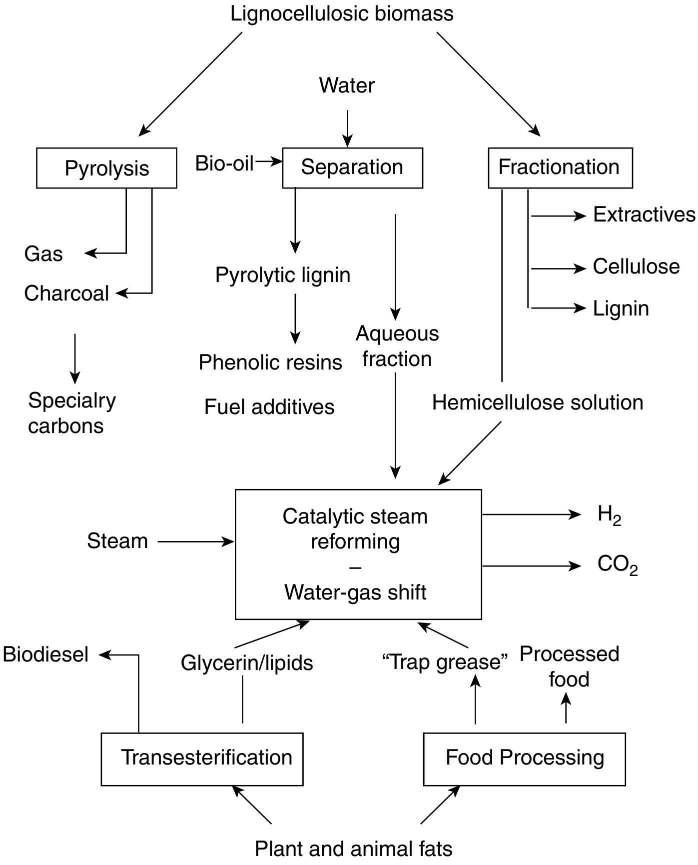

Fig. 4. Biorefinery concept (25).

of components that can be separated into valuable chemicals and fuels. Unlike crude oil, bio-oil contains a significant number of highly reactive, oxygenated components derived mainly from constitutive carbohydrates and lignin. Using a "bio-refinery" concept (see Fig. 4) that mimics the multiprocess petroleum refinery, these biomass-based components can be transformed into a variety of products, including hydrogen. Multiproduct strategies are designed to produce high value chemicals, such as phenolic resins and fuel additives, in conjunction with hydrogen (25).

Although hydrogen produced from biomass is not currently cost competitive, research is focused on bringing down costs of biomass-derived hydrogen with process improvements throughout the production chain, including feedstock collection and preparation, process operation, and product recovery and purification (24,25).

High Temperature Nuclear Thermochemical Cycles. Hydrogen produced using nuclear power may also provide an environmental advantage over traditional energy supplies. The Nuclear Energy Research Initiative (NERI) supports R&D to identify and evaluate new and innovative concepts for

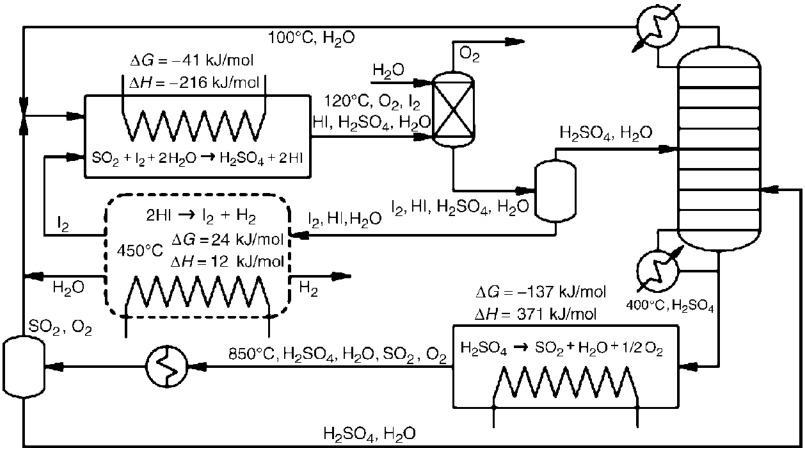

Fig. 5. Process schematic showing heat integration for the S–I thermochemical water-splitting cycle (27).

producing hydrogen using nuclear reactors. The research includes investigation of hydrogen generation processes compatible with advanced reactor systems, such as the helium gas-cooled reactor. Advanced nuclear reactors that are designed to operate at high temperatures (700–950°C), the "Gen IV" reactors, could be used to produce hydrogen using thermochemical cycles (26). These cycles have the potential to be substantially more efficient than the use of nuclear reactors as a source of electric power to electrolyze water. A large number of multistep chemical cycles have been reviewed for potential integration with these reactors. The most promising are the sulfur–iodine (S-I) and the calcium–bromine (UT-3) cycles.

The three reactions of the sulfur–iodine cycle are

$$\begin{aligned} I_2 + SO_2 + 2\,H_2O &\rightarrow 2\,HI + H_2SO_4 \\ H_2SO_4 &\rightarrow SO_2 + H_2O + \tfrac{1}{2}O_2 \\ 2\,HI &\rightarrow I_2 + H_2 \end{aligned}$$

A process schematic for the S–I thermochemical cycle is shown in Figure 5.

The UT-3, or C–B, cycle consists of four reactions:

$$\begin{aligned} Br_2 + CaO &\rightarrow CaBr_2 + \tfrac{1}{2}O_2 \\ 3\,FeBr_2 + 4\,H_2O &\rightarrow Fe_3O_4 + 6\,HBr + H_2 \\ CaBr_2 + H_2O &\rightarrow CaO + 2\,HBr \\ Fe_3O_4 + 8\,HBr &\rightarrow Br_2 + 3\,FeBr_2 + 4\,H_2O \end{aligned}$$

The overall reaction in both cases is

$$H_2O \rightarrow H_2 + \tfrac{1}{2}\,O_2$$

The viability of large-scale hydrogen production using thermochemical cycles requires demonstration of the basic chemical reactions within a number of promising candidate cycles, development of corrosion-resistant materials, and process control and integration, in addition to the development of the advanced nuclear reactor concepts (28).

Photolytic Hydrogen Production. Direct water splitting, where the only inputs to the system are sunlight and water, is sometimes called the "Holy Grail" of the Hydrogen Economy. Water-splitting processes, including photoelectrochemical and photobiological, are the subjects of research efforts around the world.

Photoelectrochemical Production. Photoelectrolysis is a process whereby sunlight is used to directly split water into hydrogen and oxygen, eliminating the need for two separate systems [ie, photovoltaic (PV) power plant connected to an electrolyzer]. The process requires a light-harvesting device and appropriate water-splitting catalysts (29). The same multijunction cell technology developed and used by the PV industry is being used for photoelectrochemical (PEC) light harvesting systems with promising results. With modification, some of these semiconductors generate sufficient voltage to split water and are stable in the aqueous environment needed for electrolysis. Theoretical efficiency (photon-to-hydrogen) for tandem systems is 42%, although a practical system would be expected to achieve 18–24% efficiency (30). Low cost multijunction amorphous silicon (a-Si) systems could achieve 7–12% efficiency.

Photobiological Production. Biological hydrogen production, the production of hydrogen by microorganisms, has been an active field of basic and applied research for many years. Realization of practical processes for photobiological hydrogen production from water using solar energy could result in a novel source of sustainable and renewable energy, without greenhouse gas emissions or environmental pollution.

Two approaches to biophotolysis have been studied: nitrogen-fixing cyanobacterium (nitrogenase based); and reversible hydrogenase-based green algal systems. The nitrogenase-based system separates the reactions of photosynthetic oxygen evolution and nitrogen fixation into two cell types. This allows the simultaneous production of oxygen and hydrogen, but suffers from a high ATP (adenosine triphosphate) requirement to drive the reaction (31). The hydrogenase-based microalgal biophotolysis process requires less energy and thus could be more efficient. However, the production of hydrogen is moderated by the extreme sensitivity of the hydrogenase enzyme to oxygen (32,33).

Photosynthetic organisms utilize sunlight to convert H_2O and CO_2 into carbohydrates, energy, and O_2. This multistep process (referred to as the "Z scheme") includes a sequence of steps wherein water is split into protons, electrons, and oxygen (H^+, e^-, O_2). The "usual" fate for the proton and electron is to be used in a sequence of reactions to provide energy to the microorganism, or to produce carbohydrates.

Certain algae and cyanobacteria that have hydrogenases with above-average oxygen tolerance have been identified (32,33). Using innovative isolation techniques, these organisms have been separated from the general population and are being further characterized for their use for renewable and sustainable hydrogen production. With the identification and isolation of active organisms, and with the development of appropriately engineered systems, hydrogen production efficiency (photons-to-hydrogen) could reach 24%. Further research and significant engineering will be required before microorganisms will produce cost-effective hydrogen in sufficient quantities to impact the Hydrogen Economy.

4. Hydrogen Storage

The specific energy of hydrogen on a weight basis (J/kg) makes it an ideal fuel for NASA and space applications where "weight costs money". However, the low energy density of hydrogen on a volume basis (J/m^3) is a problem for applications on Earth (refer to Table 1). For transportation applications, the hydrogen storage system weight and volume can be critical factors: increased vehicle weight has a negative impact on fuel efficiency and performance; and consumers will not accept a significant reduction of trunk space to accommodate bulky storage vessels. For stationary applications, storage container weight is usually not a major concern, although storage container volume could be an issue, especially in urban areas. For portable applications, both weight and volume are important.

4.1. Commercial Hydrogen Storage Technologies. Practically, hydrogen can be stored as a liquid or compressed gas to increase the volumetric energy density. Liquefaction of hydrogen is an energy-intensive process, with a third or more of the energy content of the stored hydrogen needed to condense the hydrogen. The theoretical energy requirement for liquefaction of hydrogen is 12.1 MJ/kg (10% on a LHV basis), although the actual requirements range from 28–46 MJ/kg (24–38%), depending on the process (34). The volumetric energy density of liquid hydrogen (not considering the volume of the insulated tank) is ~8500 MJ/m^3. If we consider the entire storage system, the overall volumetric energy density is ~4900 MJ/m^3.

Compressed hydrogen tanks at 350 bar (~35 MPa) contain 2700 MJ/m^3 of hydrogen (~1950 MJ/m^3 when considering the outside volume of the storage container, in addition to the actual volume of the gas), which is generally agreed to be insufficient for commercialization of hydrogen vehicles. Composite tanks, such as carbon fiber-wrapped tanks with polymer liners, have been developed and successfully tested at pressures of 700 bar as possible solutions for hydrogen storage on board vehicles (35). The volumetric energy density of hydrogen at 700 bar is 4700 MJ/m^3, without considering the storage container itself. Current designs have an overall system energy density of ~3,400 MJ/m^3. With proper tank design and vehicle integration, this may provide the driving range that the consumer desires without compromising vehicle space.

Hydrogen can also be stored in a "solid-state" form by reaction with certain metals and metal alloys. With changes in temperature and/or pressure, metal/metal hydrides can be made to reversibly and cyclically adsorb and desorb hydrogen (36). A large number of metal hydride systems have been studied and characterized. The best hydrides from a weight % hydrogen storage perspective, such as Li- and Mg-based alloys, have high desorption temperatures (>250°C), which makes them impractical for low temperature PEM fuel cell applications. The best hydrides that desorb at low temperatures, such as $LaNi_5$ and TiFe, tend to have very low storage capacities of 2 wt% or less.

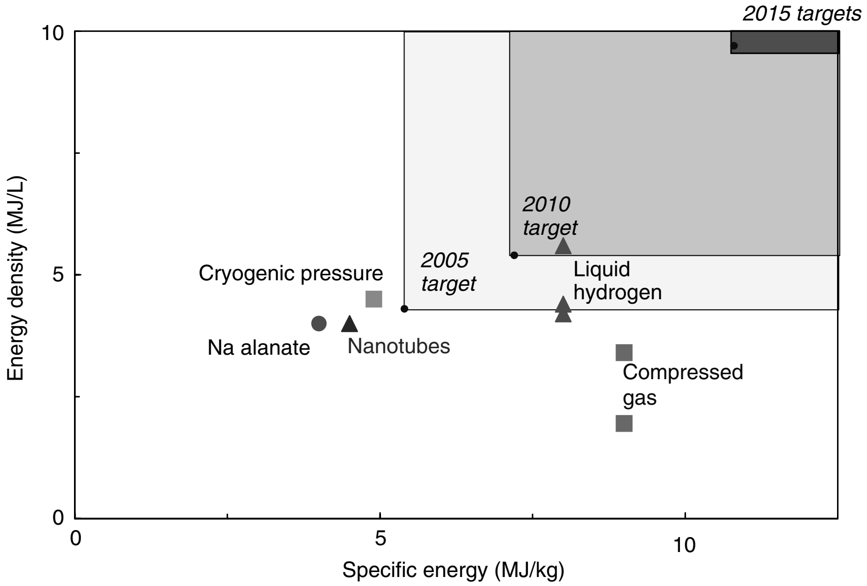

Fig. 6. Hydrogen storage system performance (37).

4.2. Future Hydrogen Storage Technologies. On-board hydrogen storage remains a critical technical barrier for hydrogen-fueled vehicles. This is a particular challenge for PEM fuel-cell vehicle applications, where hydrogen must be liberated at temperatures compatible with the waste heat of the fuel cell ($<80^\circ$C). Figure 6 illustrates the current status of hydrogen storage technologies and the technical targets that must be met for hydrogen fuel cell vehicle commercialization, according to automakers. In pursuit of technical solutions, the development of nontraditional hydrides and carbon materials has received much attention and support.

Complex Metal Hydrides. Alanates are considered to be the most promising of the complex hydrides studied to date for on-board hydrogen storage applications (38). They have been the focus of extensive research to increase the hydrogen storage capacity of the materials, extend the durability and cycle lifetime, and modify the kinetics to make the temperature and pressure for uptake and release more attractive. The most studied of these is $NaAlH_4$, which entails a two-step decomposition process

$$\mathrm{NaAlH_4} \leftrightarrow \tfrac{1}{3}\,\mathrm{Na_3\,AlH_6} + \tfrac{2}{3}\mathrm{Al} + \mathrm{H_2} \leftrightarrow \mathrm{NaH} + \mathrm{Al} + \tfrac{3}{2}\,\mathrm{H_2}$$

Using $NaAlH_4$ as a model system, researchers are developing synthesis and doping processes to improve properties and to reduce cost and complexity of production. By determining the mechanism of enhanced kinetics through experimental analysis and modeling, a fundamental understanding can lead to the development of new complex hydrides.

Chemical Hydrides. Chemical hydrides are also being considered as hydrogen carriers and as hydrogen storage media. The ultimate usefulness of this approach for widespread hydrogen use will depend on the ability and the cost to regenerate the spent material, preferably at a centralized processing plant.

Sodium borohydride has been proposed as a chemical carrier for hydrogen. When reacted with water in the presence of a catalyst, hydrogen is produced along with an aqueous solution of nontoxic, nonflammable sodium borate (borax).

$$NaBH_4 + 2H_2O \rightarrow 4H_2 + NaBO_2 + \text{heat}$$

The borohydride system has been successfully demonstrated on prototype passenger vehicles such as the DaimlerChrysler Natrium. However, the economics of this system must also include the bidirectional delivery system: $NaBH_4$ must be delivered to the end user; and $NaBO_2$ must be returned to a centralized processing facility for regeneration. This bidirectional transport of the energy carrier adds to the cost and complexity of the energy storage systems. Nevertheless, researchers are investigating various concepts for low cost regeneration. A fundamental vulnerability of this concept is the thermodynamic borate/borohydride conversion efficiency limit of 75%, with a practical limitation of $<60\%$.

Because of this, there is interest in developing systems that avoid making borate. Researchers are exploring alternative boron chemistry including B–N, B–P chemistry, and B_xH_y nanoparticles, as well as the hydrogen-storing chemistry of other elements, including C–N, Si, and P.

Carbon Materials. Adsorption of hydrogen molecules on activated carbon, C_{60} structures such as fullerenes, and carbon foams has been studied as a medium for hydrogen storage. Although the amount of hydrogen stored is comparable to a system at high pressure, these carbon systems require low temperatures (ie, liquid nitrogen at 77°K) (39).

Recent work has identified nanostructured carbon as an interesting and promising material for hydrogen storage (40), although the mechanisms and characteristics of the hydrogen sorption (physi-, chemi-, or some combination) are not yet fully understood. Carbon nanostructures are being investigated by a number of research groups, with particular focus on single-wall nanotubes (SWNTs). Fundamental studies are directed at understanding the basic mechanisms (41). Theoretical calculations indicate that a mechanism based solely on physisorption of hydrogen on the exterior surfaces of carbon nanotubes is insufficient to account for reported hydrogen storage capacities (42). In addition, research is focused on modifying carbon nanotubes in an attempt to enhance the hydrogen storage capabilities using metal dopants and other additives.

5. Hydrogen Delivery and Infrastructure

Industrialized nations have complex infrastructures that have been developed over decades, with large amounts of public and private funds. We can build a hydrogen infrastructure based on this existing model—ie, central production of fuel and electricity with delivery over vast networks (highways, railways, natural gas pipelines, and power transmission lines), perhaps coupled with on-site storage of energy (such as underground storage of gasoline at service stations)—or we can devise new systems to deliver energy services efficiently and effectively.

Currently, hydrogen is transported from central production facilities via pipeline or in tube trailers as a compressed gas, or in tanker trucks as a cryogenic liquid. As the role of hydrogen changes from that of an important industrial chemical produced on site, to that of an energy carrier on par with electricity, we will need a highly efficient infrastructure optimized for delivering hydrogen. The character of that infrastructure is unknown: will it be a centralized production with vast distribution networks similar to our current infrastructure for electricity, natural gas, and gasoline; will it rely on hydrogen produced on site; or will it be some combination?

5.1. Pipeline Delivery. In the United States, a number of hydrogen pipeline networks are in operation, reliably supplying very large quantities of hydrogen to multiple industrial users, primarily in the Gulf Coast region (Texas and Louisiana), the Great Lakes (near Chicago), and Los Angeles. For example, Air Products operates a 150-mile hydrogen pipeline in Texas, with an average pipeline diameter of 4–6 in. Pipeline transport is considered the most inexpensive way to deliver hydrogen in large quantities for the future, despite the fact that there may be considerable expense associated with installing new pipelines and difficulty in securing rights of way. Hydrogen pipelines offer the most promise in that they could be used to transport hydrogen from resource-rich regions to end users far away from the source of generation.

5.2. Tanker Truck and Tube Trailer Delivery. Because the density of liquid hydrogen (LH2) is much higher than that of compressed hydrogen, even at 700 bar, LH2 is a convenient and cost-effective means of delivery for modest-to-large quantities of hydrogen. The energy penalty for liquefaction ($\sim$35%) compared to the energy penalty for compression to 700 bar ($\sim$15%) is significant. But, the reduction in the number of truck trips required to deliver a given quantity of hydrogen (based on energy or weight) as a liquid versus as a high pressure gas more than compensates for this penalty (21). Therefore, LH2 has become the delivery mode of choice for intercontinental transport by the industrial gas industry.

5.3. Other Options. On-site production of hydrogen, via a number of processes using a variety of resources as discussed above, may eliminate the need for "delivery" in the traditional sense. In this case, hydrogen is produced where it is needed. Hydrogen may still need to be stored at the production site if it is not consumed (or transferred to the consumer) immediately. Concepts that could eliminate the delivery step include, eg, on-site electrolysis (the existing grid delivers the needed resource—electricity), or small-scale reformers (existing natural gas pipelines deliver the gas to the reformer). The efficiency penalty for small-scale operation raises the cost of producing the hydrogen, but the elimination of the delivery cost, which can be as much as two to three times the hydrogen "plant-gate" cost could still render this option cost-attractive to the consumer [see (9) for information on the effect of scale on cost, and (21) for information on the effect of delivery mode and distance on cost].

6. Hydrogen Use

Hydrogen conversion devices, based on combustion or electrochemical reactions, are under development throughout the world. With additional research, development and/or commercialization, these devices will be able to provide efficient and cost-effective energy services to a wide range of applications.

Conventional reciprocating internal combustion engines (ICEs) and gas turbines can be designed to run on hydrogen or hydrogen-blended fuels. These devices, with >100 years of development, are currently powered by hydrocarbon fuels and used in commercial applications throughout the current energy economy. The ICEs provide opportunities for near- and mid-term use of hydrogen as an energy carrier by utilizing the unique combustion characteristics of hydrogen, ie, its low flammability limit and high octane rating. These optimized conventional conversion devices can achieve extraordinarily low emissions without the need for post-clean-up technologies.

William Grove (1811–1896) developed the first hydrogen–oxygen fuel cell in 1839 and, 100 years later, Francis T. Bacon (1904–1992) began work that led to the development of the alkaline fuel cells used by NASA for manned space flight. However, the cumulative investment in fuel cells and their commercial penetration lag far behind that of ICEs. The current upsurge in interest in fuel cells, particularly for vehicle applications, began in the early 1990s, and has increased significantly in the last few years.

Fuel cells are expected to play an important role in the Hydrogen Economy. Today, fuel cells are used in manned space flight to provide power for the spacecraft and drinking water for the astronauts; they are used as backup power for critical services in hospitals and banks; and they are used in an increasing number of cars and buses. Fuel cells of various types are under intense development to reduce manufacturing costs and improve their operational reliability.

6.1. Combustion Processes. Hydrogen as a fuel has many favorable combustion properties when compared to hydrocarbons. The upward propagating lean flammability limit equivalence ratio ϕ, defined as:

$$\phi = (\text{Fuel/Oxidizer})/(\text{Fuel/Oxidizer at the stoichiometric ratio})$$

for hydrogen is $\phi = 0.14$. Hydrogen also has a very high octane number (130+, compared to gasoline at 90–100). These two properties allow combustion strategies for hydrogen that are not possible with hydrocarbon flames.

Combustion of hydrogen with oxygen produces only water. When air is used as the oxidant, anywhere from trace amounts of NO_x (<5 ppm) to significant amount of NO_x may be formed, depending on the combustion temperature. The thermal NO_x production mechanism for hydrogen flames is a very strong function of temperature. At $\phi = 1$, the combustion temperature, and hence the production of NO_x, are at a maximum. If, however, combustion can be made to occur at lower temperatures ($\phi < 1$ or under dilute conditions), then the amount of NO_x produced can be substantially reduced. Because of hydrogen's low flammability limit, stable combustion of hydrogen and air can occur at temperatures where production of significant amounts of NO_x is avoided. These conditions cannot be established for hydrocarbon flames. It is precisely this feature of hydrogen combustion that researchers are using to design combustion strategies for internal combustion engines (both reciprocating and turbines) to minimize NO_x emissions and maximize thermal efficiency.

Reciprocating Internal Combustion Engines (ICEs). Hydrogen-fueled reciprocating internal combustion engines have been the focus of aggressive research and development in recent years (43). This research has focused on the optimization of hydrogen-fueled conventional reciprocating internal combustion engines to maximize efficiency and power density (power/volume), while minimizing emissions. The combustion strategy utilized is to operate extremely dilute (beyond the stability limits for hydrocarbon combustion). This combustion strategy allows control of the amount of NO_x produced to levels sufficiently low that, with a vehicle achieving 60 mile/kg of hydrogen ($\sim$60 mile/gal of gasoline equiv), the "engine-out" emissions, without after-treatment, would qualify the vehicle as a super ultra-low emissions vehicle (SULEV), by California standards. The only emission of carbon-containing compounds comes from the lubricating oil. In recent work, the engine-out emissions of hydrocarbons were 100–1000 times lower than those of the hydrocarbon-fueled ICE counterpart. In the case where a catalyst is used, these emissions are further reduced by almost a factor of 100, which puts the emissions in the parts per billion (ppb) range, three orders of magnitude lower than the most stringent regulation. This strategy can also be applied to hydrocarbon–hydrogen-blended fuels with similar results, although not as attractive as the pure hydrogen-fueled engine. Engines utilizing this lean homogenous-charge combustion strategy have been built and are in the near-prototype stage.

Researchers at the University of California at Riverside modified a Ford research engine to operate at $\phi = 1$, but with $>50\%$ exhaust gas recirculation (EGR). Since the products of stoichiometric combustion of hydrogen and air are water and nitrogen, the recirculation of these products into the reactant stream dilutes the oxygen with nitrogen and water. Hydrogen combustion is quite stable under these more dilute conditions, providing control over the combustion temperature (and hence the NO_x production), while eliminating O_2 from the exhaust stream. Engine-out NO_x production is controlled just as in the homogeneous lean combustion strategy mentioned above. Just as in the lean homogenous charge strategy, engine-out NO_x values become an engineering design point. However, unlike the lean combustion strategy, the EGR strategy allows post-treatment using a conventional catalytic converter to further reduce the NO_x. Measured tailpipe-out NO_x values were $\sim$40 ppb (corrected for water) and $\sim$50 ppb ambient. With a properly designed catalyst, a factor of $\sim$100 reduction in engine-out NO_x can be realized (44).

For many reasons, a correctly designed hydrogen-fueled reciprocating ICE is more efficient than its hydrocarbon counterpart. Because of hydrogen's wide flammability range, hydrogen-fueled reciprocating ICEs are frequently designed without a throttle. To modify the power output from these engines, one tailors the mass of injected fuel to match the power demands on the engine. The lower limit on the mass injected is limited by the lean flammability limit or idle requirements, and the limit on the upper end for the amount of mass injected is limited by the limiting equivalence ratio. A significant efficiency loss term in a conventional hydrocarbon-fueled spark-ignited reciprocating internal combustion engine is the air induction throttle. The contemporary version of these engines must operate at $\phi = 1$ due to restrictions placed on the combustion strategy by the catalytic converter and properties of hydrocarbon combustion. The power output of the engine is regulated by controlling the amount of air induced into the engine, which is accomplished by throttling the air. At low power outputs, the throttle is effectively closed causing a significant pressure drop across the throttle, thereby resulting in a significant energy loss.

As pointed out above, this limiting equivalence ratio is an engineering design point. The Ford hydrogen engine idles with an equivalence ratio of ~0.2, which is close to the lean flammability limit. Since this engine does not have a throttle, its efficiency as a function of power rises quickly and remains effectively flat for the entire power range. In typical homogenous charge hydrocarbon engines, the efficiency rises almost linearly to a peak at full throttle. This is primarily due to large losses across the throttle when it is closed (idle conditions), with the losses decreasing as the throttle opens to achieve more power. Since the hydrogen engine has no throttle, it is not plagued with throttle losses. In addition, the effective high equivalence ratio and favorable thermodynamics unique to hydrogen combustion enable more efficient engine design.

Both combustion strategies discussed above are performed in a dilute manner. This, in addition to the lower volumetric energy content of hydrogen compared to hydrocarbon fuels under the same physical conditions, results in an engine with a lower power density than its hydrocarbon spark-ignited counterpart. However, the power density of a spark-ignited hydrogen engine is about the same as a compression-ignition direct-injection engine, commonly referred to as a diesel, which has a sufficient power density to be packaged in a vehicle. Nevertheless, engine research continues in search of techniques to improve the power density. Using a modest amount of pressure boost (supercharging), research engines have achieved power densities equivalent to their spark-ignited hydrocarbon-fueled counterparts.

The combustion strategies discussed above require no unique hardware to implement. These engines are built based on state-of-the-art production hardware with costs comparable to the hydrocarbon-fueled counterpart.

Highly efficient hydrogen ICEs with zero emissions, having power densities commensurate with their spark-ignited hydrocarbon counterparts, are a practical end-use of hydrogen. While this technology has been demonstrated, work remains. Research is underway to investigate the fundamental issues associated with direct in-cylinder injection of hydrogen. If this can be achieved without increased emissions, further improvements in efficiency, power density, and engine control can be achieved. Research into injection systems, materials compatibility, and other hydrogen-specific issues is also being performed to accelerate the introduction of this technology into the market place.

Gas Turbines. The same combustion strategies discussed for the reciprocating ICEs can be applied to gas turbines for power production using hydrogen as the fuel. The gas turbine can be operated using a premixed dilute combustion strategy, with the maximum equivalence ratio limited by the engineering tradeoff between NO_x production and power output. Power density in this application is not an issue, since, at the NO_x-limited equivalence ratio, the flame temperature is above the material thermal limit. Thus, a thermal diluent needs to be employed, such as steam or EGR, to reduce the combustor gas temperature. This is particularly true when hydrocarbon fuels are used, since the flame becomes unstable below an equivalence ratio of ~0.6, well above the level needed to mitigate engine-out NO_x to acceptable levels. This necessitates NO_x after-treatment technologies such as selective catalytic reduction. Strategies ranging from hydrogen enrichment to pure hydrogen are currently being investigated, motivated by the desire to control emissions. Hydrogen enrichment of hydrocarbon fuels extends the stable lean flammability limit, and laboratory work has shown that, at 15% additional hydrogen, one can operate sufficiently lean to reduce the flame temperature and NO_x production rate to a level that meets current NO_x regulations for gas turbines, without the need for after-treatment. An economic study (45) of this technology showed that, at today's hydrogen pricing, hydrogen enrichment is cost effective when compared to conventional selective catalytic reduction technologies (see Fig. 7).

There are technical issues still to be addressed. Since turbines are flow devices, flame stability is a big issue. These combustors are prone to flash-back and/or blow-off. In addition, premixed flames are sensitive to acoustic instabilities, which can be devastating to hardware. Lean premixed combustion is the contemporary combustion strategy of choice for the turbine industry, with thousands of units in the field today. Hydrogen addition modifies these stability issues: in some cases: hydrogen addition may improve stability and in other cases it may make it worse. Understanding lean premixed combustion stability and instability is a very active area of research.

6.2. Electrochemical Processes. Fuel cells are electrochemical devices that convert chemical energy into electrical energy. In principle similar to a battery, a fuel cell will, however, continue to produce electricity (and heat) as

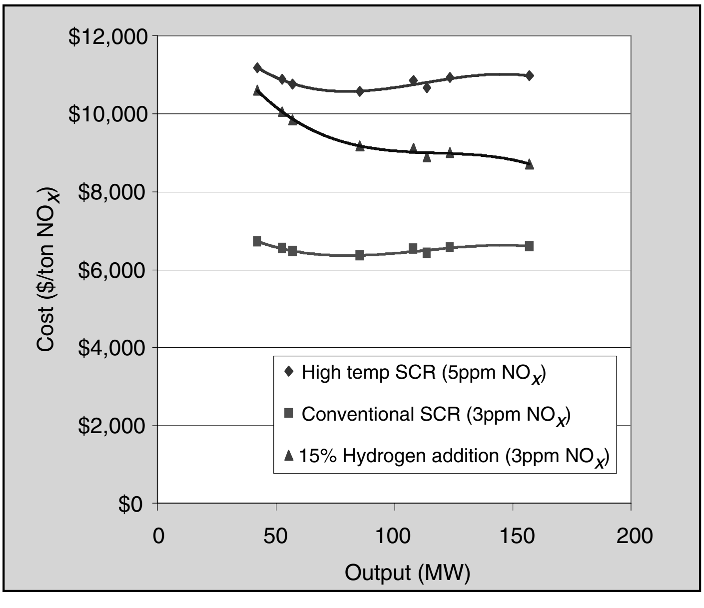

Fig. 7. Cost to retrofit gas turbines with NO_x control (45).

long as fuel and oxidant are supplied. The only "recharging" required for a fuel cell is to refill the fuel supply. For a fuel cell that is fueled directly with hydrogen, the only products are electricity, water (or water vapor) and heat.

Electrochemical devices can theoretically provide higher energy efficiencies that those that rely on combustion reactions, such as a heat engine. In 1824, Sadi Carnot defined what we now call the Carnot efficiency limit (the Second Law of Thermodynamics, as applied to heat engines), wherein the efficiency of a process is a function of its operating temperature and the temperature of the medium into which it is rejecting heat (typically above room temperature). At low temperatures, the theoretical maximum efficiency of an electrochemical device (fuel cell) operating at low current density can approach 80%, although practical efficiencies of a fuel cell power system will be much less (of the order of 40–45%). The theoretical maximum efficiency of heat engines is typically significantly less than that of an electrochemical device, especially at low and moderate temperatures. However, it is not necessarily true that the theoretical efficiency of all fuel cells is higher than the theoretical efficiency of all heat engines, especially when comparing higher temperature fuel cells and high Temperature heat engines (46).

Table 3 summarizes the main characteristics of fuel cells, characterized by electrolyte.

Alkaline Fuel Cells (AFC). Astronauts have always relied on alkaline fuel cells for the production of power, heat, and water on board their spacecraft. Fed with hydrogen on the anode side, and oxygen on the cathode side, these fuel cells can achieve efficiencies of up to 70%. The half-reactions of interest are:

$$\begin{aligned} \text{Anode}\quad & H_2 + 2\,OH^- \rightarrow 2\,H_2O + 2e^- \\ \text{Cathode}\quad & \tfrac{1}{2}\,O_2 + H_2O + 2\,e^- \rightarrow 2\,OH^- \\ \text{Overall}\quad & H_2 + \tfrac{1}{2}\,O_2 \rightarrow H_2O \end{aligned}$$

The alkaline electrolyte, usually KOH, is very sensitive to CO_2 contamination. In space applications, this is not a problem, since the fuel cells are fed directly from the oxygen and the hydrogen storage tanks on board. For terrestrial applications, however, this is a larger issue, especially if air is fed to the cathode. The unwanted side reaction is

$$2\,KOH + CO_2 \rightarrow K_2CO_3 + H_2O$$

Eventually, the OH^- ions are replaced by CO_3^{2-} ions, reducing the concentration of the active–mobile ion, and therefore the efficiency of the fuel cell. To be effective for land-based use, some sort of CO_2 capture technology would need to be incorporated into an air-blown alkaline fuel cell system.

Phosphoric Acid Fuel Cells (PAFC). An electrolyte that is tolerant to the ~400 ppm of CO_2 in our atmosphere, and perhaps the higher concentrations that would be found in a reformate stream, would be useful for earth-bound applications. In the 1970s, work to develop such an electrolyte, funded by industry and government, identified phosphoric acid (H_3PO_4) as a good choice: it is a common acid with appropriate thermal, chemical, and electrochemical properties.

Table 3. **Fuel Cell Types and Their Characteristics**[a]

Type	Mobile ion	Temperature of operation, °C	Uses	Benefits	Issues
alkaline (AFC)	OH^-	150–200	manned space flights (starting w/ Apollo missions)some interest in vehicle use	produces drinking water for astronauts and heat for the spacecraft highly reliable	extremely sensitive to CO_2
phosphoric acid (PAFC)	H^+	150–200	stationary power combined heat and power (CHP)	electricity-only efficiency of $\sim$40% improved efficiency with CHP reliable operation commercial history	cost reductions have stagnated ($3500–4500/kW)
molten carbonate (MCFC)	CO_3^{2-}	$\sim$650	stationary power CHP	electricity-only efficiency of $\sim$60% high efficiency (80–85%) with CHP fuel flexibility noble metal catalyst not required	long startup time durability cost
solid oxide (SOFC)	O^{2-}	650–1000	stationary power CHP auxiliary power units (APUs)	electricity-only efficiency of 50–60% 80–85% efficiency for CHP fuel flexibility noble metal catalyst not required solid electrolyte	long startup time durability cost
proton exchange membrane (PEMFC)	H^+	50–80	vehicles portable appliances stationary power	fast startup high power density	cost durability sensitivity to CO and H_2S

[a] See Refs. 5,46,47.

Over 300 phosphoric acid fuel cells, each with a generating capacity of 200 kW, are installed and operating around the world. Of the various types of fuel cells, the PAFC is the most mature technology with the most commercial experience on the ground, including thousands of hours of continuous operation.

The cell reactions of interest are

$$\begin{aligned} \text{Anode} \quad & H_2 \rightarrow 2\,H^+ + 2\,e^- \\ \text{Cathode} \quad & \tfrac{1}{2}\,O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O \\ \text{Overall} \quad & H_2 + \tfrac{1}{2}\,O_2 \rightarrow H_2O \end{aligned}$$

Nearly all of the commercial PAFC systems incorporate an integrated steam methane reformer, since natural gas is the primary fuel to the unit.

Hydrogen is still the reductant for the fuel cell anode: it is produced from the natural gas (methane) within the system's integrated reformer, following this reaction:

$$CH_4 + 2\,H_2O \rightarrow 4\,H_2 + CO_2$$

The overall reaction for the phosphoric acid fuel cell system fed with methane is

$$CH_4 + 2\,O_2 \rightarrow 2\,H_2O + CO_2$$

Many PAFCs are used in combined heat and power (CHP) configurations, where some of the excess heat from the reformer and the fuel cell is recovered for hot water production, to achieve higher overall energy efficiency. The relatively moderate temperature of operation minimizes the start-up time for the PAFC, although the reformer heat-up time must also be considered. Very little additional research and development is anticipated for PAFCs, and several of the traditional developers have switched their focus to other types of fuel cells.

Molten Carbonate Fuel Cells (MCFC). The molten carbonate fuel cell, with an electrolyte that is a molten mixture of alkali metal carbonates, relies on the net transfer of CO_2 from the cathode to the anode.

The cell reactions are

$$\begin{aligned} \text{Anode} \quad & H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2\,e^- \\ \text{Cathode} \quad & \tfrac{1}{2}\,O_2 + CO_2 + 2\,e^- \rightarrow CO_3^{2-} \\ \text{Overall} \quad & H_2 + \tfrac{1}{2}\,O_2 + CO_2(\text{cathode}) \rightarrow H_2O + CO_2(\text{anode}) \end{aligned}$$

Unlike the PAFC and its external reformer, the MCFC's operating temperature is high enough to allow internal reforming, with very high conversion efficiency. In addition, a wider variety of hydrocarbon fuels can be used directly. These are important features, as they reduce the complexity of the system components and increase the flexibility of operation.

Opportunities for combined heat and power production are significant, given the high operating temperature. A number of MCFC plants are being operated in the United States, Europe, and Asia as near-commercial facilities.

Solid Oxide Fuel Cells (SOFC). The SOFC uses a solid ytrria-doped zirconium oxide ceramic as the electrolyte, thus circumventing the liquid electrolyte management issues of the AFC, PAFC, and MCFC. The high operating temperature also allows internal reforming of a wide variety of fuels.

The half-reactions of interest are

$$\begin{aligned} \text{Anode} \quad & H_2 + O^{2-} \rightarrow H_2O + 2\,e^- \\ \text{Cathode} \quad & \tfrac{1}{2}\,O_2 + 2e^- \rightarrow O^{2-} \\ \text{Overall} \quad & H_2 + \tfrac{1}{2}\,O_2 \rightarrow H_2O \end{aligned}$$

Several designs have been developed and tested, including tubular and planar configurations. The tubular layout reduces the high temperature gas-tight sealing issues, whereas the planar designs are easier and more economical to produce and can yield higher power densities (much shorter current path).

The ceramic nature of the SOFC lends itself to sulfur tolerance, although a critical issue remains, mainly the tolerance of the anode material. Recent work (48) has identified strontium lanthanum chromate anode materials that can withstand sulfur concentrations up to 5000 ppm at 1000°C. This is particularly encouraging for coal-based processes (such as the ZEC technology process), since robust, sulfur-tolerant fuel cells are important for achieving high, overall efficiencies.

As with the MCFC, there are excellent opportunities for combined heat and power applications for the SOFC.

Proton Exchange Membrane Fuel Cells (PEMFC). The PEM fuel cell was initially developed for NASA for use in the first Gemini spacecraft, but was not reliable enough even for relatively short-duration missions, and was replaced by batteries for the remaining Gemini missions. These difficulties with the PEM system led to the selection of the AFC for the Apollo and subsequent missions. The development of the PEMFC languished for decades, until improvements made at Los Alamos National Laboratory led to a resurgence of interest in the late 1980s and early 1990s (49).

The centerpiece of the PEM fuel cell is the solid, ion-conducting polymer membrane. The membrane is typically made from a tough, Teflon-like material invented by DuPont called Nafion. This material is unusual in that, when saturated with water, it conducts positive ions, but not electrons: exactly the characteristics needed for an electrolyte barrier. The membrane is sandwiched between the anode and cathode electrode structures, which are porous conducting films, ~50 μm thick. The electrodes consist of carbon particles that have nanometer-size platinum particles bonded to them, in a porous matrix of recast Nafion. The carbon particles provide the electron-conducting path, while the Nafion provides an ion-conducting path to the membrane. A schematic of a PEM fuel cell is shown in Figure 8.

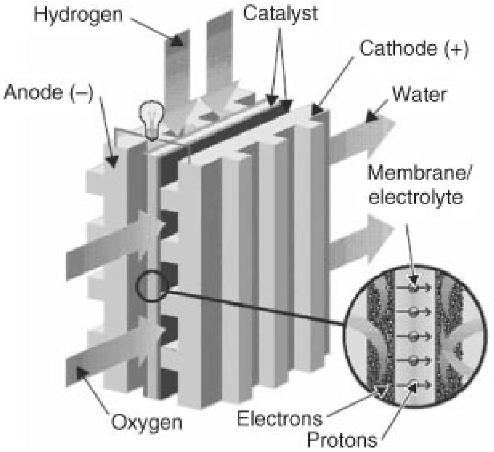

Fig. 8. Schematic of a single PEM cell.

The cell half-reactions of interest are

$$\text{Anode}\quad H_2 \rightarrow 2\,H^+ + 2\,e^-$$

$$\text{Cathode}\quad \tfrac{1}{2}\,O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O$$

$$\text{Overall}\quad H_2 + \tfrac{1}{2}\,O_2 \rightarrow H_2O$$

In addition to having catalytic, electric-, and ion-conducting properties, the electrodes and the backing material that supports them are crucial to the water management of the cell. Water management and the control of gas flows in and out of the cell are key to efficient cell operation. If there is too little water at the cathode, the membrane begins to lose the ability to conduct ions. However, if there is too much water, it floods the porous electrodes and prevents oxygen from diffusing to the catalytically active sites. Thus, water produced at the cathode must continually be removed.

For a typical design optimization, a PEM fuel cell develops a potential of ~0.7 V between the anode and cathode, depending on current density, temperature, gas pressure, flow, and other operating conditions. To get a sufficiently high overall voltage, a number of cells are placed in series to create a fuel cell stack. Because the electrochemically active area of each cell has a characteristic current density (typically several hundred to more than a thousand milliamperes per square centimeter, depending on design and operating conditions), the desired electrical current for a specific application can be achieved by changing the cross-sectional area of the cells. Through proper design and selection of operating conditions, PEMFC stacks generating as much as 100 kW have been produced.

The low temperature (hence fast-starting), high power density PEMFC is (perhaps) uniquely suited for the transportation sector, and all major automakers have aggressive programs to develop and/or utilize PEM fuel cell stacks for passenger vehicles. The PEM fuel cells are also being developed for stationary power applications and for use with small appliances, including portable electronics.

Significant reductions in noble metal (typically platinum) catalyst loading have been achieved (by a factor of 20 or more), although additional work is still needed. Further reductions in catalyst loading or the development of non-noble metal catalysts, improved durability and reliability, improved resistance to poisons such as CO and H_2S, and significant manufacturing improvements will be needed for PEM fuel cells to be able to cost-effectively compete with conventional ICEs and turbines in all energy sectors.

7. Economic and Environmental Aspects

Much of the emphasis in this article has been on hydrogen energy RD&D and the current and future technologies that will enable widespread use of hydrogen energy systems. Though the technological thrust is indeed a critically important aspect to discuss, it is also important to consider the long-term environmental, socioeconomic, and political impacts of hydrogen to affect the level of understanding and acceptance by the general public.

Hydrogen is an energy carrier similar in many ways to electricity. The public accepts electricity without question, even though they do not necessarily understand the technical requirements of the electrical energy system. In attempting to gain acceptance of hydrogen systems, we must go beyond the technical aspects, and point to the social, economic, political, and environmental benefits, in order to succeed on a commercial basis.

Prior to September 11th, the primary driver behind hydrogen technologies was local air quality and global climate change: a hydrogen fuel cell vehicle would only emit water, and no CO_2. Of course, it matters how the hydrogen was produced, since hydrogen produced from natural gas or coal without CO_2 sequestration produces significant greenhouse gas emissions at the point of production. Since renewable-based production of hydrogen was assumed to be uneconomic in the foreseeable future, the Hydrogen Economy was a long-term prospect left to visionaries.

The stark reality of 9/11 once again brought energy security (and global vulnerability to oil supply disruption) to the forefront. Do countries continue to rely on imported oil from unfriendly places, or can they reduce or even eliminate that vulnerability by relying on technology and innovation? Economic security can be significantly impacted by political uncertainty, price instability, and supply fluctuations in energy markets. In addition to the obvious first-order issues associated with energy security (the implications of continues dependence on petroleum from unfriendly or unstable suppliers halfway around the world), the second-order impact also needs to be considered. While the developed world can reasonable expect to be able to devote an ever-increasing fraction of its gross domestic product to energy imports, this may not hold true in poorer and developing countries. These countries may not be able to buy energy, or sufficient energy, to continue their development efforts. A significant and growing disparity between rich and poor nations will certainly not be conducive to world stability.

Given that hydrogen can be produced from so many different resources, a shortage in one or even two resources can be compensated for by using other resources to produce the hydrogen we need for energy services. Hydrogen allows us to remove energy from the security equation, as well as the environmental equation. It is this that makes hydrogen different from other possible solutions to security, air quality, and climate change challenges. This difference is an essential component in understanding why this transition to hydrogen energy is important, and why we need to rethink the link between resources, fuel, and energy services.

Most existing energy infrastructure is aging. Maintaining, fortifying, and expanding our existing “wire” electric grid is, and will continue to be, expensive. Deregulation will likely result in the cost being greater and passed on to the consumer. The natural gas distribution infrastructure is vulnerable to attack, and in some regions of the world, unable to meet demand due to capacity limits. Expansion of domestic oil production, both off-shore and in environmentally sensitive regions, such as the Arctic National Wildlife Refuge (ANWR), is costly and unpopular. Protecting oil supplies requires a large military presence in a very unstable part of the world.

The flexibility in production and use makes hydrogen unique among fuels and energy carriers: We could conceivably use our hydrogen-powered fuel cell vehicles as electric power generators, and we could refuel our vehicles at home using local resources. We could provide power to our neighbors, or, when needed, receive electric services from an independent, neighborhood minigrid. Power fluctuations, brown-outs, and widespread black-outs would be a distant memory, as would lines at the gasoline pumps and highly variable energy bills.

Jules Verne may have been more of a fortune teller than a science fiction writer. In 1874, he wrote about hydrogen in his novel “The Mysterious Island”. He got most of it right. The demonstration of the first fuel cell, by Sir William Grove in 1839, had already provided an essential part of the sustainable energy cycle. It has taken what seems like a long time to get from there to here, and we still have far to go. Significant research and development are still required to realize all of the benefits of hydrogen and fuel cells. Around the world, universities, industry, private and national research institutions, and federal, state and local governments are all working together to turn this “science fiction” into commercial reality.

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