

AN OVERVIEW OF HYDROGEN PRODUCTION AND STORAGE SYSTEMS WITH RENEWABLE HYDROGEN CASE STUDIES

A CLEAN ENERGY STATES ALLIANCE REPORT

by Timothy Lipman, PhD

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Summary

Hydrogen is already widely produced and used, but it is now being considered for use as an energy carrier for stationary power and transportation markets. Approximately 10-11 million metric tonnes of hydrogen are produced in the US each year, enough to power 20-30 million cars or 5-8 million homes.¹ Major current uses of the commercially produced hydrogen include oil refining (hydro-treating crude oil as part of the refining process to improve the hydrogen to carbon ratio of the fuel), food production (e.g., hydrogenation), treating metals, and producing ammonia for fertilizer and other industrial uses.

In addition to the conventional hydrogen production methods of steam methane reforming (SMR) and grid-powered electrolysis, a new suite of renewable production options is emerging. These include using renewable power directly for electrolysis, various biogas production options using gasification or pyrolysis processes or biomass fermentation with microorganisms, and newly developed photo-electrochemical and thermo-chemical processes including using microbial electrolysis cells as well as tailored molecules that can facilitate the splitting of water molecules into hydrogen and oxygen with lower energy requirements than conventional electrolysis.

Codes and standards for hydrogen storage and transport have evolved greatly over the past 10-15 years and now cover most hydrogen applications being considered. Hydrogen is now being transported by trucks and pipelines, and is stored in vessels that are certified by ASME for stationary use or by the US Department of Transportation (DOT) for transportation/delivery uses.

Examples of producing hydrogen using renewable resources include hydrogen production in a high-temperature, molten carbonate fuel cell "tri-generation" system that uses landfill gas, solar photovoltaic electrolysis for hydrogen to be used as a vehicle fuel at Honda's US headquarters in Torrance, California, and a California winery that is generating hydrogen on a demonstration basis using a new type of "microbial electrolysis cell" that is generating a mix of hydrogen and methane from winery wastewater.²

Challenges to expanded use of hydrogen for stationary power production include better education and training of local codes-and-standards officials on the processes for hydrogen system permitting, continued efforts to bring down the costs of electrolyzers to enable renewable hydrogen production, improved efficiency and performance of steam methane reformers (particularly in smaller sizes), current relatively high costs for hydrogen storage and piping systems, and improvements in other scientific processes and technologies for producing hydrogen with low to zero emissions of greenhouse gases and costs that can ultimately be competitive in the energy marketplace.

¹ Source is EIA, 2008. See reference list for full citation.

² For additional information on these applications see the following sources: *Fuel cell tri-generation:*

www1.eere.energy.gov/hydrogenandfuelcells/pdfs/renewable_hydrogen_workshop_nov16_heydorn.pdf Honda solar PV station: http://world.honda.com/FuelCell/SolarHydrogenStation/ California winery with microbial electrolysis cell:

http://abclocal.go.com/kgo/story?section=resources/lifestyle_community/green&id=7039560

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Introduction

Hydrogen is already widely produced and used, but it is now being considered for use as an energy carrier for stationary power and transportation markets. Although hydrogen is the most abundant element in the universe, where it appears naturally on the earth's crust it is bound with other elements such as carbon and oxygen instead of being in its molecular "H₂" form. Molecular hydrogen is produced for various uses, and this can be done in various ways, as discussed below.

Approximately 10-11 million metric tonnes of hydrogen are produced in the US each year (EIA, 2008). For reference, this is enough to power 20-30 million cars (using 700 to 1,000 gallon energy equivalents per car per year) or about 5-8 million homes. Globally, the production figure is around 40.5 million tonnes (equal to about 44.4 million short tons or about 475 billion cubic feet), and is expected to grow 3.5% annually through 2013 (Freedonia Group, Inc., 2010). Major current uses of the commercially produced hydrogen are for oil refining, where hydrogen is used for hydro-treating of crude oil as part of the refining process to improve the hydrogen to carbon ratio of the fuel, food production (e.g., hydrogenation), treating metals, and producing ammonia for fertilizer and other industrial uses.

Because much of the hydrogen produced in the US is done in conjunction with oil production, much of this hydrogen is produced in three states: California, Louisiana, and Texas. This hydrogen is produced from steam reforming of natural gas, the most prevalent method of hydrogen production. There are other significant production facilities up the Mississippi River valley and in the Northeast. Figure 1 shows where various types of production facilities are located in the US, including both merchant and "captive" (i.e., for internal use) producers. A key point here is that vast amounts of hydrogen are currently produced and used in the US and around the world. It is a widely used industrial gas, with a well developed set of codes and standards governing its production, storage, and use.³ However, for fuel cell applications a high level of hydrogen purity is typically more important than for many industrial applications and thus can often entail higher costs of delivery.⁴

A growing use of hydrogen is to support emerging applications based on fuel cell technology along with other ways to use hydrogen for electricity production or energy storage. More than 50 types and sizes of commercial fuel cells are being sold, and the value of fuel cell shipments reached \$498 million in 2009. Approximately 9,000 stationary fuel cell systems and 6,000 other commercial fuel cell units were shipped that year. The 15,000 total represented 40% growth over the previous year. In addition, 9,000 small educational fuel cells were shipped. (US DOE, 2010)

³ For the latest details on hydrogen codes and standards, see: <u>www.hydrogenassociation.org/safety/codesStandards.asp</u> and <u>www.hydrogenandfuelcellsafety.info/index.asp</u>, as well as the standards themselves (e.g., NFPA 55 and CGA H-5-2008 and CGA G-5.4-2005).

⁴ For example ISO 14687-2 and Society of Automotive Engineers (SAE) standard J2719 currently specify purity standards for fuel cell applications with 99.97% overall hydrogen purity and additional allowable levels of key impurities (e.g. 0.2 ppm carbon monoxide and additional upper limits on sulfur compounds, formaldehyde, etc.).



Figure 1: Industrial Hydrogen Facilities in the US Source: NREL, 2006

As shown in Figure 2 below, there is significant potential to produce hydrogen using renewable resources. Very little of this potential is used at present (the facilities shown above in Figure 1 are mostly associated with natural gas or refinery products). The renewable production potential in the US ranges from as high as 650,000 kilograms per square kilometer per year (kg/km²/yr) in some areas to less than 50,000 kg/km²/yr. Large parts of the country have production potential greater than 100,000 kg/km²/yr (NREL, 2006). For reference, at the US average population density of about 30 people per square kilometer, 100,000 kg/km²/yr would be enough for about 3,300 kilograms per person per year, or enough to drive about 200,000 miles in a 60-mpg equivalent hydrogen-powered car.⁵

⁵ Using the close approximation that one kilogram of hydrogen has the same energy content as a gallon of gasoline.



Figure 2: Estimated US Hydrogen Potential From Renewable Sources Source: NREL, 2006

As for overall hydrogen production potential, a 2009 analysis by the National Renewable Energy Laboratory (NREL) titled *Hydrogen Potential from Coal, Natural Gas, Nuclear, and Hydro Resources* examined the combined hydrogen production potential from those energy sources, building on a previous study that examined the potential from renewable wind, solar, and biomass. The study found that total US production from coal, natural gas, hydro-electric, and nuclear power could be about 72.5 million metric tonnes per year, or enough to power about 35 million homes, if 30% of the current annual production capacity from those resources were devoted to hydrogen production (Milbrandt and Mann, 2009). This would be enough hydrogen to displace 80% of the 396 million tonnes of gasoline used in the US in 2007 (Milbrandt and Mann, 2009). The previous 2007 study titled *Potential for Hydrogen Production from Key Renewable Resources in the United States*, that focused on wind, solar, and biomass, found that the total production potential in the US from these renewable resources would be about 1 billion tonnes per year, or more than 10 times the potential from the other (coal, natural gas, hydro-electric, and nuclear) resources (Milbrandt and Mann, 2007).

Thus, the hydrogen resource potential in the US is large, but the challenge is to tap economically into that resource to deliver clean, end-use energy for buildings and vehicles. The region of the country with the highest renewable hydrogen production potential (the Midwest/Great Plains) is not close to the largest population centers on the East and West Coasts. This implies considerable need for hydrogen transport and delivery infrastructure.

A key point related to hydrogen for energy production is that it is a substance that is not "found" like crude oil or natural gas, but rather "made" like electricity from one of many different means. As with electricity, the environmental impacts of hydrogen use vary significantly by production method and its accompanying value or fuel chain. This paper reviews several of these hydrogen production methods and then considers a few recent case studies of hydrogen production using renewables. A range of potential hydrogen production methods and pathways is presented below in Figure 3. There are various emerging additional pathways also possible, but these are mostly at the laboratory scale at present and not the focus of this review.⁶



Figure 3: Example Hydrogen Production Pathways (Source: EIA, 2008)

For a literature review of the environmental impacts of hydrogen produced from various means, and more details about some of these fuel pathways, see National Academy of Engineering and Sciences (2004), Lipman (2005), and US DOE (2010). A recent US DOE review of hydrogen production methods explores several of these as well as some of the more longer term hydrogen production methods such as photo-electrochemical and high temperature thermochemical.⁷

Also, for further details on the environmental impacts of hydrogen production for vehicle applications for various production methods and stages (feedstock production/delivery, fuel production, fuel delivery, and fuel end-use), the Argonne National Laboratory Greenhouse Gases, Regulated Emission, and Energy Use in Transportation (GREET) model is available to registered users through the model's website. It is an Excel spreadsheet model with a graphical-user interface that runs in the PC/Windows environment.⁸

⁶ For more on emerging hydrogen production technologies and systems, a good source of information is the

⁷ See: <u>www.hydrogen.energy.gov/annual_progress08_production.html</u>.

⁸ See: www.transportation.anl.gov/modeling_simulation/GREET/index.html

The Current Hydrogen Market

The current "merchant" and "captive use" hydrogen market is, as noted above, dominated by uses for oil refining, food production, metals treatment, and fertilizer manufacture. Power production uses relatively little of the hydrogen, perhaps on the order of 10-20 million kilograms per year in the US, or about 0.1% of the total. This figure is based on an estimate by FuelCell Energy (FCE) that their fuel cell systems produced over 400 million kWh of electricity through 2009, using about 30 million kilograms of hydrogen over the past several years (Fuel Cell Energy, 2011). The FCE systems represent a significant part of the fuel cell market -- approximately 1/3 to 1/2 of the total installed base in the country (Adamson, 2008).

For purposes of understanding the hydrogen market, it is useful to distinguish between captive hydrogen production (where the hydrogen is produced and used onsite, such as at oil refineries) and merchant hydrogen where the hydrogen is produced for delivery to other locations as an industrial gas. Further, a distinction can be drawn between on-purpose hydrogen, where hydrogen production is the main goal, and by-product hydrogen, where hydrogen is produced as a by-product from another process (e.g., chlor-alkali production).

As shown in Table 1, on-purpose captive hydrogen production at oil refineries accounts for about 25% of total US production (2.7 million tonnes per year). Production for ammonia represents about 21% of total US production (2.3 million tonnes per year), and a small amount of captive production is used for methanol production and other uses. On-purpose merchant hydrogen production was about 1.6 million tonnes in 2006, or about 15% of the US total. Finally, by-product hydrogen production amounted to about 3.8 million tonnes in 2006, or nearly 36% of total US production. Most of this by-product hydrogen was from catalytic reforming at oil refineries and from chlor-alkali production (EIA, 2008).

Production Capacity (Thousand Metric Tons per Year)			
2003	2006		
2,870	2,723		
2,592	2,271		
393	189		
18	19		
976	1,264		
2	2		
201	313		
43	58		
<1	<1		
7,095	6,839		
	2.8		
2,977	2,977		
462	478		
NA	389		
3,439	3,844		
0,534	10,683		
to "byproduct" un	nits where hydrogen is		
	3,439 0,534 to "byproduct" un heries and other p 25C Industrial Gas ational Laborator		

Table 1: Overview of US Hydrogen Production Capacity (Source: EIA, 2008)

As shown in Figure 4, the demand for hydrogen in oil refineries is growing in order to satisfy the increasing demand for vehicle fuels and tightening environmental regulations. Since 1982, refinery hydrogen plant capacity has increased by 59%, or by about 1.2% per year. Overall, hydrogen production capacity in the US has been growing by about 7-10% per year (EIA, 2008).





Hydrogen Pipelines

As of 2006, there were approximately 1,213 miles of hydrogen pipeline in the US, as reported by the US Energy Information Administration (EIA, 2008). Most of these pipelines are in Texas (847 miles), Louisiana (290 miles), Alabama (31 miles), Indiana (15 miles), and California (13 miles). Virtually all (an estimated 99%) of the transportation of hydrogen in the US is by pipeline as a compressed gas (typically at pressures below 1,000 psi), mainly for oil refinery use and ammonia production. Hydrogen transmission by pipeline dates back to the 1930's in the U.S., and has had a good safety record (EIA, 2008).

As an example, a hydrogen pipeline in California connects Carson and nearby Wilmington, associated with oil refineries in the area, as shown in Figure 5. The existing pipeline was installed by Air Products and Chemicals, Inc. to connect various refineries and to balance their capacities and needs for hydrogen for "hydro-treating" crude oil as part of the gasoline production process.



Figure 5: Los Angeles Area Hydrogen Pipeline Source: Air Products and Chemicals, Inc. (undated)

Several new or extended pipelines are being contemplated by various groups, including a proposal by Air Product and Chemicals Inc. to build a 180-mile long segment to connect its pipeline networks in Texas and Louisiana. This would create the world's largest network with the ability to supply over one billion cubic feet of hydrogen per day by the middle of 2012 (Air Products and Chemicals, Inc., 2010).

Among the other hydrogen pipelines being contemplated is one between Chevron's refinery in Richmond, California and a group of refineries in nearby Martinez. This pipeline would be approximately 20 miles long and would provide opportunities for additional uses of the hydrogen along the pipeline alignment path. However, the project has not yet been fully approved and permitted as of April 2011.

Hydrogen Production Methods

Hydrogen in molecular form can be produced from many different sources, and in many different ways. In the context of energy systems, hydrogen is best thought of as an energy carrier, more akin to electricity than the fossil fuels that we extract from the earth's crust. Hydrogen can be produced from any hydrocarbon fuel because by definition these fuels contain hydrogen. Hydrogen can also be produced from various biological materials and from water. The "water-splitting" process is called electrolysis, and it is the oldest known electrochemical process.

Hydrogen is most typically produced today through the steam reformation of natural gas, but also is produced through electrolysis and as a by-product of some industrial processes such as chlor-alkali production.

Steam Methane Reforming

Steam methane reforming (SMR) is the process by which natural gas or other methane stream, such as biogas or landfill gas, is reacted with steam in the presence of a catalyst to produce hydrogen and carbon dioxide. When starting with natural gas, SMR is approximately 72% efficient in producing hydrogen on a lower heating value basis (U.S. DOE, 2010). The efficiency can be somewhat lower with sources of methane that include sulfur or other impurities that require a pre-treatment cleanup step to remove the impurities upstream of the SMR process.

SMR produces a hydrogen rich gas that is typically on the order of 70-75% hydrogen on a dry mass basis, along with smaller amounts of methane (2-6%), carbon monoxide (7-10%), and carbon dioxide (6-14%) (Hirschenhofer et al., 2000). Costs of hydrogen from SMR vary with feedstock cost, scale of production, and other variables and range from about \$2-5 per kilogram at present (delivered and stored at high pressure) (NAS/NAE, 2004). Delivered costs as low as about \$1.60 per kilogram are believed to be possible in the future based on large centralized production and pipeline delivery, and delivered costs for small-scale decentralized production are projected to be on the order of \$2.00-2.50 per kilogram (EIA, 2008; NAS/NAE, 2004).

Gasification of Coal and Other Hydrocarbons

In the partial oxidation (POX) process, also known more generally as "gasification," hydrogen can be produced from a range of hydrocarbon fuels, including coal, heavy residual oils, and other low-value refinery products. The hydrocarbon fuel is reacted with oxygen in a less than stoichiometric ratio, yielding a mixture of carbon monoxide and hydrogen at 1200° to 1350°C. Hydrogen can be produced from coal gasification at delivered costs of about \$2.00-2.50 per kilogram at present at large scale, with delivered costs as low as about \$1.50 per kilogram believed to be possible in the future (NAS/NAE, 2004). Hydrogen can also be produced through pyrolysis-based hydrocarbon gasification processes in the absence of oxygen, with similar estimated delivered costs at large scale (NAS/NAE, 2004).

<u>Electrolysis of Water</u>

Electrolysis is the process by which water molecules are split directly into hydrogen and oxygen molecules using electricity and an electrolyzer device. The overall electrolysis reaction is:

$$e^{-} + H_2O -> \frac{1}{2}O_2 + H_2$$

The two most common types of electrolyzers are alkaline (use a potassium hydroxide electrolyte) and PEM (use a solid polymer membrane electrolyte). A schematic of an alkaline electrolysis system is provided in Figure 7. The electrolysis reaction produces pure oxygen as a by-product along with pure hydrogen. The oxygen can then be used for productive purposes such as enriching the oxygen content of greenhouses for food production.



Figure 7: Hydrogen Production by Alkaline Electrolysis (Source: Teledyne Energy Systems)

Hydrogen can be produced via electrolysis of water from any electrical source, including utility grid power, solar photovoltaic (PV), wind power, hydropower, or nuclear power. Electrolysis is currently done at a wide range of scales, from a few kW to up to 2,000 kW per electrolyzer (see Figure 8).



Figure 8: Megawatt Scale Hydrogen Production By Electrolysis (Source: Norsk Hydro)

Based on estimated cost ranges by the National Academy of Sciences/Engineering and the US Department of Energy (that agree closely and are cited below), grid power electrolysis in the US would produce hydrogen at delivered costs of \$6-7 per kilogram (kg) at present, with future potential of about \$4 per/kg. Wind electrolysis-derived hydrogen would cost about \$7-11 per kg at present, with future potential delivered costs of \$3-4 per kg, including the full costs of production from the wind power system. Solar hydrogen would be more expensive, on the order of \$10-30 per /kg at present, with future delivered costs of \$3-4 per kg estimated to be possible (NAS/NAE, 2004; EIA, 2008).

<u>Hydrogen from Biomass</u>

Biomass conversion technologies can be divided into thermo-chemical and biochemical processes. Thermo-chemical processes tend to be less expensive because they can be operated at higher temperatures and therefore obtain higher reaction rates. They involve either gasification or pyrolysis (heating biomass in the absence of oxygen) to produce a hydrogen-rich stream of gas known as "syngas" (a blend of hydrogen and carbon monoxide). They can utilize a broad range of biomass types.

In contrast, enzyme-based biochemical "digester" type processes are at present mainly limited to wet, sugar-based feedstocks but could include cellulosic feedstocks in the future with continued improvements in process techniques and systems. At medium production scale and liquid distribution by tanker truck, current delivered costs of hydrogen from biomass would be in the \$5-7 per kilogram range. However at larger production scales and coupled with pipeline delivery, delivered costs as low as \$1.50 to \$3.50 per kg are believed possible. Pyrolysis of biomass, another production option, also offers potentially low costs of delivered hydrogen, with factory bulk costs potentially as low as about \$1 per kilogram possible with large-scale production and pipeline delivery in the longer term (NAS/NAE, 2004). However, it is important to note that pyrolysis requires large-scale production to approach those costs, and that this has not yet been realized on a commercial scale. A more near-term effort is focused on achieving a plant-gate cost of \$2.90 per kg around 2010 with costs competitive with gasoline by 2015, focusing on the key research area of "fluidizable" catalysts that avoid high rates of attrition in the catalyst material (Magrini-Bair et al., 2003).

Also, depending on application, there are potential additional cleanup costs that may need to be added to these bulk estimates of hydrogen produced from biomass for the provision of high-purity hydrogen (e.g., for low-temperature fuel cell applications for transportation and stationary markets), and of course hydrogen transport costs. Each of these additional costs (purification and transport) can easily reach another \$1 per kg or more, depending on the specific requirements and scale of production.

High Temperature Fuel Cells

High temperature fuel cells based on molten carbonate (MCFC) or solid oxide (SOFC) technology operate at sufficiently high temperatures to run directly on methane. This is sometimes called "internal reforming." Thus, MCFC and SOFC systems do not need a pure or relatively pure hydrogen stream as do proton exchange membrane (PEM) and phosphoric acid (PAFC) systems, but can run directly on natural gas or biogas or landfill gas. Furthermore, such systems can be designed to produce additional purified hydrogen as a by-product (e.g. for use as a vehicle fuel), by feeding additional fuel and then purifying the hydrogen-rich "anode tail gas" from the fuel cell into purified hydrogen. This concept is discussed in some detail in the case studies section below.

Depending on the source of the methane, some cleanup of the methane stream may be required. However, projects such as the Sierra Nevada Brewery in Chico, California have successfully demonstrated MCFC systems running on a blend of natural gas and brewery wastewater treatment digester gas. These and other wastewater treatment and landfill gas opportunities, such as the one discussed below as a case study, are attractive opportunities for renewably powered fuel cell systems. Currently in California, the Public Utilities Commission Self-Generation Incentive Program (SGIP) provides an installation incentive of \$2.50 per Watt for fuel cell systems running on a trenewable fuel (see www.cpuc.ca.gov/PUC/energy/DistGen/sgip for details).

Other Methods of Hydrogen Production

Hydrogen can also be produced via other means, including from algae, by direct solar electrochemical processes, and from various nuclear-power-assisted pathways. These methods are discussed in previous reviews (Lipman, 2005) and are not the focus of this paper. However, significant additional progress in some of these areas has been made in recent years, and some of them appear to be promising opportunities for producing hydrogen from renewable sources with less energy loss and potentially lower costs and fewer GHG emissions than is currently typical of industry practice.

Hydrogen Production Costs

Table 2 presents a recent and "internally consistent" set of hydrogen production costs (i.e., not including delivery) by various methods that are either used at present or that are possible in the future, as reported by the US EIA and based on analysis by the National Academies and the US Department of Energy. These and other estimates were used to report the production cost ranges by production methods that were discussed in the preceding sections of this paper. Note that some of the cleanest methods of producing hydrogen are currently the most expensive (e.g. based on electrolysis from wind or other clean electricity sources) but biomass gasification offers a renewable hydrogen pathway with costs that can potentially be competitive with fossil sources.

Technology and Fuel	Capacity MGPD	Overnight Capital Cost			Hydrogen Production Cost (Dollars per Kllogram)			
		Miliion Dollars	Dollars per MGPD	Capacity Factor (Percent)	Capitai*	Feed- stock	O&M	Total
Central SMR of Natural Gas ^b	379,387	\$181	\$477	90	\$0.18	\$1.15	\$0.14	\$1.47
Distributed SMR of Natural Gas ^e	1,500	\$1.14	\$760	70	\$0.40	\$1.72	\$0.51	\$2.63
Central Coal Gasification w/ CCS ^d	307,673	\$691	\$2,245	90	\$0.83	\$0.56	\$0.43	\$1.82
Central Coal Gasification w/o CCS ^d	283,830	\$436	\$1,536	90	\$0.57	\$0.56	\$0.09	\$1.21
Biomass Gasification [®]	155,236	\$155	\$998	90	\$0.37	\$0.52	\$0.55	\$1.44
Distributed Electrolysis [†]	1,500	\$2.74	\$1,827	70	\$0.96	\$5.06	\$0.73	\$6.75
Central Wind (Electrolysis) ⁹	124,474	\$500	\$4,017	90	\$1.48	\$1.69	\$0.65	\$3.82
Distributed Wind (Electrolysis) ^h	480	\$2.75	\$5,729	70	\$3.00	\$3.51	\$0.74	\$7.26
Central Nuclear Thermochemical	1,200,000	\$2,468	\$2,057	90	\$0.76	\$0.20	\$0.43	\$1.39

Table 2: Estimated Hydrogen Production Costs (Source: EIA, 2008)

SMR – Steam Methane Reforming; CCS – Carbon Capture and Sequestration; MGPD – thousand kilograms per day; O&M – Operations and Maintenance.

Note: Table excludes transportation and delivery costs and efficiency losses associated with compression or transportation. *For all cases a 12-percent discount rate is used. Economic life of 20 years assumed for distributed technologies and 40 years for all other technologies. Average United States prices for 2007 are used where practicable.

Assumes industrial natural gas price of \$7.4 per million Btu and industrial electric price of 6.4 cents per kilowatthour.

⁶Assumes commercial natural gas price of \$11 per million Btu and commercial electric price of 9.5 cents per kilowatthour. ⁴Assumes coal price of \$2.5 per million Btu.

*Assumes biomass price of \$2.2 per million Btu (\$37.8 per ton).

Assumes commercial electric price of 9.5 cents per kilowatthour.

⁹Excludes opportunity cost of wind power produced.

^hAssumes grid supplies 70 percent of power at 9.5 cents per kliowatthour and remainder at zero cost.

^IIncludes estimated nuclear fuel cost and co-product credit as net feedstock cost, decommissioning costs included in O&M. Sources: The National Academies, Board on Energy and Environmental Systems, The Hydrogen Economy: Opportunity, Costs, Barriers, and R&D Needs (Washington, DC, February 2004), web site <u>www.nap.edu/catalog/10922.html</u>: and U.S. Department of Energy, Hydrogen Program, DOE H2A Analysis, web site <u>www.hydrogen.energy.gov/h2a_analysis.html</u>.

In the current hydrogen market, deliveries of industrial-grade high purity (99.95%+) hydrogen at medium to large volumes are typically priced at around \$4-5 per 100 SCF (\$17-21 per kilogram), plus freight, rental, and hazmat charges. For smaller volumes of between 4 and 15 kilograms, or about 1,600 to 6,100 SCF, gas costs are estimated to vary widely from \$5 to \$20 per 100 SCF (\$21-83 per kilogram) depending on service model, delivery frequency, and distance from the gas supplier fill plant (Cohen and Snow, 2008).

Hydrogen Storage and Delivery

Hydrogen is a widely used and stored industrial gas with a well-developed set of codes and standards governing its use. Hydrogen is typically stored in steel ASME-certified vessels, or in composite vessels that currently are DOT certified, but not yet fully ASME certified, for stationary uses. The applicable codes are the ASME Boiler and Pressure Vessel Code, Section VIII, for stationary uses, and 49 Code of Federal Regulations for transportation uses. Additional applicable codes and standards include CGA G-5.4 (piping) and G-5.5 (hydrogen vent systems), CGA H-5 (storage) and NFPA 55.

Some applications of hydrogen storage are now using higher than previously used pressure levels of up to 875 bar (12,500 psi), for refueling vehicles up to about 700 bar (10,000 psi). These higher pressure levels are requiring additional testing and certification of high-pressure vessels, typically made out of composite materials for weight considerations. The current installations using these higher-pressure systems are typically being operated under individual permitting approval based on Cal OSHA or other local guidelines, while ASME certification of the high-pressure composite vessels is still being achieved.

Figures 9 and 10 show a typical DOT-certified hydrogen tube trailer and a DOT-certified cryogenic liquid transportation trailer, respectively. Typical 22-foot and 44-foot tube trailers are available, depending on the volume of hydrogen needed. The larger 44-foot trailers typically hold 85,000 to 112,000 standard cubic feet (SCF) of hydrogen at 2,400 to 2,800 psi of pressure. For applications where hydrogen demands are such that tube trailers become cumbersome, delivery of hydrogen as a cryogenic liquid becomes more attractive owing to its higher energy density. However, that requires somewhat higher amounts of energy than compression to even 3,600 or 5,000 psi for bulk gas delivery. These higher pressure levels for ambient temperature compressed hydrogen distribution are being explored as an alternative to the currently used methods of lower pressure (2,400-2,800 psi) gas and cryogenic liquid delivery (see below for more details).



Figure 9: Compressed Hydrogen Gas Tube Trailer – 30 Cylinders and 43,260 SCF (105 kg) Capacity



Figure 10: Cryogenic Liquid Hydrogen Trailer – 13,000 gallon (3,500 kg) capacity

Because hydrogen is somewhat bulky and expensive to transport, US DOE has been funding research to improve the energy efficiency and cost of transporting hydrogen by truck, pipeline, and other means. Recent research has focused on higher pressure levels of 3,600 psi (up from current standard industry practice of 2,400-3,000 psi), and testing of a hydrogen storage and transportation delivery system that would hold 600 kilograms of hydrogen in a total of four pressure vessels as pictured in Figure 11.



Figure 11: Next Generation Hydrogen Delivery System Undergoing Testing – 3,600 psi ISO Container for 600 kg of Transport Storage (Source: Baldwin, 2009)

The 600 kilograms transportable in the higher pressure tank system would be enough hydrogen for approximately 150 vehicle fills or to produce about 10 MWh of electrical power with a stationary fuel cell system (or approximately enough to power 10 houses for a month) (Baldwin, 2009). Moving to 5,000 psi of pressure, also under investigation, would allow a total of 800 kg to be stored and transported in the same size tubes (Baldwin, 2009).

Once delivered for stationary uses, hydrogen is typically stored in what is known as "ground storage" in ASME-certified pressure vessels (see Figure 12 below), or in liquid hydrogen "Dewar" systems if the hydrogen was delivered as a cryogenic liquid (see Figure 13). These ASME pressure vessels and liquid hydrogen storage systems must be tested and re-certified every five years. When compressed gas ground storage systems are refueled by hydrogen tube trailer delivery truck, this is called "bump stop" or "field bump" delivery. For many applications this is preferable to a smaller-scale "cylinder swap" model because the frequency of deliveries can be significantly reduced with the larger storage capacity (Cohen and Snow, 2008).



Figure 12: ASME Certified Hydrogen 'Ground Storage' Systems (Source: Cohen and Snow, 2008)



Figure 13: Cryogenic Liquid Hydrogen Storage at the California Fuel Cell Partnership (Source: http://www.nrel.gov/hydrogen)



Figure 14: DOT Certified Conformable Composite Storage for Vehicle Applications by Thiokol (Source: http://www.nrel.gov/hydrogen)

In addition to compressed gas and cryogenic liquid, hydrogen can also be stored in various metal hydrides, in chemical forms such as "chemical hydrides or carriers," and in high surface area adsorbents among other methods. These are mostly of interest for onboard vehicle storage where weight and volume are at a premium.

The various methods of hydrogen storage have trade-offs with regard to the energy "penalties" involved, along with their characteristics related to safety, weight, cost, rate of energy transfer, and other factors. For further details, see:

www1.eere.energy.gov/hydrogenandfuelcells/storage/current_technology.html.

Renewable Hydrogen Case Studies

Honda's Solar Photovoltaic Hydrogen Electrolysis Station

In early 2010, Honda Motor Company in Torrance, California opened a new more compact and efficient solar-hydrogen refueling station. Pictured below (Figure 15), the new station is designed to demonstrate what could be envisioned at the household level, where solar PV panels would be used to produce the electricity needed for hydrogen production through electrolysis. The system uses a 48-panel, 6-kilowatt solar PV system. Honda's first station dates back almost ten years to 2001, with a second-generation one built in 2003 and subsequent demonstration of PV panels made by a Honda solar power technology subsidiary known as Honda Soltec Co. in 2008 (Honda, 2010).

The most noteworthy feature of the new station is that the use of a new type of high-differential pressure electrolyzer eliminates the need for the compressor. This is expected to improve system efficiency by about 25% compared to the previous station, while also reducing the size and cost of other key components (making this the most compact hydrogen refueling system in the world according to the company). The station demonstrated by Honda has a modest capacity and flow rate, allowing for only 0.5 kg of hydrogen produced over an 8-hour period. However, the company says this would be sufficient for a consumer with a consistent commute to drive 10,000 miles per year (Honda Motor Company, 2010).

An interesting feature of the station is that it is designed to take advantage of "net metering" and potential future "smart grid" developments by exporting electrical power to the grid during the day and then using a similar amount of energy at night during off-peak times (when power is typically cheaper and more plentiful).



Figure 15: Honda's New Solar Hydrogen Fueling System (Source: Honda Motor Company, 2010)

Fuel Cell Energy and Air Products and Chemicals, Inc. Hydrogen and Electricity "Tri-generation" System

FuelCell Energy (FCE) of Danbury, Connecticut, has teamed up with Air Products and Chemicals, Inc. (APCI) to demonstrate renewable hydrogen production based on the FCE molten-carbonate fuel cell technology and a novel hydrogen gas clean-up system. This system, called the "DFC-

H2[®]" system, has undergone initial testing at FCE's research laboratories and is now being readied for deployment at a landfill site at the Orange County Sanitation District in southern California (Patel et al., 2010). See Figure 16 and Figure 17.



Figure 16: "DFC-H2[®]" System Being Tested Prior to Field Deployment (Source: Patel et al., 2010)



Figure 17: Hydrogen, Electricity, and Heat "Trigeneration" System Schematic (Source: Air Products and Chemicals Inc., undated)

The basic concept behind the energy station is that hydrogen and electricity are co-produced, where the electricity is produced using methane (natural gas or biogas) as a feedstock in the high-temperature fuel cell, but additional hydrogen is produced within the fuel cell stack leading to a hydrogen-rich stream of gas leaving the fuel cell unit. This hydrogen rich "anode tail gas" can then be purified for other uses, such as fuel cell vehicles or other types of fuel cells (e.g., PEM and PAFC) that require pure hydrogen. The following schematic presents the concept, and how there are also opportunities for waste heat recovery to help boost overall efficiency.

FCE and APCI have recently released a technical paper about the system that suggests that 125 kilograms per day of hydrogen can be produced along with an electrical output of 250 kW, based on over 8,500 hours of system testing and a "pressure swing adsorption" (PSA) process for hydrogen separation. The purity of the product hydrogen was measured at 99.99%, while also meeting a target of 0.2 ppm of carbon monoxide.

The company believes that a novel electro-chemical hydrogen separation unit, that they are also testing, could offer up to a 50% reduction in operating cost compared to the more conventional PSA unit, while offering an overall electrical power plus hydrogen production efficiency increase to 68% from 66% (with no waste heat recovery) on a lower-heating value basis (Patel et al., 2010).



Figure 18: Hydrogen and Electricity Co-Production Systems With "Smart Grid" Interaction Capability (Source: Patel et al., 2010)

Napa Wine Company – Hydrogen Production by Microbial Electrolysis

The first out-of-laboratory demonstration of a renewable method for hydrogen production from wastewater using a microbial electrolysis cell (MEC) system is underway at the Napa Wine Company in Oakville, California. The refrigerator-sized hydrogen generator takes winery wastewater, and using bacteria and a small amount of electrical energy, converts the organic material into hydrogen. A typical winery in California can generate up to 10 to 12 million gallons of wastewater per year (Wine Business Monthly, 2010).

According to microbial fuel cell scientist Dr. Bruce Logan, "an MEC is an electrolysis cell in which exo-electrogenic bacteria oxidize biodegradable substrates and produce electrons and protons at the anode. Hydrogen gas is produced at the cathode through a recombination of electrons with protons, assisted by an additional voltage supplied by an external power source" (Wine Business Monthly, 2010).

Experiments have determined that the bacteria can produce an anode working potential of around 0.3V and that only an additional 0.11V are needed to produce hydrogen in theory -- but that in practice more like an additional 0.25V are needed due to over-potential at the cathode (Logan and Regan, 2006). This means that it appears that approximately halving the energy needed for electrolysis is possible with MECs, but with still unexplored overall system efficiency. The complete system includes maintaining MEC operating conditions, delivering feedstocks to the production facility, replacing other expendable materials, and performing any gas separation and cleanup needed.





Dr. Bruce Logan has spent more than 13 years developing a process that converts biodegradable liquid wastes into hydrogen fuel. Here he is pictured with a microbial electrolysis cell unit, or reactor, being used in a field study at the Napa Wine Company.

Figure 19: Microbial Electrolysis Cells (Sources: www.engr.psu.edu/ce/enve/logan/bioenergy/mfc_photos.htm; www.winebusiness.com/wbm/?go=getArticle&dataId=74087) The MEC-based production concept requires two key steps. First, one group of bacteria turns unused sugar and unwanted vinegar from improper fermentation into electricity. Only a small amount of electricity is produced, however, and not enough to reach the 1.2 volts necessary to split water in a typical electrolysis reaction. Therefore, some additional electricity from the power grid is also used. Second, another group of bacteria uses the electricity to split water molecules into oxygen and hydrogen in what is known as "microbial electrolysis" (Discovery News, 2009).

About 1,000 liters of wastewater per day are being processed at the Napa Wine Company, and Logan estimates that there is 10 times more energy in the wastewater in the form of recoverable hydrogen than it would take to process it (Science Daily, 2009).





One of the biggest problems that the project has had to overcome so far is the bacteria variability of the run-off water, making production rates difficult to predict because the bacteria have to build to a certain level of concentration to be effective. Another issue is that much of the hydrogen is being consumed by "methanogenic" microbes before leaving the solution, leading to much greater production of methane than hydrogen. While this methane could then be "reformed" into hydrogen by SMR, direct production would be far preferable from an overall energy-use standpoint. Dr. Logan's team is working in the laboratory to improve this hydrogen-to-methane production ratio.

Another key finding so far is that fermentation products in the wastewater, such as those coming from the winery, appear to be beneficial to the process (Wine Business Monthly, 2010). While hydrogen production rates are still very limited, eventually the company would like to use more of the hydrogen to operate vehicles such as forklifts and electrical power systems such as the wastewater treatment pumps.

Conclusion

In conclusion, hydrogen is a highly promising energy carrier and fuel for stationary and transportation uses, but the potential expanded use of hydrogen involves many technical and infrastructure-related challenges. Approximately 10-11 million metric tonnes of hydrogen are used each year in the US, but mostly in internal industrial settings. Delivering this hydrogen to smaller merchant end-uses, such as small (<1 to 5 MW) fuel-cell power plants or hydrogen refueling stations is likely to be challenging. This is now being done in certain places, but for smaller-scale applications it is more common for hydrogen to be made onsite from either natural gas or electricity.

In addition to the more conventional methods of SMR, gasification, and grid-powered electrolysis, a new suite of renewable production options is emerging. These include using renewable power directly for electrolysis, various biogas conversion options, and newly developed photo-electrochemical and thermo-chemical processes. Also being investigated are use of tailored molecules that can facilitate the splitting of water molecules into hydrogen and oxygen with lower energy requirements than conventional electrolysis, and a range of biological and algae-based methods.

Furthermore, codes and standards for hydrogen storage and transport have evolved greatly over the past 10-15 years and now cover most hydrogen applications being considered. Hydrogen is now being transported by various means including trucks and pipelines, and is stored in vessels that are either certified by ASME for stationary use or US DOT for transportation/delivery uses. However, additional codes and standards developments are required, particularly with regard to transferring carefully negotiated "best practices" in lead municipalities to other municipalities that are only now starting to experience the commercial introduction of hydrogen and fuel cells.

There are several examples around the US and the world where hydrogen is being produced using renewable resources, at various scales and for different applications. These include hydrogen production from landfill gas using a fuel cell "tri-generation" system, direct solar electrolysis for hydrogen to be used as a vehicle fuel, and a winery that is demonstrating the generation of hydrogen from wastewater using a "microbial electrolysis cell."

In addition to the codes and standards and hydrogen distribution issues mentioned above, there are other challenges to expanded use of hydrogen for its most attractive near-term uses -- stationary power production, backup power, and initial transportation applications such as buses, forklifts, and airport vehicles. These include the need for continued efforts to: 1) bring down the costs and improve durability of electrolyzers to enable hydrogen production from renewables; 2) improve efficiency and performance of steam methane reformers; 3) address the relatively high present costs for hydrogen storage and piping systems; and 4) make improvements in other scientific processes and technologies for producing hydrogen with low to zero emissions of greenhouse gases. Subsequent to laboratory-scale experiments, field-testing and full systems analysis will be important for further validation and improvement of low-carbon emission hydrogen production systems. A comprehensive suite of RD&D activities that address these integrated challenges offers the best chance for introducing these technologies in ways that can ultimately be competitive in the energy marketplace.

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