Hydrogen Production Science and Technology

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Article Outline

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Definition of the Subject

This chapter examines the topic of hydrogen production from a range of different feedstocks and through various production processes. These processes include electrolysis, gasification, pyrolysis, fermentation, photosynthetic algae, as well as through emerging photo- and thermo-electrochemical, high temperature fuel cell, and nuclear cycle–assisted systems. Hydrogen is a widely used industrial molecule and energy carrier that can readily be converted into electricity through fuel cells, now being used in new markets such as vehicle fuel and stationary power production. Hydrogen is expected to be more widely used in the global energy economy moving forward, based on emerging markets and rapid technological progress in production and distribution methods.
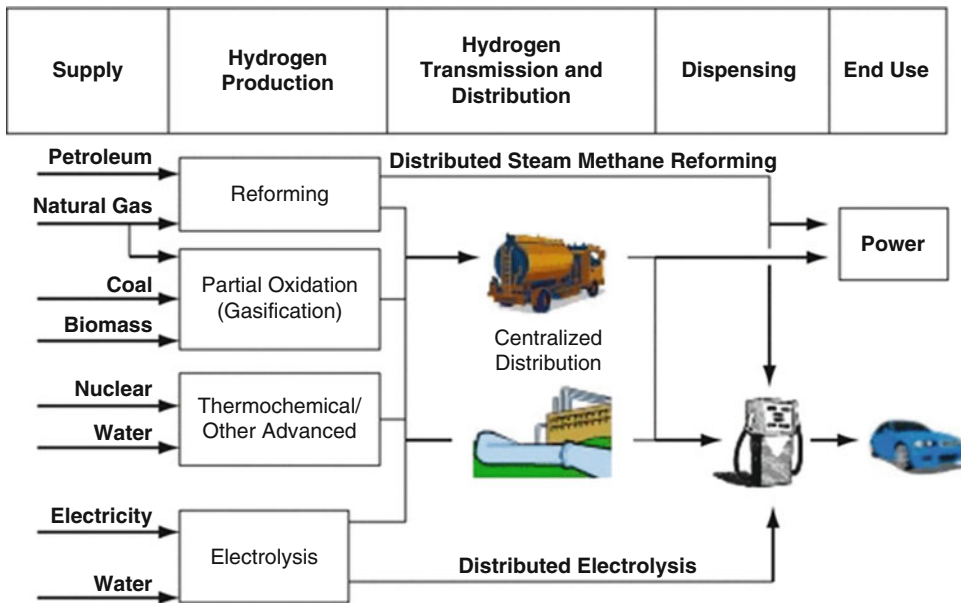
Introduction

Hydrogen is an abundant element that is currently produced in molecular form for a wide range of industrial uses. In recent years, it is also starting to be used for stationary power production in fuel cell systems and to power fuel cell electric vehicles including buses, forklifts, and passenger cars. One highly compelling attribute of hydrogen is that it can be produced in many different ways and using a variety of feedstocks; however, it does have to be *produced* through one of a variety of processes rather than simply "discovered" and delivered to market as is, for example, natural gas.

Approximately 10–11 million metric tonnes of hydrogen are produced in the USA each year [1]. For reference, this is enough to power 20–30 million cars (using 700–1,000 gallon energy equivalents per car per year) or about 5–8 million homes. Globally, the production figure was estimated at 22 million metric tonnes in 2013, with growth at 3.5% annually reaching about 27 million metric tonnes in 2018 [2]. 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.

A range of potential hydrogen production methods and pathways is presented in Fig. 1. These include reformation, gasification, electrolysis, and other advanced processes. In addition to these well-established pathways, there are various emerging production pathways also possible. These are mostly at the laboratory scale and present and include such concepts as direct "photoelectrochemical" water splitting; a wide array of biological processes involving biogas conversion, algae, and microbial electrolysis cells; and other novel methods such as high-temperature thermochemical systems.

This entry reviews a variety of established and emerging hydrogen production methods and their current status. Key remaining issues and research and development (R&D) challenges are highlighted for many of the pathways.

Hydrogen Production Science and Technology, Fig. 1 Example hydrogen production pathways. (Source: [1])

Review of Hydrogen Production Methods

Hydrogen in molecular form can be produced from many different sources and in many different ways. Hydrogen is most typically produced today for industrial uses through the steam reformation of natural gas (known as "steam methane reforming") and from other hydrocarbons in oil refinery locations but also is produced through electrolysis of water and as a by-product of some industrial processes such as chlor-alkali production. While hydrogen production methods often have several aspects and can be grouped in various ways, they can be organized as follows for purposes of this review:

- Reformation of fossil hydrocarbons and bio-derived liquids
- Gasification of coal and other hydrocarbons
- Electrolysis of water
- Biomass gasification and pyrolysis
- Biological production
- Nuclear-related pathways
- Photo-electrochemical methods
- High-temperature thermochemical methods
- Fuel cell-based co-production

Figure 2 presents a potential timeline for these production methods to become commercial, along with their anticipated scale per production facility.

A review of the primary of these production pathways is presented below, along with identification of key remaining challenges for those that are not yet commercially viable. A section that compares production cost estimates of hydrogen by several of the methods is then presented followed by the overall conclusions of this entry.

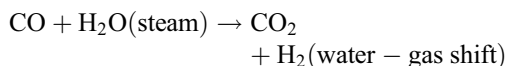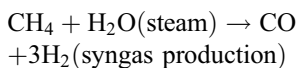### Reformation of Fossil Hydrocarbons and Bio-derived Liquids

The most widely used hydrocarbon reformation process is steam methane reforming (SMR). SMR is the process by which natural gas, other hydrocarbon, or other methane-rich stream such as biogas or landfill gas is reacted with steam in the presence of a catalyst to produce hydrogen and carbon dioxide. In the SMR process, carbon monoxide is first produced with hydrogen (this blend is known as "syngas"), and then a series of water-gas shift reactions converts the carbon monoxide to carbon dioxide and additional hydrogen through the injection of additional steam. The water-gas shift occurs first in a high-temperature step at about 350 °C and then in a lower-temperature
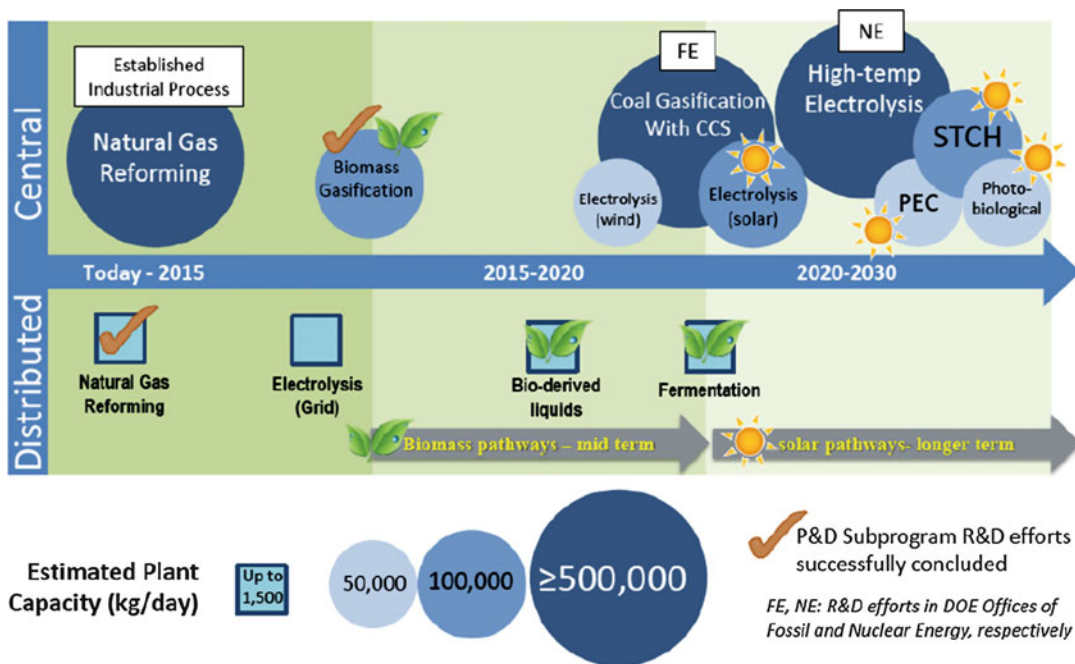
Hydrogen Production Science and Technology, Fig. 2 Estimated readiness and scale of hydrogen production pathways. (Source: [3])

step at about 190–210 °C. Four hydrogen molecules are produced for every one carbon dioxide molecule, making SMR a relatively low-carbon process when, for example, the use of SMR-based hydrogen is used in a fuel cell vehicle compared with the use of gasoline in a combustion engine vehicle on a "full fuel cycle" basis [4, 5].

The overall SMR reactions are as follows:

$$CH_4 + H_2O(steam) \rightarrow CO$$
$$+3H_2(syngas\ production)$$

$$CO + H_2O(steam) \rightarrow CO_2$$
$$+ H_2(water - gas\ shift)$$

$$Overall: \quad CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

SMR produces a hydrogen-rich gas that is typically on the order of 70–75% hydrogen on a dry basis, along with smaller amounts of methane (2–6%), carbon monoxide (7–10%), and carbon dioxide (6–14%) [6]. The efficiency of the SMR process using natural gas as a feedstock is typically about 74% on an LHV basis [7].

Bio-liquids such as ethanol, sugars, and bio-oils can also produce hydrogen through reformation processes as well as via gasification and pyrolysis. Anderson and Carole [8] provide a useful review of the key advantages and disadvantages of various feedstocks as well as potential feedstock prices, hydrogen yield rates, and commercial production timeframes. They examine ethanol, glucose, glycerol, sorbitol, ethylene and propylene glycol, cellulose/hemicellulose, methanol, and bio-oils as potential hydrogen feedstocks that are viable for use in reformation processes. They find that ethanol, glucose, glycerol, and bio-oils are potentially viable in the 2012–2017 timeframe, while sorbitol, ethylene and propylene glycol, cellulose/hemicellulose, and methanol are possible in the 2017+ longer-term timeframe.

For the medium-term feedstocks, they find that the highest yield rates are possible for ethanol (0.26 kg hydrogen/kg ethanol) and crude glycerol (0.24 kg hydrogen/kg crude glycerol), with lower rates possible for pure glycerol (0.15 kg hydrogen/kg pure glycerol), glucose (0.13 kg hydrogen/kg glucose), and bio-oils (0.13 kg hydrogen/kg

bio-oil). The longer-term options all have similar yield rates, ranging from 0.22 kg hydrogen/kg of feedstock (for methanol and propylene glycol) to 0.13 kg hydrogen/kg for sorbitol and cellulose/hemicellulose, while ethylene glycol has a more intermediate estimated hydrogen yield of 0.15 kg per kg of feedstock [8]. Based on the feedstock prices and yield rates presented, it appears from this analysis that glucose, crude glycerol, and cellulose/hemicellulose could be particularly attractive from a rough feedstock cost and yield rate perspective (not yet considering any differences in capital equipment and process energy required).

Key technical challenges for achieving hydrogen cost goals from bio-derived liquids (previously set by the US DOE at under $3.00 per kg in 2017) include advances in catalyst systems, purification technologies, and system integration. A key issue is catalyst deactivation due to coking, when products from side reactions become deposited on the catalyst. An additional important area of research is low-temperature (<500 °C) reforming, including aqueous-phase reforming that can be applied to glucose, ethylene glycol, sorbitol, glycerol, and methanol. Advantages include reduced energy intensity, better characteristics for the water-gas shift reactions, minimization of decomposition reactions (that can lead to the coking issue described above), and compatibility with membrane separation/purification techniques [8].

## Gasification and Pyrolysis 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 1,200° to 1,350 °C. Hydrogen can also be produced through pyrolysis-based hydrocarbon gasification processes in the absence of oxygen.

The chemistry of hydrogen production from gasification of coal and other heavy hydrocarbons is complex, involving molecular cracking, POX, steam gasification, water-gas shift, and methanation reactions. The first stages involve progressive devolatilization of the feedstock with increasing temperature, yielding a mix of oils, phenols, tars, and light hydrocarbon gases. This is followed by water-gas shift reactions, where additional hydrogen along with carbon dioxide are produced from carbon monoxide and water, and methanation reactions where methane (which can be later reformed into additional hydrogen) instead of hydrogen is formed with any remaining carbon monoxide. Depending on temperature and pressure conditions, the "syngas" produced from hydrocarbon gasification can have varying amounts of carbon dioxide, methane, and water, along with trace other components [9]. Several metals and metal oxides have been found to catalyze the gasification reactions and can alter the kinetic constants. Iron oxides such as Fe_2O_3 and Fe_3O_4 affect the rates of steam gasification of coal and other hydrocarbons, and some gasification reactions are also catalyzed by nickel- and calcium-based substances [9].

One study [10] examined the potential life cycle impacts of hydrogen produced through gasification and pyrolysis of coal, along with two other pathways – the thermochemical sulfur-iodine cycle and the thermochemical "Westinghouse" cycle that both make use of solar thermal energy (or other source of waste heat such as from nuclear power) and sulfuric acid to produce hydrogen. These other chemical cycles are discussed in more detail in the thermochemical and nuclear power-assisted hydrogen production sections later in this review. The study uses SimaPro™ life cycle analysis software for the analysis, which includes major indices for human health impacts, ecosystem impacts (including air, water, and soil impacts), and resource use.

The study referenced above finds that, of these four methods of hydrogen production, from a life cycle (system construction and operation) perspective, gasification of coal has the lowest human health impacts and almost as low ecosystem quality impacts as the Westinghouse cycle, while the Westinghouse cycle has the lowest
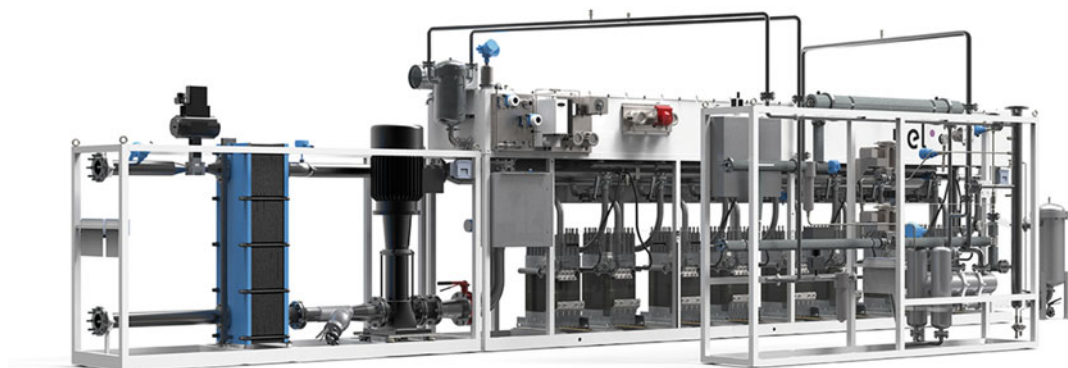
Hydrogen Production Science and Technology, Fig. 3 Commercial hydrogen production system for proton-exchange membrane electrolysis. (Source: [12])

resource impacts. The sulfur-iodine cycle has somewhat higher ecosystem impacts, comparable human health impacts to the Westinghouse cycle, and comparable resource impacts to coal gasification (i.e., somewhat higher than for the Westinghouse cycle). Pyrolysis of coal, meanwhile, has by far the highest impacts across all three categories, primarily because the amount of hydrogen produced through coal pyrolysis is about 3.5 times lower than for gasification per unit of coal used as feedstock [10].

An interesting aspect of gasification is that it could lend itself to carbon dioxide capture, owing to the large scale of many gasification systems and the production of carbon dioxide through the water-gas shift reactions. Particular attention has focused on calcium oxide (CaO) as an inexpensive carbon dioxide acceptor, yielding calcium carbonate that could then be sequestered [11]. This could prevent the product carbon dioxide from entering the atmosphere, if appropriate geological or oceanic reservoirs are available in the area for long-term storage.

Electrolysis of Water

Electrolysis is the process through which water molecules are split into hydrogen and oxygen molecules using electricity and an electrolyzer device. Electrolyzers are effectively fuel cell devices that operate in reverse. The overall electrolysis reaction is:

$$e^- + H_2O \rightarrow \text{½}O_2 + H_2 \,(\text{"water splitting"})$$
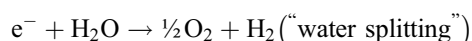
The two most common types of electrolyzers are alkaline (using a potassium hydroxide electrolyte) and PEM (using a solid polymer membrane electrolyte). A picture of a commercial hydrogen electrolysis system is provided in Fig. 3. The electrolysis reaction produces pure oxygen as a by-product along with pure hydrogen. The oxygen can then be used for productive purposes such as enriching the oxygen content of greenhouses for food production. Hydrogen electrolyzers based on both alkaline and PEM technology have now been well established at the megawatt scale. The PEM system pictured in Figure 3 is capable of producing up to about 16,000 SCF of hydrogen per hour, or around 900 kg/day, with a high level of hydrogen purity [12].

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. The ▶ "Electrochemical Hydrogen Production" entry of this encyclopedia reviews the basic science and materials issues with electrochemical hydrogen production in detail.
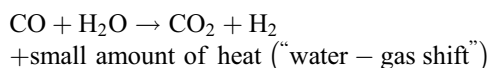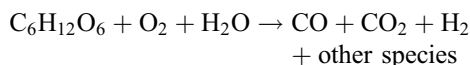
Electrolysis is currently done at a wide range of scales, from a few kW to up to 2,000 kW per electrolyzer device. Additional research involves high-temperature electrolysis, where heat that is co-produced from another process, such as

nuclear power as discussed below, is used to generate steam that can then be electrolyzed into hydrogen and oxygen with less electrical energy input than with lower-temperature electrolysis.

Biomass Gasification and Pyrolysis

Biomass conversion technologies can be divided into thermochemical and biochemical processes. Thermochemical 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 fermentative-type processes (discussed below) 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.

Biomass feedstocks can be gasified in a similar manner as fossil hydrocarbons as discussed above and can also be converted through pyrolysis. Gasification involves POX and/or steam reforming to produce a combination of gas and char products, where the char can then be reduced to ultimately produce a mix of hydrogen, carbon monoxide, carbon dioxide, and methane. Water-gas shift can then be used to produce additional hydrogen from carbon monoxide and water, and the methane can also be further reformed into additional hydrogen using SMR. Example chemical reactions include these, using glucose as an example hydrocarbon [13]:

$$C_6H_{12}O_6 + O_2 + H_2O \rightarrow CO + CO_2 + H_2 \\ + \text{ other species}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \\ + \text{small amount of heat } (\text{"water} - \text{gas shift"})$$

A key issue with biomass gasification is the formation of tar that occurs during the process, which is an unwanted product because it cannot be readily reformed into hydrogen. In order to minimize tar formation, careful design of the gasifier, incorporation of additives or catalysts, and careful control of operation variables can be effective strategies [13].

Biomass can also produce oxygenated oils through pyrolysis (without oxygen input), which can then be cracked and steam reformed to produce hydrogen and carbon dioxide syngas. An advantage of this method is that bio-oils are easier to transport than either biomass or hydrogen, and hydrogen can thus be produced in a two-step process at different locations with optimization of feedstock supply and hydrogen distribution [13].

A recent area of research has included the production of hydrogen from relatively high water content municipal and food waste streams. A recent investigation has established a process for first converting food wastes into a solid fuel called hydro-char. This process of hydrothermal carbonization followed by steam gasification has been reported to produce 28.8 mmol of hydrogen per gram of dry waste. The study determined that the steam gasification produces more hydrogen than an alternative process of supercritical water gasification. Using the identified steam gasification process, the maximum hydrogen yield was achieved at 450 °C in the presence of a potassium carbonate (K_2CO_3) catalyst [14].

Depending on application, there are potential additional cleanup steps (with associated costs) that may need to be added for hydrogen produced from biomass and municipal wastes for the provision of high-purity hydrogen (e.g., for low-temperature fuel cell applications for transportation and stationary markets). These may be similar to those required for hydrogen production from other fossil hydrocarbons but with considerable variability in both cases depending on the nature of the application requirements and fuel feedstock (i.e., biogas, natural gas, or refinery coke), the amount of sulfur present, and other factors related to details of the production process.

Additional Biological Production Methods

There are a wide range of additional biological production methods, beyond gasification or

pyrolysis and reformation of biomass and reformation of biogases. These include:

- Photolytic hydrogen production from water
- Photosynthetic bacterial hydrogen production including dark fermentative methods
- Hydrogen production from algae
- Microbial electrolysis cells
- Other concepts such as combined biological systems

The primary of these additional biological production methods (the first four from the above list) are briefly discussed below.

Photolytic Hydrogen Production from Water

The photolytic hydrogen process produces hydrogen from water directly, without the use of a more conventional electrolyzer device. This is accomplished through the use of a photo-electrochemical (PEC) cell that employs a semiconductor material and involves movement of electrons through the material. This is similar to the operation of solar photovoltaic systems, but where instead of the current being collected, it is immediately used at the site of the PEC to split water molecules in either an aqueous or flat-plate type of system.

In the photo-electrochemical water-splitting process, discussed in detail in the ▶ "Photocatalytic Hydrogen Production" entry in this encyclopedia [15], a photo-anode is subjected to solar radiation, generating an electronic charge and an electron-hole pair (as in photovoltaics). Second, however, oxidation of water occurs at the holes of the anode, yielding molecular oxygen. Then hydrogen ions and electrons are transported from the photo-anode by way of an electrolyte (for the hydrogen ions) and an electrical connection (for the electrons), forming molecular hydrogen as the hydrogen ions are reduced with the electrons at the cathode. PEC cells can thus use sunlight as the only energy input to produce hydrogen [16].

Since only some of the solar spectrum involves photons with sufficient energy to generate these voltage levels, multilayer photovoltaic junction materials can be used to allow multiple low-energy photons to be grouped together to exceed the electrolysis threshold. For example, early research investigated $GaInP_2$/GaAs "p/n, p/n tandem cells" at the National Renewable Energy Agency, that incorporated a top $GaInP_2$ junction with a band gap of 1.83 eV, to absorb the visible part of the light spectrum, with a bottom GaAs junction with a band gap of 1.42 eV to absorb the near-infrared portion that gets transmitted through the top junction. This type of system was shown to have a hydrogen production efficiency of 12.4%, based on the estimated hydrogen yield and the incident light intensity of 1,190 mW/cm^2, consistent with theoretical calculations showing a 24% maximum efficiency. However, efficiencies of more like 10–16% are expected for practical two-layer devices of these types [16].

The selection of semiconductor materials for the photo-anode is critical for PEC cells, as discussed extensively in the ▶ "Hydrogen via Direct Solar Production" contribution to this encyclopedia [17]. Key issues identified in the entry are for the semiconductor to have the proper bandgap (the level of energy in electron volts needed, between about 1.6 and 2.0 eV for the primary cell) and the ability to avoid immediate recombination of the charge carriers.

Challenges to PEC cell-based hydrogen production include materials issues including corrosion problems and uncertain performance over time. The lifetimes of current cells being tested in laboratories are on the order of hundreds of hours where tens of thousands of hours of operation are needed for practical systems [18, 19]. Furthermore, there are challenges with the physical assembly of the supramolecular complexes needed for PEC cells, in order to make sure that the various sequential reactions needed are not restricted at any step by poor collection and distribution to the water substrate of the reducing equivalents. It is also important to note that understanding the factors that control multi-electron photochemistry is still at an early stage, meaning that there are both knowledge deficiencies and opportunities for future system improvements.

Practical PEC systems of several different designs can be contemplated, and four of these have undergone recent economic analysis for the

US Department of Energy for an example 10 tonnes per day hydrogen production plant. Of the four types studied – single-bed aqueous suspension, dual bed aqueous suspension, fixed flat panel, and tracking concentrator – the first type was estimated to have the lowest costs of hydrogen produced ($1.63/kg) compared with $3.19/kg for the dual bed suspension system, $4.05/kg for the tracking concentrator system, and $10.36/kg for the fixed flat panel system [20]. These estimates are consistent with findings from a recent study where the lowest-cost PEC options are estimated to be able to produce hydrogen in the range of $1.34–2.27/kg at the production site [21].

Photosynthetic Bacterial Hydrogen Production
A number of fermentative processes for producing hydrogen using bacteria strains are being investigated. These can generally be categorized into "photobiological" methods where solar energy is captured to help drive the fermentation process or those that use organic materials that were previously produced from photosynthetic process contain hydrogen that is associated with the fixation of carbon. Key issues with the direct photobiological methods are the relatively low conversion efficiencies of solar systems and the fact that oxygen is produced along with hydrogen, creating safety risks as well as difficulties in regulating the oxygen level in the fermentative environment (an important factor to the efficacy of these systems) [22].

Another option that involves conversion of existing organic materials to hydrogen is known as anaerobic or "dark" fermentation. This process uses some type of hydrogenase as an enzyme (the two main types being NiFe and FeFe hydrogenases), uses pyruvate as a key intermediate in the fermentation pathway, and works best with carbohydrate-rich feedstocks. Fermentation of proteins does not yield much hydrogen because protein amino acids are mostly fermented in pairs through "Strickland" reactions where one amino acid is an electron receptor for oxidation of the second amino acid, without hydrogen production [22]. Fermentation of carbohydrate-rich materials such as glucose can yield a series of products following the pyruvate intermediary, including

formate that yields hydrogen and acetyl-CoA that yields acetate and acetal dehyde that can be further processed into ethanol with the addition of NADH. This is known as "enteric-type mixed-acid fermentation."

As with other biological hydrogen production methods that tend to be relatively slow in terms of yields, low yield rates for practical systems are a constraint for photosynthetic/bacterial methods as well. Based on known metabolic pathways, thermodynamic and metabolic limitations restrict hydrogen production to a maximum of 4 moles of hydrogen per mole of glucose [22]. This is because acetate is necessarily produced as well as hydrogen and carbon dioxide, effectively "locking up" half of the available hydrogen. Strategies to increase yields include optimizing parameters for the fermentation bioprocesses, attempting to limit competing reactions in order to channel more reductant for hydrogen production, decreasing hydrogen partial pressures in the reactor vessels (but then leading to more dilute streams of product gas), using thermophilic strains of bacteria that increase output at higher temperatures (but then requiring additional reactor vessel heating), and identifying and employing more active hydrogenases as enzymes [22].

Hallenbeck [22] reviews these strategies in some detail and concludes that it will be difficult to exceed the "Thauer limit" of 4 moles of hydrogen produced per mole of glucose, even though it is theoretically possible to produce 12 moles of hydrogen per mole of glucose by the reaction:

$$C_6H_{12}O_6 + 6H_2O \rightarrow 12H_2 + 6CO_2$$
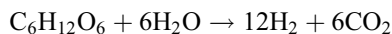
The existing conversion efficiency of only 33% (maximum) of this theoretical limit is too low for practical systems unless additional steps can be employed to convert more of the organic feedstock into useful products. These have been proposed in the forms of a second stage fermentation for methane production, a second stage photo-fermentation for additional hydrogen production, and (more radically) metabolic engineering to develop novel hydrogen producing pathways. Active research continues to address

the current limitations, with the goal of developing more efficient and complete conversion levels in practical systems.

Hydrogen Production from Algae

The ability of various strains of algae to produce hydrogen has been studied for some time, with particular attention on unicellular green algae and potential combination of hydrogen production from green algae with additional hydrogen production from bacteria in a co-production concept. Melis and Melnecki [23] have proposed this type of system, where photosynthesis is employed in the first step to produce algae biomass and hydrogen gas using the [Fe]-hydrogenase enzyme. In the second stage, the green algal process is coupled with production of an anoxygenic bacteria (such as *Rhodospirillum rubrum*) to produce adenosine triphosphate (ATP), which is required for the evolution of hydrogen using the nitrogenase enzyme. Finally, during a third stage, fermentative bacteria such as *Clostridium pasteurianum* catabolize the algae/bacteria biomass and further enhance the hydrogen yield [23].

In a recent review of microalgae for hydrogen production system progress, Kethorn et al. [24] highlight developments in bioreactor design to improve hydrogen yields for a given amount of light input. They examine recent research studies, along with some older studies, and report that the latest results indicate that hydrogen production rates of up to about 1.3 ml/l/h are now demonstrated based on the widely investigated *C. Reinhardtii* strain of bacteria, up from around 0.6 ml/l/h in some earlier studies. This strain has shown a high level of sustained hydrogen production with better oxygen tolerance than other strains. They discuss the trade-offs associated with different bioreactor designs as well as the use of mutant *C. Reinhardtii* and other types of bacteria [24].

Key areas of continuing research with algal-based hydrogen production systems include limiting oxygen evolution during the algal growth phase, exploring the role of sulfate availability to the chloroplasts to regulate the rate of photosynthesis, examining various means for further increasing hydrogen yields to enable more

practical hydrogen production systems, and improving bioreactor design schemes for maximized production [23, 24].

Microbial Electrolysis Cells

In a related concept to photosynthetic biological production, microbial electrolysis cells (MECs) can be used to produce hydrogen by providing some of the voltage potential needed for electrolysis, thus reducing energy requirements. Experiments have determined that the bacteria can produce an anode working potential of around 0.3 V and that only an additional 0.11 V are needed to produce hydrogen in theory – but that in practice more like an additional 0.25 V are needed due to overpotential at the cathode [25]. 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.

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 V 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" [25].

One of the biggest problems that practical systems have to overcome is the bacteria variability of the runoff 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 can be 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.

Research is underway in the laboratory to improve this hydrogen-to-methane production ratio [25].

Nuclear-Related Pathways

Many nuclear energy-based hydrogen production schemes are possible. These include nuclear thermal conversion of water using various chemical processes such as the sodium-iodine cycle, electrolysis of water using nuclear power, and high-temperature electrolysis that additionally would use nuclear system waste heat to lower the electricity required for electrolysis. The basic concept is that heat from nuclear plants can be used to assist the production of hydrogen in various ways, with over 100 identified cycles that could benefit from association with nuclear power [26].

A recent US national laboratory study examined hydrogen production costs from nuclear cycles based on the sulfur-iodine (S-I) thermochemical water-splitting cycle, a hybrid sulfur (HyS) thermochemical water-splitting cycle (a modified Westinghouse type cycle), and a high-temperature steam electrolysis (HTSE) cycle. The study focused on various sensitivities associated with cost estimates for these systems and generally found somewhat higher expected costs than have been reported previously (see Table 1 for details).
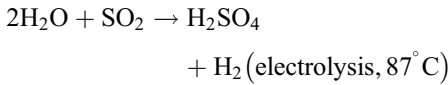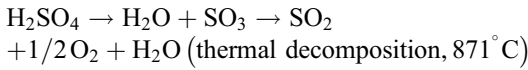
The S-I cycle has been studied since the 1970s and involves a three-step chemical reaction process. The first produces HI and sulfuric acid (H_2SO_4) from I_2, SO_2, and water at about 120 °C; the second produces SO_2, water, and O_2 from the H_2SO_4 at about 830 °C (assisted with heat from nuclear power); and the third produces I_2 and H_2 from the initial HI at about 450 °C [27]. The sulfur and iodine compounds are recovered and reused. Based on a reactive distillation design, hydrogen production costs of about $7.27/kg are believed possible with this design with a system producing 380 tonnes per day of hydrogen, assuming some future system cost reductions [28].

The HyS design differs from S-I in that it uses thermal input energy for oxygen generation and a separate low-temperature electrolysis step for hydrogen generation but also involves sulfuric acid decomposition. The HyS cycle was first explored by Westinghouse in the 1980s and is sometimes called the "Westinghouse hybrid cycle." The key steps in the Westinghouse HyS cycle are [29]:

Hydrogen Production Science and Technology, Table 1 Estimated hydrogen production costs

Technology and fuel	Production capacity (1,000 kg/day)	Hydrogen production cost ($/kg)				Source
		Capital	Feedstock	O&M	Total	
Central SMR of natural gas	380	$0.16	$1.15	$0.14	$1.47	[1]
Distributed SMR of natural gas	1.5	$0.40	$1.72	$0.51	$2.63	[1]
Central coal gasification with CCS	308	$0.83	$0.56	$0.43	$1.82	[1]
Central coal gasification w/out CCS	284	$0.57	$0.56	$0.09	$1.21	[1]
Biomass gasification	155	$0.37	$0.52	$0.55	$1.44	[1]
Distributed electrolysis	1.5	$0.96	$5.06	$0.73	$6.75	[1]
Central wind electrolysis	124.5	$1.46	$1.69	$0.65	$3.82	[1]
Distributed wind electrolysis	0.5	$3.00	$3.51	$0.74	$7.26	[1]
Central nuclear thermochemical	1,200	$0.76	$0.20	$0.43	$1.39	[1]
Nuclear S-I	343.5	$2.61	$0.35	$5.31	$7.27	[28]
Nuclear HyS	343.5	$1.48	$0.22	$2.25	$4.95	[28]
Nuclear HTSE	343.5	$1.05	$0.03	$3.15	$4.23	[28]
Single-bed aqueous PEC	1	–	–	–	$1.63	[20]
Dual bed aqueous PEC	1	–	–	–	$3.19	[20]
Fixed panel PEC	1	–	–	–	$4.05	[20]
Tracking concentrator PEC	1	–	–	–	$10.36	[20]

Notes: *CCS* carbon capture and sequestration, *HTSE* high-temperature steam electrolysis, *HyS* hybrid sulfur cycle, *O&M* operations and maintenance, *PEC* photo-electrochemical cell, *S-I* sulfur-iodine, *SMR* steam methane reforming

$$H_2SO_4 \rightarrow H_2O + SO_3 \rightarrow SO_2$$
$$+1/2\,O_2 + H_2O \left(\text{thermal decomposition}, 871^\circ C\right)$$

$$2H_2O + SO_2 \rightarrow H_2SO_4$$
$$+ H_2 \left(\text{electrolysis}, 87^\circ C\right)$$

Hydrogen production costs of about \$4.95/kg are believed possible with this type of hybrid system design with a system producing 345 tonnes per day of hydrogen [28]. A schematic of the HyS cycle is presented in Fig. 4.

The third design explored in the recent study, HTSE, involves electrolysis of water at about 800 °C, assisted with heat from nuclear power systems. Key elements of the system include sweep gas coupling heat exchangers, process coupling heat exchangers, solid oxide electrolyzer systems, and feed and product purification systems. Hydrogen production costs of about \$4.23/kg are believed possible with HTSE with a system producing 345 tonnes per day of hydrogen [28].

Thermochemical Production Methods

In this set of pathways, high-temperature (500–2,000 °C) heat is used to drive chemical reactions to produce hydrogen, including via direct thermolysis of water. This can be done in conjunction with solar thermal power, nuclear power, or other heat sources. Of the over 200 pathways that have been identified, several are being pursued by the US DOE for further research [30].

Thermochemical production typically involves the use of metal oxides in a two-step process where a metal oxide is first decomposed into the metal and oxygen in an endothermic step and then the metal is then combined with water to re-form the metal oxide and hydrogen in a second exothermic step [31]. In one example known as the zinc oxide cycle, zinc oxide powder passes through a reactor heated by a solar concentrator operating at about 2,300 K. At this temperature, the zinc oxide dissociates to zinc and oxygen gases. The zinc cools, separates, and reacts with water to form hydrogen gas and solid zinc oxide:
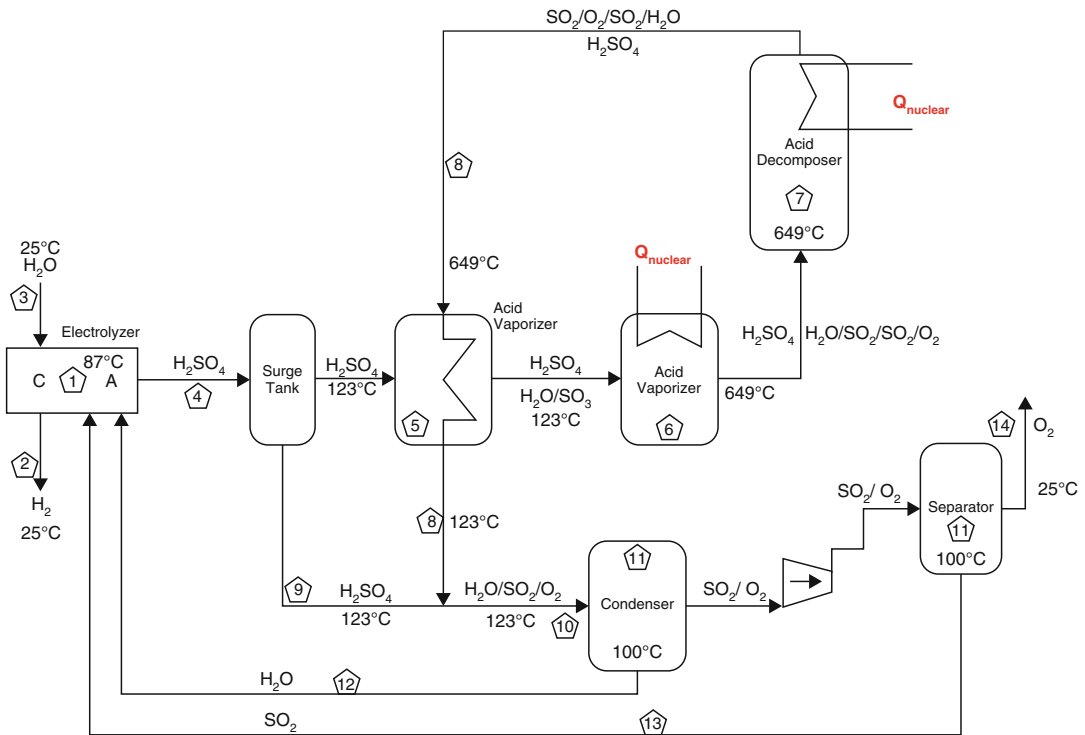
Hydrogen Production Science and Technology, Fig. 4 Westinghouse hybrid sulfur cycle schematic. (Source: [27])

$$2\,ZnO + heat \rightarrow 2\,Zn + O_2$$

$$2\,Zn + 2\,H_2O \rightarrow 2\,ZnO + 2H_2$$
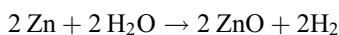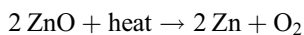
The net result is hydrogen and oxygen, produced from water, where the hydrogen can be separated and purified for subsequent use. The zinc oxide can be recycled and reused to create more hydrogen through subsequent phases of the process. Key limitations at present include the rapid reoxidation of the zinc vapor and challenges with keeping the receiver windows clean when the system is coupled with solar thermal systems for delivery of the heat required [31].

An additional type of thermochemical system has been proposed that would also involve a photon component, essentially coupling thermochemical and photo-electrochemical hydrogen production pathways. One concept would use a carbon dioxide/carbon monoxide cycle, where carbon dioxide molecules would absorb near-ultraviolet photons and high temperatures and dissociate into carbon monoxide, helping to enable the production of hydrogen. Research has demonstrated that this can be done at temperatures of around 2,000–2,500 K, which would be compatible with solar thermal concentrator systems [31].

Other concepts involve modifications to the Westinghouse cycle discussed above, including a proposed sulfur-ammonia cycle that makes use of solar power in two ways – to drive both a solar photo-catalytic reactor and a sulfuric acid decomposition reactor. The process would use ammonia, sulfuric acid, and aqueous ammonium sulfate – $(NH_4)_2SO_4$ – at various stages, with the principal advantages using solar photons to directly produce the chemical energy of hydrogen along with using solar heat in the thermochemical step, thus eliminating the need for electrical energy input [31].

Fuel Cell Co-production

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. A detailed review of this concept for hydrogen production can be found in the ► "Hydrogen Production from High-Temperature Fuel Cells" entry in this encyclopedia [32].

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 cleanup system. The system was tested at a landfill site at the Orange County Sanitation District in southern California starting in 2012, with performance expectations based on prior hydrogen tri-generation analysis work at the University of California-Irvine [33]. A figure of the system installation is presented in Fig. 5.

The basic concept behind the tri-generation system 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.

Analysis of this type of system suggests that 125 kg/day of hydrogen can be produced along with an electrical output of 250 kW, based on over 8,500 h of system testing and a pressure-swing adsorption (PSA) process for hydrogen
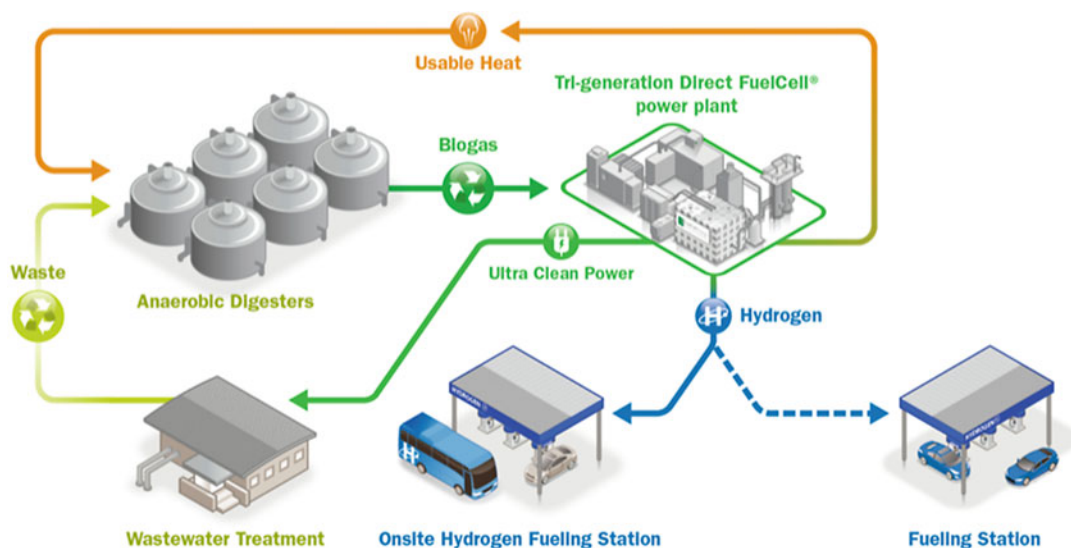
Hydrogen Production Science and Technology, Fig. 5 Fountain Valley, California tri-generation pilot project. (Source: [34])

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 project team believes that a novel electrochemical hydrogen separation unit, that they are also testing, could offer up to a 50% reduction in operating cost compared to the more conventional PSA hydrogen purification 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 [35].
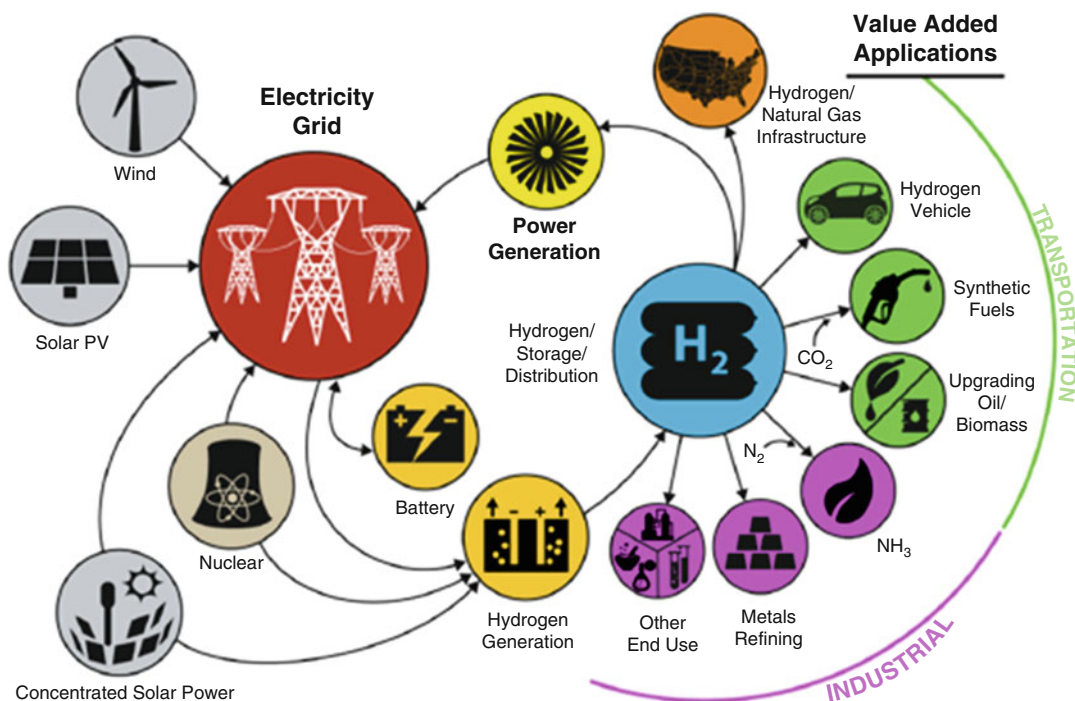
Hydrogen Production Costs

Table 1 presents a set of hydrogen production-only costs (i.e., not including delivery if centralized production) by some of the production methods discussed in this entry that are either used at present or that are possible in the future. These estimates are all as reported by the US Energy Information Administration or based on analysis for the National Academy of Science or the US Department of Energy. These and other estimates were used to report the production cost ranges by production method that were discussed

in the preceding sections of this entry. 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.

These results are consistent with reported progress in a broad review that shows a similar range in production cost estimates. The review shows similarly that the lowest-cost PEC options are estimated to be able to produce hydrogen in the range of \$1.34–2.27/kg, at the lower end of the spectrum of all hydrogen production methods and becoming comparable to conventional SMR and other methods. In comparison with other renewable hydrogen production options, the review study suggests that the biological methods discussed above are promising, but efforts are still needed to improve their production rates. Meanwhile, low conversion efficiencies in combination with high capital costs are the key restrictions for water-splitting technologies to compete with more conventional methods [36].

In comparison with these basic hydrogen production cost projections, in the current hydrogen

Hydrogen Production Science and Technology, Fig. 6   Concept for hydrogen at scale. (Source: [38])

market, deliveries of industrial-grade high-purity (99.95%+) hydrogen at medium to large volumes of hundreds to a few thousands of kilograms are typically priced at around $4–5 per 100 standard cubic feet (SCF) (or $17–21/kg), plus freight, rental, and hazmat charges. For smaller volumes of between 4 and 15 kg, or about 1,600–6,100 SCF, gas costs are estimated to vary widely from $5 to $20 per 100 SCF ($21–83/kg) depending on service model, delivery frequency, and distance from the gas supplier fill plant [37]. Hydrogen delivery to the site of use can add considerable costs depending on delivery distance, providing an advantage for onsite production where possible.

Hydrogen at Scale

With hydrogen as an energy carrier now proliferating in stationary and transportation power markets, and produced in quantities of tens of millions of metric tonnes per year globally, future planning is now considered a further scale-up of hydrogen production to meet a range of value-added applications for industry and transportation. Shown in Fig. 6 is a concept for a scaled-up and more deeply embedded role for hydrogen in the global economy. Initial analysis of this concept has shown a significant ability to divert fuels production away from the use of fossil fuels, providing the potential for major energy system and emissions benefits. The "H2@Scale" concept by the US Department of Energy shown in the figure considers the potential to increase the role of hydrogen in the US energy economy from approximately 1.2 quadrillion BTUs (or "Quads") at present to up to 9.2 quads by 2040 by expanding its role in industrial, transportation, and power generation markets [38]. Note that along with the hydrogen generation pathways shown in the figure, additional pathways for hydrogen generation are possible based on biological production, municipal and forest wastes, wastewater treatment, and advanced solar-based applications as discussed above.

Conclusion

In conclusion, hydrogen is a 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 USA and about 40 million tonnes globally but mostly in internal industrial settings. Dispensing hydrogen to wider consumer and fleet-use markets, such as for private and fleet vehicles and for stationary power uses, involves considerable challenges due to hydrogen's low-energy density (by volume) and other unusual characteristics (i.e., small molecule size, relative ease of ignition in mixes with air, and need for high gas purity when used in certain applications such as in PEM fuel cells).

There are many available and emerging hydrogen production pathways based on a myriad of thermochemical, photochemical, and electrochemical mechanisms and reactions. Perhaps the most compelling aspect of hydrogen as a potential fuel is the incredible diversity in the means and methods by which it can be produced – literally by everything from basic algae to high-temperature fuel cells using ceramic materials and customized catalysts. Hydrogen can be produced from a wide range of feedstocks – from fossil sources such as natural gas or coal to a variety of renewable sources including those based on solar power and wind, geothermal, and biomass energy.

The varied options for hydrogen production include pathways using fossil hydrocarbons or biogas using gasification or pyrolysis processes, steam methane reforming, electrolysis of water, nuclear power-assisted cycles including the sulfur-iodine cycle, fermentative, algae-based, and other biological pathways. Also included are more recently developed electrochemical and thermochemical processes including the use of PEC cells, microbial electrolysis cells, and tailored molecules that can facilitate the splitting of water molecules into hydrogen and oxygen with lower energy requirements than conventional electrolysis.

Of these, several pathways have been studied with regard to potential production costs at commercial-scale operations. While cost estimates are somewhat preliminary for some of the more novel production methods, particularly attractive hydrogen production costs appear possible for centralized SMR of natural gas, gasification of coal and biomass, nuclear thermochemical systems, and single-bed aqueous photo-electrochemical methods. Also potentially attractive are smaller-scale decentralized production systems based on SMR or electrolysis, as these can avoid the expense and difficulty of transporting bulky hydrogen gas or cryogenic liquid by generating the hydrogen close to the point of end use.

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