



Review

An overview of hydrogen production technologies

J.D. Holladay*, J. Hu, D.L. King, Y. Wang

Pacific Northwest National Laboratory, 902 Battelle Blvd., Richland, WA 99352, USA

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ABSTRACT

Currently, hydrogen is primarily used in the chemical industry, but in the near future it will become a significant fuel. There are many processes for hydrogen production. This paper reviews the technologies related to hydrogen production from both fossil and renewable biomass resources including reforming (steam, partial oxidation, autothermal, plasma, and aqueous phase) and pyrolysis. In addition, electrolysis and other methods for generating hydrogen from water, hydrogen storage related approaches, and hydrogen purification methods such as desulfurization and water-gas-shift are discussed.

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Contents

1. Introduction	244
2. Fuel processing	246
2.1. Hydrocarbon reforming	246
2.1.1. Hydrocarbon reforming reactions	246
2.2. Desulfurization	248
2.3. Pyrolysis	248
2.4. Plasma reforming	248
2.5. Aqueous phase reforming	250
2.6. Ammonia reforming	250
3. Non-reforming hydrogen production	251
3.1. Hydrogen from biomass	251
3.1.1. Biomass gasification	251
3.1.2. Biological hydrogen	251
3.2. Hydrogen from water	254
3.2.1. Electrolysis	254
3.2.2. Thermochemical water splitting	256
3.2.3. Photoelectrolysis	256
4. Conclusion	257
References	258

1. Introduction

The U.S. light vehicle fleet is over 225 million, traveling over 7 billion miles a day, and consuming 8 million barrels of oil a day [1–4]. Despite being the 3rd largest oil producer in the world, the

* Corresponding author. Tel.: +1 509 373 1473; fax: +1 509 376 3108.
 E-mail address: jd.holladay@pnl.gov (J.D. Holladay).

Nomenclature

APR	aqueous phase reforming
ATR	autothermal reforming
BEAMR	bioelectrochemically assisted microbial reactor
CPOX	catalytic partial oxidation
DBD	dielectric barrier discharge
DOE	Department of Energy
E_{ap}	applied potential
E_g	band gap energy
fd	ferredoxin
ΔH	heat of reaction
ΔH_c	heat of combustion (lower heating value)
HDS	hydrodesulfurization
I	current
IPEC	incident-photon-to-electron-conversion
MEC	microbial electrolysis cells
pqH_2	plastiquinone
PEM	proton exchange membrane
POX	partial oxidation
P/R	photosynthesis/respiration ratio
PrOx	preferential oxidation
R_{ex}	external resistance
SOEC	solid oxide electrolysis cell
SOFC	solid oxide fuel cell
Δt	time increment in seconds
VOC	volatile organic compounds
WGS	water-gas-shift

amount of imported petroleum is expected to rise to 60% by 2025 [3,4]. Since the first oil embargo in the 1970s there has been interest in developing alternative fuels to power our society [1,2,5,6]. The decline and stabilization of oil prices following the embargo decreased the interest in alternative fuels. However, with substantial uncertainty in the world today, particularly in the Middle East, increased demand from developing countries has caused the cost of oil to increase substantially in the past few years [3]. In addition to cost there are significant environmental concerns with petroleum usage. Recent analysis estimated that pollutants may be high enough to affect public health and/or the environment in areas where 50% of Americans live [7]. Light vehicles are responsible for a significant amount of carbon dioxide and volatile organic compound (VOC) emissions, and a majority of carbon monoxide and nitrogen oxide (NOx) emissions produced in the United States [8]. To deal with these issues, there has been an effort to diversify our energy supply particularly for the transportation sector and to find cleaner fuels. But alternative fuels are not available everywhere—one location may prefer ethanol, another may be dominated by biodiesel, or gasoline, or methane. Most of these fuels require a different engine technology for efficient operation. However, hydrogen can be produced from all of these feedstocks as well as many others making it a universal fuel. Recently there has been international attention on the development of new hydrogen technologies as a potential solution to the current fears and to increase energy and economic security. For example the U.S. Department of Energy has developed a multi-year plan with aggressive milestones and targets for the development of hydrogen infrastructure, fuel cells, and storage technologies [3,9]. The targeted hydrogen cost is \$2–4 kg⁻¹ (energy equivalent of 1 gallon of gasoline) delivered [3,9]. In addition to using the hydrogen from these processes as energy directly in fuel cells, the hydrogen rich streams can be used for the production of gasoline, methanol, ethanol, and other high value chemicals. Fig. 1 shows the conceptual flow sheet of hydrogen production technologies. The purpose of this paper is to provide

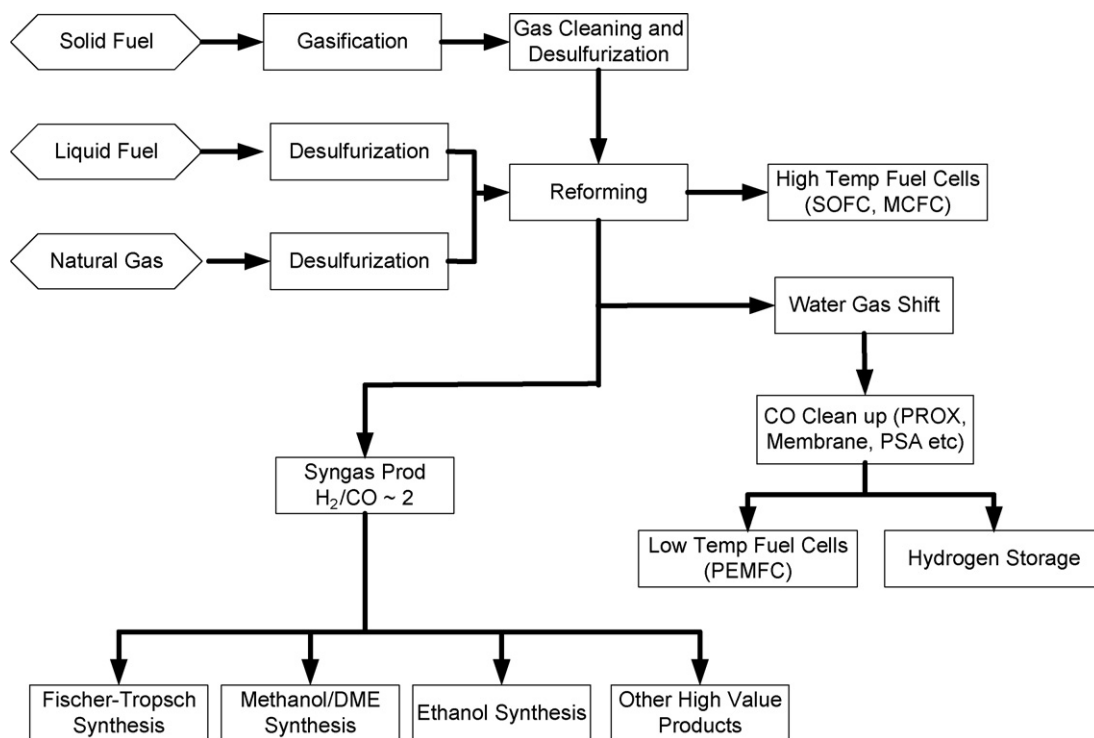


Fig. 1. Fuel processing of gaseous, liquid, and solid fuels for hydrogen production.

a brief summary of significant current and developing hydrogen production technologies. The areas to be examined include: hydrogen production using fuel processing technologies and, hydrogen from alternative resources such as biomass and water.

2. Fuel processing

Fuel processing technologies convert a hydrogen containing material such as gasoline, ammonia, or methanol into a hydrogen rich stream. Fuel processing of methane is the most common hydrogen production method in commercial use today. Most hydrocarbon fuels contain at least some amount of sulfur which poisons the fuel processing catalyst. This presents perhaps the biggest challenge to reforming. As a result, desulfurization will also be discussed. In addition, hydrocarbon reforming, plasma reforming, aqueous reforming, and pyrolysis will also be presented.

2.1. Hydrocarbon reforming

There are three primary techniques used to produce hydrogen from hydrocarbon fuels: steam reforming, partial oxidation (POX), and autothermal reforming (ATR). Table 1 summarizes the advantages and challenges of each of these processes. The reforming process produces a gas stream composed primarily of hydrogen, carbon monoxide and carbon dioxide. Endothermic steam reforming of hydrocarbons requires an external heat source. Steam reforming does not require oxygen, has a lower operating temperature than POX and ATR, and produces the reformat with a high H₂/CO ratio (~3:1) which is beneficial for hydrogen production. However, it does have the highest emissions of the three processes. Partial oxidation converts hydrocarbons to hydrogen by partially oxidizing (combusting) the hydrocarbon with oxygen. The heat is provided by the “controlled” combustion. It does not require a catalyst for operation, has minimal methane slip, and is more sulfur tolerant than the other processes. The process occurs at high temperatures with some soot formation and the H₂/CO ratio (1:1 to 2:1) is favored for the feeds to hydrocarbon synthesis reactors such as Fischer-Tropsch. Autothermal reforming uses the partial oxidation to provide the heat and steam reforming to increase the hydrogen production resulting in a thermally neutral process. Autothermal reforming is typically conducted at a lower pressure than POX reforming and has a low methane slip. Since POX is exothermic and ATR incorporates POX, these processes do not need an external heat source for the reactor. However, they require either an expensive and complex oxygen separation unit in order to feed pure oxygen to the reactor or the product gas is diluted with nitrogen. Steam reforming is typically the preferred process for hydrogen production in industry [10–14].

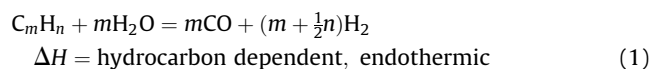
Since all three processes produce large amounts of carbon monoxide, one or more water-gas-shift (WGS) reactors – typically a high temperature reactor and low temperature reactor – are used. The high temperature (>350 °C) reactor has fast kinetics, but is

limited by thermodynamics to the amount of carbon monoxide that can be shifted. Therefore, a lower temperature reactor (210–330 °C) is used to convert the carbon monoxide to a lower level. High temperature WGS reactors commonly use an iron catalyst, and lower temperature reactors often use a copper catalyst [10–14].

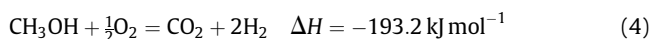
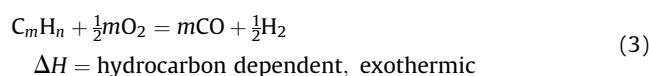
2.1.1. Hydrocarbon reforming reactions

The reforming, WGS, and oxidation reactions can be generalized as follows for hydrocarbon and methanol fuels [18–20]:

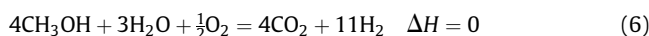
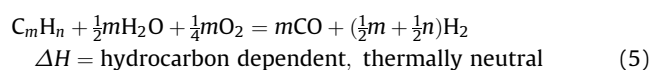
Steam reforming



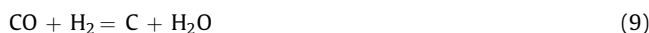
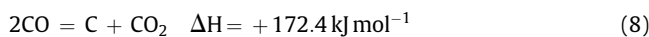
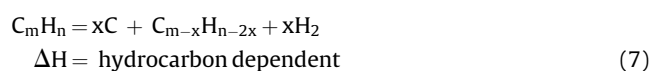
Partial oxidation



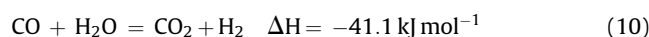
Autothermal reforming



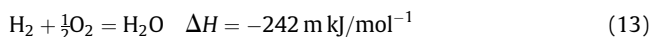
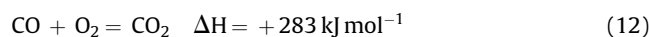
Carbon (coke) formation



Water-gas-shift



CO oxidation



The enthalpies are reported at ambient temperature and pressure with reactants and products in the gas phase.

Table 1
Comparison of reforming technologies (adapted from [15–17])

Technology	Advantages	Disadvantages
Steam reforming	Most extensive industrial experience Oxygen not required Lowest process temperature Best H ₂ /CO ratio for H ₂ production	Highest air emissions
Autothermal reforming	Lower process temperature than POX Low methane slip	Limited commercial experience Requires air or oxygen
Partial oxidaiton	Decreased desulfurization requirement No catalyst required Low methane slip	Low H ₂ /CO ratio Very high processing temperatures Soot formation/handling adds process complexity

Table 2

Minimum reaction temperatures required for avoiding coke formation during iso-octane reforming at thermodynamic equilibrium [10–14,21,22]

Reactants	Technology	Oxygen/ carbon ratio	Minimum temperature to avoid coke formation (°C)
$C_8H_{18} + 4(O_2 + 3.76N_2)$	POx	1	1180
$C_8H_{18} + 2(O_2 + 3.76N_2) + 4H_2O$	ATR	1	1030
$C_8H_{18} + 8H_2O$	SR	1	950
$C_8H_{18} + 4(O_2 + 3.76N_2) + 8H_2O$	ATR	2	575
$C_8H_{18} + 8H_2O$	SR	2	225

Fuel processing reactors are designed to maximize hydrogen production (Eqs. (1)–(6) and (10)–(12)) and minimize carbon formation (Eqs. (7)–(9)) using appropriate operating conditions (temperature, pressure residence time, etc.) and catalysts [10–14,19,21]. Table 2 lists the minimum reaction temperatures required for minimizing carbon formation, using iso-octane reforming as an example.

2.1.1.1. Steam reforming. Fuel processing requires modest temperatures (>180 °C for methanol, DME, and other oxygenated hydrocarbons that can be readily activated, and >500 °C for most conventional hydrocarbons) [10–14,19,21]. The catalysts can be divided into two types: non-precious metal (typically nickel) and precious metals from Group VIII elements (typically platinum or rhodium based). Due to severe mass and heat transfer limitations, conventional steam reformers are limited to an effectiveness factor for the catalyst which is typically less than 5% [23]. Therefore, kinetics and thus the activity of the catalyst are rarely the limiting factors with conventional steam reformer reactors [12], so less expensive nickel catalysts are used almost universally in industry. The mass and heat transfer limitations have been shown to be overcome by employing microchannel-based reactors, enabling intrinsic kinetics of steam reforming to be exploited [11,24]. In these systems, the noble Group VIII metals, particularly Rh [25], are preferred since they exhibit much higher specific activities than nickel catalysts [12,26,27]. However, the high cost of Rh is driving some researchers to develop alternative catalysts such as Co-based catalysts [28,29]. Intermediate and high temperatures required for steam reforming may promote carbon formation, and steam to carbon ratios (~2.5 or higher) higher than stoichiometry are required to gasify coke when a nickel-based catalyst is used. Coke formation is much less over the noble Group VIII metals. Promoters, such as magnesia or potassium or other alkaline components, are added to the catalyst support to minimize the coke formation [30]. Steam reforming is commonly used in industry for the production of hydrogen from methane where high thermal efficiencies of up to approximately 85%, based on the higher heating values, have been achieved [31].

2.1.1.2. Partial oxidation. Partial oxidation (POX) of hydrocarbons and catalytic partial oxidation (CPOX) of hydrocarbons have been proposed for use in hydrogen production for automobile fuel cells and some commercial applications [32–35]. The non-catalytic partial oxidation of hydrocarbons in the presence of oxygen typically occurs with flame temperatures of 1300–1500 °C to ensure complete conversion and to reduce carbon or, in this case, soot formation [12]. Catalysts can be added to the partial oxidation system to lower the operating temperatures. However, it is proving hard to control temperature because of coke and hot spot formation due to the exothermic nature of the reactions [13,21,32–35]. For natural gas conversion, the catalysts are typically based on Ni or Rh; however, nickel has a strong tendency to coke and Rh cost

has increased significantly. Krummenacher et al. [34] have had success using catalytic partial oxidation for decane, hexadecane, and diesel fuel. The high operating temperatures (>800 °C and often >1000 °C) [34] and safety concerns may make their use for practical, compact, portable devices difficult due to thermal management [36]. Typically the thermal efficiencies of POX reactors with methane fuel are 60–75%, based on the higher heating values [31].

2.1.1.3. Autothermal reforming. Autothermal reforming adds steam to catalytic partial oxidation. It consists of a thermal zone where POX or CPOX is used to generate the heat needed to drive the downstream steam reforming reactions in a catalytic zone [22,37–39]. Therefore the temperature profile in the reactor is characterized by a sharp rise in the thermal zone, and then the temperature steadily decreases in the catalytic zone due to the endothermic reactions. The heat from the POX negates the need for an external heat source, simplifying the system and decreasing the start-up time. A significant advantage for this process over SR is that it can be stopped and started very rapidly while producing a larger amount of hydrogen than POX alone. For ATR to operate properly both the oxygen to fuel ratio and the steam to carbon ratio must be properly controlled at all times in order to control the reaction temperature and product gas composition while preventing coke formation [22,37,38]. There is some expectation that this process will gain favorability with the gas–liquids industry due to favorable gas composition for the Fischer-Tropsch synthesis, ATR's relative compactness, lower capital cost, and potential for economies of scale [15]. For methane reforming the thermal efficiency is comparable to that of POX reactors 60–75%, based on the higher heating values, and slightly less than that of steam reformers [31].

2.1.1.4. Preferential oxidation and water-gas-shift. The reforming process produces a product gas mixture with significant amounts of carbon monoxide, often 5% or more [13,19,21]. To increase the amount of hydrogen, the product gas is passed through a water-gas-shift reactor to decrease the carbon monoxide content while increasing the hydrogen content. Typically, a high temperature is desired in order to achieve fast kinetics, but results in high equilibrium carbon monoxide selectivity and decreased hydrogen production. Therefore, the high temperature WGS reactor is often followed by a low temperature reactor to decrease CO content to 1% or less. TeGrotenhuis et al. [40,41] have demonstrated the potential of using microreactors to build a gradient temperature WGS reactor that contains the high temperature WGS and low temperature WGS in a single unit for >2–3 kW_e units. The most common catalyst for WGS is Cu based [13,19,21], although some interesting work is currently being done with molybdenum carbide [42], platinum-based catalysts [43,44], and Fe–Pd alloy catalysts [45].

To further reduce the carbon monoxide, a preferential oxidation reactor or a carbon monoxide selective methanation reactor can be used [13,19,21]. Sometimes the term selective oxidation is used in place of preferential oxidation, but this is misleading. Selective oxidation refers to carbon monoxide reduction within a fuel cell, typically a PEMFC; whereas preferential oxidation occurs in a reactor external to the fuel cell [19]. The PrOx and methanation reactors each have their advantages and challenges. The preferential oxidation reactor increases the system complexity because carefully measured concentrations of air must be added to the system [13,19,21]. However these reactors are compact and if excessive air is introduced, some hydrogen is burned. Methanation reactors are simpler in that no air is required; however, for every carbon monoxide reacted, three hydrogen molecules are consumed. Also, the carbon dioxide reacts with the hydrogen, so

careful control of the reactor conditions need to be maintained in order to minimize unnecessary consumption of hydrogen. Currently, preferential oxidation is the primary technique being developed [19]. The catalysts for both these systems are typically noble metals such as platinum, ruthenium, or rhodium supported on Al_2O_3 [13,19,21]. Alternatively, a membrane (ceramic or more commonly a palladium alloy) or pressure swing adsorption can be used to produce high purity (>99.999%) hydrogen.

2.2. Desulfurization

Current hydrogen production comes primarily from processing natural gas, although with the substantial advances in fuel cells there is increased attention to other fuels such as methanol, propane, gasoline, and logistic fuels such as jet-A, diesel, and JP8 fuels [14]. With the exception of methanol, all of these fuels contain some amount of sulfur, with the specific sulfur species dependent on the fuel type and source.

The typical approaches to organo-sulfur removal can be categorized as chemical reaction technologies and adsorptive technologies. Chemical reaction approaches include hydrodesulfurization (HDS) and alkylation. Most commercial large-scale applications use HDS; therefore, substantial process and catalyst optimization has occurred. In this process, HDS catalysts partially or completely hydrogenate the sulfur-bearing molecules, resulting in a release of sulfur as H_2S [46–49].

The second chemical reaction approach, selective alkylation of organo-sulfur molecules, has been demonstrated at the pilot scale, but to date it has not been implemented on a large commercial scale [50]. This technology increases the molecular weight of the sulfur bearing molecules which increases their boiling point. This enables distillation approaches to remove the sulfur. This approach does not require high-pressure hydrogen, which is a potential advantage over HDS. However, the olefin content in the fuel will vary, and it may be necessary to intentionally add olefins (or alcohols) to the fuel to convert all the sulfur-bearing molecules and to achieve the desired physical and chemical characteristics of the fuel. There is some evidence that alkylation process may occur on a limited basis in the course of HDS operation [47,48].

As the name implies, adsorptive approaches employ adsorbents for sulfur removal from the fuel. Most often this is achieved by (1) adsorption of the entire sulfur containing molecule in activated carbon, modified zeolites or other materials or (2) adsorption onto metal surfaces such as nickel, wherein nickel sulfide is formed, and the remainder of the hydrocarbon is recovered [46–48]. The former approach is conceptually quite simple to operate, as it can in principle be carried out at ambient temperature and pressure using conventional fixed-bed equipment. The other approach is more complicated, requiring a fluid bed operating at elevated temperatures and pressures. Adsorptive approaches suffer from limited capacity of the material. Adsorbent implementation to hydrocarbon fuels with high levels of sulfur such as JP-8 and diesel would require significant quantities of adsorbent, dual beds (to allow simultaneous adsorption and regeneration) with switching between beds, as well as significant logistical issues associated with disposal of spent adsorbents. For low sulfur fuels (<50 ppm sulfur) such as natural gas, adsorbent technologies can make sense depending on the adsorbent capacity and the reactor's capacity [51]. For gas phase sulfur, such as contained in natural gas, activated carbon is the absorbent of choice [46]. Finally, the sorbent materials tend to be very selective to the types of sulfur containing molecules they adsorb. Therefore, a cocktail approach may be necessary to ensure that all the sulfur is removed.

2.3. Pyrolysis

Pyrolysis is another hydrogen-producing technology where the hydrocarbon is decomposed (without water or oxygen present) into hydrogen and carbon [52]. Pyrolysis can be done with any organic material [53–56] and is used for the production of hydrocarbons [55,56] and carbon nanotubes and spheres [57,58]. Since no water or air is present, no carbon oxides (e.g., CO or CO_2) are formed, eliminating the need for secondary reactors (WGS, PrOx, etc.). Consequently, this process offers significant emissions reduction. However, if air or water is present, for example the materials have not been dried, and then significant CO_2 and CO emissions will be produced. Among the advantages of this process are fuel flexibility, relative simplicity and compactness, clean carbon by-product, and reduction in CO_2 and CO emissions [52,54,56,59–66]. The reactions can be written in the following form [52]:



One of the challenges with this approach is the potential for fouling by the carbon formed, but proponents claim this can be minimized by appropriate design [59]. Since it has the potential for lower CO and CO_2 emissions and it can be operated in such a way as to recover a significant amount of the solid carbon which is easily sequestered [52,53,55,59,61–64,67], pyrolysis may play a significant role in the future.

2.4. Plasma reforming

In plasma reforming the overall reforming reactions are the same as conventional reforming; however, energy and free radicals used for the reforming reaction are provided by a plasma typically generated with electricity or heat [68–77]. When water or steam is injected with the fuel, H, OH, and O radicals in addition to electrons are formed, thus creating conditions for both reductive and oxidative reactions to occur [78]. Proponents maintain that plasma reforming overcomes many limitations of conventional techniques such as cost and deterioration of the catalysts, size and weight requirements, sluggish response, and limitations on hydrogen production from heavy hydrocarbons [70–72,77]. In addition, they can also be configured to operate at lower temperatures than traditional reforming [70–72,77]. In the cases where no catalysts are used to assist the reforming, the process is highly sulfur tolerant [70–72,77]. The main reported disadvantages include the electrical requirements and high electrode erosion at elevated pressures [71]. Plasma reforming technologies have been developed to facilitate POX, ATR and steam reforming, with the majority of the reactors being POX and ATR [74]. There are essentially two main categories of plasma reforming: thermal and non-thermal [74].

In thermal plasma reforming a high electric discharge (>1 kW) is used. A great deal of power is consumed in raising both the electrons and the neutral species to a very high temperature (5000–10,000 K). Even more power is required to cool the electrodes to stop the metals from vaporizing at these high temperatures [71,74,76]. Fig. 2 shows methane conversion as a function of power input for a thermal plasma reactor [71]. In this case 16 MJ of energy were consumed for each kg of hydrogen produced [71]. This technology has been demonstrated in pyrolysis processes, and (with and without catalysts) in steam reforming, ATR and POX processes [71]. Conventional reforming catalysts (nickel-based with alumina support) have been explored [71,76]. Reduction in power consumption is a significant challenge for this technology [74].

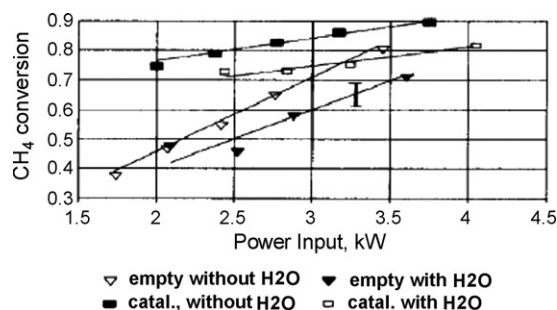


Fig. 2. Methane conversion as a function of power input (Copyright Elsevier [71]). *Empty reactor:* plasmatron air = 0.4 g/s, fuel = 0.27 g/s, additional air = 0.7 g/s. In the case of water addition, 0.2–0.5 g/s H₂O added. *Catalytic case:* plasmatron air = 0.35 g/s, fuel = 0.25–0.5 g/s, additional air = 0.5–1 g/s. In the case of water addition, 0.5–0.8 g/s water.

In non-thermal plasmas, only the electron temperatures are increased to high temperatures (>5000 K), while the bulk species temperature does not increase significantly [68–70,72–76]. Since only the electrons are directly excited, only a few hundred watts of power are required [74]. Four types of non-thermal plasma reformers have been described in the literature: gliding arc plasma, dielectric barrier discharge (DBD), microwave plasma, and corona discharge [68–70,72–75]. The first three use dynamic discharge to create the plasma (Fig. 3 of sliding arc discharge example), while the corona discharge generates the plasma with a static discharge [74]. The chief differences between these technologies is how the current and discharge power are controlled via the power supply, flow rate and design [74]. In the gliding arc plasma the reactor has two diverging electrodes down the length of the reactor [72,74,77,79]. An arc is formed where the gas enters by applying a high voltage. The gas pushes the arc down the length of the reactor. As the gas reaches the end of the reactor the arc is turned off, and another arc is formed at the gas entrance [72,74,77,79]. The advocates of this reactor claim that it is a flexible technology able to operate over a wide range of gas flow rates, the discharge power can be controlled by acting on the electrode or the voltage, it operates with AC or DC currents, and has a simpler power supply compared to the corona and microwave plasma reactors [74].

The DBD reactor is typically an annular configuration. The gases flow in a millimeter gap between the high voltage electrode encased in a non-conductive material such as quartz, with the outer shell being the ground electrode [68,69,80]. This process has been used to create hydrogen and in hydrocarbon synthesis (C₂, C₃, and C₄) using methane as the feed gas. It was found that when a pure methane feed was used, carbon black and a plasma polymerized carbon film were produced [68,69,80]. Therefore co-feeds such as water, carbon monoxide and carbon dioxide were used as well as catalysts [68,69,80]. Carbon dioxide is particularly interesting since the process could be used to eliminate a “green house” gas as well as produce useful hydrocarbons [80].

Unlike the gliding arc and DBD plasma, the microwave plasmas does not use an electric arc. It uses, as its name indicates, microwaves

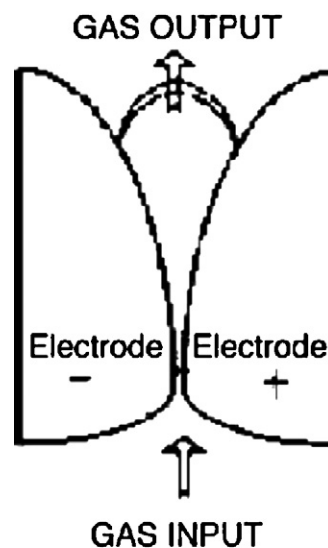


Fig. 3. Example of dynamic discharge in a sliding arc non-thermal plasma reactor (Copyright Elsevier [74]).

[78]. This technique produces electrons with temperatures from 4000 to 6000 K, while heavier particles have temperatures closer to 2000 K [78]. However, some researchers indicated that this process requires more electric energy than the hydrogen generated can produce with a fuel cell, suggesting that further improvements may be necessary [78].

The corona plasma technique is similar to the gliding arc in set up, but not in operation. In the gliding arc the plasma is pushed down the length of the reactor, but in the corona the plasma is generated between the electrodes through the length of the reactor [73,81]. The plasma is created using fast rising electric pulses (i.e. 10 ns rise time and 100 ns pulse) [73,81]. An advantage of this technique is that the length of the electric pulses is shorter than the time between pulses, resulting in relatively low power being consumed compared to other plasma technologies [81]. For example, operating the reactor with a 10 ns rise time and 100 ns pulse duration at 2000 Hz results in electricity only being used approximately 0.02% of the time. This technology has been used to crack hydrocarbon streams prior to them entering traditional reforming reactors, or as the reformer themselves both with and without catalysts [73,81].

Paulmire et al. [74] compared the efficiency of several plasma reactors. They used the following equation to define efficiency in their case [74]:

$$\eta = \frac{(\dot{n}_{\text{CO}} + \dot{n}_{\text{H}_2})\Delta H_{\text{H}_2}}{\dot{n}_{\text{fuel}}\Delta H_{\text{fuel}} + P_{\text{elec}}} \quad (15)$$

Table 3
Plasma Reformer Efficiencies (adapted from [74])

Technology	Fuel	Experimental Conditions			Products (dry vol.%)				Reformate Temperature (K)	Efficiency, η
		Chemical Reaction	Air Ratio	S/C	H ₂	CO	CO ₂	CH ₄		
Gliding arc non-thermal	Diesel	ATR	0.4	1.8	23	17	6.2	1.2	1000–1300	85
Corona discharge + catalyst	Iso-octane	ATR	0.28	1	46	16	16	–	900–1100	55
Gliding arc thermal	Iso-octane	POx	0.25	–	22	15	2	3	1200	9
Gliding arc thermal	Diesel	POx	0.25	–	23.5	23	0.1	0.03	1200	9
Microwave	Hexane	SR	–	2	66	25	4	–	?	?

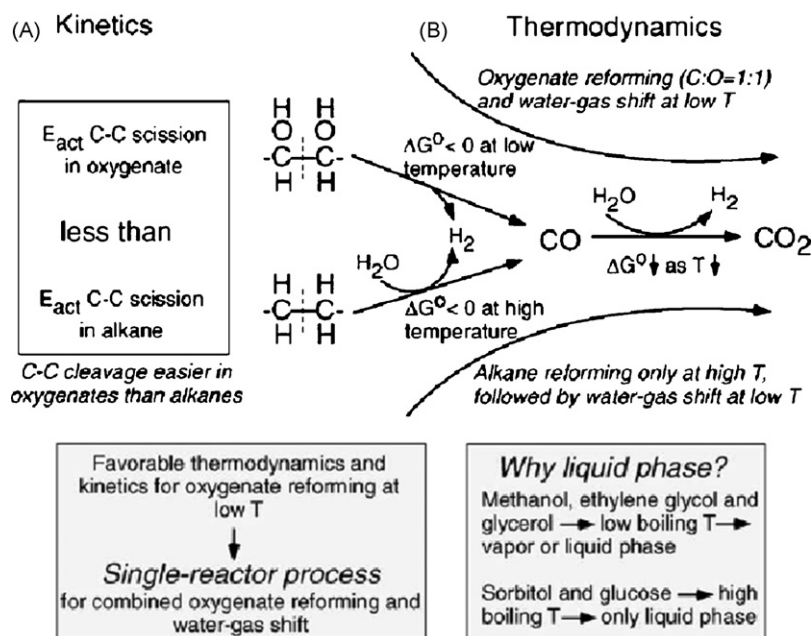


Fig. 4. (A) Reaction pathways for aqueous reforming of oxygenated hydrocarbons. (B) Summary of thermodynamic and kinetic considerations for aqueous phase reforming (Copyright Elsevier [2]).

where n_{CO} and n_{H_2} are the molar flows of carbon monoxide and hydrogen, respectively, which when multiplied by the lower heating value of hydrogen (ΔH_{H_2}) is the energy in the outlet stream (assuming all the carbon monoxide is converted to carbon dioxide in a WGS reactor). The outlet energy is divided by the input energy (n_{fuel} is the molar flow of the fuel multiplied by the lower heating value of the fuel, ΔH_{fuel} , plus electric power for the plasma generation, P_{elec}) to find the efficiency. Of the cases investigated, a gliding arc non-thermal plasma appeared to be the most efficient (Table 3).

2.5. Aqueous phase reforming

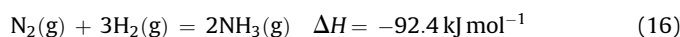
Aqueous phase reforming (APR) is under development to process oxygenated hydrocarbons or carbohydrates to produce hydrogen [2,68,82–97]. These reactors often operate at pressures up to 25–30 MPa and temperatures ranging from 220 to 270 °C. The reforming reactions are rather complex (see the reaction pathways for hydrogen production from oxygenated hydrocarbons in Fig. 4a), but can be summarized to follow the reaction pathways in Eq. (1) for reforming followed by Eq. (10) for the WGS [86]. Most research to date has been focused on supported Group VIII catalysts, with Pt-containing catalysts having the highest activity. Even though they have lower activity, nickel based catalysts have been evaluated due to nickel's low cost [86]. The advantages of APR reactors include elimination of the need to vaporize water and feedstock which eliminates a system component and also enables fuels that cannot be vaporized such as glucose to be processed without first degrading them. APR occurs at low temperatures which favors WGS to increase the hydrogen yield while suppressing CO. Thus the reforming and WGS occur in a single step eliminating multiple reactors (Fig. 4b) [2]. The advocates of this technology claim that this technology is more amiable to efficiently and selectively converting biomass feedstocks to hydrogen. Aqueous feed concentrations of 10–60% were reported for glucose and glycols [98,99]. Catalyst selection is important to avoid methanation, which is thermodynamically favorable, along with Fischer Tropsch products such as propane, butane, and hexane [2,88,89]. Rozmiarek [99] reported an aqueous phase

reformer-based process that achieved >55% efficiency¹ with a feed composed of 60% glucose in water. However, the catalyst was not stable during long-term tests (200 days on stream) [99]. Finally, due to moderate space time yields, these reactors tend to be somewhat large. However, this may be improved through the use of microreactor technology [36]. Improving catalyst activity and durability is an area where significant progress can be made.

2.6. Ammonia reforming

Ammonia reforming has been proposed primarily for use with fuel cells for portable power applications [36,100–106]. It is an inexpensive fuel that, due to its use in fertilizer production, has an extensive distribution system including thousands of miles of pipeline [107]. Pure ammonia has an energy density of 8.9 kWh/kg, which is higher than methanol (6.2 kWh/kg), but less than diesel or JP-8 (13.2 kWh/kg) [106]. Proponents quickly point out that ammonia's strong odor makes leak detection simple, reducing some of the risk [103]. Another challenge is that PEM fuel cells require ammonia levels to be reduced below ppb levels to ensure long life, since exposure of ammonia to the acidic PEM electrolyte causes severe and irreversible loss in performance. The losses are cumulative since the ammonia will build up in the electrolyte [108]. However, for SOFC, ammonia can be fed directly to the fuel cell without any reforming [103,105].

Ammonia cracking is endothermic and is regarded as the reverse of the synthesis reaction. In industry, ammonia synthesis occurs at approximately 500 °C and 250 atm, and its synthesis is represented by the following reaction [103]:



Typical catalysts used in both ammonia synthesis and cracking include iron oxide, molybdenum, ruthenium, and nickel. Ammonia cracking operates at temperatures around 800–900 °C, and unlike ammonia synthesis, low pressures are preferred [102,103]. The

¹ Efficiency = lower heating value of hydrogen produced divided by the lower heating value of the feedstock. This includes gas clean-up using a pressure swing absorption system.

high temperatures can be obtained by either burning some of the hydrogen produced by ammonia cracking or carrying a second fuel such as propane or butane which is combusted.

3. Non-reforming hydrogen production

Hydrogen is produced by many methods other than reforming. A brief description of some of the biomass-based approaches, along with production of hydrogen from water, is included here. Although chemical hydrides are typically considered hydrogen storage materials, a very brief review will also be provided.

3.1. Hydrogen from biomass

In the near term, biomass is the most likely renewable organic substitute to petroleum. In the United States it is second only to hydropower as a primary energy source among renewable resources [109]. Biomass is available from a wide range of sources such as animal wastes, municipal solid wastes, crop residues, short rotation woody crops, agricultural wastes, sawdust, aquatic plants, short rotation herbaceous species (i.e. switch grass), waste paper, corn, and many more [1,79,109–125]. For hydrogen generation, the current biomass technologies include: gasification, pyrolysis, conversion to liquid fuels by supercritical extraction, liquefaction, hydrolysis, etc. followed in some cases by reformation, and biological hydrogen production [123]. A brief description of gasification and biological hydrogen production will be given here. Conversion to liquid fuels is beyond the scope of this paper.

3.1.1. Biomass gasification

Gasification technology, commonly used with biomass and coal, is very mature and commercially used in many processes. It is a variation of pyrolysis and, therefore, is based upon partial oxidation of the materials into a mixture of hydrogen, methane, carbon monoxide, carbon dioxide, and nitrogen known as a producer gas [119]. Since pyrolysis and steam reforming have been described previously, only a brief examination of the salient differences occurs here. The gasification process typically suffers from low thermal efficiency since moisture contained in the biomass must also be vaporized [1]. It can be done with or without a catalyst [113,118,122,126] and in a fixed bed or fluidized bed reactor, with the fluidized bed reactor typically yielding better performance [118]. Addition of steam and or oxygen to the gasification process results in steam reforming and produces a syngas stream (H_2 to CO ratio of 2:1), which can be used as the feed to a Fischer-Tropsch reactor to make higher hydrocarbons, or to a WGS for hydrogen production [118,123]. Superheated steam (900 °C) has been used to reform dried biomass to achieve high hydrogen yields as seen in Fig. 5 [1]. Gasification, even at high temperatures of 800–1000 °C, produces a significant amount of tar in the product gas (Fig. 5). Therefore, a secondary reactor, which utilizes calcined dolomite or nickel catalysts, is used to catalytically clean and upgrade the product gas [118]. Ideally, oxygen should be used in these plants; however, oxygen separation unit operations are cost prohibitive for small-scale plants. This limits the gasifiers to the use of air resulting in significant dilution of the products as well as the production of NOx. Low cost, efficient oxygen separators are needed for this technology. For hydrogen production, a WGS process can be employed to increase the hydrogen concentration, and then a separation process used to produce pure hydrogen [114]. Several processes have been proposed to decrease the amount of tar produced in the gasification reactor. For example, the employment of an Rh/CeO₂/M (M = SiO₂, Al₂O₃, and ZrO₂) catalyst for use in the gasification process has been found to reduce the tar formation [118]. Much cheaper catalysts would be required to make such an

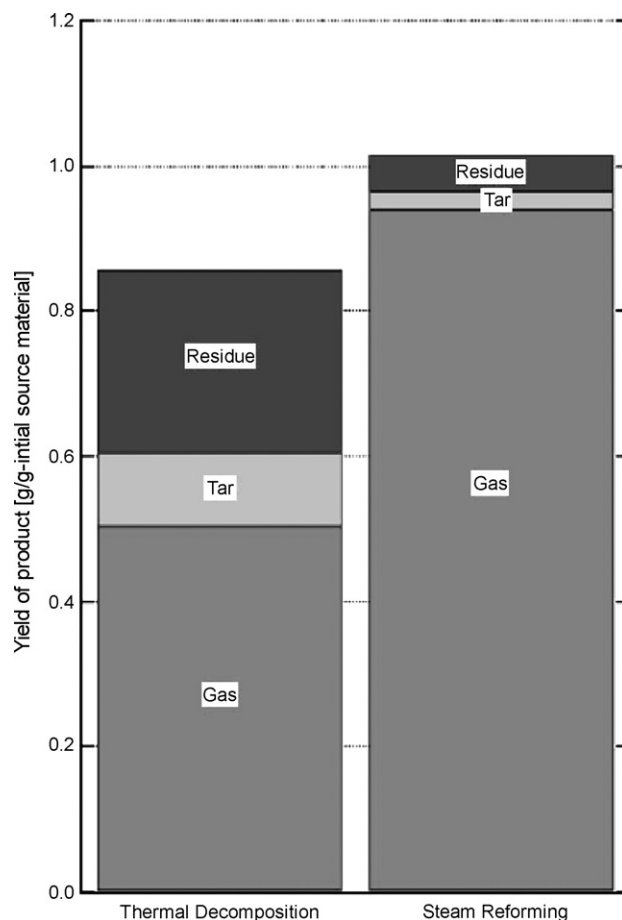


Fig. 5. Production yield for thermal decomposition and superheated steam reforming (Copyright Elsevier [1]).

approach viable. Typically, gasification reactors are built on a large scale and require massive amounts of material to be continuously fed to them. They can achieve efficiencies 35–50% based on the lower heating value [9,20,127]. One of the problems with this technology is that a tremendous amount of resources must be used to gather the large amounts of biomass to the central processing plant. Currently, the high logistics costs typically limit the gasification plants to be located. Development of smaller efficient distributed gasification plants may be required for this technology for cost effective hydrogen production using this technology.

3.1.2. Biological hydrogen

Due to increased attention to sustainable development and waste minimization, research in bio-hydrogen has substantially increased over the last several years [128–155]. The main bio-process technologies used for bio-hydrogen production include: photolytic hydrogen production from water by green algae or cyanobacteria (also known as direct photolysis), dark-fermentative hydrogen production during the acidogenic phase of anaerobic digestion of organic material, photo-fermentative processes, two stage dark/fermentative, and hydrogen production by water-gas-shift [132,137,156]. It should be noted that only a small fraction of naturally occurring microorganisms have been discovered and functionally characterized [9]. In addition, the known organisms are being modified to improve their characteristics. The feeds for biological hydrogen are water for photolysis processes and biomass for fermentative processes. Brief descriptions with their advantages and limitations will be presented here. There are several recent

review articles that provide in-depth descriptions of the reaction pathways and types of enzymes being used in bio-hydrogen production and the interested reader is referred to them for more details [132,137,148,156–158].

3.1.2.1. Direct photolysis. Photosynthesis uses solar energy to convert carbon dioxide and water to carbohydrates and oxygen. For some organisms, excess solar energy is “vented” by production of hydrogen via direct photolysis of water. Researchers are trying to engineer algae and bacteria so the majority of the solar energy is diverted to hydrogen production, with enough diverted to carbohydrate production to solely maintain life. Direct photolysis of water is done in two ways. First it can use green algae’s photosynthesis capabilities to generate oxygen and hydrogen ions. The process occurs along the thylakoid membrane where two photosystems are located (Fig. 6). The first step is the splitting of water into oxygen using solar radiation. The hydrogen in this reaction is bound in the plastoquinone (pqH_2) molecule (Sorensen 30–35). The pqH_2 is conveyed down the membrane to the cytochrome b_6f which transfers the stored energy from pqH_2 to plastocyanin (pc). The pq is recycled back to photosystem II. Additional solar radiation is absorbed in photosystem I which is used to transfer the chemical energy in pc to ferredoxin (fd). The fd is used to convert the NADP to $NADPH_2$. The NADPH₂ by means of the Benson-BassHam-Calvin Cycle converts CO₂ to carbohydrates. However, under anaerobic conditions or when too much energy is captured in the process some organisms vent the excess electrons by using a hydrogenase enzyme which converts the hydrogen ions in the fd to hydrogen gas [20,159]. The advantage of this technology is that the primary feed is water, which is inexpensive and available almost everywhere [156]. Currently, this process requires a significant surface area to collect sufficient light. Unfortunately, these microorganisms in addition to producing hydrogen, produce oxygen, which, when sensed by the organism, causes it to cease hydrogen production [135,156]. Therefore work is being done to either, identify or engineer less oxygen sensitive organisms, separate the hydrogen and oxygen cycles, and/or change the ratio of photosynthesis (oxygen production) to respiration (oxygen consumption) in order to prevent oxygen buildup [9]. The addition of sulfate to the solution has been found to depress oxygen production and sensitivity; however, the hydrogen production mechanisms are also suppressed [20,159]. Since oxygen and hydrogen are co-produced in a mixed gas, significant safety and separation issues occur. Recent innovative research has resulted in substantially increased light utilization efficiency of up to 15% compared to the previous utilization of ~5%

[160]. For photosynthetic to biomass, efficiency is as high as 2% on coral reefs, but averages 0.2% globally. This translates into a maximum theoretical efficiency for photosynthetic hydrogen production of about 1% [20]. Proponents of photolytic hydrogen production claim that 10–13% is achievable by engineering the organisms to better utilize the solar power [159]. However, the 2007 light–hydrogen efficiency is ~0.5% [161]. Another challenge is achieving continuous hydrogen production under aerobic conditions. The U.S. DOE target is 10 min of continuous operation by 2013 (2006 status was 1 s) [9]. This technology has significant promise, but also tremendous challenges.

3.1.2.2. Dark fermentation. Dark fermentation uses primarily anaerobic bacteria, although some algae are also used, on carbohydrate rich substrates grown, as the name indicates, in the dark [132,135,156]. For fermentative processes, the biomass used needs to be biodegradable, available in high quantities, inexpensive, and have a high carbohydrate content [116,156]. Pure, simple sugars, which are easily biodegradable such as glucose and lactose are preferred, but are not readily available in high quantities and/or are relatively expensive [156]. Major biomass wastes which can be readily utilized for bio-hydrogen are listed in Table 4.

The pathways are dependent on the type of bacteria used. Standard fermentative pathway has a theoretical maximum production of 4 moles of hydrogen per mole of glucose. Currently fermentative processes produce 2.4 to 3.2 moles of hydrogen per mole glucose [9,135]. However, it may be possible to change the fermentative pathway using molecular engineering with the objective to increase hydrogen production’s theoretical maximum to 12 moles hydrogen per mole glucose [9]. The gas produced is a mixture of hydrogen, carbon dioxide, methane, carbon monoxide, and some hydrogen sulfide [132]. Therefore a separation step is required to produce high purity hydrogen. For dark fermentation processes, the partial pressure of hydrogen is a factor; as the hydrogen pressure increases the hydrogen production decreases [132]. The obvious solution to this limitation is to remove the hydrogen as it is generated. The fermentation process produces acetic, butyric and other organic acids, which is a more significant problem. These acids can depress hydrogen yield by diverting the metabolic pathway toward organic chemical production. In addition, their production requires subsequent wastewater treatment which adds cost and complexity to the system. This pathway either needs to be eliminated to maximize hydrogen production and simplify the process or it needs to be taken advantage of by the integrated multi-step processes described below [9].

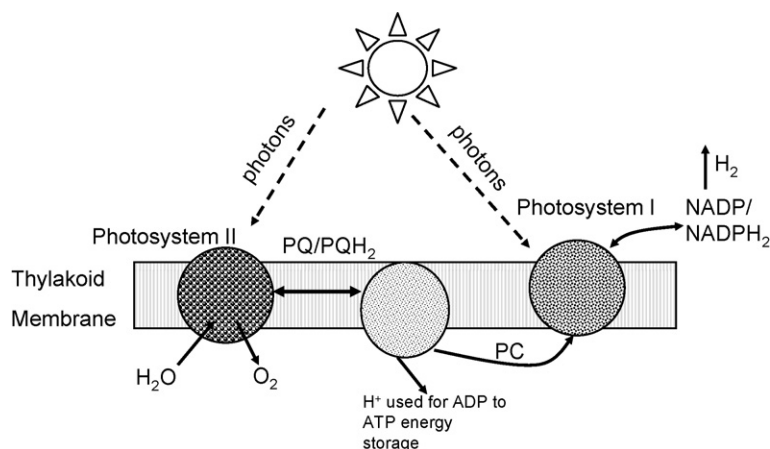


Fig. 6. Direct photolysis process.

Table 4
Biomass waste that is readily utilized for bio-hydrogen production [132,156]

Biomass material	Comments
Starch agricultural and food industry waste	Must be hydrolyzed to glucose or maltose, followed by conversion to organic acids and finally hydrogen
Cellulose agricultural and food industry waste	Must be finely ground and go through delignification, then it is processed as starch
Carbohydrate rich industrial waste	May require pretreatment for removal of undesirables and for nutritional balancing, then it is processed as starch
Waste sludge from wastewater treatment plants	May require pretreatment, the converted to organic acids and finally converted to hydrogen

3.1.2.3. Photo-fermentative processes. Photo-fermentative processes, also called photosynthetic bacterial hydrogen production, capitalize on the nitrogenase functionality of purple non-sulfur bacteria to evolve hydrogen. In this process light harvesting pigments such as chlorophylls, carotenoids, and phycobilins scavenge light energy which is transferred to membrane reaction centers similar to those in photolytic organisms (algae). Sunlight converts water into protons, electrons, and O₂ [20]. The nitrogenase catalyst is used to react the protons and electrons with nitrogen and ATP to make ammonia, hydrogen and ADP [20]. Since oxygen inhibits the nitrogenase, cyanobacteria separate nitrogen fixation and oxygen generation either spatially or temporally [20]. In nature the bacteria use the hydrogen by-product to fuel other energy requiring processes via the *uptake hydrogenase* enzyme. Therefore, researchers are trying to genetically modify the bacteria to suppress this enzyme [20]. The process is done in deficient nitrogen conditions using primarily infrared light energy and, preferably, reduced organic acids although other reduced compounds can be used [132,135,156]. The advantages of this process are that oxygen does not inhibit the process, and that these bacteria can be used in a wide variety of conditions (i.e. batch processes, continuous cultures, and immobilized in carrageenan, agar gel, porous glass, activated glass, or polyurethane foam) [132,135,156]. The disadvantages are the limited availability of organic acids, the nitrogenase enzyme is slow, the process requires a relatively high amount of energy, and hydrogen re-oxidation [135,156]. To increase the nitrogenase activity and decrease the energy requirements, the proper ratio of carbon to nitrogen nutrients must be maintained. Enzyme engineering approaches are under development to decrease the nitrogenase sensitivity to high levels of nitrogen nutrients. In addition, hydrogen re-oxidation is being addressed by microengineering to deactivate hydrogenase enzymes in the bacteria. The hydrogenase enzymes recycle the hydrogen produced by the nitrogenase to support cell growth. Finally, photosynthetic organisms are not efficient as solar collectors, collecting on average (over day and night) an energy flow of approximately 100–200 W/m² [20]. Current efficiency is approximately 1.9% [9,20]. The theoretical limit for this technology is 68% according to the U.S. DOE [9].

3.1.2.4. Microbial electrolysis cells. Microbial aided electrolysis cells (MEC), also called bioelectrochemically assisted microbial reactor (BEAMR), use electrohydrogenesis to directly convert biodegradable material into hydrogen [162–164]. The MEC is a modified microbial fuel cell. In a microbial fuel cell, exoelectrogens (special microorganisms), decompose (oxidize) organic material and transfer electrons to the anode. The electrons combine at the cathode, after traveling through an external load, with protons and oxygen forming water. A MEC operates in anaerobic state (no oxygen at the cathode) and an external voltage is applied to the cell rather than generated by it. The added energy is required since acetate substrate decomposition is not spontaneous under standard conditions [162–164]. Hydrogen production occurs at the cathode via Eq. (17).



The theoretical potential for hydrogen production in neutral pH (pH 7) is -0.61 V , V_{Cat} vs. Ag/AgCl [164]. Exoelectrogens generate an anode potential of approximately $V_{\text{an}} = -0.5 \text{ V}$. Therefore the minimum applied potential ($V_{\text{app}} = V_{\text{an}} - V_{\text{Cat}}$) is 0.11 V [164]. For acetate, the actual applied voltage is $>0.3 \text{ V}$ due to electrode overpotentials and ohmic resistance [164].

The design of MEC systems initially used similar components as used in PEM fuel cells [164]. However, flat electrode designs limited the surface area for the exoelectrogens and the membranes increased the ohmic resistances so alternative designs were developed. The most recent design uses a graphite brush for the exoelectrogen substrate (anode) and no membrane separator [162]. This design succeeded to decrease the applied voltage from 1.0 V using a gas diffusion membrane and 0.5 V with a Nafion membrane to 0.4 V in the membraneless design. The efficiency is a function of the lower heating value of the hydrogen divided by the lower heating value of the organic material plus the electrical energy provided [162].

$$\eta = \frac{n_{\text{Hydrogen}} \Delta H_{\text{c,Hydrogen}}}{\sum_1^n (I E_{\text{ap}} \Delta t - I^2 R_{\text{ex}} \Delta t) + n_{\text{substrate}} \Delta H_{\text{c,substrate}}} \quad (18)$$

where I is the current, E_{ap} the applied voltage, Δt (s) the time increment for n data points measured during the batch cycle, and R_{ex} is an external resistance which was 10Ω by Call and Logan [162]. Using Eq. (18), the efficiency was raised from 23% with a gas diffusion membrane and 53% with a Nafion membrane to 76% in the membraneless reactor [162]. Under these conditions a hydrogen production rate of $3.12 \text{ m}^3 \text{ H}_2/(\text{m}^3 \text{ reactor day})$ [162]. However, the methane production rates also increased to an average of 3.5% methane in the production gas [162]. To control the methanogenesis in these reactors, strategies involving intermittent draining and air exposure or in situ air-sparging have been proposed [162]. However, these strategies will result in more complex systems with significantly increased operations and maintenance requirements, translating into more expensive systems. In addition to methane suppression, continuous operation, decreasing the pH, operating under carbon limited conditions, increasing the microorganisms tolerance to impurities, and examining other feedstocks are all issues to be addressed.

3.1.2.5. Multi-stage integrated process. Multi-stage hydrogen production has been implemented to maximize the hydrogen production from the feed [156]. Initially, the process consisted of two stages, dark fermentation followed by photo fermentation [156], but three or even four stages have since been proposed in different configurations (Fig. 7) [9]. In this process, the biomass material is first fed to a dark fermentation reactor where the bacteria decompose the feedstock to hydrogen and an organic acid rich effluent. Since the effluent has organic acids in it, this eliminates the challenge of developing a supply of organic acids for the photo-fermentative process. Since the photo-fermentative process uses primarily infrared light, the sunlight is first filtered through a direct photolysis reactor where the visible light is utilized, but the infrared light is not [9]. The fourth stage is the use of a microbial electrolysis cells which produces hydrogen, not electricity

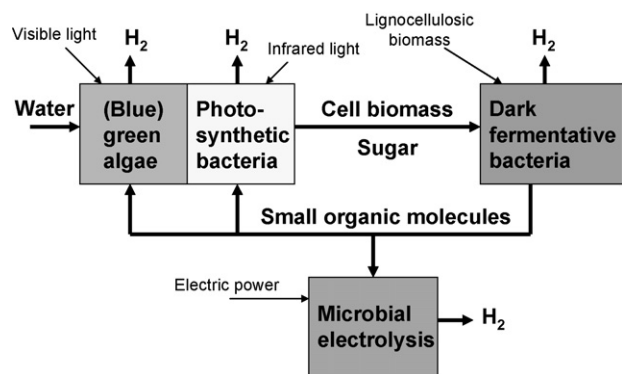


Fig. 7. Multi-stage integrated biohydrogen system (adapted from [9]).

[9]. This cell utilizes the same organic acids, but does not require light. Therefore, it can operate during the night or other times of low light [9]. The effluent from the first stage contains ammonia, which inhibits the second stage, so some dilution and neutralization to adjust the pH to 7 is required prior to feeding it to the second stage [156].

Integration of multiple processes produces significant challenges for the reactor engineering, system design, process control, and operation and maintenance. The challenges with the co-production of hydrogen and oxygen from photolytic hydrogen production include:

- Photosynthetic and respiration capacity ratio. Green algae and cyanobacteria become anaerobic when their photosynthesis/respiration (P/R) capacity ratio is 1 or less. Under such anaerobic conditions, photosynthetic water oxidation produces H_2 instead of starch, and the oxygen evolved by photosynthesis is consumed by respiration, to produce CO_2 . Currently, this process is achieved by nutrient deprivation, with the drawback that the resulting P/R ≤ 1 ratio is achieved by partially decreasing the quantum yield of photosynthesis. Alternative mechanisms to bring the P/R ratio to 1 need to be investigated, particularly those methods that focus on achieving a P/R ratio of 1 without changing the quantum yield of photosynthesis. Two further issues will need to be investigated under these conditions: (1) rate limitations due to the non-dissipation of the proton gradient and (2) the ability of the culture to take up a variety of exogenous carbon sources under the resulting anaerobic conditions [9].
- Co-culture balance. To extend the adsorption spectrum of the H_2 -photoproducing cultures to the infrared (700–900 nm), the possibility of co-cultivating oxygenic photosynthetic organisms with anoxygenic photosynthetic bacteria that absorb light in the visible (400–600 nm), thus potentially competing with green algae for these latter wavelengths. Strategies need to be devised to either maintain the appropriate biomass ratio of the two organisms as suspensions in the same cultures. The competition

for organic carbon substrates between two organisms in the same medium also needs to be investigated [9].

- Concentration and processing of cell biomass. In an integrated system, cell biomass from either green algae/cyanobacteria or photosynthetic bacteria can serve as the substrate for dark fermentation. The green algal and cyanobacterial cell walls are made mostly of glycoproteins (sugar-containing proteins), which are rich in sugars like arabinose, mannose, galactose, and glucose. Purple photosynthetic bacterial cell walls contain peptidoglycans (carbohydrate polymers cross-linked by protein, and other polymers made of carbohydrate protein and lipid). Pretreatment of cell biomass may be necessary to render it more suitable for dark fermentation. Methods for cell concentration and processing will depend on the type of organism used and how the biological system is integrated [9].

3.1.2.6. Water-gas-shift. Finally, certain photoheterotrophic bacteria in the family Rhodospirillaceae have been found which can grow in the dark by feeding only upon CO [132]. The oxidation of the CO to CO_2 was determined to follow the WGS reaction (Eq. (10)), but uses enzymes rather than metal to catalyze the process. Since it occurs at low temperatures and pressures, thermodynamics favor a high conversion of CO to CO_2 and H_2 [132]. Its conversion rate is actually relatively high compared to other biological processes, but it does require a CO source and darkness [132].

3.1.2.7. Production rates comparison. Levin et al. [132] compiled a table comparing hydrogen synthesis rates by different technologies which is adapted in Table 5. Although there have been some advances since Levin et al. published their findings in 2004, the table does provide order of magnitude estimates for the approximate size of the reactors for hydrogen production. One of the major challenges to this technology is the slow hydrogen production rate. For example, a 5 kW PEM fuel cell, sufficient to provide residential power, requires approximately 119.5 mol H_2 /h (95% H_2 utilization, 50% efficiency). Therefore a bioreactor ranging from 1 to 1700 m^3 would be required to provide the hydrogen [132]. The complete system with controls and balance of plant equipment is not included in the size estimate.

3.2. Hydrogen from water

There has been a great deal of research in splitting water to make hydrogen and oxygen; in fact its commercial uses date back to the 1890s [165]. Water splitting can be divided into three categories: electrolysis, thermolysis, and photoelectrolysis.

3.2.1. Electrolysis

Water splitting in its simplest form uses an electrical current passing through two electrodes to break water into hydrogen and oxygen. Commercial low temperature electrolyzers have system efficiencies of 56–73% (70.1–53.4 kWh/kg H_2 at 1 atm and 25 °C)

Table 5
Hydrogen production rate of different types of bio-hydrogen processes (adapted from [9,132,162])

Bio-hydrogen system	H_2 synthesis rate (reported units)	H_2 synthesis rate (converted units)	Bio-reactor volume (m^3) for 5 kW PEMFC
Direct photolysis	4.67 mmol H_2 /(l 80 h)	0.07 mmol H_2 /(l h)	1707
Indirect photolysis	12.6 mmol H_2 /(μg protein h)	0.355 mmol H_2 /(l h)	337
Photo-fermentation	4.0 ml H_2 /(ml h)	0.16 mmol H_2 /(l h)	747
WGS	0.8 mmol H_2 /(g cdw min)	96 mmol H_2 /(l h)	1.24
Dark fermentation	Various	8.2–121 mmol H_2 /(l h)	1–14.75
MEC	3.12 $m^3 H_2$ /(m^3 reactors day)	5.8 mmol H_2 /(l h)	21
Multi-stage	Not available, but assumed higher than individual stages		

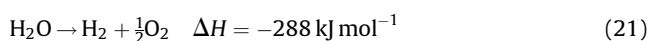
[159]. It is essentially the conversion of electrical energy to chemical energy in the form of hydrogen, with oxygen as a useful by-product. The most common electrolysis technology is alkaline based, but more proton exchange membrane (PEM) electrolysis and solid oxide electrolysis cells (SOEC) units are developing [165–167]. SOEC electrolyzers are the most electrically efficient, but are the least developed of the technologies. SOEC technology has challenges with corrosion, seals, thermal cycling, and chrome migration. PEM electrolyzers are more efficient than alkaline, do not have the corrosion and seals issues that SOEC, but cost more than alkaline systems. Alkaline systems are the most developed and lowest in capital cost. They have the lowest efficiency so they have the highest electrical energy costs.

Electrolyzers are not only capable of producing high purity hydrogen, but recently, high-pressure units (pressures > 1000 psig) are being developed [168]. The advantage of high-pressure operation is the elimination of expensive hydrogen compressors. Currently, electrolysis is more expensive than using large-scale fuel processing techniques to produce hydrogen. And, if non-renewable power generation is used to make the electricity for electrolysis, it actually results in higher emissions compared to natural gas reforming [169,170]. However, it should be noted, that if the hydrogen must be shipped in cylinders or tankers, then on site production via electrolysis may be less expensive. Several different approaches have been proposed to address these shortcomings. These include using renewable sources of energy such as solar, wind, and hydro, to produce the electricity [168,170], or excess power from existing generators to produce hydrogen during off-peak times [171], and high temperature electrolysis. There have been several studies on the cost of using renewable energy for electrolysis, all reaching the conclusion that as the cost of natural gas increases renewable energy will become economically competitive at central production facilities as well as at distributed generation points especially if carbon dioxide and other pollutants are included in the analysis [5,172,173].

3.2.1.1. Alkaline electrolyzer. Alkaline electrolyzers are typically composed of electrodes, a microporous separator and an aqueous alkaline electrolyte of approximately 30 wt% KOH or NaOH [20,159]. In alkaline electrolyzers nickel with a catalytic coating, such as platinum, is the most common cathode material. For the anode, nickel or copper metals coated with metal oxides, such as manganese, tungsten or ruthenium, are used. The liquid electrolyte is not consumed in the reaction, but must be replenished over time because of other system losses primarily during hydrogen recovery. In an alkaline cell the water is introduced in the cathode where it is decomposed into hydrogen and OH⁻ [127]. The OH⁻ travels through the electrolytic material to the anode where O₂ is formed. The hydrogen is left in the alkaline solution [127]. The hydrogen is then separated from the water in a gas liquid separations unit outside of the electrolyser [127]. The typical current density is 100–300 mA cm⁻² and alkaline electrolyzers typically achieve efficiencies 50–60% based on the lower heating value of hydrogen [159]. The overall reactions at the anode and cathode are:



Overall:



3.2.1.2. Proton exchange membrane electrolyzer. PEM electrolyzers build upon the recent advances in PEM fuel cell technology [127]. PEM-based electrolyzers typically use Pt black, iridium, ruthenium, and rhodium for electrode catalysts and a Nafion membrane which not only separates the electrodes, but acts as a gas separator [159,166]. In PEM electrolyzers water is introduced at the anode where it is split into protons and oxygen [127]. The protons travel through the membrane to the cathode, where they are recombined into hydrogen [127]. The O₂ gas remains behind with the unreacted water. There is no need for a separations unit. Depending on the purity requirements a drier may be used to remove residual water after a gas/liquid separations unit. PEM electrolyzers have low ionic resistances and therefore high currents of >1600 mA cm⁻² can be achieved while maintaining high efficiencies of 55–70% [20,159]. The reactions at the anode and cathode are:



Overall is the same as for alkaline electrolyzers:



3.2.1.3. Solid oxide electrolysis cells. Solid oxide electrolysis cells (SOEC) are essentially solid oxide fuel cells operating in reverse. These systems replace part of the electrical energy required to split water with thermal energy, as can be seen in Fig. 8 [174]. The higher temperatures increase the electrolyzer efficiency by decreasing the anode and cathode overpotentials which cause power loss in electrolysis [174,175]. For example, an increase in temperature from 375 to 1050 K reduces the combined thermal

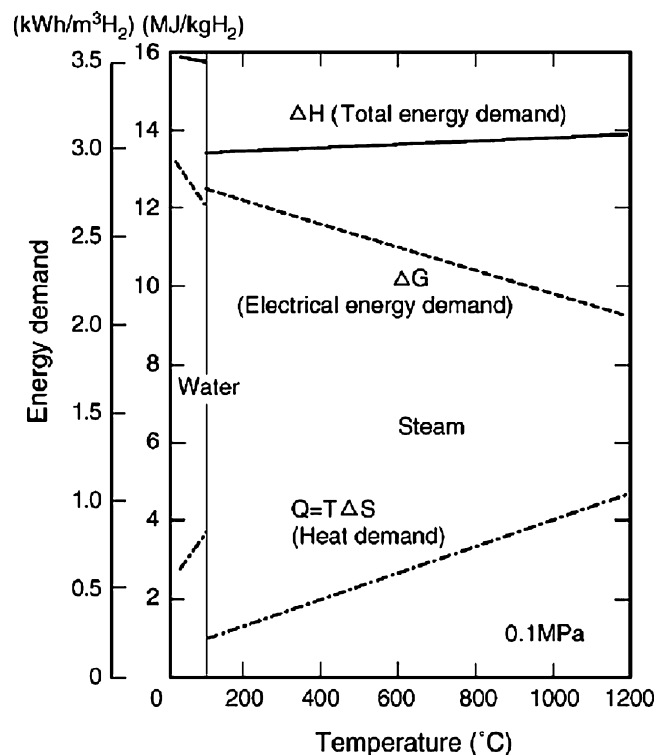


Fig. 8. Energy demand for water and steam electrolysis (Copyright Elsevier [174]).

and electrical energy requirements by close to 35% [175]. A SOEC operates similar to the alkaline system in that an oxygen ion travels through the electrolyte leaving the hydrogen in unreacted steam stream [127]. The reactions are shown in Eqs. (17)–(19).

Other advantages for high temperature electrolysis with a solid oxide based electrolyzer include: the use of a solid electrolyte which, unlike KOH for alkaline systems, is non-corrosive and it does not experience any liquid and flow distribution problems [165,174]. Of course the high temperature operation requires the use of costly materials and fabrication methods in addition to a heat source [165]. The materials are similar to those being developed for solid oxide fuel cells (SOFC), yttria stabilized zirconia (YSZ) electrolyte, nickel containing YSZ anode, and metal doped lanthanum metal oxides [165,174], and have the same problems with seals which are being investigated.

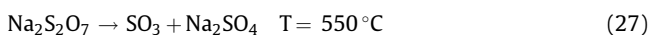
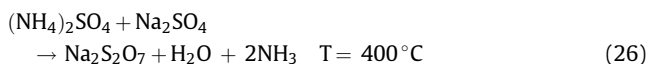
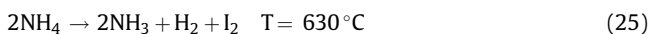
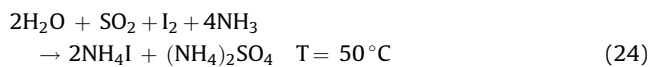
High temperature electrolysis efficiency is dependent on the temperature and the thermal source. The efficiency as a function of electrical input alone can be very high with efficiencies 85–90% being reported [127]. However, when the thermal source is included the efficiencies can drop significantly. For example, SOEC operating from advanced high temperature nuclear reactors may be able to achieve up to 60% efficiency. In addition to using conventional combustion or nuclear energy to produce the high temperature source, solar energy is under development and may result in higher efficiencies [173–181].

Combining SOEC with a SOFC for co-generation of hydrogen and electricity has been proposed [182]. In this hybrid system a SOFC and SOEC are manifolded into the same stack and fed the same fuel, such as natural gas. Hydrogen is then produced by the SOEC and electricity is produced by the SOFC. Proof-of-concept short stacks have been demonstrated with efficiencies of up to 69% [182]. However, the fuel utilization is still relatively low at approximately 40% and coking is a serious issue in addition to the other challenges faced by SOEC [182].

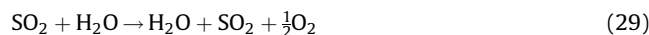
3.2.2. Thermochemical water splitting

In thermochemical water splitting, also called thermolysis, heat alone is used to decompose water to hydrogen and oxygen [165,183]. It is believed that overall efficiencies of close to 50% are achievable using these processes [184]. It is well known that water will decompose at 2500 °C, but materials stable at this temperature and also sustainable heat sources are not easily available [165]. Therefore chemical reagents have been proposed to lower the temperatures. Research in this area was prominent from the 1960s through the early 1980s. However, essentially all R&D stopped after the mid-1980s, until recently. There are more than 300 water splitting cycles referenced in the literature [9,127,185]. All of the processes have significantly reduced the operating temperature from 2500 °C, but typically require higher pressures. Three example cycles are:

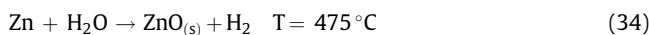
Ispra Mark-10 [165]:



Sulfuric acid decomposition [184]:



ZnO/Zn [185]:



In choosing the process there are five criteria which should be met [165]. (1) Within the temperatures considered, the ΔG of the individual reactions must approach zero. This is the most important criterion. (2) The number of steps should be minimal. (3) Each individual step must have both fast reaction rates and rates which are similar to the other steps in the process. (4) The reaction products cannot result in chemical-by-products, and any separation of the reaction products must be minimal in terms of cost and energy consumption. (5) Intermediate products must be easily handled [165].

Currently, there are several processes which meet the five criteria, such as the Ispra-Mark 10, 11, 13, 15, UT-3 process, and the sulfuric acid decomposition process; however, they are still not competitive with other hydrogen generation technologies in terms of cost and efficiency which is the major focus of research in those processes [165,184]. In addition, these processes require large inventories of highly hazardous corrosive materials. The combination of high temperatures, high pressures, and corrosion results in the need for new materials. Finally, several of them such as the hybrid sulfur Ispra-Mark 11 process require inefficient electrochemical steps which need to be improved [165,184].

It is believed that scaling up the processes may lead to improved thermal efficiency overcoming one of the principle challenges faced by this technology [184]. In addition, a better understanding of the relationship between capital costs, thermodynamic losses, and process thermal efficiency may lead to decreased hydrogen production costs [184]. The current processes all use four or more reactions, and it is believed that an efficient two reaction process may make this technology viable [184]. The U.S. DOE has active projects investigating several of these processes focused on improving materials, lowering cost, and increasing efficiency [9,183].

3.2.3. Photoelectrolysis

Photoelectrolysis uses sunlight to directly decompose water into hydrogen and oxygen, and uses semiconductor materials similar to those used in photovoltaics. In *photovoltaics*, two doped semiconductor materials, a p-type and an n-type, are brought together forming a p–n junction [165]. At the junction, a permanent electric field is formed when the charges in the p- and n-type of material rearrange. When a photon with energy greater than the semiconductor material's bandgap is absorbed at the junction, an electron is released and a hole is formed. Since an electric field is present, the hole and electron are forced to move in opposite directions which, if an external load is also connected, will create an electric current [159,186]. This type of situation occurs in *photoelectrolysis* when a photocathode, p-type material with excess holes, or a photoanode, n-type of material with excess electrons, is immersed in an aqueous

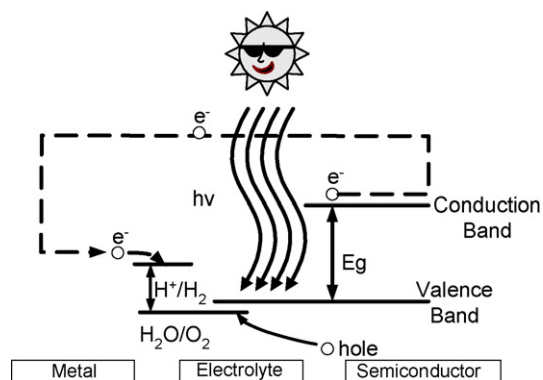


Fig. 9. Energetic diagram of n-type semiconductor photoelectrochemical cells.

electrolyte, but instead of generating an electric current, water is split to form hydrogen and oxygen (Fig. 9) [5,159,165,186]. The process can be summarized for a *photoanode-based* system as follows: (1) a photon with greater energy than the bandgap strikes the anode creating an electron–hole pair. (2) The holes decompose water at the anode's front surface to form hydrogen ions and gaseous oxygen, while the electrons flow through the back of the anode which is electrically connected to the cathode. (3) The hydrogen ions pass through the electrolyte and react with the electrons at the cathode to form hydrogen gas [5,159,165,186]. (4) The oxygen and hydrogen gasses are separated, for example by the use of a semi-permeable membrane, for processing and storage.

Various materials have been investigated for use in photoelectrodes such as thin-film WO_3 , Fe_2O_3 and TiO_2 , as well as n-GaAs, n-GaN, CdS, and ZnS for the photoanode; and CIGS/Pt, p-InP/Pt, and p-SiC/Pt for the photocathodes [180,187–189]. The materials for the photoelectrodes and the semiconductor substrate determine the performance of the system. The hydrogen production efficiency is generally limited by imperfections in the crystalline structure, bulk and surface properties of the photoelectrodes, the material's resistance to corrosion from the aqueous electrolytes, and the ability to drive the water decomposition reactions [5,159,165,186]. In order to maximize the efficiency of this process, the energetics of the electrochemical reaction must be harmonized with the solar radiation spectrum, which is a non-trivial problem. A mismatch of the solar radiation and materials can produce photo-generated holes that can cause surface oxidations leading to either a blocking layer on the semiconductor surface or corrosion of the electrode via dissolution [5,159,165,186].

Current photoelectrodes used in PEC that are stable in aqueous solutions have a low efficiency for using photons to split water to produce hydrogen. The target efficiency is $>16\%$ solar energy to hydrogen. This encompasses three material-system characteristics necessary for efficient conversion: (i) the band gap should fall in the range sufficient to achieve the energetics for electrolysis and yet allow maximum absorption of the solar spectrum. This is 1.6–2.0 eV for single photoelectrode cells, and 1.6–2.0 eV/0.8–1.2 eV for top/bottom cells in stacked tandem configurations; (ii) have a high quantum yield ($>80\%$) across its absorption band to reach the efficiency necessary for a viable device; (iii) straddle the redox potentials of the H_2 and O_2 half reactions with its conduction and valence band edges, respectively. The efficiency is directly related to the semiconductor band gap (E_g), i.e., the energy difference between bottom of the conduction band and the top of the valence band, as well as the band edge alignments, since the material or device must

have the correct energy to split water. The energetics are determined by the band edges, which must straddle water's redox potential with sufficient margins to account for inherent energy losses. Cost efficient, durable catalysts with appropriate E_g and band edge positions must be developed. To achieve the highest efficiency possible in a tandem configuration, “current matching” of the photoelectrodes must be done. Electron transfer catalysts and other surface enhancements may be used to increase the efficiency of the system. These enhancements can minimize the surface over-potentials in relationship to the water and facilitate the reaction kinetics, decreasing the electric losses in the system. Fundamental research is on-going to understand the mechanisms involved and to discover and/develop appropriate candidate surface catalysts for these systems [5,180,187–198].

In addition to semiconductor devices for photoelectrolysis, it is possible to use suspended metal complexes in solution as the photochemical catalysts [165,199]. Typically, nano-particles of ZnO , Nb_2O_5 and TiO_2 (the material of choice) have been used [165,199]. Two of the most promising dyes are the N3 dye and the Black dye. The N3 dye is cis- $\text{RuL}_2(\text{NCS})_2$ with L standing for 2,2'-bipyridyl-4,4'-dicarboxylic acid [199]. The black dye is (tri)cyanato-2,2'-bipyridyl-4,4'-tricarboxylate $\text{Ru}(\text{II})$ [199]. The advantages of these systems include the use of low cost materials and the potential for high efficiencies [199]. Current research involves overcoming the low light absorption and unsatisfactory stability in time for these systems [5].

4. Conclusion

There is a tremendous amount of research being pursued in the development of hydrogen generation systems. Currently, the most developed and most used technology is the reforming of hydrocarbon fuels. In order to decrease the dependence on fossil fuels, significant development in other hydrogen generation technologies from renewable resources such as biomass and water is being done. Table 6 summarizes the technologies, along with their feedstocks and efficiencies. How the efficiency is calculated depends on the technology. The most mature technologies are reforming and gasification. Electrolysis coupled with renewable energy is near term low emission technology. Longer term technologies include biohydrogen, thermochemical water splitting, and photoelectrolysis. While significant progress has been made in development of these alternative hydrogen production systems, more technical progress and cost reduction needs to occur for them to compete with traditional large scale reforming technologies at this time. However, for smaller scale hydrogen production at distributed facilities the technologies, particularly electrolysis, may be cost competitive. In addition, it is important to note that hydrogen can be produced from a wide variety of feed stocks available almost anywhere. There are many processes under development which will have a minimal environmental impact. Development of these technologies may decrease the world's dependence on fuels that come primarily from unstable regions. An often over-looked impact is that by producing and using hydrogen internal to one's country keeps money and jobs from being exported. The “in house” hydrogen production may increase both national energy and economic security. The ability of hydrogen to be produced from a wide variety of feedstocks and using a wide variety of processes makes it so that every region of the world may be able to produce much of their own energy. It is clear that as the technologies develop and mature, hydrogen may prove to be the most ubiquitous fuel available.

Table 6
Technology summary table

Technology	Feed stock	Efficiency	Maturity	Reference
Steam reforming	Hydrocarbons	70–85% ^a	Commercial	[31]
Partial oxidation	Hydrocarbons	60–75% ^a	Commercial	[31]
Autothermal reforming	Hydrocarbons	60–75% ^a	Near term	[31]
Plasma reforming	Hydrocarbons	9–85% ^b	Long term	[74]
Aqueous phase reforming	Carbohydrates	35–55% ^a	Med. term	[99]
Ammonia reforming	Ammonia	NA	Near term	
Biomass gasification	Biomass	35–50% ^a	Commercial	[9,20,127]
Photolysis	Sunlight + water	0.5% ^c	Long term	[161]
Dark fermentation	Biomass	60–80% ^d	Long term	[9,135]
Photo fermentation	Biomass + sunlight	0.1% ^e	Long term	[9,20]
Microbial electrolysis cells	Biomass + electricity	78% ^f	Long term	[162]
Alkaline electrolyzer	H ₂ O + electricity	50–60% ^g	Commercial	[20,159]
PEM electrolyzer	H ₂ O + electricity	55–70% ^g	Near term	[20,159]
Solid oxide electrolysis cells	H ₂ O + electricity + heat	40–60% ^h	Med. Term	[127]
Thermochemical water splitting	H ₂ O + heat	NA	Long term	
Photoelectrochemical water splitting	H ₂ O + sunlight	12.4% ⁱ	Long term	[159,186]

NA = not available.

^a Thermal efficiency, based on the higher heating values.

^b Based on Eq. (15) and does not include hydrogen purification.

^c Solar to hydrogen via water splitting and does not include hydrogen purification.

^d Percent of 4 mol H₂ per mole glucose theoretical maximum.

^e Solar to hydrogen via organic materials and does not include hydrogen purification.

^f Overall energy efficiency including the applied voltage and energy in the substrate. It does not include hydrogen purification.

^g Lower heating value of hydrogen produced divided by the electrical energy to the electrolysis cell.

^h High temperature electrolysis efficiency is dependent on the temperature the electrolyzer operates at and the efficiency of the thermal energy source. For example, SOEC operating from advanced high temperature nuclear reactors may be able to achieve up to 60% efficiency [127]. If thermal energy input is ignored, efficiencies up to 90% have been reported [127].

ⁱ Solar to hydrogen via water splitting and does not include hydrogen purification.

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