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Review and evaluation of hydrogen production methods for better sustainability

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ABSTRACT

This paper examines various potential methods of hydrogen production using renewable and non-renewable sources and comparatively assesses them for environmental impact, cost, energy efficiency and exergy efficiency. The social cost of carbon concept is also included to present the relations between environmental impacts and economic factors. Some of the potential primary energy sources considered in this study are: electrical, thermal, biochemical, photonic, electro-thermal, photo-electric, and photo-biochemical. The results show that when used as the primary energy source, photonic energy based hydrogen production (e.g., photocatalysis, photoelectrochemical method, and artificial photosynthesis) is more environmentally benign than the other selected methods in terms of emissions. Thermochemical water splitting and hybrid thermochemical cycles (e.g. Cu–Cl, S–I, and Mg–Cl) also provide environmentally attractive results. Both photoelectrochemical method and PV electrolysis are found to be least attractive when production costs and efficiencies are considered. Therefore, increasing both energy and exergy efficiencies and decreasing the costs of hydrogen production from solar based hydrogen production have a potential to bring them forefront as potential options. The energy and exergy efficiency comparisons indicate the advantages of fossil fuel reforming and biomass gasification over other methods. Overall rankings show that hybrid thermochemical cycles are primarily promising candidates to produce hydrogen in an environmentally benign and cost-effective way.

Introduction

One of the major challenges of the twenty first century is keeping up with the growth in global energy demand due to increasing population and rising standards of living. For instance, in 2011, 15 TW–energy was consumed by approximately seven billion people world-wide. By 2050, these numbers are expected to escalate to 30 TW and nine billion people, respectively [1]. Fig. 1 demonstrates world's fuel shares of total primary energy supply (TPES), electricity generation, and the resulting CO_2 emissions. From Fig. 1, it can be seen that 85% of the global energy supply was met by fossil fuels in 2011. However, because of their limited nature and nonhomogeneous distribution, fossil fuels are not expected to keep up with the increase in energy demand. Also, fossil fuel

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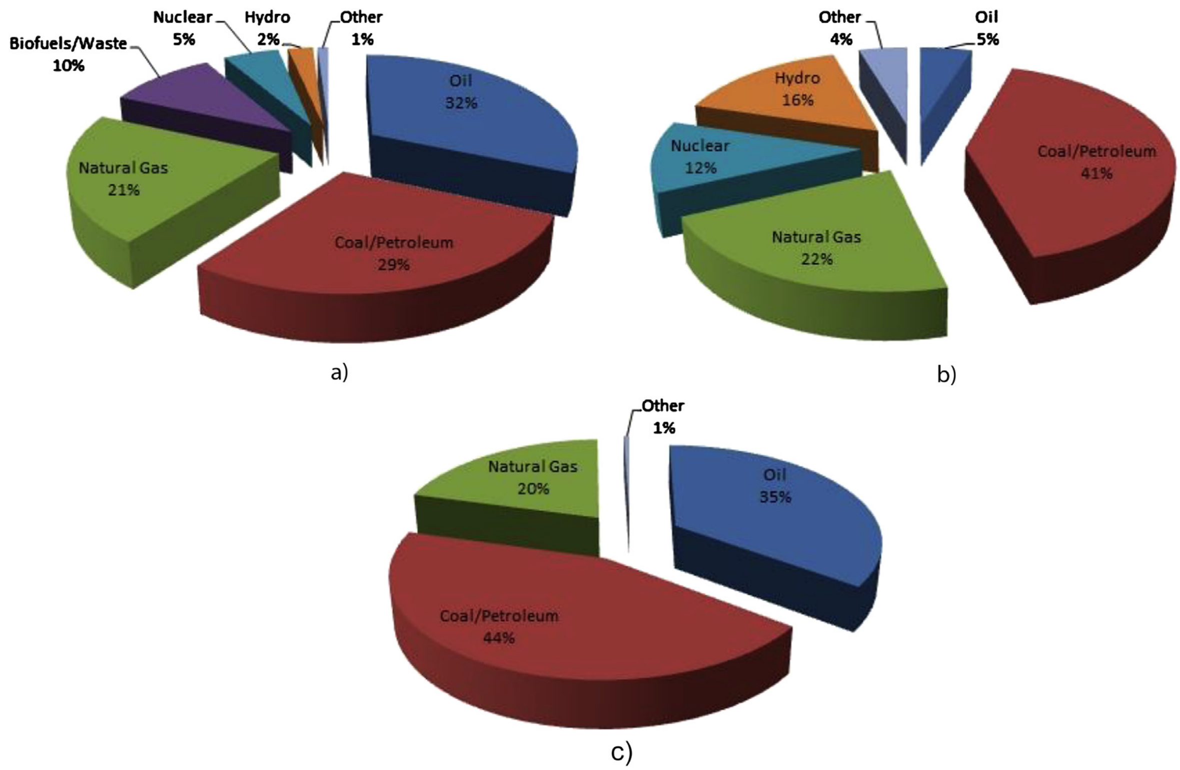

Fig. 1 – World's fuel shares of (a) total primary energy supply (TPES), (b) electricity generation, and (c) CO_2 emissions in 2011 (Other includes geothermal, solar, wind, heat, and waste etc.) (Data from Ref. [1]).

reserves are getting less accessible as the easily-accessible ones are consumed, and the prices of fossil fuels keep increasing due to accessibility loss and political uncertainties of the countries holding worlds' fossil fuel supplies. Along with economic issues, greenhouse gas (mainly CO_2) emissions as a result of fossil fuel utilization, and their contribution to global warming, have been raising serious environmental concerns. Therefore, switching to a non-fossil fuel energy source could greatly reduce the CO_2-related emissions and their adverse effect on global warming.

Reducing the dependence on fossil fuels and minimizing environmentally harmful emissions can be achieved by sustainable energy sources. With near-zero or zero end-use emissions and continually replenished resources, hydrogen can be an ideal sustainable energy carrier. Some of the advantages of hydrogen can be listed as: (i) high energy conversion efficiencies; (ii) production from water with no emissions; (iii) abundance; (iv) different forms of storage (e.g. gaseous, liquid, or in together with metal hydrides); (v) long distance transportation; (vi) ease of conversion to other forms of energy; (vii) higher HHV and LHV than most of the conventional fossil fuels (Table 1). On the other hand, most of the hydrogen production methods are not mature, resulting high production costs and/or low efficiencies [3].

Here, we go further to compare hydrogen with other conventional fuels in terms of Environmental Impact Factor (EIF), Greenization Factor (GF) and Hydrogen Content Factor (HCF) to emphasize the importance of hydrogen as a unique option, through the following equations:

$$EIF = \frac{kg\ CO_2\ product\ of\ combustion\ reaction}{kg\ fuel} \tag{1}$$

$$GF = \frac{EIF_{max} - EIF}{EIF_{max}} \tag{2}$$

$$HCF = \frac{kg\ of\ H_2 in\ the\ fuel}{kg\ fuel} \tag{3}$$

where EIF_{max} is the maximum value of EIF among the evaluated options. In this specific case with 3.6, coal is selected as the EIF_{max}.

As can be seen from Fig. 2, with increasing hydrogen content (HCF), the energy sources become greener (increasing GF) and the environmental impact (EIF) decreases. This is a clear advantage of hydrogen in terms of reducing carbon-related emissions. In order to take full advantage of the hydrogen economy, it needs to be produced from renewable or vast

Table 1 – Higher and lower heating values of hydrogen and common fossil fuels at 25 °C and 1 atm (Data from Ref. [2]).

Fuel	HHV (kJ/g)	LHV (kJ/g)
Hydrogen	141.9	119.9
Methane	55.5	50.0
Gasoline	47.5	44.5
Diesel	44.8	42.5
Methanol	20.0	18.1

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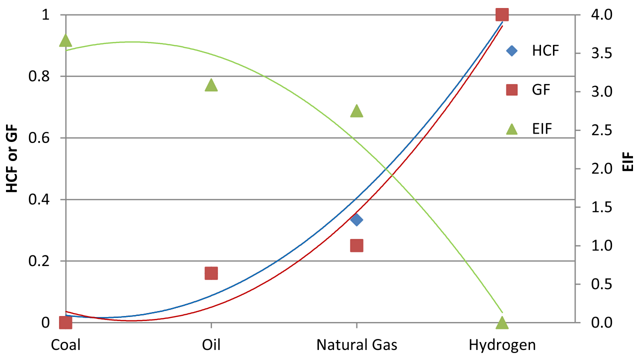

Fig. 2 – Hydrogen Content Factor (HCF), Greenization Factor (GF), and Environmental Impact Factor (EIF) of hydrogen and other fossil fuels.

sources at low costs. In the literature, there are several studies focusing on how hydrogen can be one of the most effective solutions playing a significant role in providing better environment and sustainability i.e.[4–6]. Among the possible hydrogen production methods studied in the literature, natural gas steam reforming is the most commonly used process, resulting heavy GHG emissions. Around 50% of the global hydrogen demand is met by natural gas steam reforming, 30% comes from oil reforming, 18% from coal gasification, 3.9% from water electrolysis, and 0.1% from other sources [7]. In order to remove the adverse effects of fossil fuel utilization on the environment, human health, and the climate, hydrogen should be produced from clean and abundant sources with environmentally benign methods [8,9]. This concept is called as “green hydrogen production”.

Green hydrogen technologies are not quickly accessible with sensible effectiveness and expense. For instance, studies on effectiveness and cost of PV electrolysis for large and small scale hydrogen production show that PV electrolysis is currently expensive (>$5/kg for H_2) and it cannot reach high conversion efficiencies (with energy and exergy efficiencies less than 5%) [10].

Hydrogen production from renewable energy sources and water has previously been studied in the literature by various authors. Analysis of high temperature water dissociation, thermochemical water splitting, water electrolysis, and photolysis has been conducted by Lodhi [11], which is considered as one of the early works. Later, Lodhi [12] classified solar, sea/ocean, hydro, wind, and nuclear energy as green primary sources to produce hydrogen. In Ref. [12], green material sources to generate hydrogen are listed as fresh and sea water, hydrogen sulfide, and biomass. Hydrogen production methods can be classified as “green” based on their primary energy source and/or the material hydrogen is extracted from Ref. [13]. Cost assessment of centralized and distributed hydrogen production and transportation issues (i.e. compression, distribution, and storage) are studied by Lemus and Duart [14].

Hydrogen can also be produced by mimicking photosynthesis reactions. These methods are summarized by Alstrum-Acevedo et al. [15]. Catalytic hydrogen production

Table 2 – Overview of hydrogen production methods by primary energy and material source (Modified from Ref. [2]).

Method			Source: Primary energy	Source: Material	Brief description
M1	Electrolysis		Electrical	Water	Direct current is used to split water into O_2 and H_2 (electrochemical reaction)
M2	Plasma arc decomposition			Fossil fuels	Cleaned natural gas is passed through plasma arc to generate H_2 and carbon soot
M3	Thermolysis		Thermal	Water	Thermal decomposition of water (steam) at temperatures over 2500 K
M4	Thermochemical processes	Water splitting		Water	Cyclical chemical reactions (net reaction: water splitting into H_2)
M5		Biomass conversion		Biomass	Thermocatalytic conversion
M6		Gasification			Conversion of biomass into syngas
M7		Reforming			Conversion of liquid biomass (biofuels) into H_2
M8	PV electrolysis		Photonic	Water	PV panels are used to generate electricity
M9	Photocatalysis				Water is split into H_2 by using the electron-hole pair generated by the photocatalyst
M10	Photoelectrochemical method				A hybrid cell simultaneously produces current and voltage upon absorption of light
M11	Dark fermentation		Biochemical	Biomass	Biological systems are used to generate H_2 in the absence of light
M12	High temperature electrolysis		Electrical + Thermal	Water	Electrical and thermal energy are used together to drive water splitting at high temperatures
M13	Hybrid thermochemical cycles				Electrical and thermal energy are used together to drive cyclical chemical reactions
M14	Coal gasification				Conversion of coal into syngas
M15	Fossil fuel reforming				Fossil fuels are converted to H_2 and CO_2
M16	Biophotolysis		Photonic + Biochemical	Biomass + Water	Biological systems (microbes, bacteria, etc.) are used to generate H_2
M17	Photofermentation				Fermentation process activated by exposure to light
M18	Artificial photosynthesis				Chemically engineered systems mimic photosynthesis to generate H_2
M19	Photoelectrolysis		Electrical + Photonic	Water	Photoelectrodes and external electricity are used to drive water electrolysis

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methods from biomass (i.e. gasification, pyrolysis, and sugar conversion are reviewed by Tanksale et al. [16]. Acar and Dincer [3] presented a comparative cost, environmental impact, and technical assessment of natural gas steam reforming, coal gasification, water electrolysis via wind and solar energies, biomass gasification, thermochemical water splitting with a Cu–Cl and S–I cycles, and high temperature electrolysis.

In this study, a comprehensive classification of hydrogen production methods from renewable and non-renewable sources is presented, and these methods are discussed, assessed and compared. The primary energy sources evaluated in this study are electrical, thermal, photonic, biochemical, electro-thermal, photo-biochemical, and electro-photonic. A total of 19 hydrogen production methods are compared based on energy and exergy efficiencies, production cost, global warming potential (GWP), acidification potential (AP), and social cost of carbon.

Hydrogen production methods

As an abundant element, hydrogen can be found in many substances in nature (i.e. fresh and sea water, biomass, hydrogen sulfide, and fossil fuels). In order to produce hydrogen with zero or low environmental impact ("green" hydrogen), all CO_2 and other pollutants must be processed (i.e. separated or sequestrated) when hydrogen is extracted from fossil fuels. Thermal, electrical, photonic, and biochemical energy are the primary energy sources to generate hydrogen.

Table 2 shows an overview and brief description of hydrogen production methods assessed in this study along with their primary energy and material sources. The electrical and thermal energy can be generated from fossil fuels (has to be processed to be considered as "clean"), renewable energies (i.e. solar, wind, hydro, wave, ocean, and thermal), biomass, nuclear, or recovered energy. The photonic energy comes from solar irradiation, while biochemical energy is recovered from organic matter. In addition to four major primary sources listed in Table 2 (electrical, thermal, biochemical, and photonic), there are also hybrid forms of energy such as electrical-thermal, photonic-biochemical, and electrical-photonic. Water, biomass, and fossil fuels are the material sources evaluated in this study. As mentioned before, in cases where fossil fuel is utilized, hydrogen production process includes CO_2 separation and sequestration.

Electrolysis

Currently the most basic industrial process for almost pure hydrogen production is water electrolysis, and its significance is expected to increase in the future. Water electrolysis is based on the movement of electrons which are supported by an external circuit. Alkaline, polymer membrane, and solid oxide electrolyzers are the key electrochemical hydrogen production technologies. Table 3 summarizes the typical specifications of alkaline, polymer membrane (PEM), and solid oxide electrolyzers (SOE). Of the parameters listed in Table 3, efficiency and the current density are the most important parameters. Efficiency of an electrolysis cell is calculated based on the ideal and actual energies needed to drive the reaction.

Catalysts are used in order to increase current density and rate of electrolysis reactions. Platinum is one of the most commonly used heterogeneous catalysts – applied to the surface of the electrodes. Homogeneous catalysts can also be used during electrolysis. Due to their high turnover rates, homogeneous catalysts are less expensive than the heterogeneous ones. In the literature, there are some homogeneous catalysts with turnover rates of 2.4 mol of hydrogen per mole of catalyst and second [18].

Since electrolyzers (especially PEM electrolyzers) are highly sensitive to the purity of water, desalination and demineralization must be applied before electrolysis process. For instance, if brine (or sea water) is supplied to an electrolyzer, it is more likely to produce chlorine rather than oxygen. There are several methods available in the literature to stop side reactions (like chlorine evolving reaction) during electrolysis; one of them is utilization of ion-selective membranes to desalinate water. This method is proposed by El-Bassuoni et al. [19]. When used as a catalyst, magnesium supports oxygen evolution reaction instead of chlorine generation [20].

Plasma arc decomposition

Plasma is an ionized state of matter which contains electrons in an excited state and atomic species. Plasma has a potential to be used as medium for high voltage electric current release due to the presence of electrically charged particles. Natural gas (mostly methane) dissociates to hydrogen and carbon black (soot) as a result of thermal plasma activity. Carbon black is in solid phase which remains at the bottom while hydrogen is collected in gas phase. The decomposition reaction of methane to hydrogen and carbon is written as

$$CH_4 \rightarrow C_{(s)} + 2H_{2_{(g)}}, \quad \Delta H = 74.6\ MJ/kmol \tag{4}$$

Reaction (1) is studied by Fulcheri et al. [21]; their thermal plasma reactor has 3 electrodes connected to a 3 phase

Table 3 – Typical specifications of alkaline, polymer membrane (PEM), and solid oxide electrolyzers (SOE) (Data from Ref. [17]).

Specification	Alkaline	PEM	SOE
Technology maturity	State of the art	Demonstration	R&D
Cell temperature, °C	60–80	50–80	900–1000
Cell pressure, bar	<30	<30	<30
Current density, A/cm^2	0.2–0.4	0.6–2.0	0.3–1.0
Cell voltage, V	1.8–2.4	1.8–2.2	0.95–1.3
Power density, W/cm^2	Up to 1.0	Up to 4.4	–
Voltage efficiency, %	62–82	67–82	81–86
Specific system energy consumption, kWh/Nm^3	4.5–7.0	4.5–7.5	2.5–3.5
Hydrogen production, Nm^3/hr	<760	<30	–
Stack lifetime, hr	<90,000	<20,000	<40,000
System lifetime, yr	20–30	10–20	–
Hydrogen purity, %	>99.8	99.999	–
Cold start up time, min	15	<15	>60

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voltage. Plasma gas is introduced to 2 of the 3 electrodes and methane is inserted from the top of the reactor. Their results show a 100% pure hydrogen production with zero CO_2 emissions (solid state carbon black remains at the bottom of the reactor). Plasma arc decomposition can be classified as "high temperature pyrolysis". Gaudernack and Lynum [22] states that plasma cracking has a potential to reduce hydrogen production cost by at least 5%, compared to large scale steam methane reforming with carbon dioxide sequestration.

Water thermolysis

Water thermolysis, also known as single step thermal dissociation of water, reaction can be written as

$$H_2O \xrightarrow{heat} H_2 + \frac{1}{2}O_2 \tag{5}$$

In order to accomplish a reasonable degree of dissociation, the reaction requires a heat source which could provide temperatures above 2500 K. For instance, at 3000 K and 1 bar, the degree of dissociation is 64%. One of the challenges of this production method is the separation of H_2 and O_2. The existing semi-permeable membranes can be used at temperatures up to 2500 K. Therefore, the mixture needs to be cooled down before being sent to the separation process. The experimental solar thermolysis of water study conducted by Baykara [23] achieve 90% of the equilibrium at a residence time of 1 ms and temperature of 2500 K. The results also show that if the product gases are rapidly cooled to 1500–2000 K (in few milliseconds); recombination of H_2 and O_2 can be avoided by effective hydrogen separation with the use of palladium membranes.

Thermochemical water splitting

Thermochemical water splitting cycles have a major advantage of not requiring catalysis to drive the individual chemical reactions. Except water, which is the material source of hydrogen production, all chemicals used in the thermochemical cycle can be recycled. Other advantages of thermochemical water splitting cycles can be listed as: (i) no need for O_2–H_2 separation membranes, (ii) reasonable temperature requirement range of 600–1200 K, and (iii) zero or low electrical energy requirement.

Balta et al. [24] summarized the review articles on thermochemical water splitting available in the literature. Being fully developed and demonstrated in Japan and the US, the S–I cycle are considered as technically viable. On the other hand, the commercial viability of these cycles needs to be proven. The first reaction of S–I cycles is thermally driven and it can be written as.

$$H_2SO_{4_{(aq)}} \xrightarrow{heat\ (300-500^\circ C)} H_2O_{(g)} + SO_{3_{(g)}} \tag{6}$$

The product gases (H_2O and SO_3) are separated heated up to 800–900 °C. Then SO_3 gas is decomposed thermally according to:

$$SO_{3_{(g)}} \xrightarrow{heat\ (800-900^\circ C)} \frac{1}{2}O_{2_{(g)}} + SO_{2_{(g)}} \tag{7}$$

After separation from O_2, SO_2 undergoes an exothermic reaction with iodine and water which occurs at low temperatures spontaneously:

$$SO_{2_{(g)}} + I_{2_{(g)}} + 2H_2O_{(l)} \rightarrow 2HI_{(g)} + H_2SO_{4_{(aq)}} \tag{8}$$

Lastly, HI thermally decomposes into H_2 at temperatures around 425–450 °C:

$$2HI_{(g)} \xrightarrow{heat\ (425-450^\circ C)} H_{2_{(g)}} + I_{2_{(g)}} \tag{9}$$

Since there are no side reactions happening during S–I cycle, it is reasonably straightforward to separate and reuse the chemicals used in Reactions (3)–(6). Because of the relatively high reaction temperature requirements of S–I cycles, there are not many sustainable thermal energy sources available to drive the individual reactions in the cycle. Nuclear, concentrated solar, and biomass combustion heat can be listed as possible sustainable thermal energy sources to drive the S–I cycle reactions. In the hybrid version of S–I cycles, hydrogen generating reaction is supported electrochemically.

Thermochemical conversion of biomass, gasification, and biofuel reforming

When using biomass to extract hydrogen, the moisture content should be kept below a certain level by drying or supercritical steam gasification. Some of the examples of biomass are wood sawdust and sugar cane. The general biomass conversion is:

$$\alpha C_lH_mO_n + \beta H_2O \xrightarrow{heat} aH_2 + bCO + cCO_2 + dCH_4 + eC + f\mathrm{Tar} \tag{10}$$

where $C_lH_mO_n$ is the general chemical symbol of the biomass. Tar is the undesired product of this reaction since it has adverse effect on the process (i.e. slugging and fouling). There are numerous catalysts used to control, minimize, and prevent the formation of tar as a result of Reaction 7.

In order to produce hydrogen, solid biomass undergoes the following gasification reaction:

$$C_xH_y + xH_2O \xrightarrow{high\ temperature\ heat} \left(\frac{y}{2} + x\right)H_2 + xCO \tag{11}$$

In this regard, fixed bed, moveable bed and fluidized bed are treated as the common types of gasifiers used in the gasification process. Based on the amount of provided heat, the process is called either autothermal or thermal. In autothermal gasification, the required heat is provided by the partial oxidation in the gasifier. Hydrogen production from liquid biofuels (i.e. ethanol and methanol) occurs via thermochemical processes.

PV electrolysis, photocatalysis, and photoelectrochemical method

PV based electrolysis process includes photovoltaic (PV) panels, DC bus bar, AC grid, accumulator battery set, electrolyzer and hydrogen storage canisters. PV based electrolysis is one of the most expensive hydrogen production methods; with current technology, the cost of hydrogen from PV electrolysis is about 25 times higher than that of fossil fuel alternatives.

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However, the cost of this process has been continuously decreasing and this factor is estimated to go down to 6 [25].

The photocatalysis converts photonic energy (comes from solar irradiation) to chemical energy (hydrogen). The energy carried by the photon is proportional to the frequency of the radiation and given by hν where h is the Planck constant and ν is the frequency. When a photon hits the photocatalyst, an electron-hole pair is generated and the obtained electrical charge is utilized to dissociate water. In order for a photocatalyst to split water and generate hydrogen, it should have an appropriate band gap and properly located conduction and valance bands for oxidation/reduction reactions. Furthermore, rapid generation and separation of electron-hole pairs is essential when picking an appropriate photocatalyst. In the literature, semiconductors (i.e. TiO_2) and metal oxides (i.e. Fe_2O_3) are heavily studied as photocatalysts. Also, chemically modified and engineered complex supramolecular devices are utilized to perform photocatalytic reactions. Acar et al. [26] reviewed and assessed various simple and complex photocatalysts based on their H_2 production yield, efficiency, and impact on human health and the environment. The photoreduction and photo oxidation reactions can be written as.

$$\text{Photo}-\text{reduction}: \ 2H_2O + 2e^- \xrightarrow{h\nu} H_2 + 2OH^- \tag{12}$$

$$\text{Photo}-\text{oxidation}: \ 2H_2O \xrightarrow{h\nu} O_2 + 4H^+ + 4e^- \tag{13}$$

Here, photoelectrochemical cells (PEC) convert solar energy to an energy carrier via light stimulated electrochemical processes. In a PEC, solar light is absorbed by one or both of the photoelectrodes and at least one of them is a semiconductor. PECs can produce either chemical or electrical energy. They are also used to treat hazardous aqueous wastes [27]. The working principle of the semiconductor in a PEC is similar to a PV cell. In both cases, photons with higher energy than the band gap generate electron-hole pairs and this electric field is used to oxidize/reduce water. PEC systems combine solar energy absorption and water electrolysis into a single unit. This is a clear advantage of PEC because they do not require a separate power generator such as a PV cell and therefore they are more compact. There are many kinds of photosensitive semiconductors investigated in the literature. The most promising option so far is agreed to be TiO_2. In addition to TiO_2, several other semiconductors have been studied, such as, ZnO, Fe_2O_3, $BiVO_4$, and WO_3. Metal nitrides and phosphides (i.e. Ta_3N_5 and GaP), metal oxynitrides (i.e. TaON), and n- and p-type silicon have also been investigated in the open literature. Rabbani et al. [28] coupled PEC with chloralkali cells and tested the system in batch type. Acar and Dincer [29] combined and enhanced the studies on PEC and chloralkali reactors in a continuous type hybrid system.

Dark fermentation

Biochemical energy, which is stored in organic matter, can be used by living creatures to extract hydrogen in the absence or presence of light. Dark fermentation is the conversion of biochemical energy stored in organic matter to other forms of energy in the absence of light (this case might happen when there is reduced supply of light). The bioreactors used for dark fermentation are simpler and cheaper compared to photofermentation since the process does not require solar input processing. Hydrogen production by dark fermentation has several other advantages such as the ability to produce hydrogen from organic waste and therefore control and stabilize biological waste which has a potential danger of contamination. For instance, dark fermentation can be integrated into wastewater treatment systems to produce H_2 from wastewater. Producing hydrogen from organic waste has a potential to reduce hydrogen production costs since organic waste (including wastewater) is cheap and easily available. Hydrogen production from water diluted olive oil by study by Koutrouli et al. [30] show a maximum 640 g of H_2 per tonne of olive pulp. A hydrogen production yield of around 77 g H_2 per kg of glucose is reported by Das and Veziroglu [31]. Low production capacity per unit of (production facility) capital investment is one of the major challenges of anaerobic digestion. Some of the advantages and disadvantages of dark fermentation compared to biophotolysis and photofermentation as well as the future prospects of these methods are listed in Table 4.

High temperature electrolysis

High temperature electrolysis is a method of electrolysis where steam is dissociated to H_2 and O_2 at temperatures between 700 and 1000 °C. This method is generally considered as more efficient than conventional room temperature electrolysis (efficiency increases with increasing temperature). In high temperature electrolysis, water is converted to steam by using thermal energy. The system components are either heated directly by the steam supply or indirectly by heat transfer. Thus the electrical energy need of this type of electrolysis is lower than that of conventional electrolysis methods. Another advantage of this method is the possibility of achieving zero greenhouse gas emissions when a clean heat source (i.e. solar, geothermal, and/or nuclear) is used as external heat source. However, due to high operating temperatures, the system components have to meet specific requirements for an efficient hydrogen generation. Current challenges of high temperature electrolysis can be listed as (i) chemically stable electrolyte development with high ionic and low electronic conductivity, (ii) porous, chemically stable electrode research in highly reducing/oxidizing environments with good electronic conductivity and coefficient of thermal expansion similar to the electrolyte, and (iii) engineering chemically stable materials at high temperatures and highly reducing/oxidizing environments.

Hybrid thermochemical cycles

Hybrid thermochemical cycles operate at lower temperatures compared to thermally driven water splitting cycles mentioned in Thermochemical Water Splitting. External energy needs of the individual electrochemical reactions are met by thermal and electrical energies. Since hybrid cycles operate at lower temperatures, other sustainable thermal sources apart from solar, high temperature nuclear and biomass combustion (such as recovered waste heat from nuclear and

Table 4 – Comparison of dark fermentation to biophotolysis and dark fermentation (Modified from Ref. [32]).

Process	Advantages	Disadvantages	Future prospects
Biophotolysis	Abundant supply (water)	Separation of H_2 and O_2	Near term incremental improvements possible
	Carbon independent pathway	Low conversion efficiencies	Immobilization might bring some improvement
	Only products are H_2 and O_2	Large surface area requirement	Materials science breakthrough
Photofermentation	Readily available waste streams as suply	Low volumetric production rate	Metabolic engineering is required
	Nearly complete substrate conversion	Low conversion efficiencies	Near term incremental improvements possible
		Large surface area requirement	Materials science breakthrough
Dark fermantation	Can use a variety of waste streams	Large amounts of byproducts	Metabolic engineering is required
	Simple reactor technology	Reactor-to-reactor variation	Two stage systems can extract additional energy, decrease COD
	Higher production rates	Low COD removal	

geothermal facilities) can be used to drive the involved processes.

Cu–Cl cycle is proposed as an outstanding hybrid cycle as investigated in the literature. The operating temperature of this cycle does not exceed 550 °C. Among different types of Cu–Cl cycles, "five-step" version is the most studied one. This version is composed of three thermally driven chemical reactions, one electrochemical reaction, and one physical drying step. In Cu–Cl cycles, the thermal energy source is used partially to drive the cycle directly and partially to generate the required electricity. The major advantage of Cu–Cl cycles is hydrogen generation from low grade temperature sources, especially those which can be considered as sustainable thermal energy. Nuclear heat, industrial heat, waste heat recovered from power plants, concentrated solar heat, heat resulting from municipal waste incineration, and geothermal heat can be listed as sustainable thermal energy sources.

Coal gasification

With current state of technology and worldwide coal reserves, coal is an economical and technically practical option to produce hydrogen in large scale plants. Compared to the existing methods (i.e. electrolysis), gasification is more suitable for converting coal to hydrogen. In gasification, coal is partially oxidized with steam and O_2 in a high-temperature and high-pressure reactor and the products are mainly H_2, CO, mixed with steam and CO_2 (syngas). This syngas goes through a shift reaction in order to increase the hydrogen yield. The gas product can be processed and cleaned in cases where there is a need to recover elemental sulfur or sulfuric acid. Some of the syngas can further be processed and used in gas turbines to generate electricity. Despite some advantages of coal gasification, due to high carbon content of coal, this method causes higher CO_2 emissions compared to other available hydrogen production technologies. Carbon capture and storage technologies are currently developed in order to address this issue. At present, hydrogen production cost of coal gasification is slightly higher than that of natural gas steam reforming. However, coal gasification techniques are less well-defined than those used in the steam reforming of natural gas. In terms of economics, making hydrogen from coal differs from other fossil fuels: the unit raw material costs are lower while the unit capital costs are higher for the coal gasification plants [33].

Fossil fuel reforming

Steam reforming, partial oxidation, and autothermal reforming are three main fossil fuel reforming technologies to produce hydrogen. The advantages and challenges of each of these processes are listed in Table 5. In addition to H_2, CO and CO_2 are emitted in the end of a reforming process. Steam reforming generally requires an external heat source but it does not demand oxygen to drive the process. It has a lower operating temperature and higher H_2/CO ratio than partial oxidation and autothermal reforming. In partial oxidation, hydrocarbons are partially oxidized with oxygen to produce hydrogen. The source of heat to drive this process is derived from the partial oxidation (combustion) reaction. There is no

Table 5 – Summary of fossil fuel reforming technologies (Modified from Ref. [34]).

Technology	Advantages	Disadvantages
Steam reforming	Most developed industrial process No oxygen requirement Lowest operating temperature Best H_2/CO ratio	Highest air emissions
Autothermal reforming	Lower process temperature than partial oxidation Low methane slip	Limited commercial experience Air/oxygen requirement
Partial oxidation	Reduced desulfurization requirement No catalyst requirement Low methane slip	Low H_2/CO ratio High operating temperatures Complex handling process

catalyst requirement in partial oxidation and it is more sulfur tolerant compared to steam and autothermal reforming. The pressure requirement of autothermal reforming is lower than partial oxidation. Autothermal reforming and partial oxidation do not need an external heat source. However, both of these processes require pure oxygen feed which increases complexity and cost with the addition of oxygen separation units. Compared to other fossil fuel reforming technologies, steam reforming (particularly steam methane reforming) is the least expensive and most common method to produce hydrogen.

Biophotolysis and photofermentation

Biophotolysis and photofermentation are photonic-driven biochemical hydrogen production processes from water. Kotay and Das [35] categorizes hydrogen production via biophotolysis into direct, indirect, and photofermentation. In biophotolysis, some light-sensitive microorganisms are used as biological converters in a specially designed photobioreactor. Among possible microorganisms, the most suitable ones are microalgae since they can be cultured and have a potential to generate hydrogen in closed systems which permits hydrogen capture. Cultured micro-algal strains show high hydrogen yields. The major advantage of biophotolysis is the ability to produce hydrogen from water in an aqueous environment at standard temperature and pressure. However, it is only demonstrated at laboratory scale and not yet fully developed for commercial use. The general hydrogen generation reactions with the help of photo-activated enzymes are:

$$6H_2O + 6CO_2 \xrightarrow{h\nu} C_6H_{12}O_6 + 6O_2 \tag{14}$$

$$C_6H_{12}O_6 + 6H_2O \xrightarrow{h\nu} 6CO_2 + 12H_2 \tag{15}$$

Artificial photosynthesis

Artificial photosynthesis is a bio-mimetic process mimicking the natural photosynthesis process to accomplish the following:

- PV-based electricity generation: to support the grid system.
- Dry agriculture: with this method, carbohydrates (food), liquid fuels, chemical feed stocks, and polymers for fiber manufacture can be produced with near or absolute chemical minimum water usage. This amount is thousands of times lower than the conventional agriculture water usage. The system has an enzyme bed reactor system which fixes CO_2 from the air (or other convenient sources) and it is powered by hydrogen and bioelectric transducers.
- Hydrogen production: electrolytic decomposition of water into H_2 and O_2 can be achieved by mimicking photosynthesis.

Although the technology is not mature enough to be applied to large scale manufacturing, artificial photosynthesis has a significant potential to lower global water usage and support clean energy systems by generating electricity and hydrogen from photonic energy.

Photoelectrolysis

The process where heterogeneous photocatalysts is applied on one or both of the electrodes is called photoelectrolysis. In addition to solar irradiation exposure, the electrolysis cell should be supported by electrical energy to conduct photoelectrolysis. Therefore, in photoelectrolysis, both photonic and electrical energies are converted to chemical energy (hydrogen). The photoelectrolytic hydrogen production mechanism includes the following steps: (i) generation of an electron-hole pair with the help of a photon that has sufficiently high energy (higher than the band gap of the p–n junction), (ii) flow of electrons from the anode to the cathode generating electricity current, (iii) decomposition of water into hydrogen ions and gaseous oxygen, (iv) reduction of hydrogen ions at the cathode to form hydrogen in gas form, (v) separation of the product gases, processing, and storage. The performance of a photoelectrolytic system depends on the type of photon absorbing material, their crystalline structure, surface properties, corrosion resistance, and reactivity. There usually is a trade–off between photoelectrode stability and photon energy–to hydrogen conversion efficiency: the high efficiency photoelectrodes generally have poor stability in electrolytes while the chemically stable photoelectrodes show poor water splitting efficiencies.

Summary

Key benefits, major R&D needs, and critical challenges of selected hydrogen production technologies are listed in Table 6. Given the current state of technology, natural gas based hydrogen production in large industrial plants seems to be the cheapest method available. In energy services industry,

Table 6 – Key benefits and critical challenges of selected hydrogen production methods. (Modified from Ref. [36]).

Fossil fuel reforming	Biofuel reforming	Coal and biomass gasification	Thermochemical method	Water electrolysis	Photoelectrochemical method	Biological method
Critical challenges						
High capital costs	High capital costs	High reactor costs	Cost effective reactor	Low system efficiency	Effective photocatalytic material	Efficient microorganisms for sustainable production
Design	High operation and maintenance costs	System efficiency	Long-term technology	High capital costs	Low system efficiency	Optimal microorganism functionality
High operation and maintenance costs	Design	Feedstock impurities	Effective and durable materials	System integration	Cost effective reactor	Reactor material selection
	Feedstock quality	Carbon capture and storage		Design issues	Long-term technology	Long-term technology
Major R&D Needs						
Efficiency and cost	Hydrogen yield and efficiency	Low cost and efficient purification	Robust, low cost materials	Durable and cheap materials	Durable and efficient photocatalyst	Microorganism functionality
Low cost and efficient purification	Low temperature production	Co-fed gasifiers	Ease of manufacture and application	Corrosive-resistant membranes	Low cost materials	New organisms
Feedstock pre-treatment	Low cost and efficient purification	Carbon capture and storage	System optimization	Durable, active, and cheap catalysts	Active, stable, and cheap supporting materials	Inexpensive methods
Optimization	Optimization	Hydrogen quality	High volume, low cost, flexible system design	Large scale applications	High volume production	Low cost and durable material
Automated process control	Regional best feedstock	Cost of feedstock preparation	Efficient heat transfer	Storage and production rate	System control	System optimization
Reliability	Feedstock pre-treatment	Tolerance for impurities	Reliability	Reliability	Power losses	High capacity and low cost systems
Key benefits						
Most viable approach	Viability	Low cost syngas production	Clean and sustainable	No pollution with renewable energy sources	Low operation temperature	Clean and sustainable
Lowest current cost	Existing infrastructure	Abundant and cheap feedstock	Recycled chemicals	Existing infrastructure	Clean and sustainable	Tolerant of diverse water conditions
Existing infrastructure				Integration with fuel cells		Self sustaining

secured supply is an important criterion which should be addressed by the hydrogen economy as well. Optimizing capital, operating and maintenance costs as well as developing systems with high efficiencies, low impurity levels, and emissions, and increasing the role of renewable energies are some of the critical challenges of the hydrogen economy.

In the end, in order to be able to move to a sustainable and clean energy supply, hydrogen should be produced from clean energy sources instead of fossil fuels. Production quantity, efficiency, cost, system reliability and environmental impact are some of the major concerns of hydrogen energy research. It is now widely accepted that carbon-free society is not possible without hydrogen economy. This study reviews and assesses current efforts to produce hydrogen with minimum cost, environmental and social impact as well as maximum efficiency. These efforts are to help address adverse effects of excessive fossil fuel utilization and any energy crisis that might happen in the near future with green solutions.

Comparative assessment of hydrogen production methods

Environmental impact comparison

CO_2 emissions are considered as the primary GHG sources due to their adverse impact on the environment and human health. Currently there are some methods available to mitigate the CO_2 emissions such as Carbon Capture and Sequestration (CCS), managing CO_2 as waste or a commodity in another industry, etc. Further information on CO_2 emissions and how to minimize them can be found in Refs. [37,38]. Switching to a carbon neutral economy with secured energy supply is one of the most heavily studied research topics in the literature. When produced from clean and sustainable energy sources and renewable materials, hydrogen has a potential to significantly decrease CO_2 emissions.

In order to fully understand and assess CO_2 emissions of a process, a life cycle assessment (LCA) should be conducted. LCA procedures according to ISO standards are published by the Center of Environmental Science of Leiden University as "Operational Guide to the ISO Standards" [39]. The environmental impact categories used to assess the selected hydrogen production methods in this study are based on this operational guide. Global warming potential (GWP) and acidification potential (AP) are used to evaluate the environmental impact of selected hydrogen production methods. GWP (kg CO_2 eq.) is a measure of CO_2 emissions. AP (g SO_2 eq.) indicates SO_2 discharge on soil and into water and measures the change in degree of acidity [40].

In this study, the GWP and AP LCA results published by Bhandari et al. [17] and Ozbilen et al. [41] are used as the basis of environmental impact comparison. Life cycle assessment generally has four main phases: (i) goal and scope definition to specify intention, application and stakeholders, (ii) the life cycle inventory data collection phase on material and energy flows during the life cycle – during this phase, emissions and consumed resources are identified and quantified, (iii) life cycle impact assessment (LCIA), builds on the inventory results by assessing the environmental significance of each, and (iv) LCIA results are evaluated and recommendations to reduce environmental impacts of products are discussed. The environmental impact results of selected hydrogen production methods, in terms of GWP and AP, are presented in Fig. 3. The fossil fuel based hydrogen production methods (coal gasification, fossil fuel reforming, and plasma arc decomposition) are seen to be most environmentally harmful methods. Although it has relatively low GWP, the AP of biomass gasification is the highest compared to the other selected methods. From Fig. 3, it can also be seen photonic energy and hybrid thermochemical cycle based hydrogen production are the most environmentally benign of the selected methods, in terms of CO_2 emissions and acidification potentials.

Social cost of carbon comparison

It is common knowledge that CO_2 emissions cause environmental damages and adverse effect on human health. The

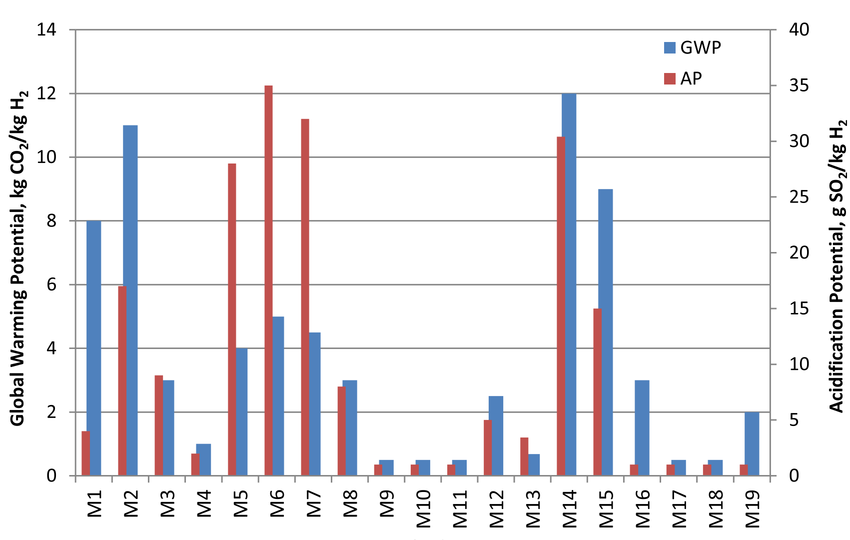

Fig. 3 – GWP and AP of selected hydrogen production methods (per kg of hydrogen).

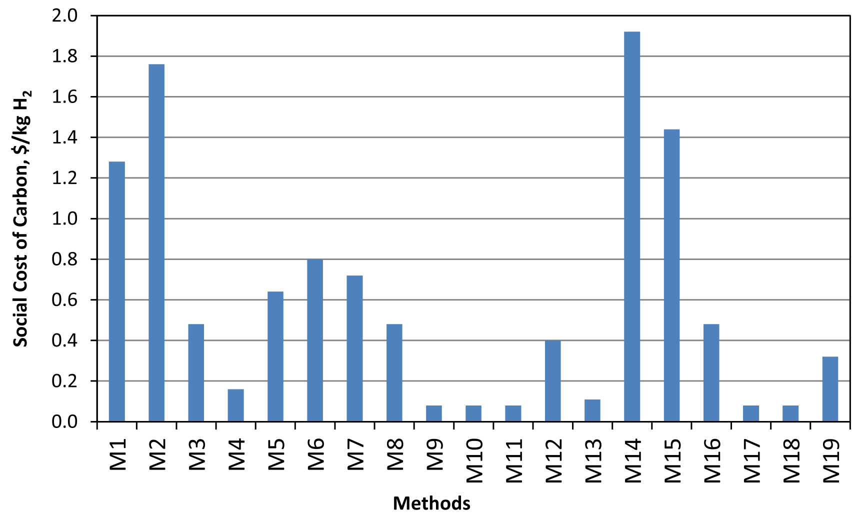

Fig. 4 – SCC of selected hydrogen production methods (per kg of hydrogen).

marginal external cost of a unit of CO_2 emissions is identified as social cost of carbon (SCC). SCC values are estimated by using an integrated assessment (IAM) framework. This framework uses a baseline socio-economic scenario, a model that identifies the relationship between emissions and temperature change, and a function to relate this temperature change to economic damages.

First step of social cost of carbon estimation is to define the reference socio-economic scenarios which are characterized by population, emissions, and production rate of the assessed technology. Climate change effect is calculated based on greenhouse gas concentrations and temperature variations. These variations from the baseline scenario and their impact on the economy are taken as the basis of SCC calculations. Next, the baseline scenarios are marginally perturbed by the addition or removal of a marginal unit of CO_2 emissions. Social welfare, which depends upon consumption and the choice of discounting parameters, is calculated for each baseline and marginally perturbed scenario. The normalized difference in expected welfare between the baseline and perturbed scenarios gives the social cost of carbon (SCC) [42].

In this study, the SCC of selected hydrogen production methods is calculated based on the results published by Parry et al. [43]. An average of $160 per tonne of CO_2 emissions is used to estimate the SCC of each hydrogen production method. Fig. 4 presents the SCC results of the selected hydrogen production methods. The results show that photonic energy and hybrid thermochemical cycle based hydrogen production are the most beneficial processes. Fossil fuel based hydrogen production methods (coal gasification, fossil fuel reforming, and plasma arc decomposition) are seen to be the most harmful ones.

Financial comparison

When it comes to calculating the cost of hydrogen production, there are several uncertainties since the cost is strongly affected by the production technology's advancement level, availability of existing infrastructure, and the feedstock prices.

The literature survey results of average hydrogen production costs (per kg of hydrogen) are presented in Fig. 5. Among

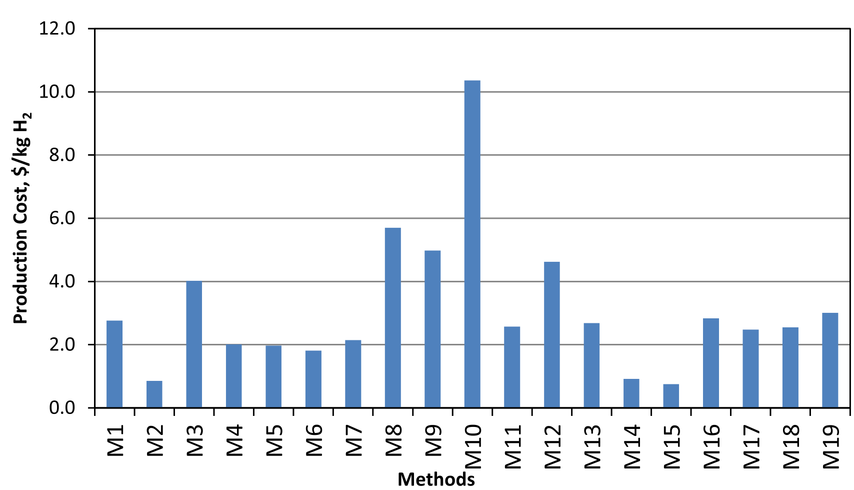

Fig. 5 – Production cost of selected hydrogen production methods (per kg of hydrogen).

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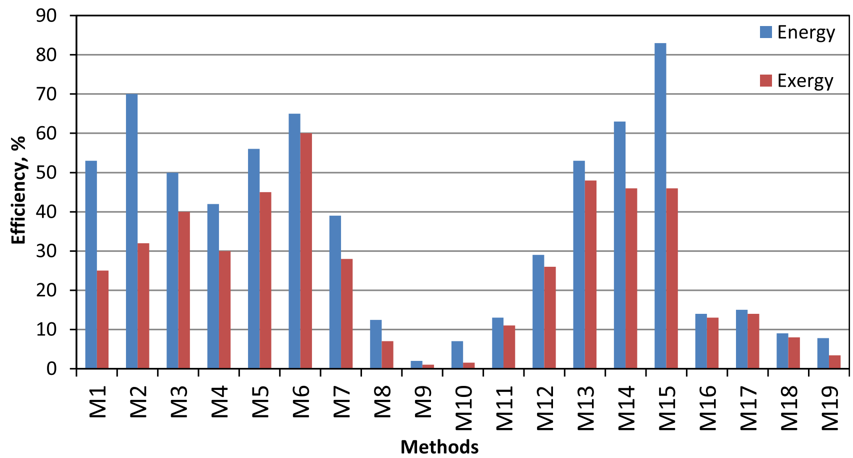

Fig. 6 – Energy and exergy efficiencies of selected hydrogen production methods.

the selected methods, hydrogen production cost of water electrolysis, thermochemical water splitting, biomass gasification, photocatalysis, coal gasification, and fossil fuel reforming are taken from Parthasarathy and Narayanan [44]. Plasma arc decomposition, thermochemical biomass conversion and reforming, dark fermentation, biophotolysis, photofermentation, artificial photosynthesis, and photoelectrolysis cost data is compiled from Uddina et al. [45]. Thermolysis, PV electrolysis, high temperature electrolysis, and hybrid thermochemical cycles' hydrogen production cost data are obtained from Ngoha and Njomo [46]. And the hydrogen production cost of photoelectrochemical method is attained from Trainham et al. [47]. According Fig. 5, the most financially advantageous methods for hydrogen production are steam methane reforming, coal and biomass gasification, and plasma arc decomposition. Thermochemical cycles and biomass conversion, as well as hybrid thermochemical cycles also seem to be competitive to fossil fuel and biomass prices. It should be noted that in this study the average of production costs are taken from the literature. Photoelectrochemical systems give the highest production cost per kg of hydrogen. However, this method is in early R&D phase and one of the major advantages of this method is its local applications. Therefore, the production costs related to PEC operation are expected to decrease in the future as PEC systems technology gets more advanced [47].

Energy and exergy efficiencies comparison

Efficiency is defined as useful output by consumed input. Energy efficiency of a hydrogen production method can be calculated as.

$$\eta = \frac{\dot{m} LHW_{H_2}}{\dot{E}_{in}} \tag{16}$$

where $\dot{m}$ is the mass flow rate of produced hydrogen, LHV is the lower heating value of hydrogen (121 MJ/kg) and $\dot{E}_{in}$ is the rate of energy input to the process. The following equation is used for exergy efficiency:

$$\psi = \frac{\dot{m} ex^{ch}_{H_2}}{\dot{E}x_{in}} \tag{17}$$

Here, $ex^{ch}_{H_2}$ is the chemical exergy of hydrogen and $\dot{E}x_{in}$ is the rate of exergy input into the process. The efficiency data used in this study are taken from Holladay et al. [34], Ismail and Bahnemannc [48], Singh and Wahid [49], Ibrahim et al. [50], Bicakova and Straka [51], and Dincer and Zamfirescu [52]. Fig. 6 presents the energy and exergy efficiency data of selected hydrogen production methods from which it can be seen that fossil fuel reforming, plasma arc decomposition, and coal and biomass gasification are advantageous over other methods. On the other hand, photonic energy based hydrogen production methods show the poorest performance among the selected production methods.

Overall comparison

In this section, the environmental, social, financial, and technical assessment results are normalized in order to compare each method effectively. GWP, AP, SCC and production costs are normalized based on the following equation:

$$Rank\ (Method\ i) = \frac{Maximum - Method\ i}{Maximum} \times 100 \tag{18}$$

The ranking is between 0 and 10, where 0 means poor performance and 10 indicates the ideal case (zero-cost and zero-emissions). Lower costs and emissions are given higher rankings. "0" is assigned to the highest cost and emissions in selected categories. For example, in terms of GWP, coal gasification method gives the highest emissions; therefore, the GWP ranking of coal gasification is assigned to be "0". Efficiencies are normalized based on the following equation:

$$Efficiency\ Rank\ (Method\ i) = Efficiency\ (Method\ i) \times 10 \tag{19}$$

The ranking range is again between 0 and 10, 0 means poor performance and 10 indicate the ideal case (100% efficiency). Higher rankings mean higher efficiencies. The normalized emissions, cost, and efficiency rankings are presented in Table 7. The hypothetical ideal case refers to zero-cost and emissions, which also means zero SCC. The energy and exergy

Table 7 – Overall comparisons of selected hydrogen production methods (Normalized).

Method		Energy efficiency	Exergy efficiency	Cost	SCC	GWP	AP
M1	Electrolysis	5.30	2.50	7.34	3.33	3.33	8.86
M2	Plasma arc decomposition	7.00	3.20	9.18	0.83	0.83	5.14
M3	Thermolysis	5.00	4.00	6.12	7.50	7.50	7.43
M4	Thermochemical water splitting	4.20	3.00	8.06	9.17	9.17	9.43
M5	Biomass conversion	5.60	4.50	8.10	6.67	6.67	2.00
M6	Biomass gasification	6.50	6.00	8.25	5.83	5.83	0.00
M7	Biomass reforming	3.90	2.80	7.93	6.25	6.25	0.86
M8	PV electrolysis	1.24	0.70	4.50	7.50	7.50	7.71
M9	Photocatalysis	0.20	0.10	5.19	9.58	9.58	9.71
M10	Photoelectrochemical method	0.70	0.15	0.00	9.58	9.58	9.71
M11	Dark fermentation	1.30	1.10	7.52	9.58	9.58	9.71
M12	High temperature electrolysis	2.90	2.60	5.54	7.92	7.92	8.57
M13	Hybrid thermochemical cycles	5.30	4.80	7.41	9.43	9.43	9.02
M14	Coal gasification	6.30	4.60	9.11	0.00	0.00	1.31
M15	Fossil fuel reforming	8.30	4.60	9.28	2.50	2.50	5.71
M16	Biophotolysis	1.40	1.30	7.27	7.50	7.50	9.71
M17	Photofermentation	1.50	1.40	7.61	9.58	9.58	9.71
M18	Artificial photosynthesis	0.90	0.80	7.54	9.58	9.58	9.71
M19	Photoelectrolysis	0.78	0.34	7.09	8.33	8.33	9.71
Ideal	(zero-emissions and cost, 100% efficiency)	10.00	10.00	10.00	10.00	10.00	10.00

efficiency of this ideal case is 100%. In terms of energy and exergy efficiency, closest performance to the ideal case is reached by fossil fuel reforming and biomass gasification. However, biomass gasification gives considerably high AP (low AP ranking) compared to other selected methods. SCC rankings of biomass gasification are also low.

Results and discussion

Electrical energy based hydrogen production

In this study, there are two electrical based hydrogen production methods which are electrolysis and plasma arc decomposition. Electrical energy based methods give higher energy and exergy efficiencies compared to thermal and photonic energy based and hybrid hydrogen production methods. In terms of production costs, electrical energy gives competitive results to already mature fossil fuel technologies. However, environmental assessment results show that hydrogen generation via electrical energy causes higher GWP and AP than the other selected methods. The normalized rankings of electrolysis and plasma arc decomposition are presented in Fig. 7. Compared to plasma arc decomposition, electrolysis option gives closer-to-ideal results in terms of GWP, AP, and SCC. This means electrolysis releases less CO_2 and SO_2 and this option has a lower social cost of carbon. On the other hand, plasma arc decomposition has higher energy and exergy efficiencies and lower production costs. Overall, the average of the normalized rankings show that electrolysis gives closer-to-ideal results compared to plasma arc decomposition. There is significant amount of research going on in the field of electrolysis since it has a potential to be coupled to renewable energy sources and produce hydrogen with zero or low emissions. However, this option is still not mature. Developing highly efficient electrolysis technologies will eventually address this issue by lowering hydrogen production costs via electrolysis.

Thermal energy based hydrogen production

Thermolysis, thermochemical water splitting, thermochemical conversion of biomass, gasification, and reforming are the thermal energy based hydrogen production technologies selected in this study. Thermal methods have considerably higher energy and exergy efficiencies, close-to-ideal GWP, SCC, and production costs compared to other selected hydrogen production options. However, these methods, especially biomass gasification, release high amounts of SO_2 (high AP). Among the thermal based production methods, biomass gasification gives the highest energy and exergy efficiencies and lowest cost of production. Thermochemical water splitting gives the lowest GWP, AP, and SCC. Biofuel reforming has the lowest energy and exergy efficiencies.

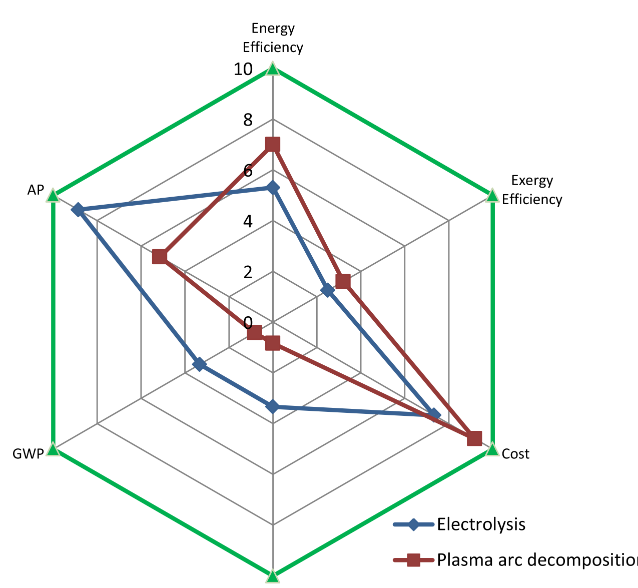

Fig. 7 – Normalized ranking comparison of electrical based hydrogen generation options.

Thermolysis gives the highest cost of production. And the most environmentally harmful thermal energy based hydrogen production among the selected ones is biomass gasification. These results are shown in Fig. 8. Among thermal based hydrogen production methods, thermochemical water splitting gives closest-to-ideal results with highest average normalized rankings and biomass (biofuel) reforming gives the lowest average normalized rankings (Table 7). Thermochemical water splitting has very good AP, GWP, and SCC rankings due to their low emissions. Any improvement that could increase energy and exergy efficiencies of this method would eventually reduce the production costs, bringing this method even closer to an ideal hydrogen production method level with maximized efficiency and minimum emissions and cost possible.

Photonic energy based hydrogen production

The photonic hydrogen production methods selected in this study are: PV electrolysis, photocatalysis, and photoelectrochemical method. Hydrogen generation using solar (photonic) technologies is still in early R&D phase. Therefore, compared to other selected primary energy sources, this option gives lower rankings in terms of energy and exergy efficiencies and production costs. However, photonic based hydrogen production has very low CO_2 and SO_2 emissions and low SCC as well. Therefore, environmental and social impact assessment gives almost ideal case normalized rankings to these methods. Among these options, PV electrolysis gives the highest energy and exergy efficiencies. However, this option also gives the highest CO_2 and SO_2 emissions and SCC. Photocatalysis gives the lowest efficiencies and lowest cost. Photoelectrochemical method is in early R&D phase. However, it gives almost ideal case rankings in terms of emissions and social impact comparison. However, this option by far gives the highest production costs and lower efficiencies. These findings are illustrated in Fig. 9. On average, photocatalysis gives the closest-to-ideal (highest ranking) and PV electrolysis gives the lowest rankings among solar based hydrogen production options.

Hybrid hydrogen production methods

High temperature electrolysis, hybrid thermochemical cycles, biophotolysis, photofermentation, artificial photosynthesis, and photoelectrolysis are the hybrid hydrogen production options evaluated in this study. The hybrid energy sources are electro-thermal, photo-biochemical, and electro-photonic. Compared to electrical, thermal, and photonic only hydrogen production, hybrid methods generate hydrogen in an environmentally benign way. Compared to single primary energy methods, GWP, AP, and SCC rankings of hybrid methods are closer to the ideal case. There is a need to increase energy and exergy efficiencies and lower production costs of these methods to make them technically and financially feasible. In terms of energy and exergy efficiencies, hybrid thermochemical cycles give highest results compared to other hybrid options. Artificial photosynthesis and photoelectrolysis show the lowest efficiencies. Photofermentation gives the lowest production costs and hybrid thermochemical cycles are the most expensive hydrogen production option. Photonic based hybrid methods (such as photofermentation, artificial photosynthesis, and photoelectrolysis) have the highest GWP, AP, and SCC rankings (lowest emissions). Overall normalized rankings of hybrid hydrogen production methods are presented in Fig. 10. The average rankings of hybrid production methods show that hybrid thermochemical cycles have the highest ranking (closest to ideal case) and high temperature electrolysis gives the lowest ranking (least ideal option).

Overall comparison

In order to compare financial, technical, social, and environmental impact of selected hydrogen production methods

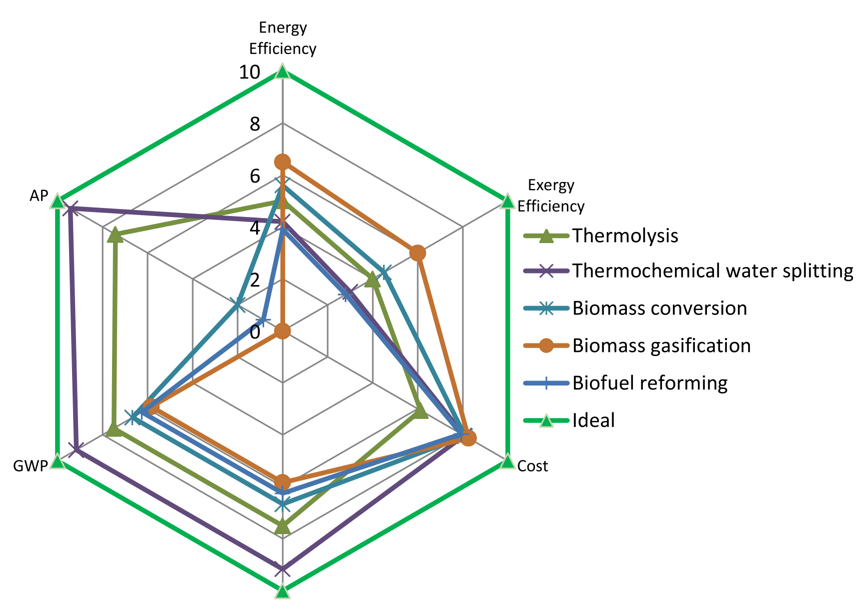

Fig. 8 – Normalized ranking comparison of thermal based hydrogen generation options.

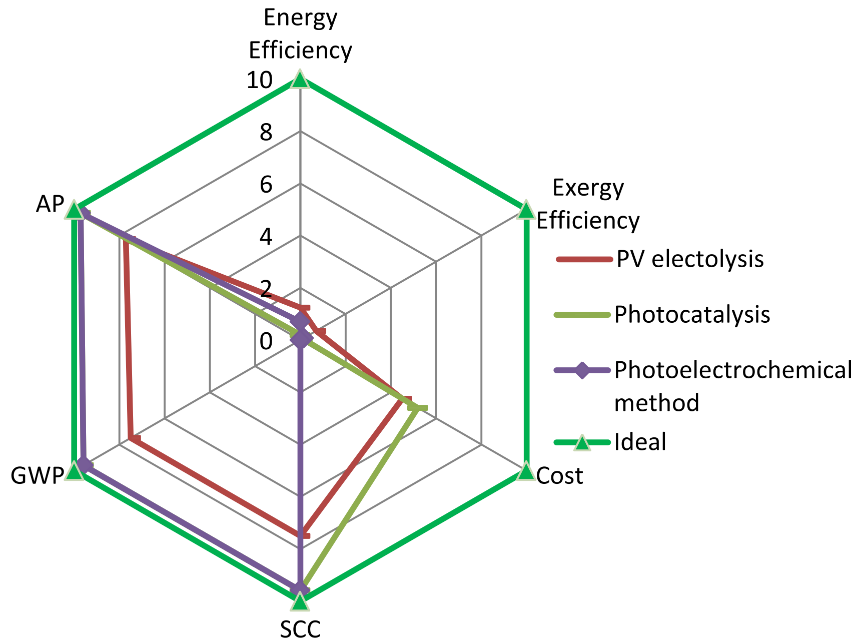

Fig. 9 – Normalized ranking comparison of photonic based hydrogen generation options.

based on their primary energy sources, average values of normalized GWP, AP, SCC, cost, energy and exergy rankings of each energy source are taken as basis. These average values are summarized in Table 8 and presented in Fig. 11. The average normalized rankings show that electrical based hydrogen production show the highest energy efficiency and lowest production cost. However, electrical based hydrogen production also gives the highest GWP and SCC due to high emissions of plasma arc decomposition. Thermal based hydrogen production has the highest exergy efficiency and AP. This is caused by the high SO_2 emissions of biomass gasification. Photonic based hydrogen production seems to be the most environmentally benign one, immediately followed by hybrid production methods. However, both options show low efficiencies and high production costs. On average, hybrid hydrogen production methods have the highest rankings (6.32/10), followed by thermal (5.82/10), photonic (5.18/10), and electrical (4.74/10) based hydrogen production. There is usually a trade-off between efficiency-cost and environmental-social impact. Among selected hydrogen production methods, there is a wide range of technical advancement. Already mature, late R&D-mature technologies give higher efficiencies and lower costs compared to early R&D-phase ones (such as photoelectrochemical method). Another

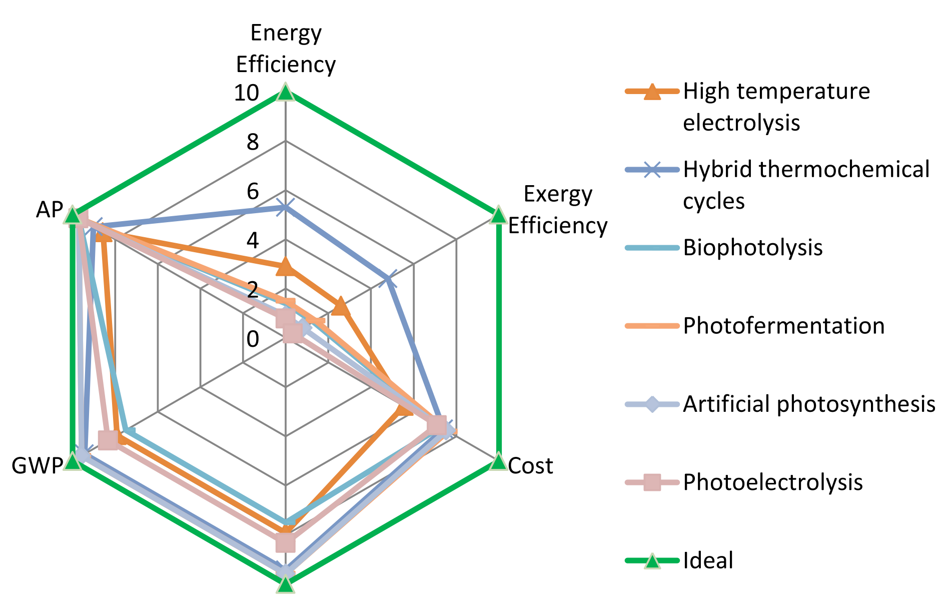

Fig. 10 – Normalized ranking comparison of hybrid hydrogen generation options.

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Table 8 – Overall comparisons of selected hydrogen production methods based on primary energy sources (Normalized).

	Energy efficiency	Exergy efficiency	Cost	SCC	GWP	AP
Electrical	6.15	2.85	8.26	2.08	2.08	7.00
Thermal	5.04	4.06	7.69	7.08	7.08	3.94
Photonic	0.71	0.32	3.23	8.89	8.89	9.05
Hybrid	2.13	1.87	7.08	8.73	8.73	9.41
Ideal	10	10	10	10	10	10

important factor is the availability of large scale production (such as fossil fuel reforming and coal gasification). Large scale production options have lower costs than the early R&D-phase, small and distributed ones.

Efficient and low cost hydrogen generation with minimum environmental and social adverse effect is the goal of successful transition to hydrogen economy. In order to reach this goal, there is significant amount of research going on to improve the performance of existing methods and find new promising ways to generate hydrogen. The methods mentioned so far can be used alone, or together with other alternatives in order to reach this target. Because of their limited and non-renewable nature and resulting GHG emissions, hydrogen from fossil fuels is not considered as sustainable. However, these methods can be used during the transition to hydrogen economy as the renewable hydrogen production techniques are being developed.

Conclusions

This study comparatively evaluates and assesses environmental, financial, social, and technical performance of 19 selected hydrogen production methods. Electrical, thermal, photonic, electro-thermal, photo-biochemical, and electro-photonic are the primary energy sources of these selected methods. Material resources of these methods are water, biomass, and fossil fuels. Six criteria are selected for comparison purposes: global warming potential (GWP), acidification potential (AP), social cost of carbon (SCC), production cost, and energy and exergy efficiencies. The results of this study can be listed as:

- Fossil fuel reforming has the highest (83%) and photocatalysis (less than 2%) has the lowest energy efficiency among selected options. In general, photonic (solar) based hydrogen production options have low energy efficiencies.
- Biomass gasification has the highest exergy efficiency (60%), followed by fossil fuel reforming (around 45–50%). Again, photonic based hydrogen production options have lowest exergy efficiencies compared to other selected options.
- The production cost evaluation shows that fossil fuel reforming (\$0.75/kg H_2), coal gasification (\$0.92/kg H_2), and plasma arc decomposition (\$0.85/kg H_2) produce the cheapest hydrogen. On the other hand, as an early R&D phase method, photoelectrochemical hydrogen (\$10.36/kg H_2) is by far the most expensive one.
- GWP and AP of photonic based hydrogen production methods are almost zero. As a result, these options have very low SCC. On the other hand, fossil fuel reforming, plasma arc decomposition, biomass and coal gasification have very high GWP, AP, and SCC among the selected options.
- The average normalized rankings of individual methods show that hybrid thermochemical cycles give closest-to-ideal case results (7.57/10). This amount is the lowest for coal gasification (3.55/10).
- When selected methods are compared based on their primary energy sources, electrical based hydrogen production show the highest energy efficiency and lowest production cost. This method also gives highest GWP and SCC.
- Thermal based hydrogen production has the highest exergy efficiency and AP. Photonic based hydrogen production gives the lowest AP, GWP, and SCC.
- On average, hybrid hydrogen production methods have the highest rankings (6.32/10), followed by thermal (5.82/10), photonic (5.18/10), and electrical (4.74/10) based hydrogen production.

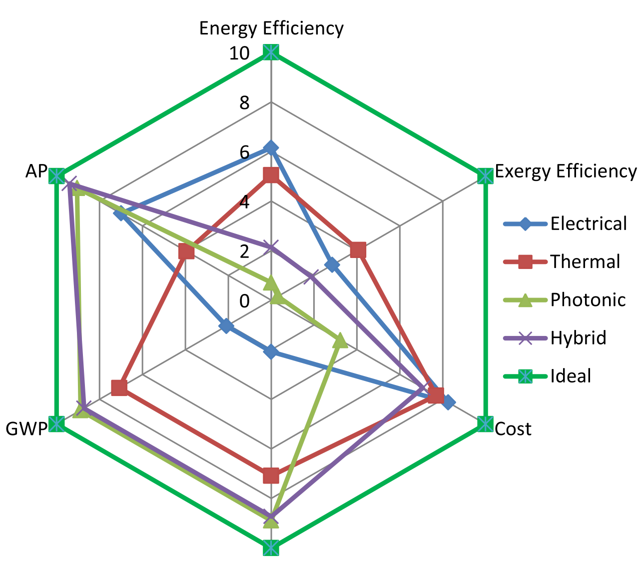

Fig. 11 – Normalized ranking comparison of hydrogen generation options based on primary energy sources.

Nomenclature

AP	Acidification Potential, g SO_2 eq./kg hydrogen produced
CCS	Carbon Capture and Storage
EIF	Environmental Impact Factor
GF	Greenization Factor
GHG	Greenhouse Gases

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GWP Global Warming Potential, g CO_2 eq./kg hydrogen produced
HCF Hydrogen Content Factor
IEA International Energy Agency
LCA Life Cycle Assessment
MTOE Million Tonnes of Oil Equivalent
NGSR Natural Gas Steam Reforming
SCC Social Cost of Carbon, $/kg hydrogen produced

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