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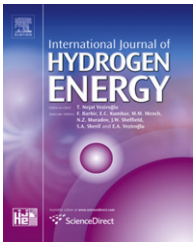

Sustainable hydrogen production options and the role of IAHE

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ABSTRACT

In this paper, some potential sustainable hydrogen production options are identified and discussed. There are natural resources from which hydrogen can be extracted such as water, fossil hydrocarbons, biomass and hydrogen sulphide. In addition, hydrogen can be extracted from a large palette of anthropogenic wastes starting with biomass residuals, municipal wastes, plastics, sewage waters etc. In order to extract hydrogen from these resources one needs to use sustainable energy sources like renewables and nuclear. A total of 24 options for sustainable hydrogen production are then identified. Sustainable water splitting is the most important method of hydrogen production. Five sustainable options are discussed to split water, which include electrolysis, high temperature electrolysis, pure and hybrid thermochemical cycles, and photochemical/radiochemical methods. Other 19 methods refer to extraction of hydrogen from other materials than water or in conjunction with water (e.g., coal gasification with CO_2 capture and sequestration). For each case the achievable energy and exergy efficiency of the method were estimated based on state of the art literature screening for each involved process. In addition, a range of hydrogen production capacity is determined for each of the option. For a transition period to hydrogen economy nuclear or solar assisted coal gasification and fossil fuel reforming technologies – with efficiencies of 10–55% including CO_2 sequestration – should be considered as a viable option. Other "ready to be implemented" technology is hydro-power coupled to alkaline electrolysers which shows the highest hydrogen generation efficiency amongst all electrical driven options with 60–65%. Next generation nuclear reactors as to be coupled with thermochemical cycles have the potential to generate hydrogen with 40–43% energy efficiency (based on LHV of hydrogen) and 35–37% exergy efficiency (based on chemical exergy of hydrogen). Furthermore, recycling anthropogenic waste, including waste heat, waste plastic materials, waste biomass and sewage waters, shows also good potential as a sustainable option for hydrogen production. Biomass conversion to hydrogen is found as potentially the most efficient amongst all studied options in this paper with up to 70% energy efficiency and 65% exergy efficiency.

1. Introduction

The world energy supply is majorly based on fossil fuels. Their use for process heat and electricity generation creates an environmental un-balance because it depletes the oxygen from the atmospheric air and it releases greenhouse gases (e.g., CO_2) with negative effect on global warming. In addition, the world dependence on conventional fossil fuels resources,

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which are mostly concentrated in Asia, is a source of geopolitical conflicts. It jeopardizes the access of future generation to a convenient energy supply and a clean and healthy environment.

The hydrogen economy has been conceptually shaped out by late 1960s and first half of 1970s as a reaction of scientists and engineers to the dependence of world energy on fossil fuels. The International Association of Hydrogen Energy (IAHE) was initiated by 1974 with the aim to develop and implement a hydrogen economy for future generations. Since then IAHE promoted the idea of hydrogen economy at all societal levels starting from general public till governments. By 2005 many countries engaged in the Kyoto Protocol to develop a cleaner energy system; hydrogen is an important part of this goal.

In a hydrogen economy, sustainable energy sources like hydro, wind, solar, biomass, geothermal, ocean thermal and nuclear are used to extract hydrogen from water (or other materials). Hydrogen is used as energy carrier (which by combustion with air forms again water) and as chemical required in many crucial processes (manufacturing of plastics, foods, fertilizers, synthetic fuels, metallurgical procedures etc). The main benefits of a hydrogen economy are:

- The problem of world dependence on fossil fuel is solved if hydrogen is used as energy storage and carrier in conjunction to renewable energy systems.
- Nuclear energy can be better utilized if it is converted in a chemical such as hydrogen.
- Many fundamental processes at industrial scale can be made pollution free as they can use hydrogen both as a material and clean source of process heat and electricity.
- Transportation can be made almost zero-polluting with hydrogen and hydrogen-based synthetic fuels which are carbon neutral.

Based on the historical perspective presented in Winter [1] a full decarbonisation of primary energy resources is expected in the next hundred years which, a time which was denoted as “the hydrogenation period”. In this period, non-sustainable energy resources such as fossil fuels will be gradually replaced with renewables and nuclear and the energy carriers will be hydrogen and electricity. The hydrogenation period follows after other two major historical periods of modern world development, namely i) mechanization (approx. 1750–1900, when the primary energy resource was coal) and ii) electrification (the 20th century, when petroleum was the most used primary energy resource of the world).

The International Journal of Hydrogen Energy published since 1975 many papers illustrating views on hydrogen economy, possibilities for its actual implementation in society, its benefits and other aspects. As early at 1976 – the mix of hydrogen and fossil fuel – was proposed as a transition phase towards a fully implemented hydrogen economy [2,3]. A series of papers were published within the journal in form of a package of concepts with the specific aim to promote the idea of hydrogen economy to a wider scope of peoples besides scientists and engineers [4,5].

Other series of conceptual papers were dedicated to specific countries and regions and the conversion of their economies to hydrogen energy. The solar energy resource of Spain can be conveniently converted to hydrogen [6]. Solar and wind were fond as best energy resources of Ceara in Brazil to be converted in hydrogen [7]. Some specific hydrogen solutions were found for the oil-rich Gulf countries. In United Arab Emirates there is the fourth largest resource of natural gas (after Russia, Iran and Qatar); consequently, it is found in [8] that the expanded use of proton exchange membrane fuel cells (PEMFC) for power generation will assure a transition to hydrogen economy – as this technology is viewed as a bridge between the natural gas exploitation of today and the future exploitation of solar and wind resources of the country to generate hydrogen [9]. The solar and wind resources were also identified as a major vector for hydrogen production in Saudi Arabia [10] denoted in present as an “Oil Kingdom” because it has one of the largest reserves of conventional petroleum in the world. By implementing a hydrogen-based energy system Saudi Arabia can be transformed in an “Energy Kingdom” [11].

The use of nuclear energy – including fusion – as a primary energy source to generate hydrogen from water was identified since early times as crucial for the implementation the future hydrogen-based energy economy [12]. A review of nuclear hydrogen production pathways is presented in Naterer et al. [13]. The next generation of nuclear reactors – known as Generation IV – will be developed for generation of power, hydrogen and high temperature process heat. The most developed technology for nuclear hydrogen production which uses high temperature process heat at >850 °C is the sulphur–iodine thermochemical cycle. A hybrid thermochemical cycle that operates at intermediate process heat temperatures of ~600 °C is currently in development by an international consortium [14].

Although hydrogen is not viewed as a natural resource – but rather an energy carrier – it is pointed out in [15] that there are few oil wells in Kansas that yield a hydrogen rich gas containing 60% hydrogen and 40% nitrogen plus traces of hydrocarbons. Other natural sources of hydrogen are water, fossil hydrocarbon, biomass and hydrogen sulphide. The Black Sea contains a major natural resource of hydrogen sulphide which occurs at a nearly constant concentration of 9.5 mg/L [16–18]. In addition, there is an anthropogenic source of hydrogen such as waste plastics, manure, landfill gas, biogas, urea containing wastes and sewage sludge [19] and other waste materials. Hydrocarbon fuels cannot be neglected as a source of energy and hydrogen during the transition period toward hydrogen economy. It order to use in a cleaner way fossil hydrocarbons as energy supply, they must be converted to hydrogen with carbon dioxide sequestration. The sequestration of carbon dioxide results in cost penalties which can be balanced through a carbon taxation policy which can be enforced by authorities. Muradov and Veziroglu [20,21] proposed a hydrogen production system which cogenerates carbon black co-product for better cost effectiveness. In this vision, fossil hydrocarbons are used as a natural resource to extract hydrogen and carbon, where hydrogen if further used as a fuel or chemical in industry, and carbon is used mostly as a valuable material in form of carbon black, carbon nano-fibres, amorphous carbon etc.

It was argued that hydrogen can be stored in large scales in depleted oil fields or in balloons under the sea at pressures of

20–50 bars. In the initial views – characterizing the years of the 1970s – hydrogen stored in large scales would be transported at long distances (~1000 km) for which the economics shows that its transportation is better than electricity [22]. In more recent years, another concept appeared, namely, hydrogen storage at small scales to satisfy power generation needs in vehicles or small power generators.

The present economic value of all hydrogen produced worldwide is about $300 billion/year. The annual growth rate is about 10% and is expected to be doubled to 20% by 2012. It is crystal clear that hydrogen economy is not possible without sustainable hydrogen production options. Several international and national associations are preoccupied to identify economically sound, sustainable methods for hydrogen production. The Organisation for Economic Cooperation and Development (OECD) and Japan Atomic Energy Agency (JAEA) co-organized a workshop in 2006 to revise the worldwide efforts to develop nuclear hydrogen production methods in a sustainable way [23]. Das and Veziroglu revise the progress on biological hydrogen production methods. A review of sustainable energies and their use for hydrogen production is presented in [24]. De Jong [25] revises sustainable methods of thermochemical hydrogen production from biomass processing. Joshi et al. [26] discuss sustainable methods of solar hydrogen production. Turner et al. [27] and Miltner et al. [28] analyse hydrogen production options from renewable sources. Alstrum-Acevedo et al. [29] discuss chemical approaches to artificial photosynthesis to split the water molecule and generate hydrogen. In Dincer and Zamfirescu [30] there are several identified routes to generate hydrogen from renewable energy. Basically there are five kinds of energies which can be used to extract hydrogen out of hydrogen containing substances, namely electric energy, thermal energy, photonic energy, energy of nuclear radiation or nuclear particles and biochemical energy. Dincer [31] further discusses hydrogen production options based on some potential driving energy sources such as electrical, thermal, biochemical, photonic, electro-thermal, photo-thermal, photo-electric, photo-biochemical, and thermal–biochemical.

This paper comprehensively expands the analysis presented by the authors in some sources [30–32] by discussing and comparing the sustainable hydrogen production options (including radiolysis as an additional basic method to generate hydrogen in conjunction to nuclear reactors) in terms of efficiency, environmental impact and sustainability, as well as identifying and analysing potential ones for hydrogen economy. Hydrogen production options are categorized based on the material from which hydrogen is extracted. The various options are compared with respect to applicability and range of hydrogen generation capacity. Furthermore, the role of International Association of Hydrogen Energy (IAHE) on sustainable hydrogen production is discussed.

2. Sustainable hydrogen production options

In order to identify pathways for sustainable hydrogen production one needs to inventory the natural resources of hydrogen, the available sources of energy which can be used to extract hydrogen from natural resources and the applicable methods of hydrogen production. These items are summarized in Fig. 1. The hydrogen containing natural resources are water, fossil hydrocarbons, biomass, hydrogen sulphide and anthropogenic wastes as indicated in Fig. 1a. Municipal sewage waters containing urea, farming wastes like manure, crops residues etc. (which are sources of biogas), other wastes which generate landfill gas, recycled plastic and cellulosic materials etc., are all anthropogenic wastes from which hydrogen can be extracted.

Sustainable energy is required to extract hydrogen from any resource in a clean, non-polluting manner. Fig. 1b lists the main energy sources that can be considered sustainable: solar, hydro, ocean thermal, tidal (including ocean currents), wind, biomass, geothermal and nuclear. The careful use of any of these sources can generate electricity and/or high temperature heat and/or nuclear radiation without or with minor environmental impact. Such energy is used for hydrogen production via one of the methods, as listed in Fig. 1c. These methods are categorized in six classes, namely electrochemical, thermochemical, photochemical, radiochemical, biochemical and hybrid (where hybrid methods refer to integrated systems that use any kind of combination of the first five listed hydrogen production methods, e.g., electro-photo-chemical, photo-bio-chemical, electro-thermo-chemical etc).

Based on the above analysis we identified five possible pathways to generate hydrogen in a sustainable manner. As indicated in Fig. 1d these are: water splitting, fossil hydrocarbons decarbonisation, hydrogen sulphide decomposition, biomass conversion to hydrogen and extraction of hydrogen from waste materials resulted from the anthropogenic activity. Each pathway corresponds to a natural resource (including the anthropogenic waste) from which hydrogen can be extracted. For any of the pathways the use of a specific combination of sustainable energy (see Fig. 1b) and hydrogen production method (see Fig. 1c) is possible. In the subsequent sections of this paper, the main options are addressed.

For the purpose of this study we categorize hydrogen production capacity in three ranges, namely low, medium and high, in the manner indicated in Table 1. The general systems configurations for sustainable water splitting are introduced in Tables 2 and 3. Water splitting pathways via sustainable methods is summarized in Table 2. The first option to consider for water splitting is water electrolysis. Depending on the kind of energy source in conjunction with the capacity (size) of hydrogen production facility, various configurations are possible.

As indicated in Table 2, proton exchange membrane electrolysis cells (PEME) are the logical choice for low production capacity, whereas alkaline electrolysers must be used in conjunction with medium production rates. For large production rate, groups of alkaline electrolyser units can be employed. The renewable sources which can be selected for low capacity hydrogen production are individual wind turbines of medium capacity, solar photovoltaic arrays and some applications involving waste heat recovery from various processes. Small capacity heat engines, based on advanced Rankine cycles with organic fluids or other fluids such as ammonia–water or CO_2 can be used in conjunction with waste heat recovery systems to generate power (with possible

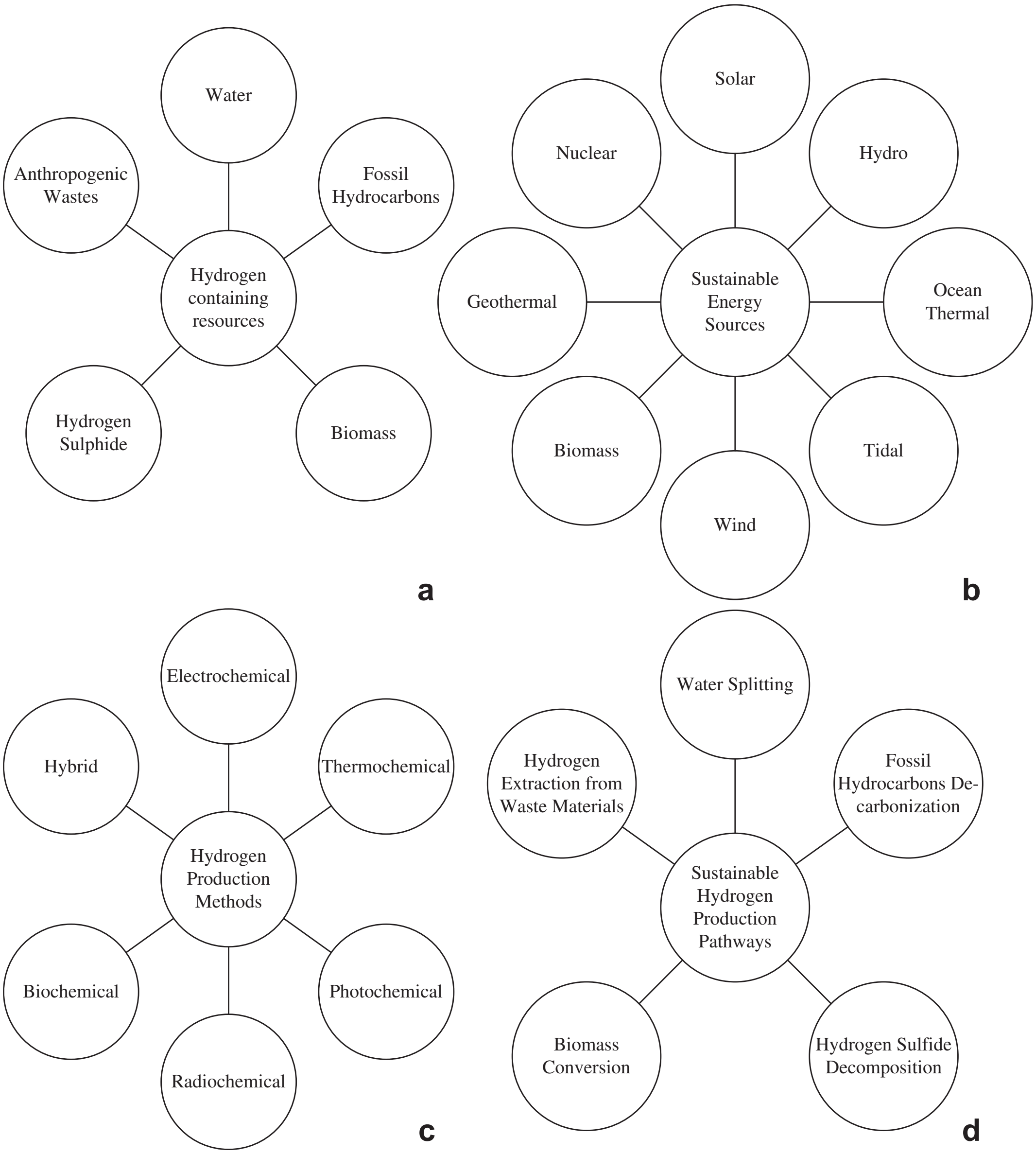


Fig. 1 – Renewable based hydrogen production sources (a), sustainable energy sources (b), methods (c) and sustainable pathways (d) for sustainable hydrogen production.

Table 1 – Capacity range of hydrogen production facilities.

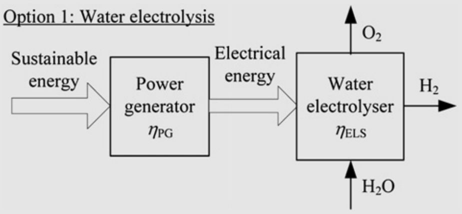
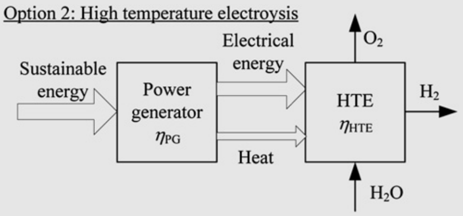
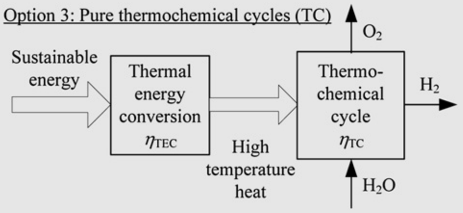
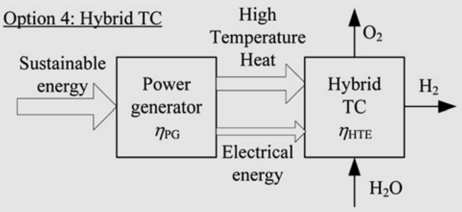
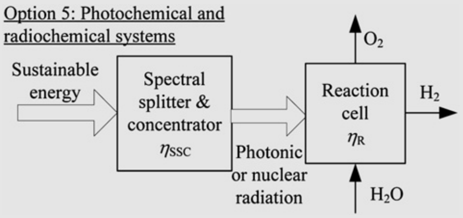
Production range	$\dot{V}$(Nm^3/day)	$\dot{m}$ (kg/day)	E (MWh/day)[a]	$\dot{E}$ (MW)[b]
Low	$\lesssim$1700	$\lesssim$70	$\lesssim$30	<0.1
Medium	1700–17,500	70–70,000	30–30,000	0.1–10
High	$\gtrsim$17,500	$\gtrsim$70,000	$\gtrsim$30,000	>10

a E represents the energy equivalent of produced hydrogen, based on LHV of hydrogen (121 MJ/kg).
b $\dot{E}$ is the rate of hydrogen production in equivalent terms calculated with $\dot{E} = E/(24 \times 3600)$.

option to cogenerate low grade heating for various applications). The generated power is further used to run a PEME and to produce hydrogen. Some promising low power heat engine developments are presented in [30–32].

An interesting option is to use low power solar dishes which generate concentrated solar radiation to run heat engines with a power spectrum of the order of few kW. The power can be either directly used (e.g., in residences) or converted to hydrogen with the help of a PEME. Concentrated solar power at medium to high capacity range is possible with solar tower settings or solar through fields. In such case, the facility should be coupled to an alkaline water electrolysis facility to generate hydrogen. Other sustainable energy sources available for “option 1” are wind farms, ocean thermal, geothermal, and nuclear. With wind farms, the generated

Table 2 – Water splitting options for sustainable hydrogen production.

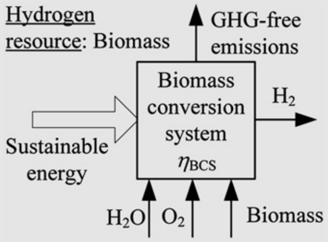
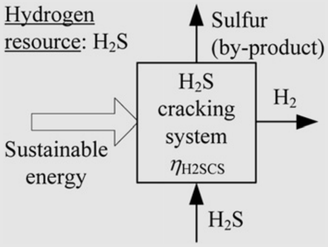
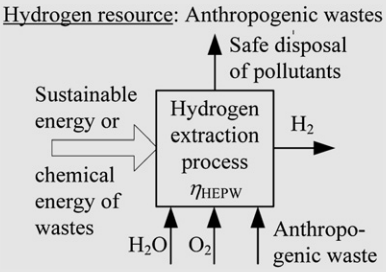
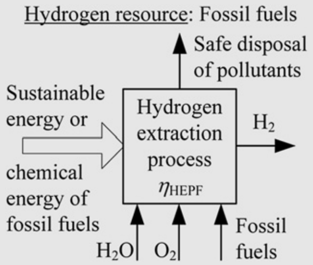
Option and system configuration	Energy input	Short description
	Wind	Wind turbine/farms + PEME/AE
	Hydro/tidal	Water turbine + AE
	OTEC	Floating NH_3–H_2O Rankine + AE
	Solar-PV	PV arrays + PEME
	Solar-CSP	Solar Rankine cycles + AE/PEME
	Geothermal	Geothermal Rankine + AE
	Nuclear	Nuclear Steam Rankine + AE
	Waste heat	Advanced Rankine + PEME/AE
	Geothermal	Geothermal Rankine + Heat exchangers + AE
	Solar-CSP	Solar Rankine cycles + Heat exchangers + AE or SOEP
	Nuclear	Gen. III–III$^+$ nuclear reactors + Heat exchangers + AE or Gen. IV nuclear reactors + SOEP/SOEO
	Solar	Concentrated solar heat and a thermochemical cycle at high temperature (e.g., S–I cycle)
	Nuclear	Gen. IV SCWR nuclear reactors coupled to the S–I thermochemical cycle
	Solar	Solar through/tower concentrators running power plant + hybrid thermochemical cycle (e.g., Cu–Cl cycle)
	Nuclear	Gen. IV SCWR coupled to a hybrid thermochemical cycle (Cu–Cl cycle)
	Solar	Photo-catalytic reactor or photo-electrochemical cells for water electrolysis
	Nuclear	Nuclear radiation used to drive radiolytic water splitting process

Notes: PEME = proton exchange membrane electrolyser; AE = alkaline electrolyser; PV = photovoltaic, SOEP = intermediate temperature solid oxide electrolysis cell with proton conduction; SOEO = high temperature solid oxide electrolysis cells with oxygen ion conduction; TC = thermochemical cycle.

power is in the medium range spectrum of capacity, thus wind farms are suitable to be coupled with water electrolysis. OTEC systems (Ocean Thermal Energy Conversion) comprise advanced power plants placed on floating platform in warm seas (oceans). The platforms also include hydrogen production system with alkaline water electrolysers. Geothermal sites with enough energy content to run power plants with production in a range above 100 kW show attractive economics; these facilities are suitable for hydrogen production with alkaline electrolysers. In the vicinity of nuclear reactors large electrolysis plants can be installed to generate hydrogen with limited electrical losses due to electricity transport. The logical choice is to use alkaline electrolyser units in conjunction with nuclear power plants.

Option 2 as given in Table 2 refers to water splitting via high temperature water electrolysis. A variety of choices are

Table 3 – Hydrogen production options from other resources than water.

Hydrogen resource and configuration	Energy input	Option	Short description
	Biomass	6	Thermochemical conversion by gasification
		7	Aerobic fermentation
		8	Anaerobic digestion
	Solar + biomass	9	Photo-biological processes (bacteria or algae process the biomass and generate hydrogen)
	Solar	10	Thermochemical $H_2S \rightarrow H_2 + S$
	Sustainable electricity[a]	11	Electrolytic of H_2S decomposition
		12	Plasma arc decomposition of H_2S
	Solar	13	Thermochemical conversion of plastics
	Biomass	14	Thermochemical conversion of biomass
		15	Bio-digestion of municipal solid wastes
		16	Landfill gas generation
		17	Bacterial sewage waters treatment to generate hydrogen
	Sustainable electricity[a]	18	Sewage waters electrolysis
	Fossil fuels[b]	19	Coal gasification with CO_2 capture and sequestration
		20	Hydrocarbons reforming with CO_2 capture and sequestration
	Nuclear	21	Coal gasification with CO_2 sequestration
		22	Nuclear assisted hydrocarbons cracking
	Solar	23	Solar assisted hydrocarbon cracking
	Sustainable electricity[a]	24	Plasma arc cracking of hydrocarbons

a Electricity derived from all sustainable sources listed in Fig. 1b.
b Energy derived from fossil fuel combustion followed by CO_2 capture and sequestration.

possible in this case. The source of sustainable energy must provide both electricity and heat. One first possibility is to use geothermal heat from large capacity geothermal heat that generate heat at 100–300 °C; one part of the geothermal heat is used to generate power with a geothermal Rankine cycle based plant; another part of the heat produced at geothermal well is used to supply heat to an electrolysis cell. Alkaline electrolysers can operate at temperatures up to 200 °C with heat supplied externally to reduce the electricity input requirements. Solar tower systems and solar through fields can be used to generate power and heat to drive (depending on the capacity and temperature level) wither alkaline electrolysers or intermediate temperature solid oxide electrolysis cells with proton conduction (SOEP). Future nuclear reactors of generations III and III$^+$ can be designed with embedded facility to generate heat and power. Although for these generations of nuclear reactors – which will be available commercially in the next decade – the temperature level is limited to 300–350 °C due to materials and safety constraints, they can be coupled with existent alkaline electrolysers which have the option to run at ~200 °C with heat input for an improved efficiency. Future generation of reactors of IV generation can operate at high temperature (500 − 1000 °C); therefore the use of SOEO (solid oxide electrolysis cells with oxygen ion conduction) or SOEP is applicable.

Pure thermochemical cycles ran with sustainable high temperature heat are indicated in Table 2 as “option 3”. This cycle are closed chemical processed that split water into hydrogen and oxygen while recycling all intermediate chemicals. The Sulphur–Iodine cycle is the most promising system for this hydrogen production option (see Analysis section for further discussion). The temperature level of high temperature heat must be over 850 °C. Only concentrated solar radiation and nuclear reactors of generation IV are capable to deliver this heat in a sustainable manner.

Option 4 refers to hybrid thermochemical cycles which require heat at an intermediate temperature level (~500 °C) and electricity to be driven. The promising candidate for this temperature level is the Cu–Cl thermochemical cycle (see Analysis section for further discussion). The input energy can be concentrated solar radiation from solar tower or solar through system or nuclear heat from VI generation SCWR (supercritical water cooled reactors). The heat input is used in part for electricity generation and in part to supply the endothermic reaction within the thermochemical cycle.

Option 5 includes those methods to split water with high energy radiation such as solar photonic radiation and nuclear radiation (e.g., gamma photons and alpha particles). The upper spectrum of solar radiation (above 450 nm, blue color) can be used directly to photo-catalytic reactions which evolve hydrogen from water. Some photo-reactors are under development for this technology. In addition, photo-electrochemical cells were developed which are able for a multi-band capture of solar photons to split water in a hybrid manner: high energy photons are directly used to split water photochemically, while low energy photons are used to generate photovoltaic currents to split water electrochemically; both methods are supposed work synergistically within a hybrid photo-electrochemical cell. Nuclear radiation from various fissionable materials can be used to split water through a radio-chemical or radio-catalytic process. Spent fuel pools generate at nuclear power plants alpha particles and gamma photons which conveniently can split water. In addition, nuclear reactors generate various fissionable materials from the range of actinides which, potentially, can be used with special radio-chemical reactors to split water molecule and generate hydrogen.

Table 3 summarizes those options to generate hydrogen from other natural or anthropogenic resources than water. Options 6–9 refer to pathways to extract hydrogen from biomass. Hydrogen production process can be done thermochemical or based on biological processes such as anaerobic or aerobic digestion, depending on the feedstock. Water is used in the process to supplement the source of hydrogen. Solar energy can be used in conjunction with some algae and bacteria to generate hydrogen via photo-biological processes.

Options 10–12 illustrate pathways to extract hydrogen out of hydrogen sulphide which is a natural resource found at geothermal sites, volcanos, and dissolved in some seas. The basic methods are thermal cracking using high temperature heat, plasma arc decomposition and electrolysis; all methods lead to generation of hydrogen with sulphur as by-product.

Hydrogen can be extracted from anthropogenic wastes as indicated in sustainable options 13–18 listed in Table 3. Plastic materials wastes resulted from human activity are an important source of hydrocarbons, from which hydrogen can be reformed using thermochemical methods. Nuclear heat can be used to gasify coal and sequester carbon dioxide or to reform fossil hydrocarbons (some nuclear research programs worldwide consider this alternative as a transition period toward a hydrogen economy). Biogas and landfill gas are other examples of hydrogen rich gas resulted from farming or municipal wastes. Sewage waters are an important source of hydrogen in towns and urban agglomerations. The sewage water contains important quantities of urea and other hydrogen rich compounds. Hydrogen can be extracted from sewage water by microbial methods or electrochemical method.

Conventional (coal, petroleum, natural gas) or nonconventional (oil shale, oil sands) fossil fuels are a source of hydrogen that cannot be neglected. Options 19–24 show sustainable methods to extract hydrogen out of them. The hydrogen content of some fossil hydrocarbon is poor (e.g., coal, oil sands) such that the extraction process may require water addition as supplementary source of hydrogen. In order to make the processes sustainable, clean energy sources such as nuclear and renewables must be used to generate high temperature heat and electricity. One class of processes involves hydrocarbon cracking to generate hydrogen and carbon black as by-product. Another process is nuclear assisted coal gasification with carbon dioxide sequestration and generation IV of nuclear reactors. In addition, autothermal processes can be applied in a sustainable manner – that is with CO_2 capture and sequestration – to generate hydrogen, e.g., coal gasification, or natural gas or petroleum reforming.

In total there were identified 24 options to generate sustainable hydrogen as shown in Tables 2 and 3. Each option requires a hydrogen resource and a form of energy as input. The form of energy is one of sustainable forms indicated in Fig. 1b, or the energy of fossil hydrocarbon provided that their combustion is done with clean methods carbon capture and sequestration (with all energy penalties applied). Table 4 shows a matrix indicating the hydrogen production option for any given form of energy input and hydrogen resource. This matrix is useful for screening the applicable hydrogen production methods for any regional context in agreement with available local resources.

3. Analysis and assessment

In this section all hydrogen production methods relevant to the sustainable options identified above (see Fig. 1c, and Tables 2 and 3) are analysed to derive their specific range of efficiency, their scale of hydrogen production and applicability. Water splitting is discussed first.

Water can be split into hydrogen and oxygen with various technologies such as electrolysis, thermolysis, thermochemical decomposition, hybrid thermochemical cycles, photolysis systems, photo-electrochemical cells, radiolysis and radiocatalysis systems. Regardless the specific method, the water

Table 4 – Matrixes indicating H_2 production options based on energy source and H_2 resource.

Hydrogen resource:		Water	Fossil fuels	Biomass	Hydrogen sulphide	Anthropogenic wastes
Energy source	Solar	1–5	19, 22	9	10–12	13, 18
	Hydro	1	22	n/a	11, 12	18
	OTEC	1	22	n/a	11, 12	18
	Tidal	1	22	n/a	11, 12	18
	Wind	1	22	n/a	11, 12	18
	Biomass	n/a	n/a	6–9	n/a	14–17
	Geothermal	1–2	22	n/a	11, 12	18
	Nuclear	1–5	20,21, 22	n/a	11, 12	18
	Wastes[a]	1	22	n/a	11, 12	18
	Fossil fuels[b]	n/a	23, 24	n/a	n/a	n/a

a Refers to anthropogenic wastes such as waste process heat or combustible wastes.
b Assumes clean fossil fuel combustion with carbon dioxide capture and sequestration n/a = not applicable.

splitting process occurs according to the following overall equation

$$2H_2O \rightarrow 2H_2 + O_2 \tag{1}$$

Water electrolysis can be conducted with proton exchange membrane electrolysers (PEME) or alkaline electrolysers (AE). The system is configured according to general layout listed under option 1 in Table 2. A proton exchange membrane electrolyser is a device which splits the water by electrolysis using an acidic electrolyte. Across acidic electrolytes the species that are transported are positive ions (or cations). In the case of water electrolysis the ionic transport results in a net transfer of protons from anode to cathode. Through the exterior circuit there is a net transfer of electrons from cathode to anode. The overall electrochemical reactions for acid electrolyte electrolysers is

$$\begin{cases} H_2O \rightarrow 2H^+ + 1/2O_2(g) + 2e^- & \text{in anode} \\ 2H^+ + 2e^- \rightarrow H_2(g) & \text{in cathode} \end{cases} \tag{2}$$

The most common acid electrolyte is a perfluorosulfonic acid polymer of which the most known trade name is NAFION®. The sulphonate groups present in polymeric chain make that this electrolyte behaves as a strong acid. NAFION® presents as a thin, solid membrane and is embedded between two planar electrodes known as bipolar plates. Because NAFION® Si strongly acid, the bipolar plates must be resistant to corrosion. Therefore the electrodes, especially the cathode comprises expensive metals such as Pt, Ir, Ru. The ionic species which permeates through NAFION® is the hydronium (H^3O^+) in aqueous solution. The membrane must be always wet to allow for the ionic transport. Moreover, one needs to compensate for a backward permeation process of molecular oxygen through membrane by increasing the electrical current density with ~5%.

Typical electricity consumption of commercial PEME (proton exchange membrane electrolysers) is of 23–26 MJ electric per normal cubic metre (Nm^3) of hydrogen produced or approx. 258–292 MJ per kg of hydrogen produced. Note that based on the lower heating value, the energy developed by hydrogen combustion with oxygen is 121 MJ/kg; with respect to higher heating value this is 141.8 MJ/kg. The generated hydrogen has purity higher than 99.999%. The capacity range of industrial PEME is ~0.2–60 Nm^3/h or from about 10 g/h to approx. 2.5 kg/h. The associated electrical energy consumption of commercially available PEME can go up to a maximum of 400 kW while the water consumption reaches at most 25 L/h.

The capital cost of PEME is relatively high due to the cost of the NAFION® proprietary membrane (approx. $\$600/m^2$) and the expensive catalysts. Based on the lower heating value (LHV) of hydrogen the energy efficiency of a unit is of 56–73% with 80–95% conversion. From the total electrolytic hydrogen cost, approx. 58% represents operation cost and the rest of 42% reflects the capital cost. PEME can be coupled to those electric power stations which generate in a range which extends from few kW to a few hundred kW. Wind turbine generator, photovoltaic (PV) arrays and low power organic Rankine cycles (ORC) generate power in an appropriate range and are suitable to be coupled with PEME.

As the name suggests, alkaline electrolysers comprise an alkaline electrolyte ($pH > 7$). In an alkaline electrolyte the mobile ionic species are anions (that is negative ions), respectively the hydroxyl group, OH^-. Typical electrolytes are liquid solutions of bases such as KOH or NaOH. The electrochemical reactions in an alkaline electrolyser cell are the following:

$$\begin{cases} 2H_2O \rightarrow 2e^- \rightarrow H_2(g) + 2OH^- & \text{in cathode} \\ 2OH^- \rightarrow H_2O \rightarrow 0.5O_2(g) + 2e^- & \text{in anode} \end{cases} \tag{3}$$

With an alkaline electrolyte the requirements on construction materials are less demanding with respect to acidic electrolytes, because alkaline solutions do not corrode. The concentration of electrolyte must be high enough such that it assures a good mobility of the ions. The electrodes are made of planar geometry to enhance the contact area with the electrolyte and, most importantly, they do not require expensive catalysts (normally carbon steel coated with nickel is used). Due to these characteristics, alkaline electrolysers can constructed in a cost effective manner for much larger production capacities with respect to PEM electrolysers. Commercial alkaline electrolysers operate at temperatures of 80–200 °C with production capacities in the range 5000–30,000 Nm^3/h (or equivalent 5 – 40 MW per unit with respect to LHV of produced hydrogen). The purity of hydrogen is higher than 99.7% and the energy efficiency (electricity-to-hydrogen) of commercial electrolysers is in the range of 55–90%. Note that when operating at higher temperature (e.g., over 120 °C) a part of the energy needed to split water is transmitted as heat via heat transfer to the electrolyte.

Solid oxide electrolysers emerged recently as promising technology. There are two kinds of solid oxide electrolytes based on ceramic materials: i) proton conducting which operate at temperatures of ~725–1025 K and ii) oxygen ion conducting electrolytes which operate at 1000–13,000 K. None of the solid oxide electrolyser option (with proton or oxygen ion conducting electrolyte) is available commercially, although much progress is observed for solid oxide electrolyser with oxygen ion conduction (SOEO). Solar energy is one of possible sources to drive a solid oxide electrolysis cell. Large scale systems with concentrated solar radiation deliver heat in the temperature range of 700–1000 K, and therefore these systems can be coupled to solid oxide electrolysers with proton conduction membrane (SOEP). High temperature nuclear reactors of IV generation – which are currently in early research phase – will deliver heat in a temperature spectrum compatible with SOEO. The supercritical water cooled reactor (SCWR) of generation IV is compatible with SOEP systems. The general definition for energy efficiency of solid oxide electrolysers, which are supplied with electric power and heat, is based on the Gibbs energy of the reaction (per mole of hydrogen produced):

$$\eta_{SOE} = \Delta G_R / W_{el} \tag{4}$$

where W_{el} represents the electric power supplied to the electrolysis unit per mole of hydrogen generated. Based on the analysis from [33] the average efficiency of SOE is 65%.

There are many known thermochemical water splitting cycle; however, only types of cycles show presently a significant research and development activity: i) the sulphur–iodine (S–I) cycle and ii) the copper–chlorine (Cu–Cl) cycle. In its basic implementation the S–I cycle is a pure thermochemical one which requires only high temperature heat (800–1000 °C) as input to generate hydrogen by water splitting. The cycle comprises three steps from which the first is the so-called Bunsen reaction according to $I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4$ which produces two acids (HI and H_2SO_4) which are separable by physical methods. The next step is HI decomposition by the reaction $2HI \rightarrow I_2 + H_2$ which evolves gaseous hydrogen. Another reaction is that of H_2SO_4 decomposition according to $H_2SO_4 \rightarrow H_2O + SO_2 + 0.5O_2$ which requires a solid catalyst. This cycle is mostly suitable to be coupled to solar dishes which concentrate solar radiation to produce high temperature heat in a suitable range for a thermal capacity range of around 100 kW per unit. The most promising application of the cycle is in conjunction to high temperature reactors of generation IV which – as projected – can generate thermal energy up to 2 GW per unit. The preconized efficiency of large scale S–I plants is around 45%, respectively.

The Cu–Cl cycle is a hybrid one which requires heat as an intermediate temperature level (~530 °C) and electricity as energy input. There five known configurations of the Cu–Cl cycle as indicated in Table 5 from which it results that the electricity required by the cycle can be as low as 53% of that for water electrolysis. A comprehensive review of research and development progress on Cu–Cl cycle is revised in [34,35]. Approximately a 43% net efficiency is envisioned with this Cu–Cl cycle, which is a significant margin of improvement of more than one-third over water electrolysis.

An interesting feature of photonic or nuclear radiation is its ability to interact with matter across volumes rather than surfaces. Alpha particles, gamma photons or photons from visible light can penetrate through various media. The possibility to transmit energy to every point of a volume is attractive for water splitting processes. Photonic radiation and alpha particle radiation can be used in many ways to split the water molecule, either directly (through photolysis or radiolysis) or assisted by electricity (such as in photo-electrochemical processes).

In order to use solar photons directly for water splitting, a photo-sensitizer capable to absorb solar radiation must be dissolved in solution, because water itself is transparent to the visible spectrum. Photonic-based hydrogen production systems are categorized in Fig. 2. The following systems for water splitting with solar light are analysed here – as they are found the most relevant processes in this category (photo-electrochemical): i) photo-electrochemical cell, ii) dye-sensitized electrolysis cell, iii) homogenous photo-catalysis systems with supra-molecular devices. Fig. 3 depicts the general schematics of photo-electrochemical (a) and dye-sensitized (b) electrolysis cells.

A photo-electrochemical cell is a device that uses heterogeneous photo-catalysis to drive water electrolysis and to generate hydrogen from water. The photo-catalysts can be placed at anode, or at cathode, or at both electrodes. An acid or a basic electrolyte may be used depending on the nature of electrodes materials and their resistance to corrosion. As suggested in Fig. 3a, photo-electrochemical cell can be linked to a PV array which provides part of the required energy to drive the process as electricity; the other part is due to photons that are incident on photo-electrodes. The energy efficiency of the system can be obtained as follows

$$\eta_{PEC} = \frac{\dot{n} \times LHV}{I_{T0} \times A} \tag{5}$$

where molar $\dot{n}$ is the rate of hydrogen production and LHV is the molar based lower heating value of hydrogen, I_{T0} is the solar irradiation on a tilted surface and A is the area exposed to solar radiation (including that of the PV array if applied). Depending on the band-gap of the photo-electrodes, a smaller or larger portion of incident solar radiation is absorbed. For example:

- $SrTiO_3$ photo-anode absorbs maximum 2.62% of incident solar light energy, and
- GaP photocathode absorbs maximum 21.9% of incident light energy.

The efficiency of the single photo-electrode cell with $SrTiO_3$ is 1.2% and of that of a cell with photo-electrodes at both anode and cathode is of around 6% [36]. Some recent advances on photovoltaic cells [e.g., 38–41] show that it is possible to enhance the solar energy harvesting by using systems that can generate two lower energy photons from one high energy photons. The energy of the lower energy photons is set to be

Table 5 – Cu–Cl cycle configurations and their electrical energy requirements.

Number of steps		Processes	Electricity[a]
Five		$4CuCl(aq) \rightarrow 2Cu(s) + 2CuCl_2(aq)$ at 80 °C, electrolytic	89%
		$CuCl_2(aq) \rightarrow CuCl_2(s)$, drying, no chemical reaction	
		$2Cu(s) + 2HCl(g) \rightarrow 2CuCl(l) + H_2(g)$	
		$2CuCl_2(s) + H_2O(g) \rightarrow CuO^{*}CuCl_2(s) + 2HCl(g)$	
		$CuO^{*}CuCl_2(s) \rightarrow 2CuCl(l)+1/2O_2(g)$	
Four	Option 1	$4CuCl(aq) \rightarrow 2Cu(s) + 2CuCl_2(aq)$ at 80 °C, electrolytic	89%
		$2CuCl_2(aq) + 2H_2O(g) \rightarrow Cu2OCl2(s) + 2HCl(g) + H_2O(g)$	
		$Cu_2OCl_2(s) \rightarrow 1/2O_2(g) + 2CuCl(l)$	
		$2Cu(s) + 2HCl(g) \rightarrow 2CuCl(l) + H_2(g)$	
	Option 2	$2CuCl(aq) + 2HCl(aq) \rightarrow 2CuCl_2(aq) + H_2(g)$ at 100 °C, electrolytic at 1 bar	57%
		$CuCl_2(aq) \rightarrow CuCl_2(s)$	
		$2CuCl_2(s) + H_2O(g) \rightarrow Cu_2OCl_2(s) + 2HCl(g)$	
		$Cu_2OCl_2(s) \rightarrow 2CuCl(l) + 1/2O_2(g)$	
Three	Option 1	$4CuCl(aq) \rightarrow 2Cu(s)+2CuCl_2(aq)$ at 80 °C, electrolytic	89%
		$2CuCl_2(aq) + H_2O(g) \rightarrow 2CuCl(l) + 2HCl(g) + 1/2O_2(g) + H_2O(g)$ at 400–600 °C	
		$2Cu(s) + 2HCl(g) \rightarrow 2CuCl(l) + H_2(g)$ at 430–475 °C	
	Option 2	$2CuCl(aq) + 2HCl(aq) \rightarrow 2CuCl_2(aq) + H_2(g)$ at 100 °C, electrolytic at 24 bar	53%
		$2CuCl_2(s) + H_2O(g) \rightarrow Cu_2OCl_2(s) + 2HCl(g)$	
		$Cu_2OCl_2(s) \rightarrow 1/2O_2(g) + 2CuCl(s)$	

a Given in percentage of electrical input of water electrolysis (calculated based on Gibbs free energy of the reaction).

slightly higher than the band-gap energy of the solar absorber (viz. the photo-electrode). It is also possible to convert lower energy photons into higher energy photons which then are directed to a PV cell. Although such systems may be derived for PV-electricity, they can be applied, in principle, to photo-electrolysis cells. It is found in Badescu and Badescu [37] that the incident solar radiation to electrical energy conversion efficiency may overpass 40% using up- and down photonic energy to photonic energy conversion systems. Other recent contributions in this direction are described in Refs. [38–41].

Dye-sensitized tandem electrolysis cells are hybrid devices comprising photo-electrodes and photo-sensitizers (see Fig. 3b). This type of cell has been mentioned for the first time in [42]. The cell has two compartments, one comprising an aqueous electrolyte (where electrolysis is performed), and the other an iodine-based electrolyte. The light is absorbed partially by an extremely thin photo-anode based on wolfram tri-oxide semiconductor (WO_3). This electrode is transparent to the lower visible range and infrared. The transmitted light falls on a second photo-electrode, which is sandwich-like and comprises a semiconductor layer in titanium dioxide (TiO_2). A second dye layer is deposited comprising ruthenium-bipyridyne based photo-sensitizers which absorb light in the lower visible spectrum. Through the opposite window, incident light passes a thin layer of platinum that has the role of counter electrode and it further crosses the iodine-based electrolyte from the second compartment prior being absorbed by the ruthenium-based dye (for detailed information on this system see Ref. [43]). An estimation of the energy efficiency of the tandem cell can be determined as follows. The energy portion from incident radiation carrying photons with a wavelength shorter than 477 nm (which can be absorbed by the photo-anode) is 13%. The portion of photons with wavelengths shorter than 774 nm (which can be absorbed by the dye) represents 53%. Thus the photons in the range 477–744 nm carry 40% from incident radiation. This means that the light

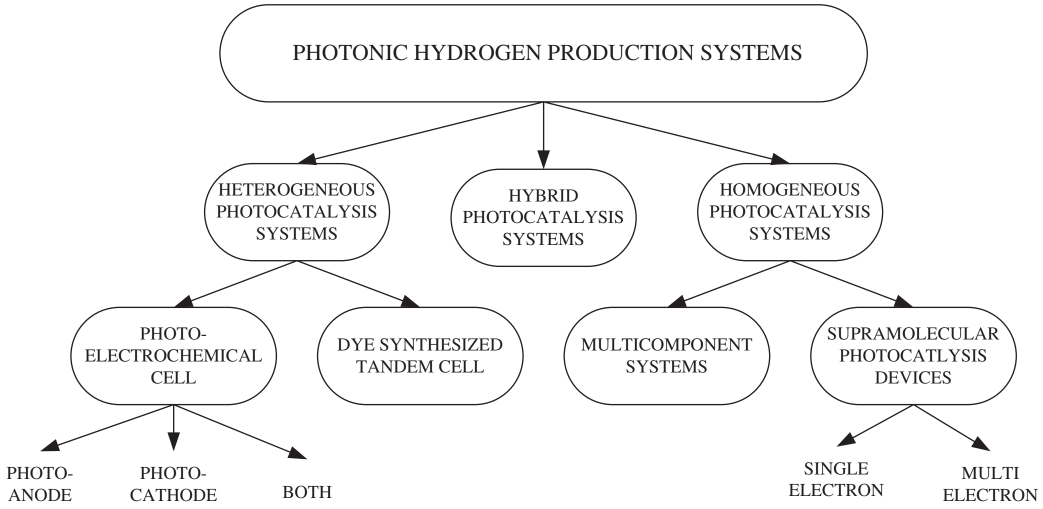


Fig. 2 – Classification of photonic based hydrogen production systems.

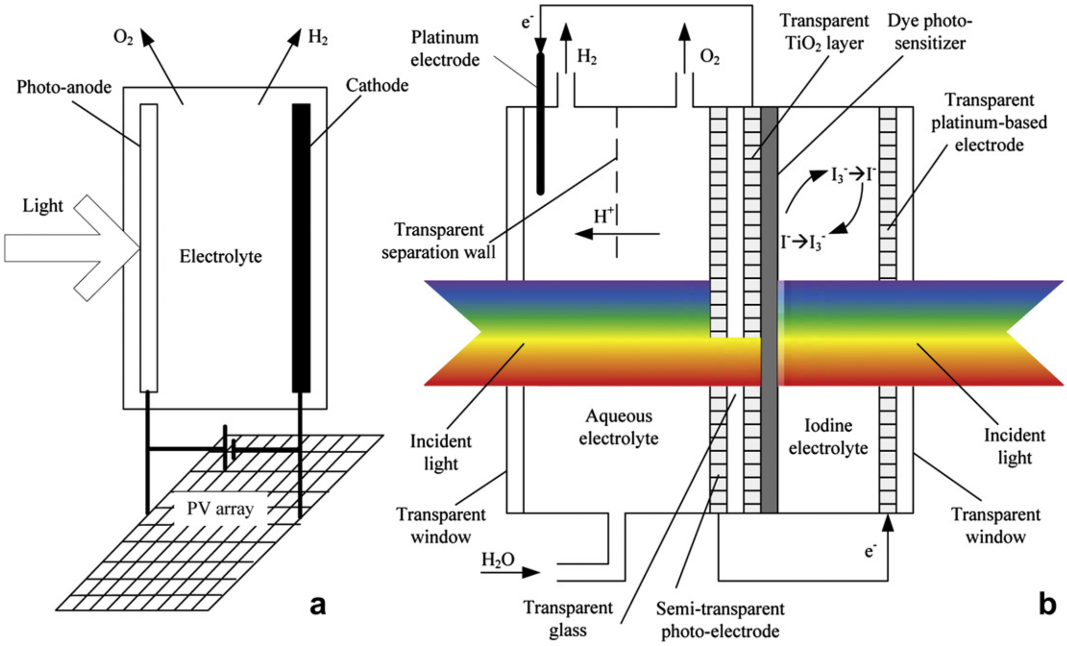


Fig. 3 – Schematics of photo-electrochemical (a) and dye-sensitized (b) electrolysis cells.

energy that crosses the photo-anode is sufficient to excite the dye. Therefore, only 13% from incident solar radiation can be used by the system and as detailed in [36] it results in a theoretical energy efficiency of 7.3% while practical implementations of the tandem cell have demonstrated 3% efficiency.

A promising approach to water splitting is homogeneous photo-catalysis with supra-molecular devices. Currently there are few known systems – demonstrated at a lab scale – that can be used to generate hydrogen from water with molecular devices; a literature revision on this is found in [36]. Sacrificial electrons donors dissolved in non-aqueous solutions were investigated by Brewer and co-workers in conjunction with proprietary supra-molecular devices which act as photo-sensitizers and photo-catalysts with multi-electrons collection at the active site [43]. The system performs the half water splitting reaction according to

$$2H_2O + h\upsilon + ED \rightarrow H_2 + 2OH^- + ED^+ \qquad (6)$$

where ED represents an electron donor consumed by the reaction.

The Brewer's systems show hydrogen evolution from water at promising rates. In all cases, *N*,*N*-dimethylaniline (DMA) is used as the electron donor [43]. The source of light generates 6.27×10^{19} monochromatic photons/ min at 460 nm. Hydrogen is produced under these conditions in a sealed batch reactor with a turnover frequency of 14 molecules of hydrogen per molecule of catalyst and hour. The energy efficiency of the system roughly reaches 1% under monochromatic radiation. The estimated energy efficiency of hydrogen production under actual solar conditions is less than 0.2% with the current lab scale system.

Water splitting by radiolysis occurs in a relatively similar manner as photolysis. In radiolysis case (with high energy gamma or X-ray photons) or ionized alpha particles are directed from a water molecule. These radiations can be derived from a nuclear reaction. Two physical processes are possible after water exposure to radiation: i) molecular excitation or ii) ionization. Molecular excitation can lead – with some probability – to the formation of molecular hydrogen and atomic oxygen. Ionization results in release of a proton, a hydroxyl and one hydrated electron. Experimental activity was performed using gamma radiation sources based on ^{60}Co in the presence of molecular catalysts dissolved in water such as BeO, SiO_2, TiO_2, ZrO_2 [44]. Production volumes of μ mol of hydrogen per mL of solution were observed.

Extraction of hydrogen from biomass via thermochemical processes (viz. biomass gasification) is identified in Table 3 under "option 6". Through biomass oxidation using air and water, a hydrogen rich gas is obtained according to the following simplified reaction [30]

$$aC_xH_yO_z + bH_2O \rightarrow cH_2 + dCO_2 + e\mathrm{Tar} \qquad (7)$$

for which the hydrogen yield varies between 40% and 65% depending on the nature of biomass. Here, some gaseous products such as CO and CH_4 where omitted as they can be further oxidized to extract more hydrogen. The temperature at which biomass gasification occurs is in the range 750–900 °C. The energy efficiency of the process defined with respect to LHV of hydrogen is around 70%.

Biomass stores chemical energy which can be manipulated by micro-organisms to generate hydrogen via chemical processes catalyzed by specific enzymes. Digestion in the absence of oxygen is called anaerobic digestion; it generates hydrogen rich gas or biogas out of which hydrogen can be extracted. Around 1.5 mol of hydrogen can be generated per mol of sucrose substrate [31] based on a series of processes catalyzed by hydrogenase and nitrogenase enzymes according to the prototypical equation

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 4CH_3COOH + 4H_2(g) \tag{8}$$

where $C_{12}H_{22}O_{11}$ represents sucrose.

In the case of aerobic fermentation (which occurs in the presence of oxygen) typically 7 mol of hydrogen can be generated per mole of glucose (see details in [24]). The energy efficiency of hydrogen production by aerobic digestion can rich remarkable high values for such substrates, e.g., 28% when molase is the substrate.

Photo-biological hydrogen generation occur under presence of biomass substrates, light and micro-organisms. This is an enzymatic process conducted by living organisms which evolve hydrogen under illumination conditions. Although this process is not developed at industrial scale it shows promises because is able to generate hydrogen at ambient temperature conditions with an efficiency which can reach 10% [24]. The prototypical reaction which generate hydrogen from glucose-based substrate is

$$C_6H_{12}O_6 + 6H_2O \overset{h\nu}{\rightarrow} 12H_2(g) + 6CO_2 \tag{9}$$

Hydrogen sulphide can be decomposed thermochemical using sustainable high temperature heat according to the reaction $H_2S \rightarrow H_2(g) + 0.5S_2$ which generates gaseous hydrogen and sulphur. The reaction enthalpy in standard conditions is 20.5 kJ/mol. The reaction temperature is in the range of 400–800 °C and is conducted catalytically using various catalysts among which Cr_2S_3 and WS_2 and Mo-based compounds give significant yields with around 25% conversion and separation of hydrogen gas product from the hydrogen sulphide reactant it is necessary [45,46]. Pressure swing absorption and selective hydrogen membrane separation techniques were proposed to extract hydrogen out of the gaseous product mixture [45,47]. Hydrogen sulphide decomposition using concentrated solar energy (see option 10 in Table 3) has been studied [48]; the obtained conversion was 15% at 770 °C.

In [49] it is proposed to install this system on floating platforms on Black Sea which are able to pump water from 2000 m depth from which hydrogen sulphide can be separated; the concentrated solar thermal system is used to decompose H_2S thermochemical and hydrogen selective membranes are used to separate hydrogen. The platform will produce around 1000 kmol hydrogen per year with sulphur as by-product at an estimated cost ten times higher than conventional steam methane reforming. An integrated system that extracts electrochemically hydrogen, sulphur, salt and drinking water from deep Black Sea waters was proposed by [16]. Based on data from [16] it results that, if renewable energy is used to drive the processes, the estimated energy efficiency for hydrogen production is ~2% when extracted from Black Sea, or ~4% if extracted from industrial waste waters containing hydrogen sulphide.

Plasma arc decomposition is another method to extract hydrogen from hydrogen sulphide using a sustainable electricity source [50]. This method can be used for very small production rates because it involves corona discharges reactors with size limited due to practical considerations. In gas phase energetic electrons are created by Corona discharge; the electrons and initiate a chain of reactions which eventually decompose the H_2S molecules.

Waste plastic materials can be decomposed via thermochemical processes evolving at around 350 °C. Recycled plastic materials – except those with polyvinyl chloride (PVC) and polyethylene terephthalate (PET) – are heated at high temperature in the absence of oxygen to recover crude oil liquids and hydrogen rich non-condensable fractions [51]. Iron-based catalysts were used to improve the yield. The gas yield is of ~50%; from it 3–5% is molecular hydrogen and the other part consists of mainly propane.

Biomass-containing materials can be separated from municipal solid waste and gasified through thermochemical processes with similar efficiency as in the case of agricultural biomass. Another option is to apply bio-digestion of solid wastes and sludge. Landfill gas generation potential of municipal wastes – with its negative effect on global warming due to methane escapes in the atmosphere – can be reduced importantly by appropriate pre-treatment of the waste. Rotting and fermentation can be applied to generate biogas and hydrogen rich gas. Municipal solid waste comprises typically up to 60% bio-waste. Units with high capacity which can generate biogas from municipal solid waste of ~10^6 kg per were shown to be feasible [24]. Around 40% of biogas is methane, which can be reformed to hydrogen based on the overall auto-thermal reaction:

$$1.315CH_4 + 1.37H_2O + 0.63O_2 \rightarrow 4H_2 + 1.315CO_2 \tag{10}$$

which has a yield of 60%; it is assumed that CO_2 emissions for municipal bio-waste are carbon neutral because they are derived from food products and cellulosic materials.

Landfill gas contains in high proportion methane. Modern landfills are equipped with gas collection system. Although the first option is to combust landfill gas in internal combustion engines for power generation, an alternative is to convert it to hydrogen with a method such auto-thermal steam methane reforming (Eq. (10)).

Sewage sludge can be processed micro-biologically in conjunction with molasses substrates to extract hydrogen [24]. A fixed bed bio-reactor with activated carbon which process sewage sludge to generate hydrogen with a rate of few standard litres per hour for one litre of feed is mentioned in [24]. Sewage bio-solids were treated in continuous flow bio-reactors with mesophilic anaerobic fermentation with a production of tens of standard litres of hydrogen per kg of volatile substances [24].

Urea rich water can be derived from municipal sewage. An emerging technology is urea electrolysis to generate hydrogen. The standard theoretical cell voltage for urea electrolysis is 0.37 V (to be compared to water electrolysis potential of 1.23 V). Alkaline electrolyte is used. At anode hydrogen evolves (three moles of hydrogen per mole of urea) while at cathode it evolves carbon dioxide and nitrogen, according to the reactions

$$\begin{cases} CO(NH_2)_2(aq) + 6OH^-(aq) \rightarrow N_2(g) + CO_2(aq) + 5H_2O(l) + 6e^- \\ 6H_2O(l) + 6e^- \rightarrow 3H_2(g) + 6OH^-(aq) \end{cases} \tag{11}$$

Fossil fuels represent an important source of hydrogen and of energy which cannot be neglected. The current reforming technology of fossil fuels results in important GHG emissions. The general chemical equation representing the hydrocarbon reforming process is

$$C_xH_y + \alpha H_2O + (x - 0.5\alpha)O_2 \rightarrow (\alpha + 0.5y)H_2 + xCO_2 \quad (12)$$

where C_xH_y represents the fossil hydrocarbon and α is a parameter determined by imposing that the enthalpy of reaction (12) is zero (this is an auto-thermal reforming process).

Allo-thermal processes are nowadays considered where the reaction heat required to conduct the reforming process is provided via a high temperature heat from sustainable source. One envisaged possibility is to couple nuclear reactors of generation IV with fossil fuel reforming or coal gasification facilities. Important reduction of carbon dioxide emissions is obtained if the reaction heat is provided from sustainable sources. Allo-thermal processes evolve according with

$$C_xH_y + 2xH_2O \rightarrow (2x + 0.5y)H_2 + xCO_2 \quad (13)$$

It can be observed from Eqs. (12) and (13) that the reduction of CO_2 emissions by allo-thermal reforming with respect to auto-thermal reforming is given by the factor

$$\beta = \frac{\alpha + 0.5y}{2x + 0.5y} < 1 \quad (14)$$

Electrical power derived from nuclear reactor is to be used for processes such as compressing carbon dioxide, transportation and sequestration. An alternative to CO_2 sequestration is proposed in Muradov and Veziroglu [20,21] (as discussed above) is to crack the hydrocarbons to generate carbon black and hydrogen. This process is done according to the reaction

$$C_xH_y \rightarrow xC + 0.5yH_2(g) \quad (15)$$

Process (15) is assumed in hydrogen production options 22–24 listed in Table 3. Hydrocarbon cracking can be pursued in various ways, including thermo-catalytically or via plasma arc decomposition [31]. Carbon black is collected out as a powder out of the decomposition reactors. Carbon black can be stored safely in silos and used when needed as ingredient for construction materials such cements, other structural materials, carbon nano-fibres, steels and metallic materials or allows. In addition, carbon black can be used as a fuel for backup power when required (e.g., in emergency situations), obviously with an environmental damage as it emits carbon dioxide in the atmosphere. Reaction (5) can be driven on the expense of energy derived from concentrated solar radiation, from nuclear reactors of IV generation, or other sources of sustainable energy.

4. Results and discussion

The sustainable options identified in Tables 2, 3 are compared from the point of view of efficiency and scale of application. Two kinds of efficiencies are studied, namely exergy and exergy efficiency. In general, efficiency is defined as useful output by consumed input. In energy efficiency both the output and inputs are expressed in terms of energy, while for exergy efficiency they are expressed in terms of exergy. The energy efficiency of a sustainable hydrogen generation facility is defined with

$$\eta = \frac{\dot{m} \times \text{LHV}}{\dot{E}_{\text{in}}} \quad (16)$$

where $\dot{m}$ is the mass flow rate of hydrogen produced, LHV is the lower heating value of hydrogen (121 MJ/kg) and E_{in} is the energy input to drive the process. The exergy efficiency is defined with

$$\psi = \frac{\dot{m} \times \text{ex}^{\text{ch}}}{\dot{\text{E}}\text{x}_{\text{in}}} \quad (17)$$

where ex^{ch} is the chemical exergy of hydrogen and $\dot{\text{E}}\text{x}_{\text{in}}$ is the exergy input into the system. Based on [52] the chemical exergy of hydrogen is 118.06 MJ/kg. From Eqs. (16) and (17) a hydrogen exergy quality factor γ can be introduced which expresses the ratio between chemical exergy and LHV of hydrogen. This factor has the value of $\gamma = 0.97$ Using γ as the hydrogen exergy quality factor the ratio between ψ and η is

$$\frac{\psi}{\eta} = \frac{\dot{E}_{\text{in}}}{\dot{\text{E}}\text{x}_{\text{in}}} \times \gamma \quad (18)$$

which is useful for determining the exergy efficiency from energy efficiency for various cases. In what follows we attempt to determine the range of energy and exergy efficiencies for systems options 1–24.

First five options refer to water spitting. Fig. 4 depicts the reaction enthalpy ΔH for equation (1) in function of the process temperature ($\Delta H = H_P - H_R$, where H is molar enthalpy and subscripts P and R represent products and reactants, respectively). It is remarked that the total enthalpy of the reaction increases with the process temperature. However, when free Gibbs energy (ΔG) is analysed

$$\Delta G = \Delta H - T\Delta S \quad (19)$$

where $\Delta G = G_P - G_R$ and $\Delta S = S_P - S_R$ (the entropy of the reaction) and T is the process temperature, one observes in Fig. 4 a quasi linear decrease of ΔG. The Gibbs energy is that form of organized energy that must be given to the reaction in form of mechanical work, or electrical work, or work corresponding to electromagnetic or nuclear radiation etc. The

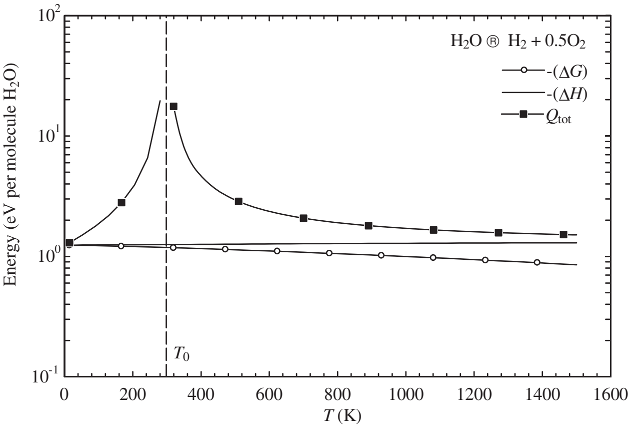


Fig. 4 – Energy required to split one water molecule (reaction enthalpy ΔH, free Gibbs energy ΔG, total heat required Q_{tot}).

entropic term $-T\Delta S$ is transmitted to the reaction in form of heat. There are some key cases to discuss:

- If water splitting is driven by electricity only, the entropic component of total enthalpy must be obtained by Joule effect heating (the electric current is dissipated as heat).
- If water splitting is driven by a radiation, the entropic term is associated with all dissipative effects due to irreversibilities, which are converted in heat and transferred to the process. The entropic term can be determined based on the difference between the energy and exergy content of the radiation.
- It water splitting is driven by heat only, the entropic term is transmitted to the process directly, while the generation of required Gibbs energy is obtained by heat to work conversion; this conversion is governed by Carnot factor and depends on the process temperature.

For the third case above, assume that the process of water splitting is driven by a heat Q_{tot} at the process temperature T. According to Eq. (19) the portion of the heat that must be converted in work form to supply the required Gibbs energy of the reaction is $(Q_{tot} - T\Delta S)$. Using the Carnot factor one expresses the Gibbs energy as follows

$$\Delta G = (Q_{tot} - T\Delta S) \times (1 - T_0/T) \tag{20}$$

where T_0 is the reference temperature of the environment.

Equation (20) can be solved for Q_{tot} for any given temperature T; the result is superimposed on the plot from Fig. 4. This shows that the process is favoured either by very low temperatures or by very high temperatures, when the input source is of thermal kind. In practical systems, a high temperature is in general obtained much cost effective than a cryogenic temperature; therefore, it appears logical to conduct water splitting process at high temperature. The challenge will remain to generate a high temperature in a non-polluting manner. Hybridization is also a good, practical option whereas the required energy is supplied partly electrically or by radiation and the remaining part as heat.

When coupled to wind turbines, the PEMEs can be used either as single units or multiple units operating in parallel, in accordance to the momentary wind conditions. Smaller capacities wind turbines (up to roughly 100 kW) require only single electrolysis units (which can operate at part load). Large capacity wind turbines will use multiple electrolysis units. The local average wind speed influences the power capacity factor of wind turbine which can be in the range of $C_p = C_p(\overline{V}) = 0.35 - 0.45$ with an ideal maximum of 0.59. The average wind speed is calculated base of a probabilistic distribution (e.g., Rayleigh), while the maximum average power generation per unit of area exposed to the wind (A) is given by

$$W/A = 0.5\rho C_p(\overline{V}) V_{RMC}^3 \tag{21}$$

where V_{RMC}^3 denotes the so-called root mean cube velocity. The ideal maximum average power per unit area is $0.5\rho\, V_{RMC}^3$; therefore, the power generation efficiency of wind turbine can be estimated through the power capacity factor calculated at average speed $\eta_{wind} = C_p(\overline{V})$; thus the energy efficiency of hydrogen production is calculated by multiplication of capacity factor and energy efficiency of PEM electrolyser according to

$$\eta_{H_2} = C_p(\overline{V}) \times \eta_{PEME} \tag{22}$$

Here, based on the rage of energy efficiency characterizing the PEME and wind turbines, $\eta_{H_2} = 0.20 - 0.33$. Note that the wind energy comes in the form of a mechanical work. Although is demonstrated in [53] that wind exergy is slightly different than wind exergy, as a first approximation the temperature (and wind chill) effect can be neglected and the exergy of wind assumed equal to the energy carried by the air stream; therefore, here it is assumed that the exergy efficiency of wind to power convertors is equal to the energy efficiency. The exergy efficiency of wind + PEM electrolysis systems can be thus estimated based on the energy efficiency η_{H_2} multiplied with a quality factor which is equal to the ration between the chemical exergy of hydrogen and its LHV. From Eq. (18) it results that $\psi = 0.19–0.32$.

As discussed also in [30] the application of wind-based PEM electrolysis leads to substantial GHG (greenhouse gas) emission reductions with respect to conventional steam methane reforming of natural gas. If all GHG emissions are taken into account starting from construction to operation phase for their entire lifecycle, the PEME-wind turbine system emit at most a levelized amount 8 g CO_2 per MJ embedded in the produced hydrogen (including hydrogen compression at ~350 bar). With conventional fossil hydrocarbon based methods, the emissions of GHG are more than ten times higher.

Wind farms are group of large capacity wind turbines installed to the same geographical location and interconnected electrically to generate power with total nameplate capacity in the range of 100–1000 MW with a capacity factor of 25–50%. Therefore, the effective power generation range of actual wind farms is 25–500 MW. This power range is suitable to drive large capacity alkaline electrolysers which can be installed at wind power generation. In principle, around 50 wind turbines can be grouped to supply a single AE unit with roughly 75–100 MW electric power. In wind farms facilities each individual wind turbine has a typical nameplate capacity of 2–3 MW. Wind farms are installed in special locations where there is enough wind resource (including on-shore and off-shore) such that operate with a high capacity factor, roughly of 40–45%.

The calculation of exergy efficiency based on Eq. (18) involves estimation of the ratio of energy and exergy input into the system. For a system which works with any radiation Eq. (18) becomes

$$\frac{\psi}{\eta} = \frac{E}{E \times EQF} \times \gamma = \frac{\gamma}{EQF} \tag{23}$$

where E is the energy supplied to the system and EQF is denoted as "Energy Quality Factor".

This factor (EQF) represents the ratio between exergy content and energy content associated with the energy supplied to the system. The estimation of SEQ depends on the nature of exergy supplied. In many cases it is customary to assume that the exergy supply is in form of a heat flux with an associated temperature. This approach is proposed to estimate the exergy of an electromagnetic or nuclear radiation. In such case, the energy quality factor is similar to Carnot factor, namely this is $EQF = 1 - T_0/T_s$.

For example, the most straight forward and simpler approach is to assume that solar radiation is equivalent to a heat flux of the same energy content and a temperature $T_s = 5700$ K, whereas the heat is diverted to Carnot a heat engine operating between the sun temperature and the terrestrial environment at the reference temperature T_0. In this case, the ratio between exergy content and energy content of solar radiation calculated from Eq. (23) is 1.024. More advanced models consider other aspects that influence the conversion of solar energy into work and therefore its associated exergy content. Some more elaborated expressions for SEQ are presented in [54–57].

If the energy is supplied to the system in form of a nuclear radiation – like in the case of nuclear reactors for power generation – it is customary to assume that the temperature of nuclear radiation is extremely high and its EQF is unity. Recent approaches consider however other aspects such as the nature of the nuclear particles (charged or neutral), the nature of the propagation (free or enclosed) etc. [58,59].

A photovoltaic (PV) water electrolysis system must comprise a commercial electrolyser plus a set of PV arrays and an electrical interconnection system that normally includes DC/AC inverters and rectifiers. In addition it must be included a hydrogen storage system, normally in metal hydrides. The factor that limits the efficiency of the system is the solar to electricity conversion with PV cells characterized by their energy efficiency, η_{PV}. A practical system has been experimented by [60] comprising double-axis sun-tracking PV arrays with an energy and exergy efficiency breakthrough as indicated in Fig. 5. The major losses of energy occur at solar radiation conversion into electricity at the level of PV arrays. For commercial system these losses account for approx. 88% with respect to the incident radiation.

More evolved multi-junction PV cells have higher efficiency which can go to about 30% but at a much higher cost. The availability on the marked of high efficient cost effective PV is nowadays very limited. The energy losses in electronics is also important because in commercial systems the electronics include at least three major components as charge regulators, backup batteries and inverter; the associated overall efficiency of electronic components (including transmission lines) is around 56%. Therefore, the electricity delivered to the electrolyser may represent approx. 7% from incident solar radiation.

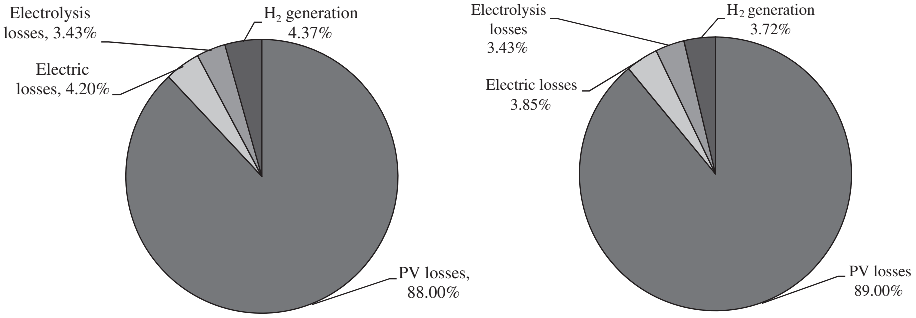
The exergy efficiency of PV-electrolyser system can be estimated based on Eq. (8) which takes in account the exergy losses through heat transfer due to PV array heating, namely

$$\psi = \psi_{PV} \times \psi_{PEME} = \frac{\dot{W}_{el} - hA \times (T_{PV} - T_0) \times (1 - T_0/T_{PV})}{\dot{E}x_S} \times \frac{\dot{E}x^{ch}_{H_2}}{\dot{W}_{el}} \tag{24}$$

where hA is the heat transfer coefficient into exposed area of the PV array, T_{PV} is the average temperature of the PV array surface, T_0 is the reference temperature of the environment, $\dot{E}x$ is exergy, subscripts "el", "solar" and "H_2" refer to the generated electrical power, to the incident solar radiation and to hydrogen, respectively, and the superscript "ch" refers to chemical exergy.

The scale of PV-electrolysers applications depends on the commercial viability of PV array systems. PV arrays are used today with capacity from below kW to couple of tens of kW electric. Many PV power plants – comprising hundreds of PV arrays installed on solar fields – were built in recent years with installed capacities approaching up to 90 MW and average capacity factors of 0.15; that is the actual levelized electric power generation can go to ~10 MW. PEM electrolysers can be coupled either to individual PV arrays or to large PV power plants. For small capacity, single PEME units are sufficient. At highest capacity, tens of PEM electrolyser units can be coupled with a PV solar field.

The systems that comprise an organic Rankine cycle (ORC) and a PEM electrolyser are discussed now. The ORC recover intermediate temperature heat from an application which waste heat. There are many examples in industry when heat is wasted at intermediate temperature level (approx. 80–200 °C). Heat can be recovered from combustion gases in actual water heating, space heating, or power generation facilities. In addition, solar radiation can be converted to high temperature solar heat with through concentrators. Both solar and waste heat recovery are sustainable energy sources that can be used in medium power ORC to generate electricity (from 1 kW range to tens of kW electric). The power is used to drive PEM electrolysers which in turn produce sustainable hydrogen. The Carnot factor associated with intermediate temperature source heat is of order of 0.2–0.4 leading to achievable electrical power generation with ORC in the range $\eta_{ORC} = 0.05–0.2$ with practical exergy efficiency of $\psi_{ORC} = 0.25–0.5$.



a Energy share **b** Exergy share

Fig. 5 – Typical energy (a) and exergy (b) shares for a PV-electrolyser hydrogen production system (based on a real system data from [35]).

Concentrated solar radiation at high installed capacity can be obtained with various techniques including solar through fields, solar dish fields and solar tower technologies. Regardless the methods of solar radiation concentration high temperature heat is eventually obtained to drive a heat engine, commonly based on Rankine cycle (either steam power plant or ORC). This setup forms a concentrated solar power (CSP) facility. If CSP is coupled to a high temperature electrolyser one can take advantage of the low grade heat that the heat engine rejects to the environment. Heat recovery can be applied to use part of the rejected heat to preheat water and the alkaline electrolyser such that some reductions of electrical energy requirements are achieved. This is an important issue for high capacity hydrogen production plants. CSP plants at high capacity operate at hot source temperature in the range of 300 °C (through systems) till 1000 °C (solar dish systems) with a characteristic Carnot factor of 48–76%. Power generation efficiency of 20–35% is practically demonstrated by those systems. CSP plants are currently available for a levelized power generation range from ~50–350 MW.

Ocean Thermal Energy Conversion (OTEC) has been studied for power generation at off shore locations. In equatorial and tropical seas the superficial seawater is warm at an almost constant temperature of 28 °C. Ocean deep sea is always cold at a constant temperature of 4 °C. The temperature difference between warm and cold water can be used to generate power with a suitable power plant installed on a floating facility. The corresponding Carnot factor for OTEC system is therefore around 0.08. In the study by [61] it is demonstrated an ammonia–water based power cycle which generates electricity with 5% energy efficiency and 62% exergy efficiency. The capacity factor of OTEC power plants is remarkably high.

Alkaline electrolysers may be used for an OTEC hydrogen production rate equivalent to 30–300 MW energy equivalent on hydrogen's LHV basis. In study by [62] it is assumed that the electrolyser has an efficiency of 84%, the OTEC facility is equipped with a desalination plant and an air separation unit which extracts nitrogen from air and an ammonia synthesis unit which combines hydrogen with nitrogen. Ammonia is transported to shores in liquid form and either sold on the fertilizers market or converted back to hydrogen with release of nitrogen in the atmosphere. It was found that the OTEC ammonia with current technology and the current tax credit applicable in USA for renewable energy (equivalent of ~2¢/kWh electric) the OTEC ammonia becomes cost-competitive with the imported ammonia which is produced from steam methane reforming or coal gasification with enormous GHG pollution worldwide. In addition, in [35] is shown that the cost of hydrogen stored and distributed as ammonia is 25% cheaper than hydrogen as cryogenic liquid, despite of the energy penalties at ammonia synthesis (to embed hydrogen) and ammonia decomposition (to release hydrogen). A capital cost breakthrough of an OTEC-hydrogen system is presented in Fig. 6.

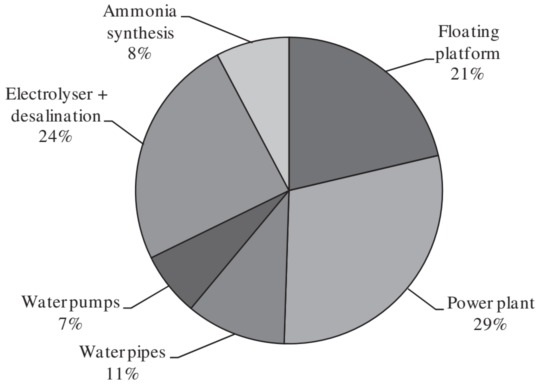


Fig. 6 – Cost shares for an OTEC hydrogen production facility (option 6).

Remark that the exergy efficiency of hydrogen production is high. This is due to a high exergy efficiency of the OTEC power generation efficiency. The use of ammonia-water as working fluid in the Rankine power plant assures an excellent match of temperature profiles at source and sink. In addition, the ocean thermal energy is the only form of solar energy which neither fluctuates nor it is intermittent. Therefore the OTEC power plant can operate steadily at it optimal design point.

Hydro-power has been used since the beginning of XIX century to generate hydrogen with alkaline electrolysers at Norsk Hydro in Norway where hydrogen was used to produce ammonia as fertilizer. Hydrogen via hydro-power and electrolysis has to compete – as a technology with hydroelectricity. In terms of efficiency, hydroelectricity reaches up to 85% hydraulic power to electric power conversion. If an alkaline electrolyser is used to generate hydrogen out of hydro-electricity, the overall efficiency, namely hydro-power to hydrogen, reaches around 60–65% which is the highest hydrogen production efficiencies among all sustainable pathways. Hydropower has a very high capacity factor (higher than 0.6). A very large spectrum of hydrogen production capacities can be obtained from hydropower. Small hydro can be coupled with PEM electrolysers, while large capacity hydropower plants can use groups of alkaline electrolysers.

Use of geothermal power to generate hydrogen has been studied in [63]. According to this study geothermal sites can cover a range of electric power generation from tens of MW to roughly 300 MW (e.g., Treiceria site in Portugal). Geothermal ORC plants can operate with an energy efficiency of 15–20%. When coupled to alkaline electrolysers, geothermal power plants can produce hydrogen with an efficiency of 10–15%.

Present generation of nuclear reactors have energy efficiency of ~30% with a predicted increase up to 50% of the IV generation of nuclear reactors. Assuming that reactor core is at a temperature of 2500 K, the Carnot factor of nuclear heat is 88%; thus, the exergy efficiency of nuclear power generation facilities is in the range of 26–44% If coupled to alkaline electrolysers, the energy and exergy efficiency of hydrogen production becomes 19–32% and 17–29%, respectively. With intermediate and high temperature steam electrolysers the expected hydrogen generation efficiency is higher; only generation IV reactors will be able to be coupled with intermediate and high temperature electrolysis systems.

The thermochemical S–I and hybrid Cu–Cl water splitting cycles have envisaged efficiencies of ~45%, based on their required energy input [34,35]. When coupled with high temperature nuclear reactors the total hydrogen generation efficiency of these systems must degrade to 40–43% due to various energy losses at heat (and electricity) transfer/

Table 6 – Energy inputs, energy and exergy efficiencies, sustainability indexes and hydrogen production rates of various sustainable options.

Option	Energy input	η (%)	ψ (%)	SI $= 1 - \psi$	$\dot{E}$ (MW)[a]
1-W	Wind	22–40	21–39	0.61–0.79	0.01–400
1-H/T	Hydro/Tidal	60–65	58–63	0.37–0.42	0.1–1000
1-O	OTEC	4–5	45–50	0.50–0.65	30–300
1-PV	Solar-PV	4–6	3–5	0.95–0.97	0.001–0.1
1-CSP	Solar-CSP	11–31	11–30	0.70–0.89	25–300
1-G	Geothermal	10–15	20–30	0.60–0.70	10–300
1-N	Nuclear	19–32	17–29	0.71–0.83	100–1000
1-WH	Waste heat	4–15	10–35	0.65–0.90	0.001–0.1
2-G	Geothermal	11–16	22–32	0.30–0.40	10–300
2-CSP	Solar CSP	12–32	12–31	0.69–0.88	25–300
2-N	Nuclear	22–35	20–33	0.67–0.80	100–1000
3-S	Solar	36–40	33–37	0.63–0.67	75–400
3-N	Nuclear	40–43	35–37	0.63–0.65	500–1500
4-S	Solar	36–40	33–37	0.63–0.67	75–400
4-N	Nuclear	40–43	35–37	0.63–0.65	500–1500
5-S	Solar	1–4	1–3	0.97–0.99	0.001–0.1
5-N	Nuclear	1–5	1–3	0.97–0.99	0.001–0.1
6	Biomass	60–70	55–65	0.35–0.45	0.5–100
7	Biomass	10–20	9–19	0.81–0.91	0.001–0.1
8	Biomass	5–20	4–19	0.81–0.96	0.001–0.1
9	Solar + biomass	3–25	2–24	0.76–0.98	0.001–0.1
10	Solar	15–25	14–24	0.76–0.86	0.01–1
11	Sustainable electricity	10–20	8–45	0.55–0.92	0.1–10
12	Sustainable electricity	10–20	8–45	0.55–0.92	0.001–0.01
13	Solar	30–40	27–36	0.64–0.73	0.1–10
14	Biomass	50–60	45–54	0.46–0.55	0.1–100
15	Biomass	5–15	4–13	0.87–0.96	0.1–10
16	Biomass	5–10	4–9	0.91–0.96	0.01–0.1
17	Biomass	5–10	4–9	0.91–0.96	0.1–1
18	Sustainable electricity	20–25	8–45	0.55–0.92	0.1–10
19	Fossil fuels	30–40	27–36	0.64–0.73	1–100
20	Fossil fuels	35–40	27–36	0.64–0.73	1–100
21	Nuclear	40–50	38–48	0.52–0.62	10–1000
22	Nuclear	50–55	48–53	0.47–0.52	10–1000
23	Solar	30–40	26–35	0.65–0.74	0.1–1
24	Sustainable electricity	10–15	8–45	0.55–0.92	0.001–0.01

[a] With respect to LHV of hydrogen.

conversion. When coupled to concentrated solar radiation, one assumes up to ∼20% optical and heat losses at the solar concentrator; thus, roughly, the system efficiency is ∼36–40%.

The efficiency range for each sustainable energy production option investigated in this paper is summarized in Table 6. The sustainability index – also discussed in [64] – is used here to determine the sustainability of each option based on the exergy efficiency of hydrogen production, according to

$$\mathrm{SI} = 1 - \psi \tag{25}$$

The key results from Table 6 are also presented graphically in Fig. 7–9 which show the range of energy efficiency, the

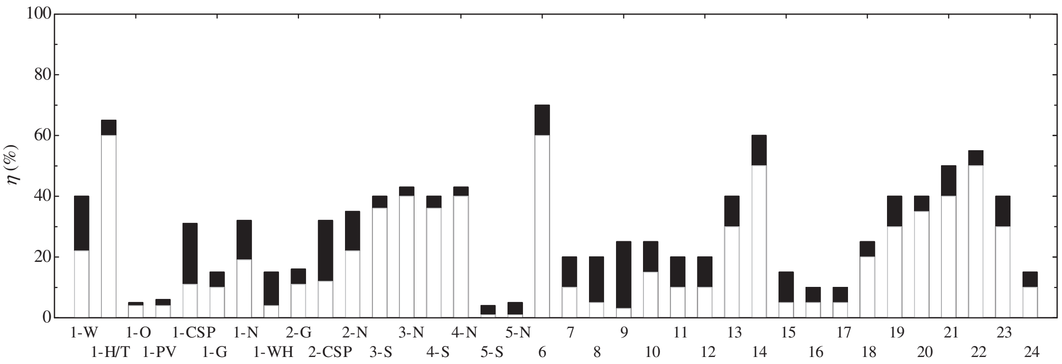


Fig. 7 – Energy efficiency ranges of the studied sustainable options of hydrogen production [*x*-axis labels indicated the option number as in Table 6; black ribbons indicate the range].

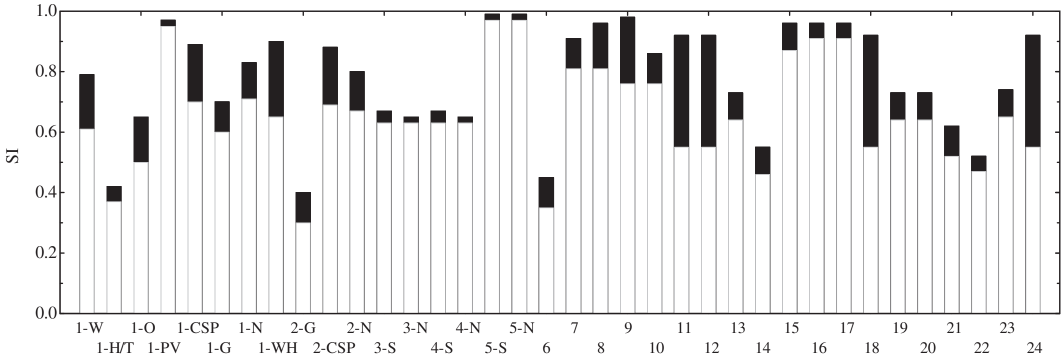


Fig. 8 – Energy efficiency ranges of the studied sustainable options of hydrogen production [*x*-axis labels indicated the option number as in Table 6; black ribbons indicate the range].

range of sustainability index and the range of hydrogen production rate for each of the studied case.

5. The role of IAHE in sustainable hydrogen production

As clearly outlined in IAHE [65], the Association strives to advance the day when "*hydrogen energy*" will become the principal means by which the world will achieve its long-sought goal of "Abundant Clean Energy for Mankind". Toward this end, the Association stimulates the exchange of information in Hydrogen Energy field through its publications and sponsorship of international workshops, short courses and conferences. In addition, the Association endeavours to inform the general public of the important role of hydrogen energy in the planning of an inexhaustible and clean energy system.

After appointment of Dr. Ibrahim Dincer as Vice President for Strategy in IAHE in 2009, Dr. Dincer was committed to play a critical role in achieving the following:

- to develop strategic plans for expansion
- to help to enhance IAHE horizons
- to promote IAHE through conferences symposia, workshops, and courses
- to develop divisions and technical groups in specific areas
- to organize outreach activities
- to organize and participate in public events
- to arrange displays about IAHE
- etc.

Dr. Dincer has played a critical a key role in bringing two key divisions on sustainable hydrogen production, bi-hydrogen and nuclear hydrogen divisions to fruition.

The mission of this bio hydrogen production division is to promote the development of biological hydrogen production as a viable process of hydrogen production through science and engineering excellence. It serves to educate scientists and engineers as well as policy makers, politicians and the general public about the use of hydrogen as an alternative energy currency, the value of biological hydrogen as a viable production technology, and the pathways to the hydrogen economy. It takes part in various national and international conferences to promote biological hydrogen production for hydrogen production. This is chaired by Dr. Richard Levin. The second division is nuclear hydrogen division which has a mission of organizing and promoting the development of nuclear systems and applications to hydrogen production. It also serves as public outreach and hydrogen advocacy to policy makers on the nuclear expansion underway worldwide. This division organizes regular activities at conferences, working sub-groups for different nuclear hydrogen technologies, and technology roadmaps that foster the emergence of

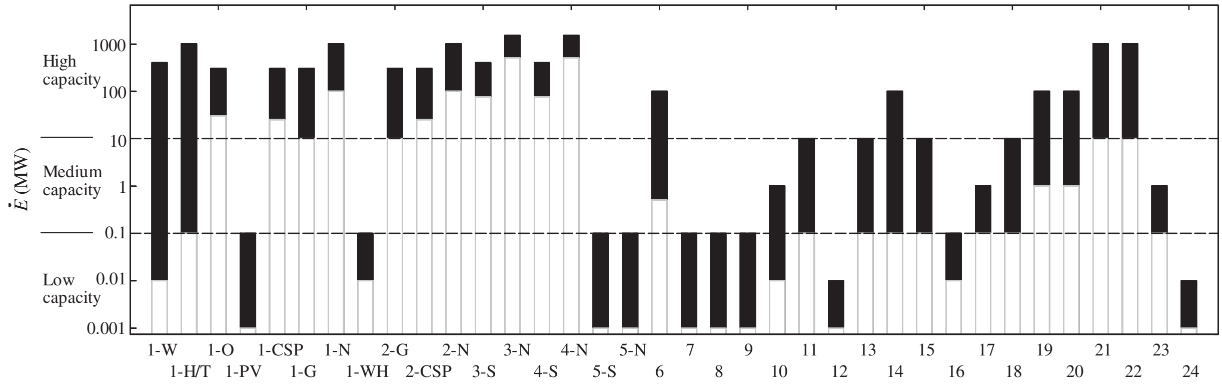


Fig. 9 – Ranges of hydrogen production rate for each hydrogen production option [*x*-axis labels indicated the option number as in Table 6; black ribbons indicate the range].

nuclear hydrogen production. There are also potential plans to enhance these activities and increase the number of key divisions to expedite the switch to hydrogen economy which is a prerequisite for the future carbon free society.

6. Conclusions

In this paper some relevant sustainable hydrogen production options are identified. In order to be sustainable, a method must be benign to the environment. Hydrogen does not exist in nature in a free way, except in few hydrogen rich natural gas wells. Therefore it must be extracted from available resources such as water, biomass, hydrogen sulphide, fossil hydrocarbons and anthropogenic wastes. Sustainable energy sources must be used for the extraction of hydrogen in order to make the overall process environmentally benign. There were found 24 options to produce hydrogen in a sustainable manner. Specifically, the following conclusions can be extracted from this study:

- Water splitting is the most important process for hydrogen production because water is the most abundant natural resource containing hydrogen.
- There are many ways to split water; the most efficient at appears to be hydro-power in conjunction to water electrolysers.
- Nuclear energy is a reasonable method to generate hydrogen at large and very large production scale using thermochemical cycles.
- Radiolytic methods of water splitting have good potential to be applied in conjunction with nuclear reactors and nuclear fuel processing systems.
- Photo-chemical and photo-bio-chemical present potential – although it is characterized by low efficiency – in conjunction to treatment of sewage waters which are a significant, cheap source of hydrogen.
- Anthropogenic wastes of all kinds must be considered as a source of hydrogen.
- Process waste heat recovery is one remarkable option to generate “clean” power and electrolytic hydrogen.
- Biological methods of hydrogen production from agricultural residuals and anthropogenic wastes present great potential.

Acknowledgements

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Nomenclature

A	area, m^2
C_p	power capacity factor
G	Gibbs free energy, kJ
E	energy, kJ
$\dot{E}$	energy rate, kW
EQF	energy quality factor
ex	specific exergy, kJ/kg
$\dot{E}x$	exergy rate, kW
I	intensity of incident solar radiation, W/m^2
h	heat transfer coefficient, W/m^{2}K
H	reaction enthalpy, kJ/mol
LHV	lower heating value, MJ/kg
$\dot{m}$	mass flow rate, kg/s
$\dot{n}$	molar rate, kmol/s
S	reaction enthalpy, kJ/molK
SI	sustainability index
T	temperature, K
V	velocity, m/s
W	work, kJ
y	stoichiometric factor

Greek letters

α	stoichiometric factor
β	GHG reduction fraction (Eq. (14))
γ	hydrogen energy quality factor
η	energy efficiency
ψ	exergy efficiency
ρ	density, kg/m^3

Subscripts

0	reference state
el	electrical
P	products
PEC	photo-electrochemical
PEME	proton exchange membrane electrolyser
PV	photovoltaic
R	reaction, reactants
RMC	root mean cube
S	sun
SOE	solid oxide electrolysis
T0	normal tilted surface
tot	total

Superscripts

ch	chemical

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