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Green methods for hydrogen production

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ABSTRACT

This paper discusses environmentally benign and sustainable, as green, methods for hydrogen production and categorizes them based on the driving sources and applications. Some potential sources are electrical, thermal, biochemical, photonic, electro-thermal, photo-thermal, photo-electric, photo-biochemical, and thermal-biochemical. Such forms of energy can be derived from renewable sources, nuclear energy and from energy recovery processes for hydrogen production purposes. These processes are analyzed and assessed for comparison purposes. Various case studies are presented to highlight the importance of green hydrogen production methods and systems for practical applications.

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1. Introduction

Many environmental issues have been caused by or relate to the production, transformation and use of energy, for example, acid rain, stratospheric ozone depletion and global climate change. Recently, a variety of potential solutions to the current environmental problems associated with the harmful pollutant emissions has evolved. Hydrogen energy systems appear to be the one of the most effective solutions and can play a significant role in providing better environment and sustainability [e.g., [1–4]].

At present, hydrogen, representing a market of roughly fifty billion US\$ for 40 Mt annual production, is mainly used as a chemical substance rather than a fuel. The most of its current uses are found as processing agent in oil refineries (e.g., for desulphurization and upgrading conventional petroleum) and in chemicals production processes (e.g., methanol, ammonia and pharmaceuticals). Prospects of future population increase with the consequence of an increased requirement of food and of various commodities

lead to the logical conclusion that the demand of hydrogen will increase too, at least to satisfy the needs of conventional transportation fuels, fertilizers and chemicals.

A consequence of the increased energy and food demand is the raise of greenhouse gases (GHG) emissions in the atmosphere. Measures to limit GHG emissions must consider hydrogen production from sustainable energy sources – that is, so-called green hydrogen production methods. Presently, hydrogen is mainly produced by steam reforming of natural gas – a process which led to massive emissions of GHG. Close to 50% of the global demand for hydrogen is currently generated via steam reforming of natural gas, about 30% from oil/naphtha reforming from refinery/chemical industrial off-gases, 18% from coal gasification, 3.9% from water electrolysis and 0.1% from other sources [5].

In the foreseen hydrogen economy of the future, green hydrogen production methods will be applied to supply hydrogen to be used directly as fuel, or to generate synthetic fuels, to produce ammonia and other fertilizers (viz. urea), to upgrade heavy oils (like oil sands), and to produce other

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chemicals [6]. Even from early time of hydrogen energy concept development, Awad and Veziroglu [7] pointed out the importance of hydrogen in removing environmental damages generated by combustion of fossil fuels. The main pollutants due to combustion are the carbon dioxide, carbon monoxide, sulfur dioxide, nitrogen oxides, ozone, lead, soot and ash. These negative effects extend from humans to water resources, farm produce, plants, forests, animals and other components of human habitat like buildings (e.g., degradation of buildings envelope due to pollution), damaging of coasts and beaches (e.g., through oil spills), effects on climate (e.g., the process of climate change with the associated temperature rise, ice melting and ocean waters rise).

Green hydrogen production technologies are not presently available with reasonable efficiency and cost. There is one green hydrogen production method – which can be considered as reference and can be realized with off-the-shelf components – namely the PV-electrolysis: it couples a photo-voltaic (PV) power generation system with a water electrolyzer. Mason and Zweibel [8] and other authors like Yilanci et al. [9] analyzed the efficiency, effectiveness and cost of this method for large and low scale hydrogen generation applications. This method is presently costly ($> \$5/\text{kg H}_2$) and generates hydrogen at very low efficiency ($< 5\%$). Other methods involve the use of one or more green energy sources to generate hydrogen directly or indirectly. Through “green energy sources” one understands renewable energy, nuclear energy, and energy derived from recovery (e.g., landfill gas, industrial heat recovery etc).

The financial, societal and political effort to convert the world economy to hydrogen is considerable. Currently, many associations exist to promote the concept of hydrogen economy at all levels of society. Several governments are committed in putting efforts toward a hydrogen economy development. One important role is played by International Association of Hydrogen Energy which – as discussed in Goltsov et al. [10] – deployed considerable activity for influencing the world hydrogen movement, general public, international and regional organizations, parliaments and governments of the world countries.

Several reviews were published in the open literature regarding hydrogen production from renewable energy sources and renewable raw materials. One of the early works analyzing hydrogen production from water by using renewable sources of energy is due to Lodhi [11] which mentions the application of high temperature water dissociation, thermochemical water splitting, water electrolysis, water photolysis. In a subsequent paper Lodhi [12] lists the green energy sources to generate hydrogen as being: the sunlight, sea/ocean energy, runoff waters, winds, fissionable materials. The materials from which hydrogen can be extracted through green methods are identified as: water, brine (sea water), hydrogen sulphide and biomass. Miltner et al. [13] classified green hydrogen production methods based on the material from which hydrogen is extracted.

Lemus and Duarte [14] emphasized a hydrogen cost paradigm: at centralized locations is higher than the cost at distributed locations because of transportation issues (which involve cost penalty at hydrogen compression, distribution and storage). Muradov and Veziroglu [5] advanced the concept of

hydrogen–carbon economy as a transition phase from a fossil fuel based economy to the future hydrogen fuel based economy. In hydrogen–carbon economy scenario, natural gas is distributed through networks over a territory. At each distributed location, the natural gas is catalytically dissociated in hydrogen and carbon powder. The hydrogen is then fed to vehicles to be used as fuel for propulsion. The carbon is collected and transported to centralized locations for further processing. There carbon can be embedded in structural materials (as component of carbon fibers, cements, steels etc), or it can be used for soil amendment. Carbon dioxide can be combusted for power generation with high efficiency in direct carbon fuel cell assisted by CO_2 sequestration in oil wells or underwater.

Regarding the green hydrogen production methods based on water electrolysis, Lemus and Duarte [14] enumerated PV-electrolysis, biomass gasification, concentrated solar power (CSP) coupled with water electrolysis, Ocean Thermal Energy Conversion (OTEC) power coupled to water electrolysis, geothermal power + electrolysis, coal gasification coupled with carbon capture and storage and water electrolysis, wind power + electrolysis, nuclear power and electrolysis, hydro-power and electrolysis, tidal power and electrolysis.

Photonic hydrogen generation methods present a considerable interest as they are essentially “green”. Regarding water photolysis, this can be done as photo-electrolysis, catalytic photolysis, bio-photolysis. There are a number of approaches to mimic photosynthesis reactions performed by green plants and cyano-bacteria. Gust et al. [15] developed a molecular bio-device capable to interact with photonic radiation and deliver electrons and protons to an ATP (adenosine tri-phosphate) synthase enzyme to generate ATP from ADP (adenosine di-phosphate); further ATP can be used to generate hydrogen from the substrate. Alstrum-Acevedo et al. [16] summarized the current chemical approaches to artificial photosynthesis for hydrogen generation. Levin and Chahine [6] reviewed the biological methods to generate hydrogen including direct and indirect photolysis, photo-fermentation, dark fermentation. Tanksale et al. [17] reviewed catalytic hydrogen production methods from biomass including gasification, pyrolysis and sugars conversion in hydrogen.

In this paper, a comprehensive classification of green methods for hydrogen production is presented, and these methods are discussed, assessed and compared for various applications, along with some illustrative examples and case studies.

2. Hydrogen production methods

Many substances found in nature contain hydrogen. Among them water – naturally found as brine (sea water), river or water, rain or well water is the most abundant. Hydrogen can also be extracted from fossil hydrocarbons, biomass, hydrogen sulfide, or some other substances. When hydrogen is extracted from fossil hydrocarbon, all carbon dioxide must be processed (separated, sequestered etc) such that no GHG or other pollutants are emitted in the atmosphere and the hydrogen extraction process can be called “green”.

The forms of energy needed to extract hydrogen from the above-listed natural resources can be classified in four

categories, namely thermal, electrical, photonic and biochemical. These kinds of energy can be obtained from green energy sources as it will be indicated subsequently. In this paper is proposed that green energy comprises renewable energy, nuclear energy, and recovered energy (like, for example, recovered industrial heat, landfill gas, wastes that can be incinerated etc).

Fig. 1 proposes various paths through which the four kinds of energies to drive hydrogen production can be obtained from green energy sources. The electrical and thermal energy can be derived from renewable energies (like solar, wind, geothermal, tidal, wave, ocean thermal, hydro, biomass), or from nuclear energy, or from recovered energy. The photonic energy is comprised in solar radiation only. The biochemical energy is that stored in organic matter (in form of carbohydrates, glucose and sugars etc) and can be manipulated by certain micro-organisms that can extract hydrogen from various substrates or it can be chemically converted to thermal energy. Biochemical energy can be assisted or not by

solar radiation to generate energy, depending on the case (viz. bio-photolysis or dark fermentation).

Table 1 lists the available green hydrogen production methods according to the energy used to drive the process. Apart from the methods that use a single form of energy (electrical, thermal, photonic or biochemical) there were identified hybrid methods that use two forms of energy (electrical + thermal, electrical + photonic, biochemical + thermal, photonic + biochemical). The table also indicates the materials/resources from which hydrogen is extracted for each of the methods. The considered hydrogen containing materials are as follows: water, biomass, hydrogen sulfide and fossil hydrocarbons. In the case that coal or fossil hydrocarbons are used in the conversion process, the hydrogen production process is devised such that all carbon dioxide emitted is separated and sequestered.

The process driving energy for each case can be obtained from green energy sources through various routes. These routes were identified for each case as they are listed in Table 2.

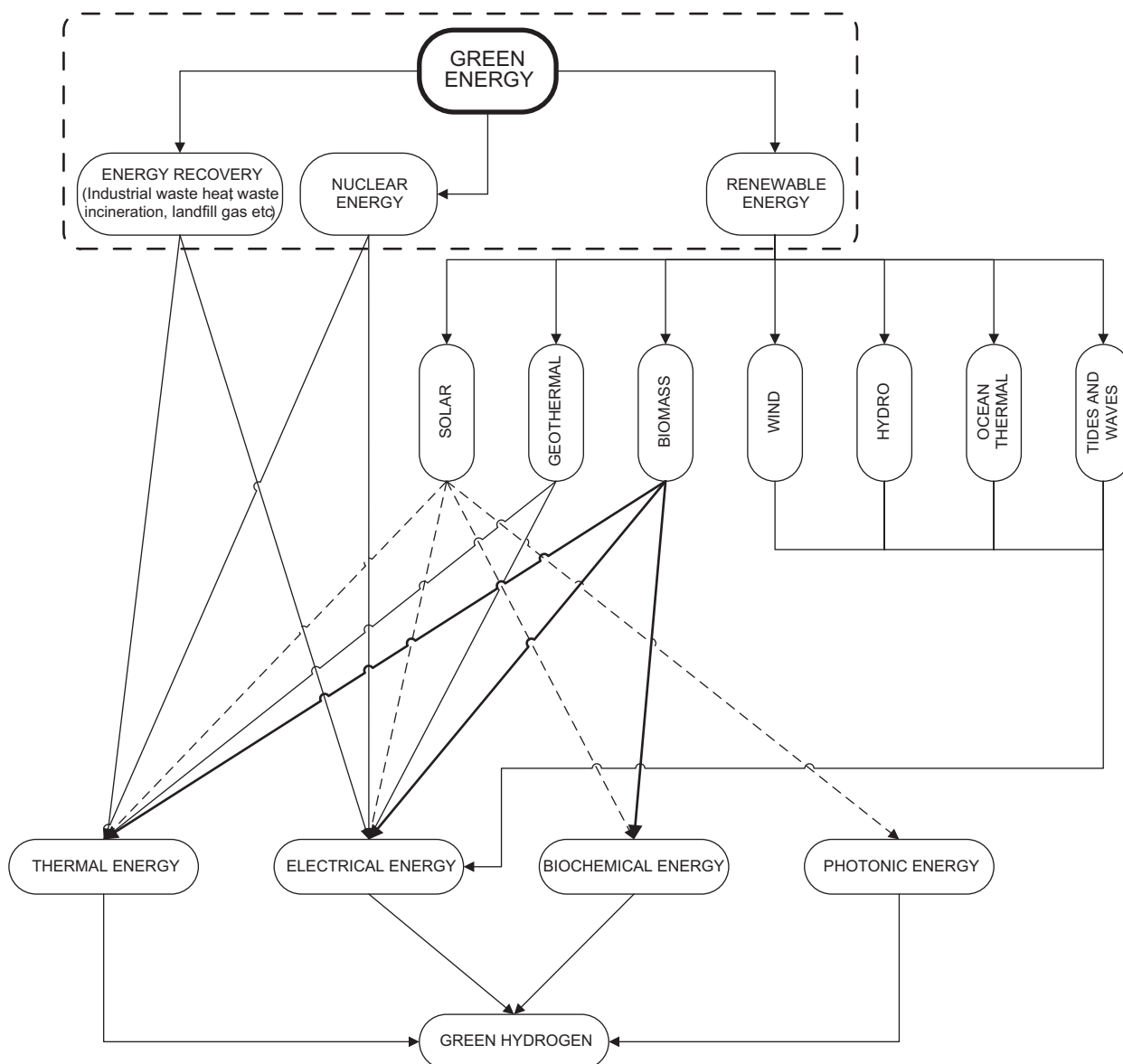


Fig. 1 – Paths of generation of basic form of energy from primary green energy sources.

Table 1 – Classification of green hydrogen production methods.

Process driving energy	Hydrogen production method		Material resources	Brief description
Electrical energy	Electrolysis		Water	Water decomposition into O ₂ and H ₂ by passing a direct current which drives electrochemical reactions.
	Plasma arc decomposition		Natural gas	Cleaned natural gas (methane) is passed through an electrically produced plasma arc to generate hydrogen and carbon soot.
Thermal energy	Thermolysis		Water	Steam is brought to temperatures of over 2500 K at which water molecule decomposes thermally.
	Thermocatalysis	H ₂ S cracking	Hydrogen sulfide	H ₂ S extracted from seas or derived from other industrial processes is cracked thermo-catalytically
	Thermochemical processes	Biomass conversion	Biomass	Thermo-catalytic biomass conversion to hydrogen
		Water splitting	Water	Chemical reactions (including or not redox reactions) are conducted cyclically with overall result of water molecule splitting.
		Gasification	Biomass	Biomass converted to syngas; H ₂ extracted
		Reforming	Biofuels	Liquid biofuels converted to hydrogen
Photonic energy	PV-electrolysis Photo-catalysis	H ₂ S splitting	Hydrogen sulfide	Cyclical reactions to split the hydrogen sulfide molecule
			Water	PV panels generate electricity to drive electrolyzer
			Water	Complex homogeneous catalysts or molecular devices with photo-initiated electrons collection are used to generate hydrogen from water
	Photo-electro-chemical method		Water	A hybrid cell is used to generate photovoltaic electricity which drives the water electrolysis process
	Bio-photolysis		Water	Biological systems based on cyanobacteria are used to generate hydrogen in a controlled manner
Biochemical energy	Dark fermentation		Biomass	Anaerobic fermentation in the absence of light
	Enzymatic		Water	Uses polysaccharides to generate the required energy
Electrical + thermal	High temperature electrolysis		Water	Uses a thermal source and electrical power to split water in solid oxide electrolyte cells
	Hybrid thermochemical cycles		Water	Use thermal energy and electricity to drive chemical reactions cyclically with the overall result of water splitting
	Thermo-catalytic fossil fuels cracking		Fossil fuels	A thermo-catalytic process is used to crack fossil hydrocarbons to H ₂ and CO ₂ , whereas CO ₂ is separated/sequestered for the process to become green
	Coal gasification		Water	Coal is converted to syngas, then H ₂ extracted and CO ₂ separated/sequestered (electric power spent)
	Fossil fuels reforming		Fossil fuels	Fossil hydrocarbons are converted to H ₂ with CO ₂ capture and sequestration (electric power spent)
Electrical + photonic	Photo-electrolysis		Water	Photo-electrodes + external source of electricity
Biochemical + thermal	Thermophilic digestion		Biomass	Uses biomass digestion assisted by thermal energy for heating at low grade temperature
Photonic + biochemical	Bio-photolysis		Biomass, water	Uses bacteria and microbes to photo-generate hydrogen
	Photo-fermentation		Biomass	The fermentation process in facilitated by light exposure
	Artificial photosynthesis		Biomass, water	Chemically engineered molecules and associated systems to mimic photosynthesis and generate H ₂ .

Basically, Table 2 indicates energy conversion routes to generate electrical, thermal, biochemical, or photonic energy from green energy sources. For thermal energy, an important parameter is the level of temperature. Note that there are specific methods for generating low, intermediate and high temperature heat. Thermolysis, thermochemical and thermo-catalytic processes and high temperature electrolysis require high temperature heat. Hydrogen sulfide splitting and hybrid thermochemical water splitting require intermediate

temperature heat. Thermophilic digestion needs low grade heat. Solar energy and biomass energy can generate high temperature heat; solar, geothermal and heat recovery from various processes are appropriate forms to generate intermediate and low temperature heat. Nuclear energy comes normally at intermediate temperature level ($\sim 300^\circ\text{C}$). Also one remarks that processes that use photonic energy (viz. photo-catalysis, photo-electrolysis etc) require solar energy as input; though they may be assisted by other forms of green

Table 2 – Production methods and energy conversion paths to generate “green hydrogen”.

Hydrogen production method		Green energy source	Conversion path	
Electrolysis (Green energy gene-rate electricity for water electrolysis) or Plasma arc decomposition (Green energy gene-rate electricity for plasma ark decom-position of nat. gas)		Solar	PV power plant or concentrated solar power (CSP) to generate electricity	
		Geothermal	Power plant (Organic Rankine Cycle – ORC, Flash cycle etc)	
		Biomass	Biomass power plant, internal combustion engines, fuel-cell plants	
		Wind	Wind power plants (grid connected or autonomous)	
		Ocean heat	OTEC – Ocean Thermal Energy Conversion plants	
		Other renew.	Tides, ocean currents and wave energy converted into electricity	
		Nuclear	Nuclear power plants	
		Recovery	Landfill gas combusted in diesel generators	
			Industrial/other heat recovery used to drive ORC or other heat engines	
Thermolysis		Solar	Incineration with pollutant capture drives Rankine power plant	
Thermocatalysis	H ₂ S cracking	Solar	Concentrated solar heat used to generate ultrahigh temperature steam	
		Solar	Concentrated solar heat used to drive the process at high temperature	
		Biomass	Low grade biomass combustion generates the process heat	
		Recovery	Landfill gas combustion, high temperature industrial heat recovery	
	Biomass conv.	Solar	Concentrated solar heat at high temperature drives the process	
		Biomass	Auto-thermal process: reaction heat comes from biomass combustion	
Thermochemical processes	Water splitting	Solar	Concentrated solar radiation generates high temperature heat	
		Geothermal	Geothermal generate electricity to drive high temperature heat pumps	
		Biomass	Dried biomass is combusted to generate high temperature heat	
		Nuclear	Nuclear electric power used to drive high temperature heat pumps	
		Recovery	Landfill gas combustion	
		Gasification	Solar	Concentrated solar heat at high temperature drives the process
			Biomass	Auto-thermal process: reaction heat comes from biomass combustion
		Fuel reforming	Solar	Concentrated solar heat at high temperature drives the process
	Biofuels		Auto-thermal process: reaction heat comes from biomass combustion	
		H ₂ S splitting	Solar	Concentrated solar heat used to drive the process at high temperature
	Geothermal		High temperature geothermal heat at ~200 °C drives the process	
	Biomass		Low grade biomass combustion generates the process heat	
		Recovery	Landfill gas combustion, high temperature industrial heat recovery	
	PV-electrolysis		Solar	Solar radiation generates electricity through PV-panels
	Photo-catalysis		Solar	UV and upper spectrum visible solar radiation drives the process
Photo-electro-chem.		Solar	All solar spectrum used by photo-electrochemical cell	
Bio-photolysis		Solar	All solar spectrum can be used	
Dark fermentation		Biomass	Biogas reactors are used for dark fermentation to generate hydrogen	
Enzymatic		Biomass	Polysaccharides are manipulated by special enzymes to extract hydrogen	
High temperature electrolysis		Solar	Concentrated solar power generates high temperature heat and electricity	
		Geothermal	Geothermal electricity coupled to high temperature heat pumps	
		Biomass	Biomass combustion generate power and high temperature heat	
		Nuclear	Nuclear power used to generate electricity and high temperature heat	
		Recovery	Recovered energy generates electricity and high temperature heat	
Hybrid thermochemical cycles		Solar	Concentrates solar power generate high temperature heat and electricity	
		Geothermal	Geothermal electricity coupled to high temperature heat pumps	
		Biomass	Biomass combustion generate power and high temperature heat	
		Nuclear	Nuclear power used to generate electricity and high temperature heat	
		Recovery	Recovered energy generates electricity and high temperature heat	
Photo-electrolysis		Solar	PV or CSP + electrolysis bath with photo-electrodes	
Thermophilic digest.		Biom. + other	Biomass energy drives the process; heat recovery or solar provides heat	
Bio-photolysis		Biomass + sol.	Biomass + photonic energy drive the process	
Photo-fermentation		Biomass + sol.	Biomass + photonic energy drive the process	
Artif. photosynthesis		Solar	Solar energy drives directly the hydrogen generation process	

energy. Another remark regards biological conversion processes: they necessary require biomass as biological substrate.

2.1. Water electrolysis

Water electrolysis is one of the most basic methods to generate almost pure hydrogen and is driven by the movement of electrons which are continuously circulated through an external circuit. The energy transmitted to a process in form of work can be quantified by Gibbs energy variation, which at infinitesimal scale is $dG = \sum d(\mu_i \eta_i) - sdT + vdp$, where μ_i is the chemical potential of specie “i” which number of mols is η_i ; obviously, the species involved in electrolysis are H_2O , H_2 , O_2 . Electrolysis occurs normally at constant pressure and temperature, thus, the work energy transmitted to the reaction in form of electrons movement (electric current) becomes $dG = \sum d(\mu_i \eta_i)$. The Gibbs free energy of the reaction influences the reaction equilibrium through the equilibrium constant which is $K_{eq} = \exp(-\Delta G/RT) = \exp(-\Delta \mu_{el}/RT)$, where R is the ideal gas constant and T is the process temperature, and $\Delta \mu_{el}$ is the electrochemical potential (which is a measure of energy stored in chemical potential and electrostatics). Further, the equilibrium constant is related to the reaction rate of the forward (k_f) and backward (k_b) reactions through the following equation $k_f = k_b K_{eq} = k_b \exp(-\Delta \mu_{el}/RT)$; thus the reaction rate is a function of electrochemical potential variation (induced by the photonic energy), $k_f = k_f(\Delta \mu_{el})$.

There are two technologies to conduct water electrolysis: the alkaline process and the proton exchange membrane (PEM) process. Table 3 summarizes the main characteristics of alkaline and PEM electrolysis systems. Two parameters are important, that is the efficiency and the current density. The electrolysis cell efficiency is defined as the ideal energy and actual energy needed to drive the reaction. From thermodynamics one can easily determine the enthalpy for water splitting reaction $H_2O \rightarrow H_2 + 0.5O_2$, which is equal with the formation enthalpy of liquid water and is $\Delta H = 285.813$ kJ/mol; a part of this enthalpy can be provided thermally at the reaction temperature in the form of increase of entropy $\Delta Q = T \times \Delta S$. At standard temperature and pressure this amount of heat is $\Delta Q = 48.689$ kJ/mol. The remaining part is the Gibbs free energy of the process and represents the minimum electrical energy that must be applied for the reaction to occur, that is – for standard condition

$\Delta G = 237.124$ kJ/mol = 2.458 eV. Two electrons are needed for one mol of hydrogen; thus the minimum potential applied at standard conditions is $V_{min} = 2.458/2 = 1.23$ V.

Electrolysis requires catalysts for improved reaction rate and current density. Platinum is normally applied on the electrodes to conduct a heterogeneous catalysis process. Alternatively, homogeneous catalysts can be dissolved/suspended in the electrolyte. Homogeneous catalysts are a promising solution for the future as they are less expensive and have high turnover rate that the commonly used rare metals. One recent example of homogeneous catalyst that act at the hydrogen evolving electrode is due to Karundasa et al. [18] showing a turnover rate of 2.4 mole of hydrogen per mole of catalyst and second.

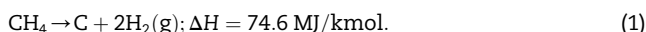
At a rate of €5/kWh electricity cost, the cost of hydrogen production through commercially available electrolysis systems goes from \$2.5 to \$3.5 per kg, while the cost obtained from an ideal electrolyzer (without losses) is \$1.95/kg. Water must be desalinated and demineralized before electrolysis. Especially PEM electrolyzers are more sensitive to the purity of water. If saline water (brine) is fed in a regular electrolyzer high chances are that ionic chlorine is evolved at the cathode rather than oxygen. El-Bassuoni et al. [19] proposed a method to generate hydrogen and desalinate sea water through electrolysis where the electrodes are surrounded by ions selective membranes having the role to stop side reactions (like chlorine evolution which being toxic should be avoided). Using magnesium as catalyst at anode also promotes oxygen evolution in the detriment of chlorine formation (see [20]).

2.2. Plasma arc decomposition

Plasma is ionized state of matter comprising atomic species and electrons in an excited state. Because of the existence of electrically charged particles, plasma can be used as medium for high voltage electric current discharge. Natural gas – comprising mostly methane – can be decomposed under the action of thermal plasma. Thermal plasma has the property of which ionized atoms and the electrons are at the same thermodynamic temperature. When methane is flown through a plasma arc it dissociates to hydrogen and carbon black (soot). The carbon black can be collected as soot at the bottom, while the hydrogen remains in gas phase. The decomposition of natural gas (methane) to hydrogen and carbon is according to

Table 3 – Parameters of typical water electrolysis cells.

Electrolysis process	Electrolyte	Ions transport	Anode reaction	Cathode reaction	Current density, A/cm ²	Efficiency, %
Alkaline	KOH 25–30% wt or NaOH, NaCl	Hydroxyl OH [−]	$4OH_{(aq)}^- \rightarrow O_{2(g)} + 2H_2O_{(l)}$	$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH_{(aq)}^-$	0.1–0.4	50–65
PEM	Polymer (NAFION)	Protons H ⁺	$2H_2O_{(l)} \rightarrow 4H_{(aq)}^+ + 4e^- + O_{2(g)}$	$4H^+ + 4e^- \rightarrow 2H_{2(g)}$	>1.6	50–75



Fulcheri et al. [21] conducted reaction (1) under high temperature thermal plasma in a reactor comprising 3 electrodes connected to a 3-phase voltage with plasma gas injected at 2 of the electrodes, and methane introduced in the reaction chamber from above. The yield of hydrogen has been 100% with no CO₂ release and formation of carbon black at the bottom of the reactor. The plasma dissociation is in fact a high temperature pyrolysis process. Based on the analysis of Gaudernack and Lynum [22] the cost of hydrogen generated through plasma cracking is reduced with at least 5% with respect to large scale production by steam methane reforming assisted by carbon dioxide sequestration.

2.3. Water thermolysis

The single-step thermal dissociation of water is known as water thermolysis and can be given as



The reaction requires a high-temperature heat source at above 2500 K to have a reasonable degree of dissociation (e.g. 3000 K for 64% dissociation at 1 bar). One drawback of this process comes from the need of an effective technique to separate H₂ and O₂ to avoid ending up with an explosive mixture. Semi-permeable membranes based on ZrO₂ and other high-temperature materials can be used with this purpose at up to 2500 K. Separation can also be achieved after the product gas mixture is quenched to lower temperature. Baykara et al. [23] studied experimentally the thermolysis of water using solar radiation. The conclusions are that the residence time in the reactor to achieve 90% of the equilibrium at 2500 K is 1 ms. Recombination of hydrogen and oxygen can be avoided if the product gas is rapidly cooled by quenching through a sharp temperature decrease of 1500–2000 K within few milliseconds. Palladium membranes can be then used for effective hydrogen separation.

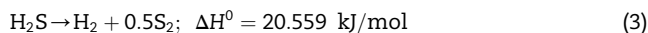
2.4. Thermo-catalytic cracking of hydrogen sulfide to generate hydrogen and sulfur

One standard liter of hydrogen sulphide embeds 76 g of hydrogen – that is about 1000 times more than the mass of pure hydrogen per unit of volume in the same conditions. Hydrogen sulphide can be found in nature in various environments: volcanoes, hot springs, well water, geothermal wells, oil wells, lakes or seas.

Recent studies [24,25] have demonstrated that deep waters of the Black Sea have a resource of 4.6 billion tons of H₂S generated by anaerobic bacterial activity which may bring a potential of extracting 270 million tons of hydrogen. At depths of over 150 m the concentration of H₂S increases steadily; close to the sea bottom at 1000–2000 m depth the concentration reaches 8–8.5 ml/l.

Presently there is not any commercially available method to produce hydrogen from H₂S. The available laboratory methods known up to date and the potential to develop a commercial thermo-catalytic process were analyzed by

Zaman and Chakma [26]. Thermo-catalytic cracking of hydrogen sulphide generates two valuable products, namely hydrogen and sulfur according to the reaction



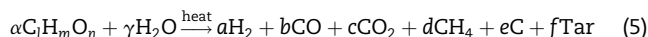
Catalytic separation membranes made from a combination of glass and alumina which allow permeation of hydrogen from the H₂S decomposition reactor represent one of the promising cracking methods. Molybdenum disulphide (MoS₂) catalyst shows excellent yield; other catalysts are based on WS₂, NiW, NiMo and alumina. Two steps thermochemical cycles extracting hydrogen from H₂S with the help of metals of various valences were also investigated; they operate according to [26]:



where M represents a metal.

2.5. Biomass thermo-catalytic conversion routes

Biomass can be used as primary energy to extract hydrogen from steam. If the moisture content is too high, either the biomass must be dried before gasification or supercritical steam gasification can be applied. The wood sawdust, sugar cane bagasse etc. are some general form of biomass that can be used to produce hydrogen. The global reaction of biomass gasification process to produce hydrogen reads



where $\alpha\text{C}_i\text{H}_m\text{O}_n$ is the general chemical representation of the biomass. The formation of tars is undesirable because of negative effect on the pipes, ducts and equipment by slugging and fouling. Tar formation can be diminished by proper control and using various catalyzes. Table 4 indicates the H₂ yield and operating parameters of typical gasifiers.

Abudala et al. [27] proposed a hydrogen production system based on steam gasification of biomass that uses wood sawdust and 4.5 kg/s of steam at 500 K. It is found that the hydrogen yield reaches 80–130 gH₂/kg biomass with 50% molar concentration in the product gas which reaches heating value of 15–20 MJ/m³. The biomass is introduced to a gasifier at an operating temperature range of 1000–1500 K.

Table 4 – Indicative parameters and H₂ yields of biomass gasifiers.

Biomass	T, °C	Steam-biomass ratio	H ₂ yield, %
Pine & eucalyptus	880	0.8	41
Pine sawdust	750	0.5	40
Mixed sawdust	750	0.51	62.5
Mixed sawdust	800	4.7	57.4
Mixed sawdust	800	1.4	48.8
Mixed sawdust	800	1.1	46
General biomass	777	1.5	59

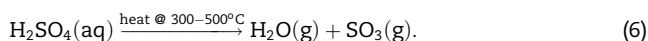
Source: Abuadala et al. [27].

2.6. Thermochemical water splitting

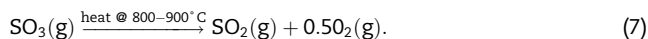
One major interest in thermochemical cycle is that they normally do not require catalysis to drive the chemical reactions. All chemicals involved in the process can be recycled except water which is the material source from which hydrogen is derived. Water-splitting thermochemical cycles are attractive for the following reasons: (i) there is no need of hydrogen-oxygen separation membranes; (ii) the temperature of the required thermal energy source is in a reasonable range (600–1200 K); (iii) there is no or very less requirement of electrical energy to drive the process.

Several review articles on the topic have been published in the open literature, as summarized by Balta et al. [28]. The sulfur–iodine (S–I) cycle operates at maximum temperature of 825–900 °C which is needed to drive the oxygen-evolving reaction. The S–I cycle has been fully demonstrated in both Japan and the US and has been shown to be technically viable. However, the commercial viability of any of these cycles has yet to be demonstrated. The equipment cost for an S–I plant with 790 tons/day of hydrogen production capacity was \$125 million. The maximum attainable one-pass HI conversion rate was reported to exceed 90% with membrane technology, whereas the equilibrium rate is about 20%.

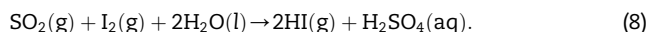
The first reaction of this cycle is the sulfuric acid decomposition to release water; this reaction is thermally driven, according to



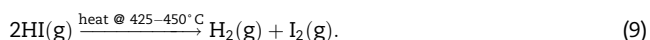
The resulted steam is separated from $\text{SO}_3(\text{g})$ and by further heating up to 800–900 °C the sulfur trioxide is decomposed thermally to release oxygen according to



The so-called “Bunsen” reaction follows a reaction in which combines the sulfur dioxide $\text{SO}_2(\text{g})$ separated from oxygen with iodine and water. The reaction is exothermic and occurs at low temperatures, spontaneously, to produce sulfuric acid as it follows



The hydrogen iodine is further decomposed thermally at 425–450 °C and generates hydrogen:

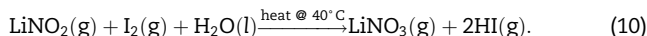


One major advantage of the sulfur–iodine cycle is due to the fact that there is no side reaction occurring during the process and the separation of chemicals is relatively straight forward. The drawback of the process is that it occurs at rather high temperature. Thus relatively less number of sustainable thermal energy sources is available to drive this process. Among the possible such sources one can list here: nuclear heat from high temperature gas-cooled reactors, concentrated solar thermal heat and biomass combustion heat. Note that the S–I cycle has a hybrid version also in which the hydrogen evolving reaction is conducted electro-chemically.

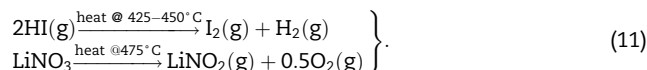
An interesting process – but less developed – is the Li– NO_3 cycle for water splitting. This thermally driven cycle evolves

completely at lower temperatures. The highest temperature required is 475 °C the LiNO_3 decomposition reaction which releases oxygen. Also the hydrogen iodine decomposition reaction is evolving at 425–450 °C.

The first reaction occurs at temperature close to the ambient and is endothermic according to

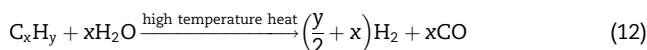


The other two reactions are also endothermic evolving at higher temperature and releasing hydrogen and oxygen according to



2.7. Biomass gasification and biofuels reforming

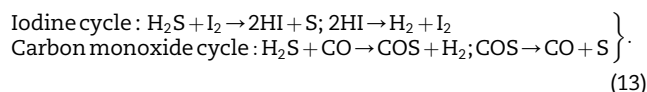
Through biomass gasification synthesis gas ($\text{CO} + \text{H}_2$) is obtained according to the following simplified reaction of solid biomass with steam:



The main parameters influencing the gasification process are discussed in Table 5. Different gasifiers are employed in the gasification process: fixed bed, moveable bed and fluidized bed. The process could be either auto-thermal or all-thermal depending on how this heat is provided. In case of auto-thermal gasification, the necessary heat is generated directly by partial oxidation in the gasifier itself. Liquid biofuels (ethanol, methanol etc) and biogas can be reformed to hydrogen via thermochemical processes which is a process rather analog with gasification.

2.8. Thermochemical cycles for hydrogen sulfide splitting

Other thermochemical cycles for hydrogen sulfide decomposition can operate with iodine or carbon monoxide:



All these processes are yet in development phase as they raise several technical problems with controlling the reactions, improving yields and reaction rates and diminishing the formation of non-desired products. For example, as shown elsewhere [26], the thermochemical cycle operating with carbon monoxide, though it is very attractive because its hydrogen releasing reaction evolves at very low temperature (373–473 K) is difficult to cycle because of the formation of CS_2 in a concurrent reaction, namely $2\text{COS} \rightarrow \text{CO}_2 + \text{CS}_2$.

2.9. PV-electrolysis

The photovoltaic driven water electrolysis comprises photovoltaic (PV) panels, DC bus bar, AC grid, accumulator battery set, electrolyzer and hydrogen storage canisters. The cost of PV-generated electricity is in continuous decline; for example

Table 5 – Parameters influencing the gasification process.

Parameter	Description	Effects
Equivalent ratio	The oxygen supplied over the stoichiometric oxygen	Higher oxidant delivered through increased air rate dilutes the product gas and reduces the efficiency; to low air rate does not suffice for partial oxidation which reduce gas production
Steam-fuel ratio	$SBR = \frac{\dot{m}_{\text{steam}} + \dot{m}_{\text{moist}}}{\dot{m}_{\text{fuel}}(1 - \text{moist}\%)}$	Influences the required energy input and product gas composition. Low SBR leads to more methane and solid carbon formation. High SBR means more syngas produced.
Process temperature	Process temperature is not constant; gasifier temperature is considered that which is after the pyrolysis zone.	Lower temperatures lead to more solid carbon and methane in the product gas. In general, optimal values are 800–900 °C; above these hydrogen yield reduces.
Process pressure	Gasification occurs at constant pressure in the gasifier.	Chemical equilibrium indicates that gasification is favored by low pressures and high temperatures. However, no substantial gain is obtained if the process runs in vacuum.

in 1998 the average cost was \$12 per installed watt and in 2008 became \$8. The efficiency of the solar cell can range from 12 to 15% typically for the silicon solar cell. However, it is as high as 25–30% for GaAs solar cells. The total efficiency of solar radiant energy transformed to chemical hydrogen energy is nearly 16% [9]. The exergy efficiency of the PV-electrolyzer system is calculated as the product of exergy efficiency of the PV system ψ_{PV} and the exergy efficiency of the electrolyzer ψ_{EL} and it is

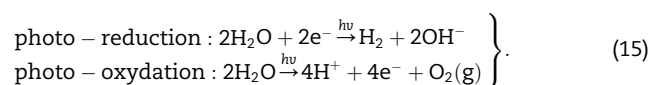
$$\psi = \psi_{\text{PV}}\psi_{\text{EL}} = \frac{V_{\text{m}}I_{\text{m}} - \left(1 - \frac{T_0}{T_{\text{cell}}}\right)hA(T_{\text{cell}} - T_0)}{\dot{E}x_{\text{solar}}} \times \frac{\dot{E}x_{\text{H}_2} + \dot{E}x_{\text{O}_2}}{V_{\text{m}}I_{\text{m}}}, \quad (14)$$

where $V_{\text{m}}I_{\text{m}}$ is the electrical power accounting of all electrical losses of the PV panel, associated electronics and electrical lines. This power is the same as that retrieved at the input of the electrolyzer. The quantity $hA(T_{\text{cell}} - T_0)$ represents the heat losses between the PV panel and the ambient due to heat transfer; some exergy losses are associated with this heat as indicated in the numerator of above equation.

2.10. Photo-catalytic water splitting

Solar radiation is in essence a source of photonic energy. As it is already known the photonic energy is proportional to the frequency of the radiation and given by $h\nu$, where h is the Plank constant and ν is the frequency. Photons can be used to dislocate electrons by their interaction with matter. While electrons are dislocated, the obtained electrical charge can be used to manipulate the valence electrons of chemical species in order to conduct chemical reactions photo-catalytically.

Complex supramolecular devices were engineered to capture photonic radiation and perform catalytic reactions at active centers. The photo-reduction and photo-oxidation of water molecule occur as follows:



2.11. Photo-electrolysis and photo-electrochemical hydrogen production

Photo-electrolysis involves application of heterogeneous photo-catalysts at one electrode which is exposed to solar radiation. Additionally, the electrolysis cell is supplied with electric power at the electrodes. Due to the action of photonic radiation the required electrical energy is reduced. Photo-electrochemical cell (PEC) is a recent implementation of photo-electrolysis which comprises photosensitive semiconductors immersed in an electrolyte and counter-electrodes. Fig. 2 presents a possible configuration of PEC. The semiconductor operates similarly as a photovoltaic cell, namely it uses the photons with energy greater than the semiconductor band gap to generate electron–hole pairs that are split by the electric field which traverses the electrolyte.

One remarkable advantage of the photo-electrochemical cell is that it actually integrates solar energy absorption and water electrolysis into a single unit. Thus, the device does not require a separate solar power generator (e.g., a PV cell) and electrolyzer and it is consequently more compact. The technology is in course of development and achieved in laboratory about 18% efficiency [29]. The lifetime of PEC experimented until present showed to be low because water corrodes the electrolyte. Many kinds of photosensitive semiconductor electrodes were investigated, one of the most promising being titanium dioxide (TiO_2); among other kinds one can list strontium titanate, carbonate oxides, NaOH oxides, tantalum oxynitride, other niobates and titanates, cadmium sulfide.

2.12. Bio-photolysis and photo-fermentation

Bio-photolysis and photo-fermentation are photonic-driven biochemical hydrogen production processes from water. According to Kotay and Das [30], production of hydrogen through bio-photolysis can be classified into direct or indirect kinds and photo-fermentation kind.

In bio-photolysis some micro-organisms sensible to light are used as biological converters in a specially designed photo-bioreactor. The most suitable micro-organisms are

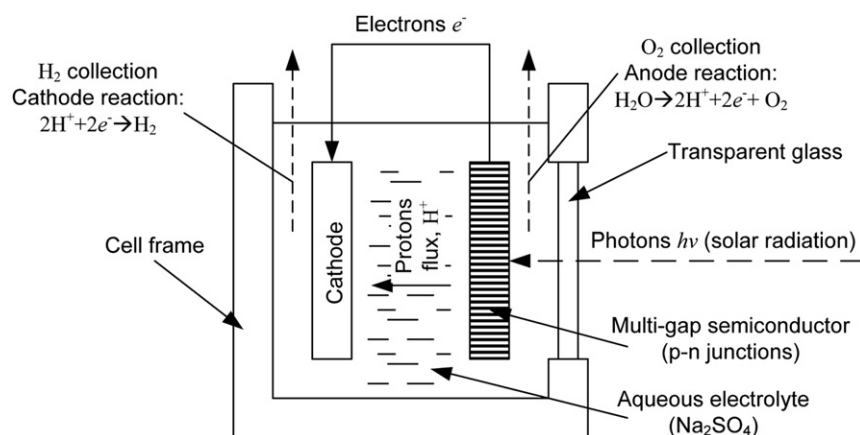
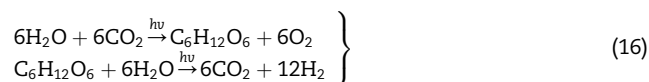


Fig. 2 – Sketch illustrating the operating principle of photo-electrochemical cell.

microalgae, because they exhibit hydrogen evolution and can be cultured in closed systems that can permit hydrogen capture. Micro-algal strains can be cultured that exhibit high hydrogen yields. One remarkable advantage of bio-photolysis is to produce hydrogen from water in an aqueous environment at standard temperature and pressure. Bio-photolysis is not yet developed for commercial use but is demonstrated at laboratory scale. According to Das and Veziroglu [31] the energy efficiency of the method can reach, potentially, 10%.

Water molecule can be split through bio-photolysis under the action of Cyanobacteria, also known as green micro-algae (*Chlamydomonas reinhardtii*) under special conditions. These micro-organisms generate and manipulate nitrogenase and hydrogenase enzymes in such a way that they may generate hydrogen and oxygen from water. According to the bacteria which were found to be hydrogen productive are mainly: *anabaena variabilis* PK84, *anabaena cylindrica*, *anabaena* AMC 414, gloebacted PCC742, *synechococcus* PCC602, *aphanocapsa montana*; also the micro-algae *chlamydomonas reinhardtii* cc124 and cc1036 proved to be hydrogen productive. The general reactions producing hydrogen from water with the help of photo-activated enzymes can be written in the following manner [31]:

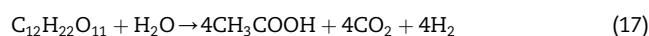


2.13. Dark fermentation and thermophilic and enzymatic digestion for hydrogen production

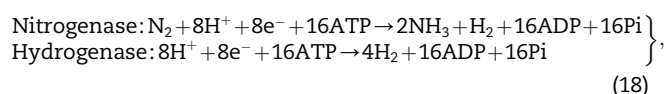
Biochemical energy is stored in organic matter can be manipulated by microbes to extract hydrogen in absence or presence of oxygen. When oxygen is completely absent or is present in very reduced quantities the biochemical conversion of organic matter to various forms of biochemical energy is called anaerobic digestion. It is therefore attractive as hydrogen production method for two important aspects: (i) it can generate hydrogen from organic waste; and (ii) is stabilized the waste which otherwise may become source of uncontrolled microbial growth with potential danger of contamination of biological species.

Experiments were made both in batch and flow reactors that generate hydrogen from various biomass substrates including sucrose and an appropriate control of hydrogen generation and hydrogen consuming bacteria present in the reactor. The production rate is about of 1.5 mol hydrogen per mol of sucrose in the substrate. Clostridium kind bacteria influence positively the hydrogen production rate under certain conditions. One major problem regarding reaction control in anaerobic digestion reactors is the inhibition of methanogens – which represent hydrogen consuming bacteria. One possibility to eliminate these bacteria – which normally are present in the organic substrate, is to heat the substrate for short duration at about 100 °C which will kill all bacterial population. Further, the biomass is seeded with hydrogen producing bacteria like Clostridium and Bacillus species.

One of the possible chemical reaction favored by the enzymes generated by hydrogen bacteria (viz. hydrogenase) is the acetic acid fermentation from sucrose:



In an organic substrate, both nitrogenase and hydrogenase enzymes contribute to hydrogen production by reducing free protons according to the general reactions:



where ADP is adenosine tri-phosphate and ADP is adenosine di-phosphate, and Pi is the shortcut for inorganic phosphate which is cleaved from the ATP molecule according to the reaction $\text{ATP} \rightarrow \text{ADP} + \text{Pi}$ which releases free energy of about 30.5 kJ/mol; this biochemical energy is used to drive the reaction.

Koutrouli et al. [32] studied hydrogen production from water diluted (1:4) olive oil using anaerobic digestion. The retention time in the bioreactor was 7.5–30 h as compared to that typical for methane formation from the same substrate, namely 10–20 days. The results show that the thermophilic bacteria production rate 1.5 times higher than that of mesophilic ones and it is at maximum 320 mol of hydrogen per tonne of olive pulp.

In a study, Das and Veziroglu [31] indicated a hydrogen yield of 7 mol H₂ per mol of glucose. The major challenge with aerobic digestion for hydrogen production is the reduced production rate per unit of capital investment in the facility. Remarkable energy conversion efficiency is observed at anaerobic digestion of molasses (which is a by-product of sugar processing), namely 28%.

2.14. High temperature electrolysis

In electrolysis a portion of the required energy can be given either in form of heat; this is $Q_{TH} = -T\Delta S(T,P)$. Thus the total energy needed to drive the reaction $\Delta H(T,P)$ can be given partially as electricity – as corresponding to energy $\Delta G(T,P)$ – and the rest transmitted as heat. One has

$$\Delta E_{TOT} = \Delta E_{EL} + \Delta E_{TH}, \quad (19)$$

where

$$\Delta E_{TOT} = -\Delta H(T,P)/(nF), \quad (20)$$

is the total equivalent electric potential difference that must be applied to the electrolytic cell and

$$\Delta E_{TH} = -T\Delta S(T,P)/(nF). \quad (21)$$

High temperature electrolysis is conducted in solid oxide electrolysis cells (SOEC). In these systems water is converted to steam with the expense of thermal energy. Moreover, the electrochemical stack is heated directly (by the supplied steam) or indirectly (through heat transfer) such that the electric energy needed by the process is only $\Delta E_{EL} = -\Delta G(T,P)/(nF)$.

When it is accounted for the efficiency of electricity generation (η_E) the electrolysis energy efficiency assuming no losses becomes

$$\eta_{EL} = \frac{\Delta H}{(\Delta H/\eta_E)} = \eta_E, \quad (22)$$

where $\Delta E_{TOT}/\eta_E$ represents the heat input needed to generate the total electricity to drive the electrolysis in that case that the process is driven only electrically. If high temperature steam electrolysis is considered, then

$$\eta_{EL} = \frac{\Delta G + Q_{TH}}{\Delta G/\eta_E + Q_{TH}} = \eta_E \times \frac{\Delta G + Q_{TH}}{\Delta G + \eta_E Q_{TH}} > \eta_E, \quad (23)$$

where $\Delta G/\eta_E$ is the amount of thermal energy needed to generate the electricity amount equivalent to ΔG . It can be observed in Eq. (23) that the factor $((\Delta G + Q_{TH})/(\Delta G + \eta_E Q_{TH})) > 1$; thus $\eta_{EL} > \eta_E$ which demonstrates that the theoretical efficiency of high temperature steam electrolysis is necessarily higher than the theoretical efficiency of liquid water electrolysis. Potentially, high temperature steam electrolysis coupled to advanced nuclear reactors can generate sustainable hydrogen with 45–55% thermal-to-hydrogen efficiency [33].

2.15. Hybrid thermochemical cycles for water splitting

Apart from thermally driven thermochemical water splitting cycles – mentioned above – three other thermochemical water

splitting cycles – called hybrid – draw special attention because they operate at lower temperature. Hybrid cycles use thermal and electrical energies to conduct certain endothermic and electrochemical reaction. As a consequence of their lower operating temperature, other sustainable thermal sources – apart from solar, high temperature nuclear and biomass combustion – can be used to drive the involved processes. The additional heat sources are nuclear reactors of present generation operating at 250–650 °C, geothermal and waste heat recovery.

One remarkable thermochemical water splitting cycle is the Cu–Cl one. The maximum temperature level required from the heat source is of about 550 °C and needed to drive the oxygen generation reaction. There are several variants of the Cu–Cl cycle from which the one that is most studied is the “five-steps” version. The 5-steps Cu–Cl cycle comprises 3 thermally driven chemical reactions, one electrochemical reaction and one physical step of drying. The energy efficiency of hydrogen production by Cu–Cl plant is close to 60%, while the exergy efficiency is around 11%. Note that the consumed exergy by the Cu–Cl plant is assumed to be thermal; however, since the Cu–Cl cycle is a hybrid one, the thermal energy source must be used partially to drive directly the cycle, and partially to generate the required electricity. The processes involved in the five-step cycle are indicated in Fig. 3.

The copper–chlorine cycle presents true advantages with respect to the other ones with regards to hydrogen generation from low grade temperature sources, especially those which can be considered as sustainable thermal energy. In these categories are envisaged nuclear heat, industrial heat, heat recovered from power plants, concentrated solar heat, heat resulting from municipal waste incineration, geothermal heat and other sources.

2.16. Artificial photosynthesis for hydrogen production

The main steps in the natural photosynthesis processes of plants and bacteria provide the models and inspiration for a totally bio-mimetic, industrial-scale technological approach to achieve the following specific goals:

- Electricity generation using photovoltaic systems. The power generated can directly be supplied to the national grid.

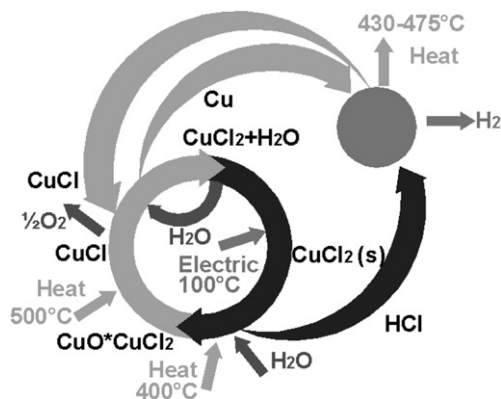


Fig. 3 – The Cu–Cl thermochemical water splitting cycle (modified from Balta et al. [18]).

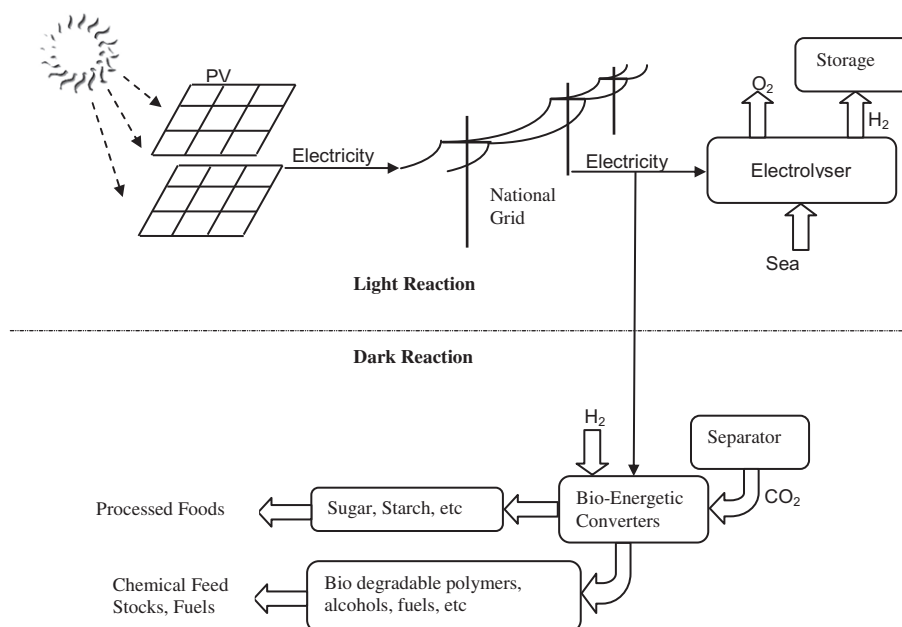


Fig. 4 – Artificial photosynthesis concept (modified from Collings and Critchley [34]).

- “Dry agriculture,” employing enzyme bed reactor systems to fix carbon dioxide from the air or other convenient sources, powered by hydrogen and bioelectric transducers drawing power from the national grid. These will produce carbohydrates (food), liquid fuels, chemical feed stocks, and polymers for fiber production. Water usage will be at or near the absolute chemical minimum and thousands of times lower than in conventional agriculture.
- Hydrogen production from sea water or other suitable water sources. Electrode systems employing catalytic surfaces modeled on the relevant high-efficiency active sites in photosynthetic organisms will achieve the electrolytic decomposition of water (into hydrogen and oxygen).

Artificial photosynthesis is a mean of achieving these above said aims of clean power generation and dry food production as shown in Fig. 4. It shows the schematic diagram of artificial photosynthesis. Figure is separated by a dashed line, upper half shows light reaction and bottom half shows the dark reaction of the photosynthesis.

2.17. Comparative remarks

As known, hydrogen can be produced from fossil fuels using such technologies as coal gasification, steam reforming of natural gas, water electrolysis and thermochemical water decomposition. Hydrogen is produced mainly from natural gas today, because this resource is available at relatively low cost and has a delivery and distribution infrastructure. For such reasons, natural gas is likely to remain a source of hydrogen in the near future, despite the associated emissions of CO₂, NO_x, etc.

Green hydrogen production requires the use of sustainable energy resources and water instead of fossil fuels. Sustainable energy sources can include renewable and nuclear energy. As

such, hydrogen facilitates the use of sustainable energy sources (solar, wind, hydro, geothermal, biomass, etc.). There are also promising biological methods, as mentioned earlier, for green hydrogen production. The main concern is the quantities produced by such methods. By looking at the methods given above, there are three key commodities, namely electricity, thermal heat and light to drive the hydrogen production processes, aside from the biological methods. So, the key question here is how to make these processes green (environmentally benign). This can only be achieved if those key drivers are supplied by green resources. In this regard, renewables become an excellent source for generating those commodities. It then becomes essential to couple hydrogen production processes with renewables.

In order to address whether or not hydrogen economy will come to reality, Fig. 5 presents a nice illustration about what kind of fuel humankind has utilized over the centuries and dependent on. It shows that humankind started with wood (with the highest carbon-hydrogen ratio) and later used coal, oil and natural gas. As clearly seen in the figure, the carbon-hydrogen ratio decreased drastically based on the use of fuel

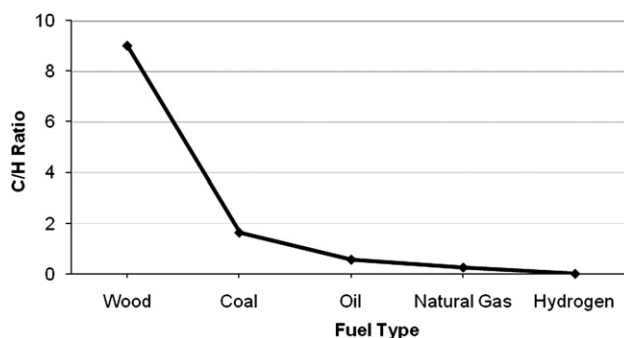


Fig. 5 – Variation of carbon/hydrogen ratio for various fuels.

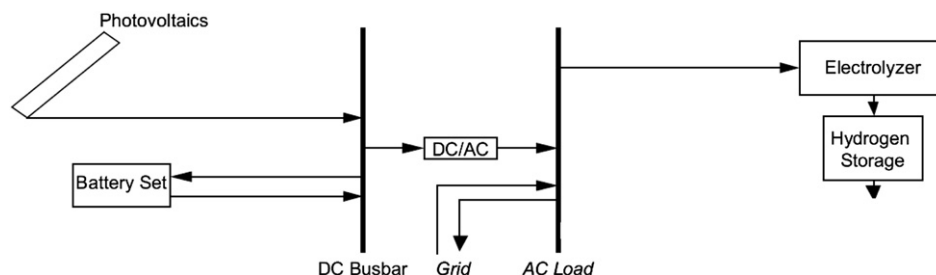


Fig. 6 – System for PV-driven water electrolysis (modified from Yilanci et al. [9]). (a) Dedicated nuclear reactor for water electrolysis (b) Co-generation of electricity and hydrogen.

Table 6 – Efficiencies of the solar-H₂ generator components from Pamukkale University.

Components	Energy efficiency (%)	Exergy efficiency (%)
PVs	11.2–12.4	9.8–11.5
Charge regulators	85–90	85–90
Batteries	80–85	80–85
1st inverter	85–90	85–90
Electrolyzer	56	52
Hydrogen tanks	100	100
Fuel cells	30–44	24.5–38
2nd inverter	85–90	85–90

Data from Yilanci et al. [9]. Energy efficiency = useful over consumed energy for each component; Exergy efficiency = useful over consumed exergy for each component.

throughout centuries. It is now crystal clear that carbon-free society is not possible without hydrogen which will bring the carbon-hydrogen ratio down to zero. One can take this as a clear justification of why hydrogen economy is necessary. This solution will help combat global warming and provide green solutions.

3. Case studies and illustrative examples

A number of illustrative examples and case studies of hydrogen generation from green energy resources are presented next.

3.1. PV-electrolysis system

This system has been installed in February 2007 in the Clean Energy Center (CEC) on the campus of Pamukkale University in Denizli, Turkey. The system is equipped with 5 kWe PV panels. Its simplified diagram is shown in Fig. 6. For performance investigation, one-half of the photovoltaic modules are on fixed tilt, and the other half are mounted on solar trackers. The fixed tilt (45° south) photovoltaic modules are located on the roof of the building. Each tracker consists of ten modules with the nominal power, 1.25 kWe.

A line feed deionizer was selected to supply the quality of water needed for the electrolyzer. A basic particle water filter was also used before the deionizer. A PEM type electrolyzer was used in the system. Metal Hydride (MH) storage tank has been used for hydrogen. The down side is that the hydrogen produced for MH storage must be of very high purity. Six OVONIC 85G250B storage tanks were chosen. The system includes also a fuel cell to generate electricity from the produced hydrogen and is connected to the grid. Table 6 lists the efficiencies of the individual system components. Average hydrogen production of the system for a week is 4.43 kg.

3.2. Nuclear routes for hydrogen production

Using nuclear energy as the primary energy source for hydrogen production is attractive because: (i) the greenhouse gases emissions associated with nuclear energy production is much more reduced than the ones with conventional fossil fuel combustion; (ii) nuclear energy is adaptable to large-scale

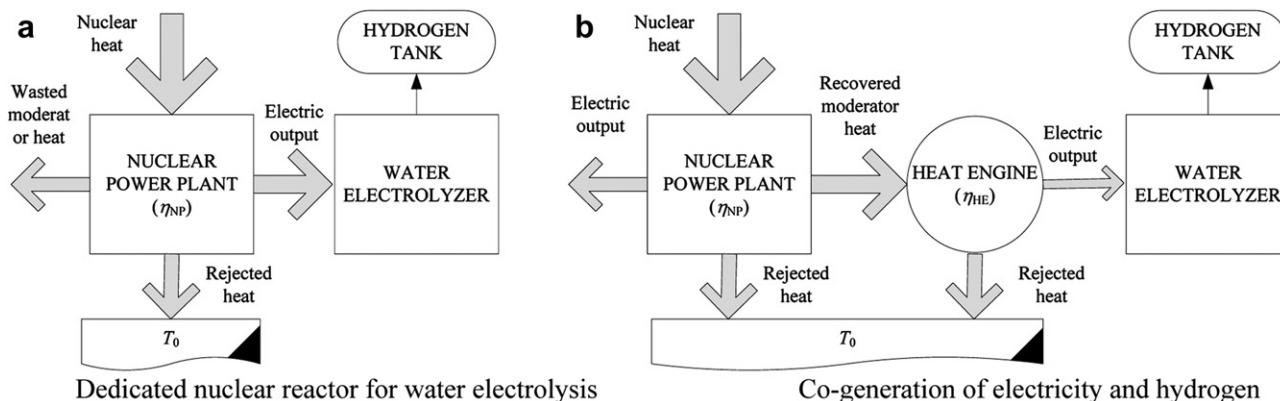


Fig. 7 – Possibilities to couple water electrolysis to nuclear reactors for (a) dedicated hydrogen production systems or (b) cogeneration systems of electricity and hydrogen.

hydrogen production. Progress in nuclear-based hydrogen production became visible in recent years by many research studied published in the open literature.

The simplest method to obtain hydrogen from nuclear power is by coupling an electrolyzer to a nuclear power plant (Fig. 7). The advantage of such system is the possibility to operate at design load without direct interference with the grid which can be under congestion in some periods of time. Another important advantage of nuclear/water electrolysis is that there is no need to modify the reactor. Such systems were applied on nuclear submarines to generate oxygen (for maintaining life) and hydrogen. It is possible to adapt the system to the existent nuclear power plants to generate off-peak electricity.

Generation of hydrogen during off-peak hours at nuclear plants allow for constant load operation at the highest efficiency and lowest electricity production cost. Also it is avoided any possible grid congestions which increases the reliability and efficiency of the electrical grid. Recall that the maximum expected efficiency of water electrolysis process is 80% even though proved concepts show less than 55%. Coupled to current light water reactors or advanced light water reactor (ALWR) the expected thermal-to-hydrogen efficiency is 27%, coupled to MHR (modular helium reactor) or AGR (advanced gas reactor) the expected efficiency is ~35%.

The typical utilization of nuclear reactors has been for electricity generation with steam power plants. Studies indicate that more benefits can be obtained if in addition to electricity a sustainable fuel like hydrogen is produced. The efficiency of power generation normally increases with increasing temperature of the working medium which, in the case of the nuclear energy utilization, leads to increased nuclear-reactor coolant temperatures and pressures. However, increases in the power generation efficiency of nuclear power plants are mainly limited by the permissible temperatures in nuclear reactors and the corresponding temperatures and pressures of the coolants. Coolant parameters are limited by the corrosion rates of materials and nuclear-reactor safety constraints.

Many studies regard nuclear reactor modifications and progress which need to meet some requirements like producing cheap electricity and high temperature heat view of efficient coupling it with a hydrogen production plant. The envisaged reactor technologies and the progress in their development are listed in Table 7. With respect to the process heat temperature level that they offer, gas-cooled reactors, molten-salt-cooled reactors, and heavy-metal-cooled reactors, appear the most promising technologies for hydrogen production. The various nuclear reactor technologies combined with thermally-driven hydrogen production processes adaptable to nuclear reactors will complement, not compete, in shaping the future nuclear-based hydrogen generation capability. Table 8 lists the envisaged thermally-driven hydrogen production methods that can be integrated with nuclear reactors.

3.3. Illustrative example of biomass gasification to produce hydrogen

It is considered steam biomass gasification for hydrogen production according to the results by Abuadala et al. [27], in

Table 7 – Progress in high temperature reactor design for hydrogen production.

Reactor type	Progress description
Advanced gas reactor (AGR)	<ul style="list-style-type: none"> - commercially available in UK; 14 units in operation with 1500 MW thermal each; - coolant temperature 650 °C to be upgraded at 750 °C - subcritical carbon dioxide coolant at 43 bar to be upgraded at supercritical pressures
High-temperature gas-cooled reactor	<ul style="list-style-type: none"> - developed by Japan Atomic Energy Research Institute (JAERI) - prototype power 30 MW cooled with helium at maximum 950 °C - adaptable to drive the S–I thermochemical water splitting cycle - advantageous concept for efficient, economic and safe nuclear
Secure transportable autonomous reactor STAR-H ₂	<ul style="list-style-type: none"> - not available yet commercially; based on proven technology from Russian submarine propulsion - demonstrated liquid lead coolant at 500 °C to be upgraded at 800 °C - 400 MW thermal capacity in compact units transportable on rail
Modular helium reactor (MHR)	<ul style="list-style-type: none"> - based on demonstrated German and US technologies - helium coolant at 850 °C at 70 bar, upgradeable to 1000 °C - meets the requirements for hydrogen production - proposed as a basis for a nuclear energy source
Sodium-cooled fast reactor (SFR)	<ul style="list-style-type: none"> - demonstrated technology in Russia, USA and France - sodium coolant at 500 °C upgradeable to 550 °C - closed fuel cycle with efficient management of actinides and conversion of fertile uranium
Molten-salt-cooled advanced high-temperature reactor	<ul style="list-style-type: none"> - only in design phase; not yet build - high-temperature (750–1000 °C) heat - molten fluoride salts coolant and a pool configuration - efficient low cost thermochemical H₂ & electricity - coated-particle graphite-matrix fuel
Super-critical water cooled CANDU reactor	<ul style="list-style-type: none"> - coolant (supercritical water) pressure of about 25 MPa - coolant temperature 625 °C - expected power generation efficiency 45%

a gasifier with 80 cm outside diameter and 50 cm height, insulated with a material with $k_{\text{ins}}/\delta = 12\text{W/m}^2\text{K}$ and $\epsilon_{\text{ins}} = 0.01$, exposed to an average wind condition of 2 m/s and with feed with sawdust wood biomass at the rate in the range 10–32 kg/s. Steam is fed at 500 K, while the temperature of the gasifier is kept in the range of 1000–1500 K. For modeling purpose the chemical formula of tars is assimilated to that of benzene.

At these conditions, the simulations performed by Abuadala et al. [27] with EES (Engineering Equation Solver) software

Table 8 – Envisaged hydrogen production methods coupled with nuclear reactors.

H ₂ production method	Description and remarks
Thermochemical cycles	Best candidate is the S–I cycle. It allows for centralized, base-load production of hydrogen and the utilization of waste heat from nuclear power plant provided that suitable temperature level upgrade methods are elaborated. Potential efficiency of the overall process can be higher than 40%. The technology is proven at lab scale but requires development to achieve commercialization phase.
Nuclear coal gasification	European research led by Germany since 1999. Requires temperatures larger than 700 °C. The gasification technology is mature and coupling with nuclear reactors can show overall efficiency of over 60%. The main advantage: carbon dioxide emissions are reduced as compared to auto-thermal processes.
Nuclear steam reforming of fossil fuels using membranes	Chemical reactions, required heats for reactions, fuel savings, CO ₂ emission reductions were investigated for natural gas and petroleum. The process temperature can be reduced down to 550 °C. High efficiency (>60%) and lower CO ₂ emissions are achievable.

indicate the variation of the product gas concentration with the biomass feed rate in the range of 50–60%. It is interesting to note that the hydrogen concentration behaves in an opposite manner as the carbon monoxide concentration. These results indicated that only 7–11% of fed biomass is converted to hydrogen. If the steam feed rate is increased in the same conditions (from 4.5 to 6.3 kg/s) the hydrogen concentration in the product gas increases with about 4%, fact that indicates the beneficial effect of steam addition. It has been found that the rise of gasification temperature from 1000 to 1500 K led to decrease of hydrogen concentration with 2%.

3.4. Cost comparison of three hydrogen production methods

The capital cost of Cu–Cl plant, as estimated by Orhan et al. [35] is roughly 10–50 millions USD for a capacity range of 1–10 tons hydrogen per day. The cost of produced hydrogen by such a large scale plant must account form many production cost components apart from the direct production costs, like taxation, depreciation, insurance, rent, overhead costs, administrative expenses, distribution and marketing expenses, research and development, financing, gross-earning expenses. A rough estimation of the contribution of individual costs to the hydrogen product price is indicated in

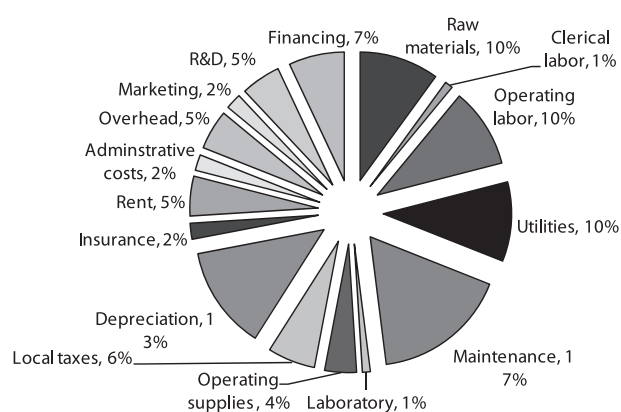


Fig. 8 – Various contributions to the total product cost of a Cu–Cl water splitting plant for hydrogen production (data from Orhan et al. [35]).

Fig. 8. Table 9 compares the hydrogen production costs with other methods.

3.5. Comparison of biomass driven high temperature steam electrolysis and Cu–Cl plant

The biomass-driven high temperature steam electrolysis system and the biomass-driven thermochemical water splitting system are compared here with respect to energy and exergy efficiencies and biomass utilization. It has been assumed that heat losses from the system are 0.5% from the reaction heats. The results were obtained by Zamfirescu et al. [36] based on standard thermodynamic analysis conducted according to first and second law.

Since the required temperature level is anyways available from the flue gas produced by biomass combustion, internal heat recovery within the Cu–Cl plant is applied. The plot from Fig. 9 shows with dashed lines the temperature level and enthalpy range of the flue gas delivering heat to the Cu–Cl plant. The highest temperature of the flue gas is 680 °C. Fig. 10 shows the energy and exergy efficiencies in function of biomass moisture content. The definitions of these efficiencies are indicated in the same figure.

The last result indicates in Fig. 10 the biomass utilization in function of technology and biomass quality. In the figure “N” represents the number of mols of biomass used per mol of hydrogen produced. The result demonstrates that the TCWS (thermochemical water splitting) consumes less biomass than HTSE (high temperature steam electrolysis) because of two reasons: (i) the requirement of electrical energy is reduced and (ii) there is not need to dry the biomass before utilization. The conclusion is that TCWS appears more attractive than HTSE.

Table 9 – Comparison of Cu–Cl hydrogen cost with other methods for 10 t hydrogen per day.

Cost item, \$/GJ	Cu–Cl plant	Off-peak electrolysis	Steam-methane reforming
Capital cost	7.7	3.2	3.1
Energy charge	0.5	1.0	0.8
Carbon charge	0	0	1.6
Hydrogen cost	2.71	2.41	2.67
Data from adapted from Orhan et al. [35].			

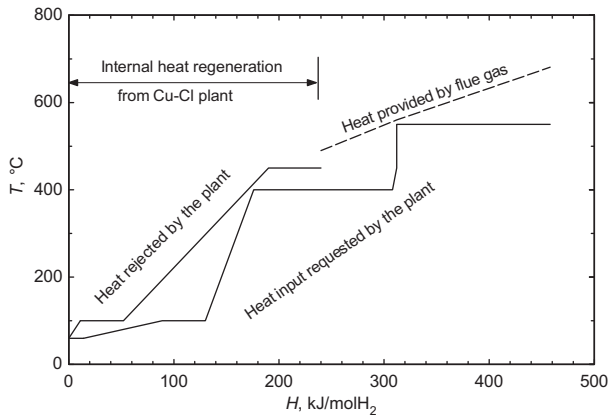


Fig. 9 – Heat input and heat rejected by the Cu–Cl plant per 1 mol of H_2 .

3.6. Energy recovery routes for electro-thermal hydrogen production

Energy recovery can be applied in various instances to generate high-grade or low-grade temperature heat. Municipal waste incineration and landfill gas combustion are typical examples of high temperature heat recovery obtained from human activity. Also various industries reject large amount of heat in the surroundings. In general such heat comes at lower grade, typically from 60 to 150 °C, or intermediate temperatures that are up to 400 °C.

Fig. 11 presents some possible routes to generate hydrogen through hybrid processes starting from energy recovery. The recovered energy is present or it is eventually converted in heat at high, intermediate or low grade. The high temperature heat can be directly used to feed hybrid processes; in this case, the heat rejected by the processes can be used to drive electricity generation through heat engine power generation

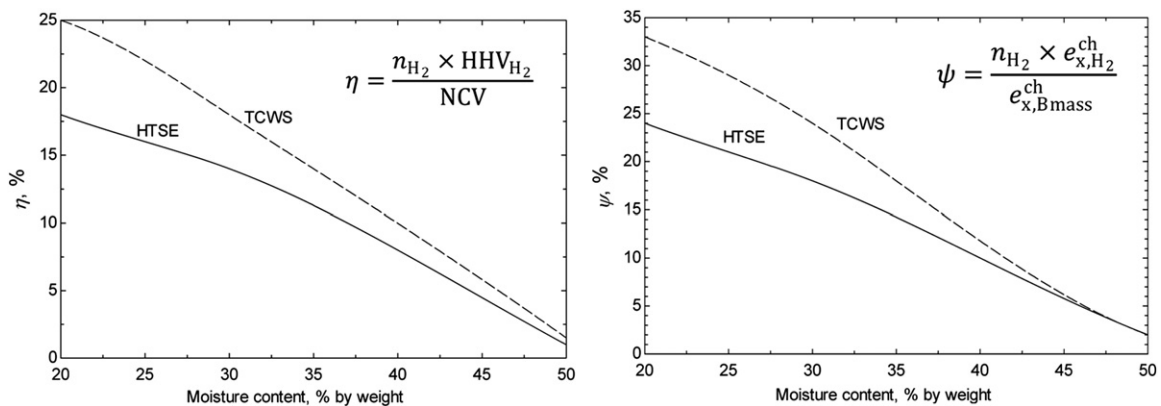


Fig. 10 – Energy (η) and exergy (ψ) efficiencies of HTSE and TCWS driven by biomass energy (data from Zamfirescu et al. [36]).

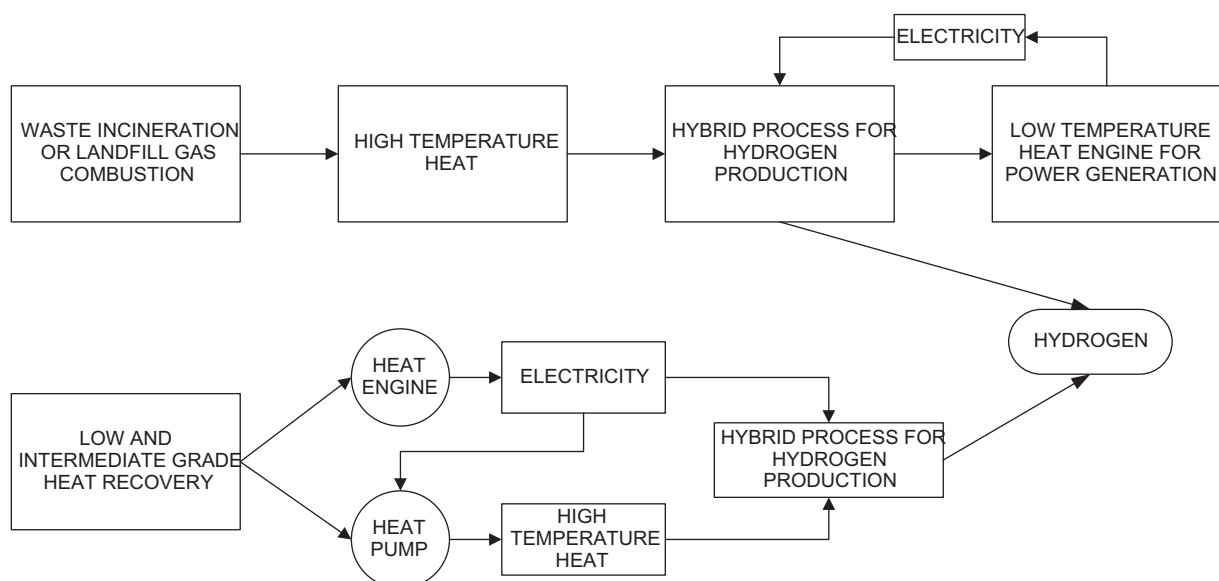


Fig. 11 – Routes to hybrid hydrogen production processes driven by energy recovery.

which is feed back to the hybrid process. Additional heat can be possibly obtained from the high temperature heat when it is the case, by using appropriate power cycles. In the case when low or intermediate heat is recovered, heat engines generators and heat pumps may be used simultaneously to obtain electricity and higher temperature heat appropriate for the process. It may be economically advantageous to drive a hybrid process in this way instead of producing electricity only and conduct water electrolysis. The economic advantage of the system depends on the temperature level of the heat source. If the level is too low, upgrading the temperature becomes not beneficial.

4. Concluding remarks

This paper identifies and categorizes the principal methods to produce green hydrogen. Material resources from which hydrogen can be extracted are many, but those of prime importance are water, sea water, hydrogen sulphide, biomass and fossil hydrocarbons. When fossil hydrocarbons or coal are used in the process, precautions must be taken to extract and sequester the resulting carbon dioxide, if it is the case, such that the production process is environmentally benign. Electrical, thermal, biochemical and photonic energy or combinations of these are identified as the key commodities to drive hydrogen production process. These basic forms of energy can be obtained from green energy sources – like renewables, nuclear or waste energy – through various conversion paths. Of course, each production method has advantages and disadvantages. Selection of these requires various criteria, namely, environmental impact, efficiency, cost effectiveness, resources and their use, commercial availability and viability, system integration options, to be considered.

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Nomenclature

A	area, m ²
E	energy, kJ
\dot{E}_x	exergy rate, kW
F	Faraday constant
G	Gibbs free energy, kJ/kg
h	heat transfer coefficient, W/m ² K
H	enthalpy, kJ
I	current intensity, A
k	reaction rate
K	equilibrium constant
n	number of mols
p	pressure, Pa
R	ideal gas constant

SBR	steam-fuel ratio
T	temperature, K
ν	specific volume, m ³ /kg
V	electric potential, V

Greek letters

η	energy efficiency
ψ	exergy efficiency
μ	chemical potential

Subscripts

0	reference state
E	electrolysis
eq	equilibrium
el	electric
EL	electric
f	forward
m	maximum
min	minimum
PV	photovoltaic
TH	thermal
TOT	total

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