



A comparative overview of hydrogen production processes



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ABSTRACT

Climate change and fossil fuel depletion are the main reasons leading to hydrogen technology. There are many processes for hydrogen production from both conventional and alternative energy resources such as natural gas, coal, nuclear, biomass, solar and wind. In this work, a comparative overview of the major hydrogen production methods is carried out. The process descriptions along with the technical and economic aspects of 14 different production methods are discussed. An overall comparison is carried out, and the results regarding both the conventional and renewable methods are presented. The thermochemical pyrolysis and gasification are economically viable approaches providing the highest potential to become competitive on a large scale in the near future while conventional methods retain their dominant role in H_2 production with costs in the range of 1.34–2.27 \$/kg. Biological methods appear to be a promising pathway but further research studies are needed to improve their production rates, while the low conversion efficiencies in combination with the high investment costs are the key restrictions for water-splitting technologies to compete with conventional methods. However, further development of these technologies along with significant innovations concerning H_2 storage, transportation and utilization, implies the decrease of the national dependence on fossil fuel imports and green hydrogen will dominate over the traditional energy resources.

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1. Introduction

The introduction of greenhouse gases (GHG) into the atmosphere due to the continuous burning of fossil fuels, pose a serious threat to the global environment and consequent climate change [1]. In addition, the growing energy demand has imposed the increase of conventional fuel prices which are declining, exposing national economies which are dependent on their import. For the long-term treatment to climate change along with the reduction of the dependence on oil imports, future energy sources must meet the requirements of being carbon-free and renewable [2–5].

The expansion of the amount of renewable sources in the supply system is restricted by their intermittent and unpredictable nature. The increase in the contribution of renewable energy sources (RES), with simultaneous adaptation of production to demand, would not be feasible without the use of energy storage systems [6–8]. The major challenge for a storage device is to maintain the energy stored as long as needed and, when required, to be able to supply it as soon as possible. For this purpose, several studies in their effort to provide a clean and reliable alternative to traditional fossil fuels, which enjoy this particular feature, were led to hydrogen technology.

Unlike fossil fuels, hydrogen is not readily available in nature. It can be however produced from any primary energy source and to be then used as the fuel either for direct combustion in an internal combustion engine or in a fuel cell, only producing water as a byproduct [9–12]. As the only carbon-free and possessing the highest energy content compared to any known fuel (Table 1), hydrogen is globally accepted as an environmentally benign secondary form of renewable energy, alternative to fossil fuels [13–15]. A further advantage is that, supported by appropriate storage technologies, hydrogen can be utilized for domestic consumption as it can be safely transported through conventional means [16–19], and in order to be fed to stationary fuel cells, it can be stored as compressed gas, cryogenic liquid or solid hydride [20–22]. Currently the annual production of hydrogen is about 0.1 GT which is mainly consumed on-site, in refining and treating metals [23,24]. A small fraction is already used to fuel driving cars while in the near future applications including power generation and heating in residential and industrial sectors are expected [23,25,26].

The major problem in utilization of hydrogen gas as a fuel is its unavailability in nature and the need for inexpensive production methods [27]. A wide variety of processes are available for H₂ production which according to the raw materials used could be divided into two major categories namely, conventional and renewable technologies. The first category processes fossil fuels and includes the methods of hydrocarbon reforming and pyrolysis. In hydrocarbon reforming process, the participating chemical techniques are steam reforming, partial oxidation and autothermal steam reforming.

The second category accommodates the methods which produce hydrogen from renewable resources, either from biomass or water. Utilizing biomass as a feedstock, these methods can be

subdivided into two general subcategories namely, thermochemical and biological processes. Thermochemical technology mainly involves pyrolysis, gasification, combustion and liquefaction, whereas the major biological processes are direct and indirect bio-photolysis, dark fermentation, photo-fermentation and sequential dark and photo-fermentation. The second class of renewable technologies regards the methods, which can produce H₂ through water-splitting processes such as electrolysis, thermolysis and photo-electrolysis, utilizing water as the only material input. The various pathways for hydrogen production are shown in Fig. 1.

Based on the extensive literature review, there has not yet been a comprehensive discussion, assessment and comparison of the operating principles along with the cost components relating to both H₂ production, storage, transportation and utilization. In this work a comparative overview of the major hydrogen production methods is carried out. The operating principles together with the technical features of the systems that comprise each technology are analyzed. Also, the raw materials used and the energy requirements relating to each method are reviewed. Finally, the associated production costs are provided and a qualitative comparison between the various production processes is undertaken, in order to evaluate the feasibility of such systems and their future contribution in the development of sustainable hydrogen economy.

In Section 2 the methods which produce hydrogen from fossil fuels are presented and discussed in detail, whereas Section 3 deals with renewable technologies. In Section 4, an overall comparison of the technical and economic aspects relating to each method is carried out and the issues concerning hydrogen storage, transportation and utilization are mentioned in Section 5. The conclusions are summarized in Section 6.

2. H₂ production from fossil fuels

There are several technologies of producing hydrogen from fossil fuels, the main of which are hydrocarbon reforming and pyrolysis. These methods are the most developed and commonly used, meeting almost the entire hydrogen demand. Specifically, up to date hydrogen was produced 48% from natural gas, 30% from heavy oils and naphtha, and 18% from coal [28–30]. Presently, fossil fuels retain their dominant role in the world hydrogen supply as the production costs are strongly correlated to fuel prices which are still kept to acceptable levels.

As in many fields of chemical and biochemical industries, membrane reactors also constitute new schemes for H₂ production from conventional fuels. A membrane is a structure which allows mass transfer under a gradient of driving forces (concentration, pressure, temperature, electric potential, etc) and is usually laterally much greater than its thickness [31]. In Fig. 2, the types of ideal continuous flows used in membrane-based separations are presented. Depending on the separation regime, membranes are classified into dense, porous and ion exchange. Based on their nature, the two major categories are biological and synthetic membranes, with the latter being distinguished in organic (polymer) and inorganic (ceramic or metallic). A suitable for H₂-production membrane should possess high selectivity for hydrogen, high permeability to operate with high flows and limited surfaces, and good chemical and structural stability. Therefore, a suitable (porous) support allowing the gases crossing, in combination with a barrier restricting the inter-diffusion in the metallic support are necessary parts for a composite membrane [32]. The common geometries of planar and tubular membranes are shown in Fig. 3.

Table 1
Higher and lower heating values for various fuels (adapted from [104]).

| Fuel | State at ambient temperature and pressure | HHV (MJ/kg) | LHV (MJ/kg) |
|----------|---|-------------|-------------|
| Hydrogen | Gas | 141.9 | 119.9 |
| Methane | Gas | 55.5 | 50 |
| Ethane | Gas | 51.9 | 47.8 |
| Gasoline | Liquid | 47.5 | 44.5 |
| Diesel | Liquid | 44.8 | 42.5 |
| Methanol | Liquid | 20 | 18.1 |

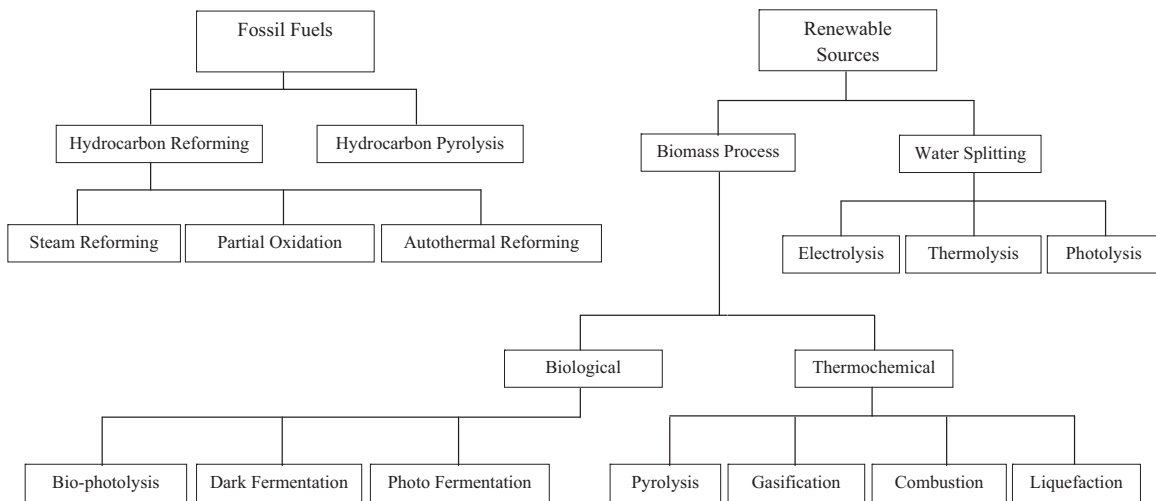


Fig. 1. Hydrogen production methods.

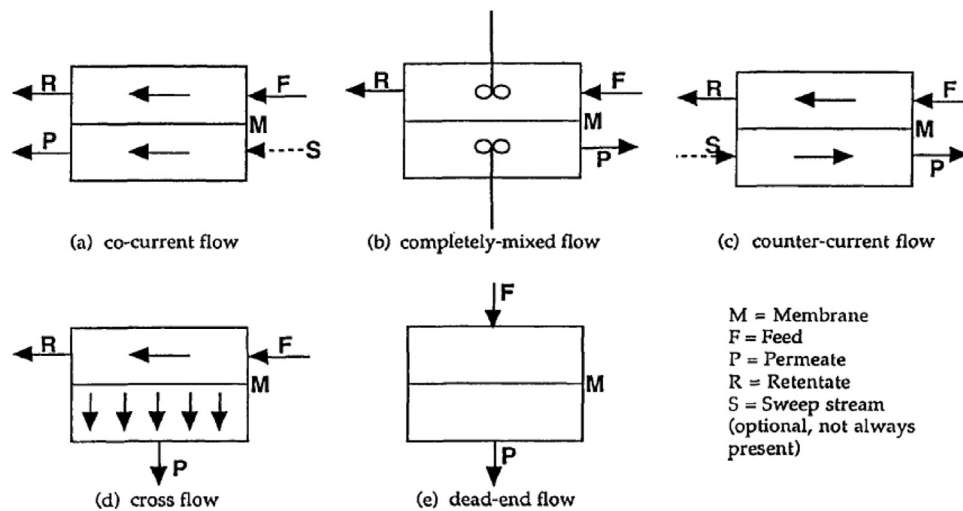


Fig. 2. The types of ideal continuous flows used in membrane-based separations [31].

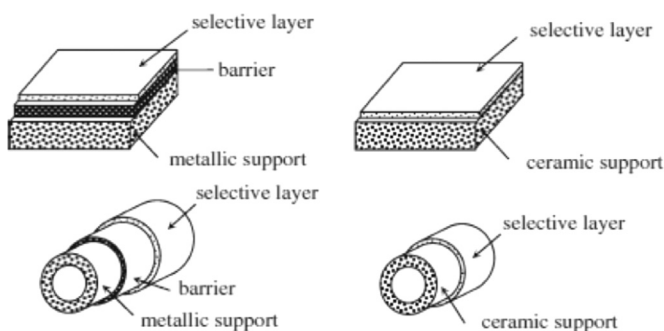


Fig. 3. The geometries of planar and tubular composite membranes [32].

2.1. Hydrocarbon reforming methods

By definition, hydrocarbon reforming is the process by which the hydrocarbon fuel is converted into hydrogen through some reforming techniques. In addition to the hydrocarbon, the other reactant for the reforming process can be either steam, and then the endothermic reaction is known as steam reforming, or oxygen, and the exothermic reaction is known as partial oxidation. When these two reactions are combined, it is termed as the autothermal reaction [33]. A typical reforming plant consists of the desulfurization unit, the reforming and clean-up sections, and the

auxiliary units such as pumps, compressor, expander, heat exchangers, coolers, combustor, etc., [34].

2.1.1. Steam reforming method

Steam reforming (SR) method basically involves a catalytic conversion of the hydrocarbon and steam to hydrogen and carbon oxides, and consists of the main steps of reforming or synthesis gas (syngas) generation, water-gas shift (WGS) and methanation or gas purification. Raw materials range from methane, natural gas, and other methane containing gases through various combinations of light hydrocarbons including ethane, propane, butane, pentane, and light and heavy naphtha. If the feedstock contains organic sulfur compounds, the reforming step is preceded by a desulfurization step to avoid poisoning the reforming catalyst which is usually based on nickel [35]. In order to produce the desired purified H_2 product and prevent coking formation on the catalyst surface, the operation parameters of reforming reaction are selected at high temperatures, pressures up to 3.5 MPa and steam-to-carbon ratios of 3.5 [34]. After the reformer, the gas mixture passes through a heat recovery step and is fed into a WGS reactor where the CO reacts with steam to produce additional H_2 and then, the mixture passes either through a CO_2 -removal and methanation, or through a pressure swing adsorption (PSA) leaving H_2 with higher purity of near 100% [36]. The CO_2 emissions can be strongly reduced by CO_2 capture and storage (CCS), through

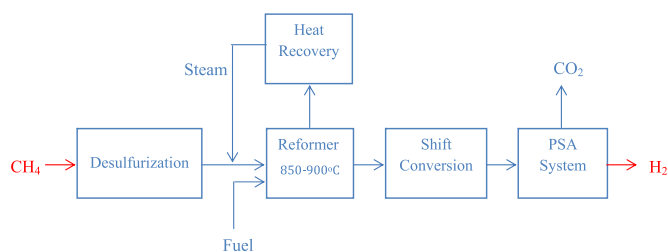
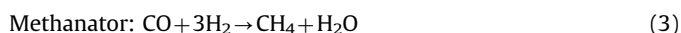
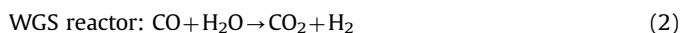
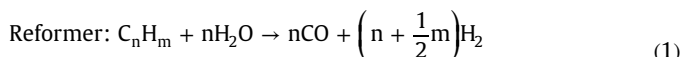


Fig. 4. Flow diagram of the steam methane reforming process.

which CO₂ is captured and injected in geological reservoirs or the ocean [37]. The main chemical reactions that take place in SR are shown in Eqs. (1)–(3).



SR of methane can be represented by applying $n=1$ and $m=4$ to the Eq. (1). Steam methane reforming (SMR) is the most common and developed method used for large-scale hydrogen production, with conversion efficiency between 74–85%. Fig. 4 depicts a simplified flow diagram of H₂ production from methane. Steam and natural gas are reacted over a nickel-based catalyst to produce syngas at temperatures of about 850–900 °C and higher quality H₂ (99,999%) is obtained by applying PSA to separate H₂ from the other components [33]. The energy requirement of 63.3 kJ/mol H₂ can be provided by 30–35% of the total amount of natural gas as a process fuel producing additional stack gases with CO₂ concentration, resulting in total emissions of up to 0.3–0.4 m³ CO₂ per m³ of H₂ produced [38]. The component costs as a percentage of the overall H₂ production cost for SMR are as follows: 60.7% feedstock, 29.1% capital investment and 10.2% O&M [36]. It is estimated that the hydrogen production cost, corresponding to plants with a design capacity of 379,387 kg/day, at 90% capacity factor and a natural gas cost of 10.00 \$/MMBtu, are 2.27 \$/kg and 2.08 \$/kg with and without carbon capture and sequestration, respectively [39].

A very promising solution is offered by membrane reactors. As the main process of producing large amounts of H₂, SMR has been extensively tested by integrating a selective membrane either directly inside the reaction environment or applied downstream to reaction units. Significant benefits arise from the first method by using palladium-based membrane reactors, combining in only one unit the chemical reaction and gas separation as can be observed in Fig. 5. In Fig. 6, a system composed of two molecules is shown. The molecular hydrogen produced in the reformer, is transported by adsorption and atomic dissociation on one side of the membrane, dissolution in the membrane, followed by diffusion, and finally desorption (on the other side) [40]. In fact, the Pb-based membrane reactors enable the same reactant conversion (methane conversions up to 90–95%) at lower temperature (450–550 °C as opposed to 850–900 °C of traditional SMR) [32].

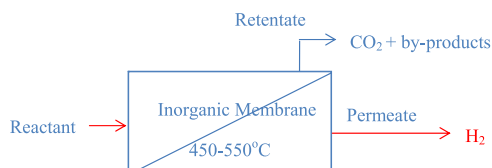
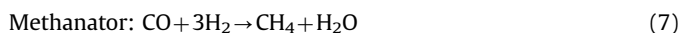
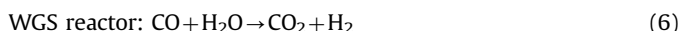
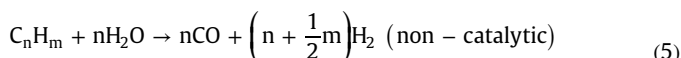
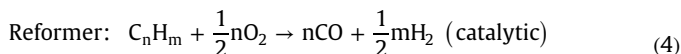


Fig. 5. Flow diagram of the membrane-integrated steam methane reforming process.

2.1.2. Partial oxidation method

Partial oxidation (POX) method basically involves the conversion of steam, oxygen and hydrocarbons to hydrogen and carbon oxides. The catalytic process which occurs at about 950 °C operates with feedstock ranging from methane to naphtha, whereas the non-catalytic process which occurs at 1150–1315 °C can operate with hydrocarbons including methane, heavy oil and coal [36]. After sulfur removal, pure O₂ is used to partially oxidize hydrocarbon feedstock and the syngas produced is further treated in the same way as the product gas of the SR process. The cost of the oxygen plant and the additional costs of desulfurization steps make such a plant extremely capital intensive [35]. In catalytic process, the heat is provided by the controlled combustion and from methane the thermal efficiency is 60–75% [41]. The catalytic and non-catalytic reforming processes are presented in Eqs. (4) and (5) respectively, whereas the chemical reactions of WGS and methanation are shown in Eqs. (6) and (7).



POX is the most appropriate technology to produce H₂ from heavier feedstock such as heavy oil residues and coal [33]. Due to the lower hydrogen-to-carbon ratios of the heavy feedstock compared to methane, a larger portion of the hydrogen produced comes from steam. Residual fuel oils can be represented by applying $n=1$ and $m=1.3$ to Eq. (5), and at 880 psi or 6 MPa, the typical composition of syngas is 46% H₂, 46% CO, 6% CO₂, 1% CH₄ and 1% N₂. After the syngas is desulfurized, shifted and purified, the component costs as a percentage of the overall H₂ production cost for POX of residual fuel oil are as follows: 34.8% feedstock, 47.9% capital investment and 17.3% O&M [36].

To represent the POX method of the feed coal, $n=1$ and $m=0$ are applied to Eq. (5) and a typical flow sheet for H₂ production is illustrated in Fig. 7. The process is referred as coal gasification and constitutes a major process through which hydrogen is obtained from coal. The reaction mechanisms of this method, resemble very much those of the POX of heavy oils distribution, however additional handling of the relatively un-reactant fuel as a solid and removing of the large amounts of ash, have a severe impact on costs. Moreover, due to the low hydrogen content of the coal, water supplies 83% of the hydrogen produced compared to 69% when heavy oil is used [35]. Using the Texaco gasifier which operates at around 800 psi or 5.5 MPa, the typical composition of syngas is 34% H₂, 48% CO, 17% CO₂, and 1% N₂. After the syngas treatment, the distribution of hydrogen cost is 25.8% feedstock, 54.6% capital investment and 19.6% O&M [36].

Studies performed for two plants both using Texaco gasifier, but one including carbon capture and sequestration and a hydrogen output of 276,900 kg/day, and the other without sequestration producing 255,400 kg/day, showed a hydrogen cost of 1.63 \$/kg and 1.34 \$/kg, respectively [39].

2.1.3. Autothermal reforming method

Autothermal reforming (ATR) method uses the exothermic partial oxidation to provide the heat and endothermic steam reforming to increase the hydrogen production. Basically, steam and oxygen or air, are injected into the reformer, causing the reforming and oxidation reactions to occur simultaneously, as shown in Eq. (8) [33].

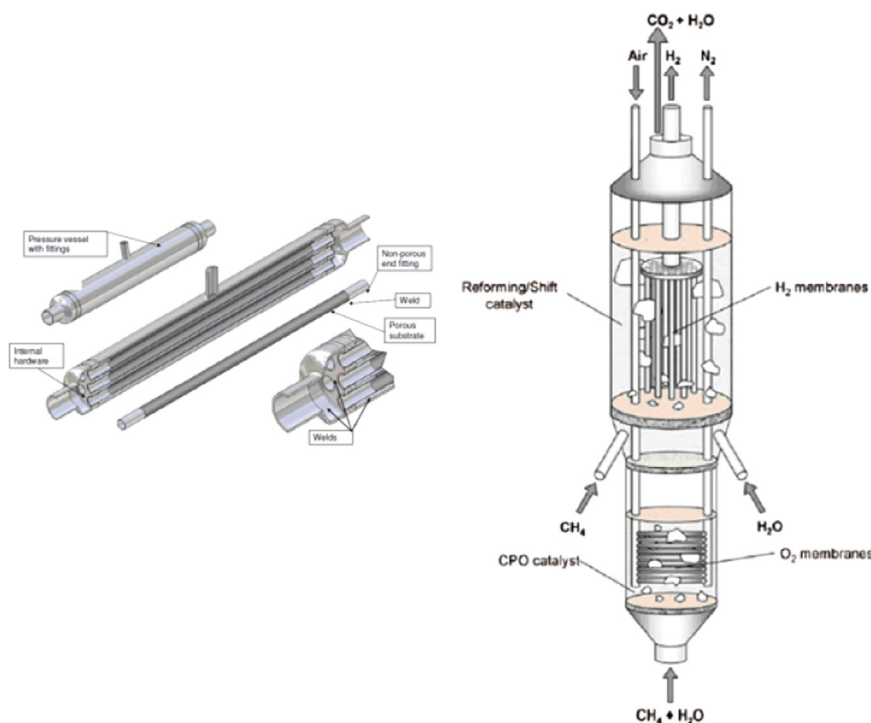


Fig. 6. Multiple membranes reactor for steam methane reforming [32].

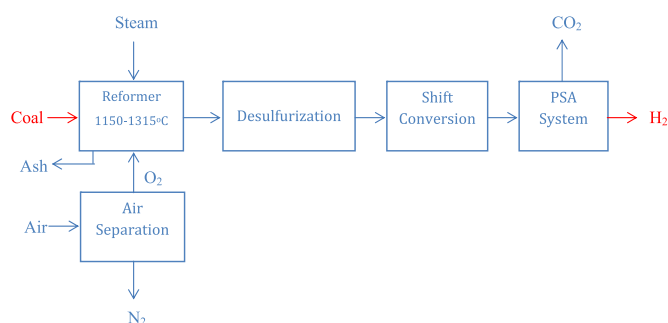
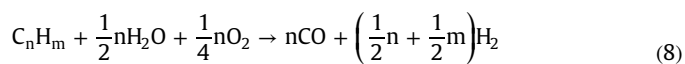


Fig. 7. Flow diagram of the partial oxidation (or coal gasification) process.



From methane (by applying $n=1$, $m=4$ to Eq. (8)), the thermal efficiency is 60–75%, while the optimum operating value has been calculated at around 700 °C inlet temperature, for ratios $S/C=1.5$ and $O_2/C=0.45$ where the maximum hydrogen yield is about 2.8 [34,41]. In Fig. 8, a simplified flow diagram of the ATR of methane is available presenting the process explained by Eq. (8). The investment costs are about 15–25% and 50% lower than SMR and

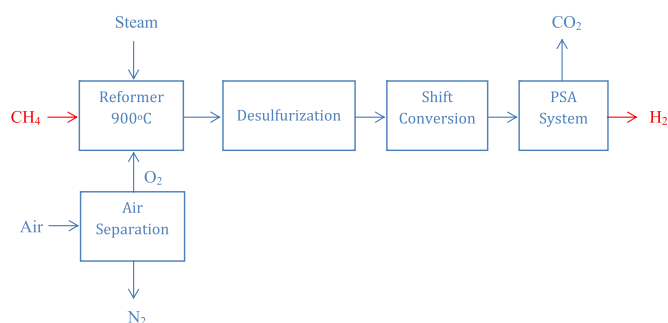


Fig. 8. Flow diagram of the autothermal reforming of methane process.

coal gasification respectively, whereas advanced large-scale ATR plants with 90% CO_2 capture at an efficiency of 73% and investment costs at nearly 499.23 \$/kW_{H2}, enable hydrogen production cost of 13.48 \$/GJ or 1.48 \$/kg of H_2 produced [37].

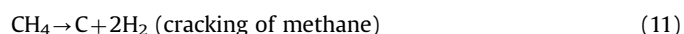
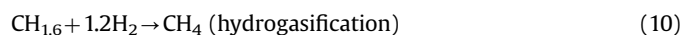
Dealing with the integration of an ATR reactor with a Pd membrane, a few simulation studies showed a small improvement in the overall system efficiency and up to 20% reduction of the fuel processor volume. According to the simulation results reported, higher CH_4 conversions were observed, and at the retentate side the concentrations of H_2 and CO_2 were lower and CO higher at each pressure investigated [42]. However, the efficiency improvement in the presence of membrane is limited due to the elevated temperature (900 °C) needed which may result in membrane detriment and the architecture of such a reactor is more complex if compared to that in the absence of membrane [32].

2.2. Hydrocarbon pyrolysis

Hydrocarbon (CHs) pyrolysis is a well-known process in which the only source of hydrogen is the hydrocarbon itself, which undergoes thermal decomposition through the following general reaction:



Thermo-catalytic decomposition of light liquid hydrocarbons (boiling point between 50 and 200 °C), is carried out with the production of elemental carbon and hydrogen, whereas in the case of heavy residual fractions (boiling point higher than 350 °C), hydrogen is produced in a two-step scheme namely, hydrogasification and cracking of methane [43]:



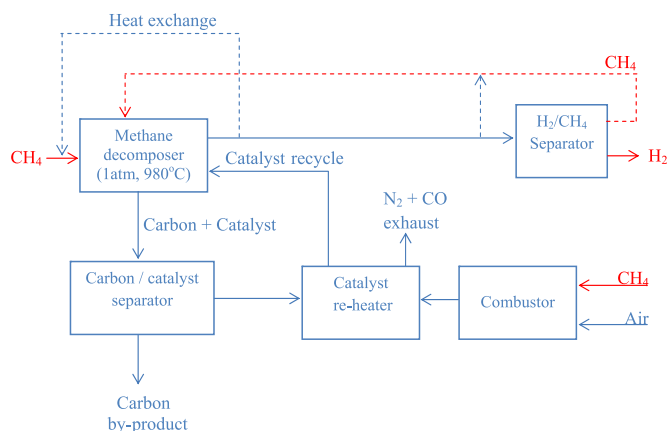


Fig. 9. Flow diagram of the methane pyrolysis process.

Direct de-carbonization of natural gas (CH_4), is effected in an air and water free environment, at temperature up to 980°C and atmospheric pressure as illustrated in Fig. 9. The energy requirement per mole of hydrogen produced (37.6 kJ/mol), is less than that for the SMR method (63.3 kJ/mol) and could be covered by combustion of approximately 15–20% of hydrogen produced in the process [38]. Moreover, pyrolysis does not include WGS and CO_2 removal steps, and the energy intensive stage of CCS is replaced by carbon management which could be used in the metallurgy and chemical industries or even can be stored underwater or on land for future use. Hence, capital investments for large plants are lower than for the processes of steam conversion or partial oxidation resulting in 25–30% lower hydrogen production cost [43]. If a market for the huge amounts of carbon that will be produced by decomposition of natural gas was found, the price of hydrogen would be further reduced [44]. From environmental points of view, it would be more advantageous to produce both hydrogen and carbon by the catalytic dissociation of natural gas, as opposed to the production of hydrogen by SMR coupled with CO_2 sequestration [45].

Continuous removal of hydrogen by membrane separation should increase the de-carbonization conversion for a given temperature. Pd-Ag alloys are typically used for H_2 separation, allowing operation at lower temperatures and reducing the coke formation. The main drawbacks of this technology are related to the hydrogen separation weakness due to the low H_2 partial pressures in the reaction mixture and membrane durability affected by high temperatures needed for the de-carbonization equilibrium [32].

3. H_2 production from renewable sources

Although hydrocarbons are currently the main feedstock used for H_2 production, the need to increase the integration of renewable technologies will become unavoidable. As the fossil fuels are declining and Greenhouse effect is attracting greater attention, the share of renewable technologies will increase in the near future while in long term, is expected to dominate over conventional technologies [1,2,46,47]. There are many processes for H_2 production from renewable resources and a brief description of some biomass-based technologies, along with approaches related to water splitting, is included here.

3.1. Biomass process

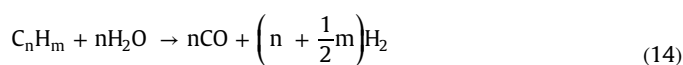
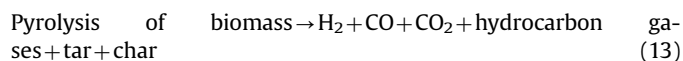
Biomass is a renewable source of primary energy derived from plant and animal material such as, energy crops and crop residues,

wood from forests and forest residues, grass, industrial residues, animal and municipal waste and a host of other materials [48]. Biomass stems from plants, is organic matter in which the energy of sunlight is stored in chemical bonds via photosynthesis [49]. Although, CO_2 is released when biomass is utilized for energy production, this amount of gaseous emission is equal to the amount that absorbed by organisms when they were still living [50]. Thermochemical and biological methods are the two modes for hydrogen production from biomass. Although biological processes are more environmentally benign and less energy intensive, as they operate under mild conditions, they provide low rates and yields ($\text{mol H}_2/\text{mol feedstock}$) of hydrogen depending on the raw materials used [29]. On the other hand, thermochemical processes are much faster and offer higher stoichiometric yield of hydrogen with gasification being a promising option based on economic and environmental considerations [51,52].

3.1.1. Thermochemical processes

Thermochemical processes constitute the technique through which biomass can be transformed into hydrogen and hydrogen-rich gases [53,54]. Hydrogen-rich gas production from synthesis gas obtained from such processes is an effective step forward for a climate with zero emission of greenhouse gases necessary for sustainable development [55]. Thermochemical technology mainly involves pyrolysis and gasification. Both conversion processes produce, among other gaseous products, CH_4 and CO which can be further processed for more hydrogen production through steam reforming and WGS reaction. Addition to these techniques, combustion and liquefaction are two less preferable methods, as they both offer low hydrogen production with the first emitting polluting byproducts and the second requiring difficult to be achieved operation conditions of 5–20 MPa in the absence of air [56].

Biomass pyrolysis is the thermochemical process of generating liquid oils, solid charcoal and gaseous compounds by heating the biomass at a temperature of $650\text{--}800\text{ K}$ at $0.1\text{--}0.5\text{ MPa}$ [48]. It takes place in the total absence of oxygen except in cases where partial combustion is allowed to provide the thermal energy needed for the process [52]. Methane and other hydrocarbon gases produced can be steam reformed and for even more hydrogen production WGS reaction is applied. After CO is converted into CO_2 and H_2 , the desired purified H_2 is obtained by PSA [57]. The individual steps of biomass pyrolysis process, shown in Fig. 10, are represented by the following equations:



The yield of hydrogen production from biomass pyrolysis depends on the type of feedstock, the type of the catalyst used, the temperature and the time of residence [51,58]. The hydrogen production cost of biomass pyrolysis is expected to be in the range

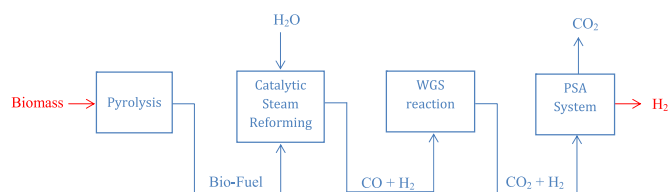
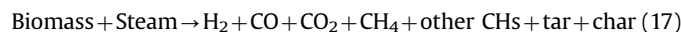
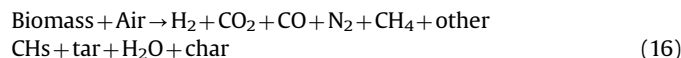


Fig. 10. Flow diagram of the biomass pyrolysis process.

of 8.86 \$/GJ to 15.52 \$/GJ (or 1.25 \$/kg to 2.20 \$/kg), depending on the facility size and biomass type [56].

Biomass gasification is the thermochemical conversion of biomass into a gaseous fuel (syngas) in a gasification medium such as air, oxygen and/or steam. It takes place at temperatures between 500 and 1400 °C, operating pressures from atmospheric to 33 bar depending on the plant scale and the final application of the produced syngas and the types of the reactor are distinguished according to the flow and velocity of the gasifying agent [57]. Fixed bed, fluidized bed and indirect gasifiers are the three main types of reactors used for biomass gasification, the most common configurations of which are shown in Fig. 11. Eqs. (16) and (17), represent the transformation of biomass into syngas, when it reacts with air or steam, respectively.



After the transformation of biomass into syngas, the gas mixture is further treated in the same way as the product gas of the pyrolysis process, as shown in Fig. 12. However, biomass type, particle size, temperature, steam-to-biomass ratio and type of catalyst used are the main parameters affecting on hydrogen yield [54,55]. In steam gasification, the yield of hydrogen is far better than fast pyrolysis while the overall efficiency (thermal-to-hydrogen) can reach up to 52% providing an effective means of renewable hydrogen production [52,59]. It is estimated that a typical route of biomass gasification-steam reforming-PSA, requires 2.4 TJ of primary energy input per TJ of hydrogen [60], and for a plant with an expected hydrogen output of 139,700 kg/day and cost of biomass in the range of 46–80 \$/dry-ton the hydrogen production cost is expected to be 1.77–2.05 \$/kg [39].

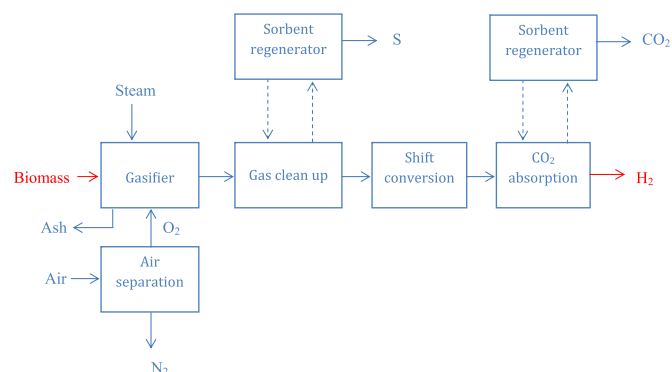


Fig. 12. Flow diagram of the biomass gasification process.

3.1.2. Biological processes

Due to increased attention to sustainable development and waste minimization, research in biological hydrogen production has substantially increased over the last several years. Most biological processes operate at ambient temperature and pressure, thus less energy intensive. Moreover, they utilize renewable energy resources which are inexhaustible and they contribute to waste recycling as they can also use various waste materials as feedstock [61].

The major biological processes utilized for hydrogen gas production are direct and indirect bio-photolysis, photo and dark fermentations, and multi-stage or sequential dark and photo-fermentation. The feeds for bio-hydrogen are water for photolysis where hydrogen is produced by some bacteria or algae directly through their hydrogenase or nitrogenase enzyme system, and biomass for fermentative processes where the carbohydrate containing materials are converted to organic acids and then to hydrogen gas by using bio-processing technologies [27,41].

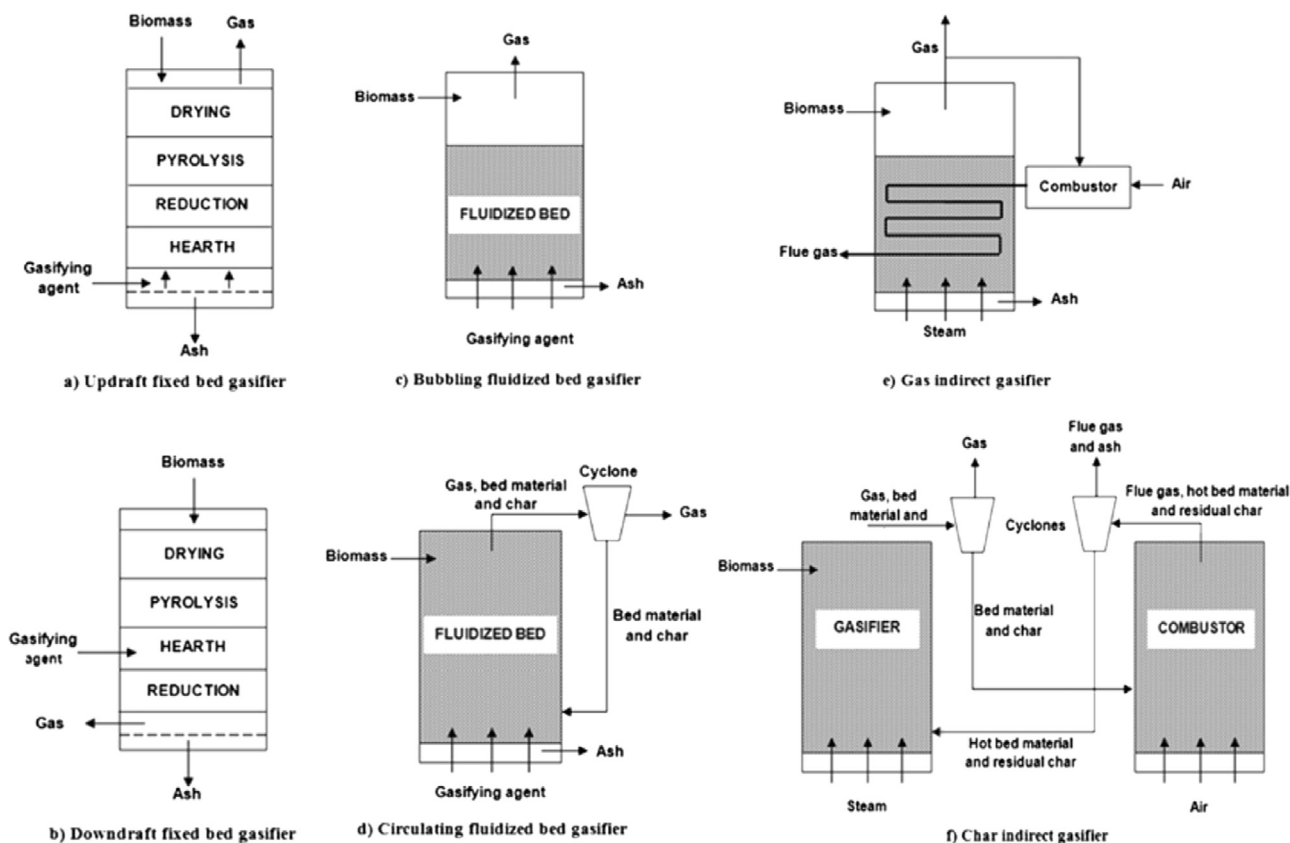


Fig. 11. Configuration of gasifiers [57].

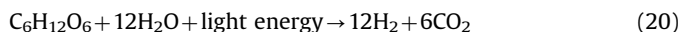
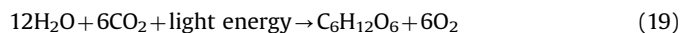
Bio-photolysis is a biological process using the same principles found in plants and algal photosynthesis, but adapts them for the generation of hydrogen gas. In green plants only CO_2 reduction takes place, as the enzymes that catalyze hydrogen formation are absent. On the contrary, algae contain hydrogen-producing enzymes and can produce hydrogen under certain conditions [61]. Green algae and blue-green algae are able to split water molecules into hydrogen ion and oxygen via direct and indirect bio-photolysis, respectively.

In direct bio-photolysis, green algae split water molecules to hydrogen ion and oxygen via photosynthesis, as observed in Fig. 13. The generated hydrogen ions are then converted into hydrogen gas by hydrogenase enzyme [27]. This enzyme is very sensitive to oxygen, and thus, it is necessary to maintain the oxygen content at a low level under 0.1% [56]. On the other hand, at full sunlight intensities 90% of the photons captured by the photosynthetic apparatus (chlorophyll and other pigments) are not used in photosynthesis but rather decaying as heat or fluorescence [62]. In order to overcome the “light-saturation effect”, mutants derived from microalgae were reported to have both reduced pigment content with smaller amounts of chlorophyll and good tolerance to oxygen, leading to higher hydrogen production [56]. The conversion of water to hydrogen by green algae may be represented by the following general reaction:



Assuming a very optimistic capital cost for photo-bioreactor of only 50 \$/m², minimal operating costs at an overall 10% solar conversion efficiency and many cost components such as engineering, gas separation and handling being not included, the hydrogen cost is estimated to 15 \$/GJ or 2.13 \$/kg of H_2 produced [62]. An increase of 20% of the capital cost implies 33.33% higher production cost [56].

In indirect bio-photolysis, the general reaction for hydrogen formation from water by cyanobacteria or blue-green algae can be represented by following reactions:



The schematic diagram of indirect bio-photolysis process can be observed in Fig. 14. Hydrogen is produced both by hydrogenase and nitrogenase enzymes and the production rate is comparable to hydrogenase-based production by green algae [56]. Although indirect bio-photolysis processes are still at the conceptual stage, assuming a total capital cost of 135 \$/m² the production cost is estimated to 10 \$/GJ or 1.42 \$/kg of H_2 [62]. Hence, the algal H_2 production could be considered as an economical and sustainable method in terms of water utilization as a renewable source and CO_2 consumption as one of the air pollutants. However, low H_2 production potential, the requirement of significant surface area to collect sufficient light and no waste utilization are the main drawbacks of this bio-hydrogen production method [27,41].

Fermentations are biochemical processes that take place with or without oxygen and perform microbial transformations of organic feed materials producing alcohols, acetone and H_2 in minimal amounts as well as CO_2 . These methods constitute an attractive approach for bio-hydrogen production as they utilize waste materials, providing inexpensive energy generation with simultaneous waste treatment [35].

Dark fermentation uses primarily anaerobic bacteria on carbohydrate rich substrates under anoxic (no oxygen present), dark conditions. As can be seen from Eqs. (21) and (22), with glucose as the model substrate, acetic and butyric acids constitute over than 80% of total end-products and theoretically the yields of H_2 are

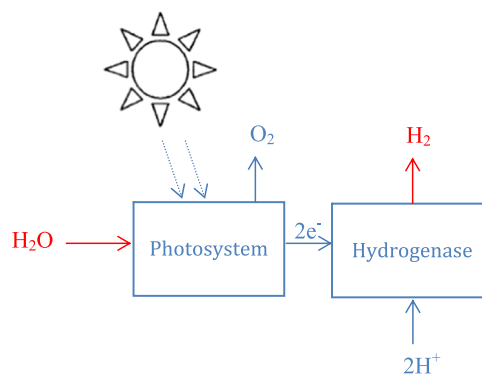


Fig. 13. Flow diagram of the direct bio-photolysis process.

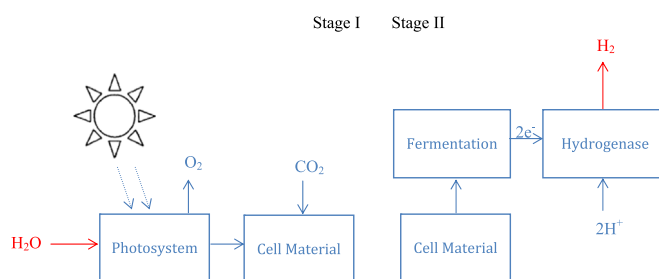
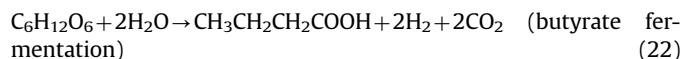
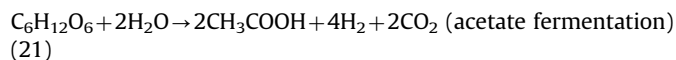


Fig. 14. Flow diagram of the indirect bio-photolysis process.

4 and 2 mol per mole of glucose in acetate and butyrate type fermentation, respectively [29].



Glucose, as the preferred source for this process, is relatively expensive and is not readily available in high quantities but can be obtained from agriculture wastes. Starch containing materials which are abundant in nature, as well as cellulose which is the major constitute of plant biomass, can be alternatively used [27]. For the optimal production, pH should be maintained between 5 and 6 as the amount of H_2 production by this process highly depends on its value [56]. Another constraint is that the hydrogen must be removed as it is generated because as the pressure increases the H_2 production tends to decrease [41]. However, dark fermentation is realized over a relatively simple process that does not rely on the availability of light sources, as can be seen from Fig. 15 [19]. Thus, much land is not a requirement and hydrogen can be produced constantly through day and night from a wide spectrum of potentially utilizable substrates including refuse and waste products [61].

The second biochemical process is photo-fermentation which is realized in deficient nitrogen conditions using solar energy and organic acids. Due to the presence of nitrogenase, some photosynthetic bacteria are capable of converting the organic acids (acetic, lactic and butyric) into hydrogen and carbon dioxide according to the following reaction [19]. With acetic acid as the reactant, the overall conversion into H_2 is presented below.

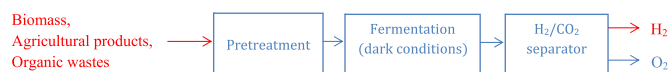


Fig. 15. Flow diagram of the dark fermentation process.

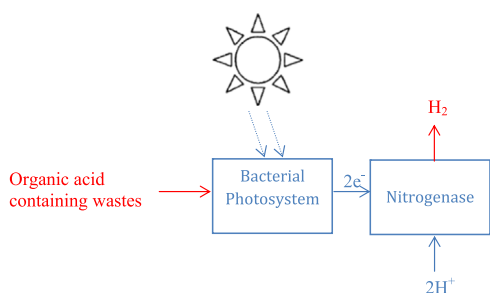
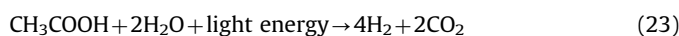
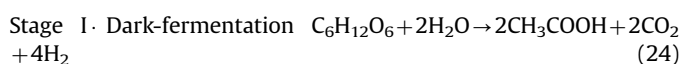


Fig. 16. Flow diagram of the photofermentation process.



Increasing light intensity has a stimulatory effect on H_2 yield and production rate, but an adverse effect on the light conversion efficiency. If industrial effluents are used for H_2 production, a major problem occurs due to the color of wastewaters which could reduce the light penetration and the presence of toxic compounds such as heavy metals which may require pre-treatment before being used [27]. Although hydrogen production under illuminated conditions is usually higher than that of the dark conditions, low solar energy conversion efficiency and demand for elaborate anaerobic photo-bioreactors covering large areas [56], as well as the limited availability of organic acids [41], are the key barriers restricting this method to compete with aforementioned process. Fig. 16 illustrates a schematic diagram representing the H_2 production by photosynthetic bacteria. Two typical configurations of photo-bioreactor types are provided in Fig. 17 while the footprint needed in terms of their volume, along with the H_2 production rates can be obtained from Table 2.

Higher hydrogen production yields and reduced light energy demand can be obtained by using hybrid systems. Such a system comprises of non-photosynthetic or anaerobic and photosynthetic bacteria. As shown in Fig. 18, variety of carbohydrates can be digested by anaerobic bacteria producing hydrogen under dark conditions and the resulting organic acids could be sources for photosynthetic bacteria to produce additional hydrogen [61]. The combination of dark and photo-fermentation is also referred as sequential dark/photo-fermentation and the two-stage process can be represented as follows:



The theoretical hydrogen yield increases to a total of 12 mol of hydrogen produced per mole of glucose while in practice the maximum reported is 7.1 mol H_2 /mol glucose [63]. The main parameters that affect the H_2 yield are: the temperature which improves the H_2 yield as it increases and the pH value which must be in the range of 4.5–6.5 and above 7 for fermentative and

Table 2

Hydrogen synthesis rate and bio-reactor volume needed for 5 kW PEMFC (adapted from [41]).

| Bio-hydrogen system | H_2 synthesis rate (mmol H_2 /h) | Bio-reactor volume (m^3) |
|-------------------------|--|-------------------------------------|
| Direct bio-photolysis | 0.07 | 1707 |
| Indirect bio-photolysis | 0.355 | 337 |
| Dark fermentation | 8.2–121 | 1–14.75 |
| Photo-fermentation | 0.16 | 747 |

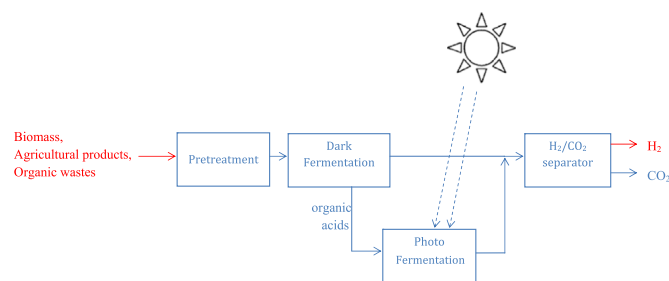


Fig. 18. Flow diagram of the sequential dark and photofermentation process.

photosynthetic bacteria, respectively [19]. Hydrogen production cost by multi-stage, sequential dark and photo-fermentation is not available but assumed lower than individual stages which, according to a recent study, are estimated to be 2.57 \$/kg and 2.83 \$/kg for dark and photo-fermentation respectively [30].

3.2. Water splitting

Water is one of the most abundant and inexhaustible raw materials in Earth and can be used for H_2 production through water-splitting processes such as electrolysis, thermolysis and photo-electrolysis [64,65]. If the required energy input is provided from renewable energy sources, the hydrogen produced will be the cleanest energy carrier that could be used by mankind.

3.2.1. Electrolysis

Electrolysis is an established and well-known method, constituting the most effective technique for water splitting [66]. The reaction, however, is very endothermic thus the required energy input is provided by electricity [67]. A typical electrolysis unit or electrolyzer, illustrated in Fig. 19, consists of a cathode and an anode immersed in an electrolyte, and generally when electrical current is applied water splits and hydrogen is produced at the cathode while oxygen is evolved on the anode side via the following reaction [68]:

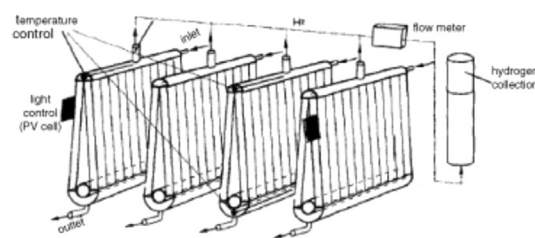
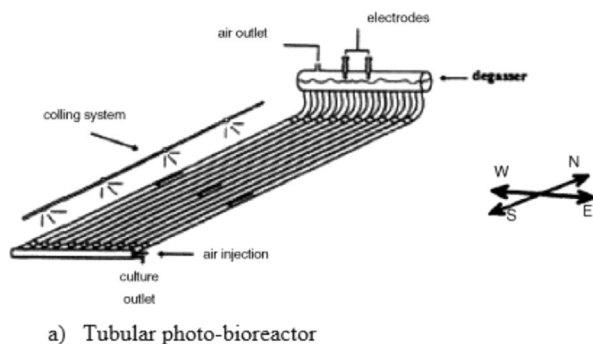


Fig. 17. Configurations of photo-bioreactors [27].

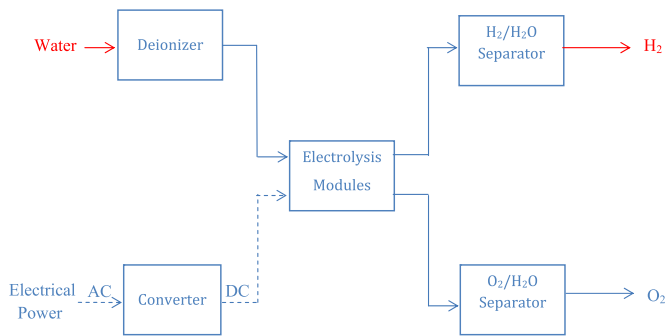


Fig. 19. Flow diagram of the water electrolysis process.

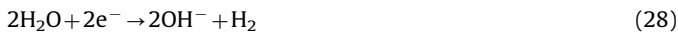
To date, the developed and commonly used electrolysis technologies are alkaline, proton exchange membrane (PEM) and solid oxide electrolysis cells (SOEC). In PEM electrolyzer water is introduced at the anode where it is split into protons (hydrogen ions, H^+) which in turn travel through membrane to the cathode in order to form H_2 , and oxygen which remains back with water. In alkaline and SOEC, water is introduced at the cathode where it is split into H_2 which is separated from water in an external separation unit and hydroxide ions (OH^-) which in turn travel through the aqueous electrolyte to the anode in order to form O_2 [67]. SOEC systems differ in that part of the electrical energy is replaced with thermal as a result the temperature increases and consequently, the H_2 is left in unreacted steam stream [41]. Overall conversions realized to both sides of each individual system can be summarized as follows:

- Alkaline and SOEC:

Anode:



Cathode:



- PEM:

Anode:



Cathode:



Although extremely pure hydrogen could be simply produced from water by electrolysis, the high consumption of electricity by electrolyzers prevents the production cost to compete with other large-scale technologies contributing with a share of about 5% to the total generation [69]. However, if the electrical energy is provided by RES such as hydro, wind and solar, the H_2 produced is the cleanest energy carrier, which can be used to store the excess electricity and improve the plant-load factor and efficiency in small scales [1,3,46,48–54]. In this way, water electrolysis offers a more sustainable and cost-effective option [79]. Commercialized alkaline electrolyzers can reach 380,000 kg H_2 annual production rates with a system energy consumption of 53.4 kWh/kg H_2 and efficiency up to 73% [80]. Hydrogen production costs of different electricity sources for electrolysis are tabulated in Table 3.

3.2.2. Thermolysis

Thermolysis or thermochemical water splitting is the process at which water is heated to a high temperature until decomposed to hydrogen and oxygen. Although simply, the decomposition of water is not effected until the temperature is very high, generally

Table 3

Hydrogen production cost of different approaches for electrolysis (adapted from [39]).

| Electricity source | Hydrogen production rate (kg/day) | Capacity factor (%) | Hydrogen cost (\$/kg) |
|--------------------|-----------------------------------|---------------------|-------------------------|
| Nuclear | 1000 | 97 | 4.15 |
| Solar thermal | 1000 | 40 | 7.00 |
| Solar PV | 1356 | 28 | 10.49 ^a |
| Wind | 62,950 | 65 | 6.46 ^a |
| | 38,356 | 76 | 5.10 |
| | 1400 | 28 | 5.78–23.27 ^b |
| | 50,000 | 41 | 5.89–6.03 ^c |

^a Based on electrolyzer cost of 500 \$/kW.

^b Based on photovoltaic cost varying from 0.75 \$/W_{peak} to 5 \$/W_{peak} and an electrolyzer cost of 450 \$/kW.

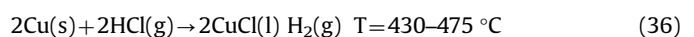
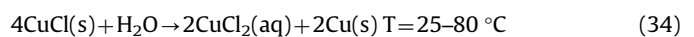
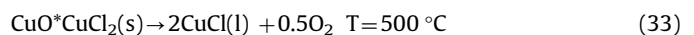
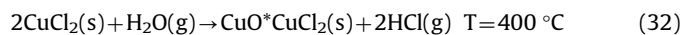
^c The cost of 6.61 \$/kg assumes the coproduction of electricity along with hydrogen whereas, 6.77 \$/kg represents the cost of only hydrogen production.

over 2500 °C, in order the Gibbs function (ΔG) to become zero and the separation of hydrogen from the equilibrium mixture become feasible [81]. Since such expenditures of considerable primary energy could not be achieved by sustainable heat sources, several thermochemical water-splitting cycles have been proposed to lower the temperature and improve the overall efficiency. Thermochemical cycles consist of a series of chemical reactions at different temperatures and constitute one of the most promising process through which heat is converted into chemical energy in the form of hydrogen [32,49,50]. Two examples of thermochemical cycle, represented by the chemical reactions (32)–(38) respectively, are shown below enabling the comparison with the single-stage water decomposition of Eq. (31).

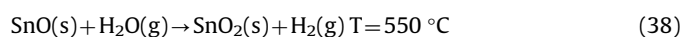
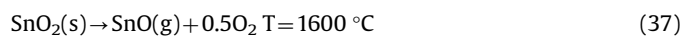
- Single-stage water decomposition [65]:



- Multi-stage Cu-Cl cycle [84]:



- Novel two-step SnO_2/SnO cycle [85]:



The still high temperature required can be supplied by solar heat or nuclear energy, with the interest be focused to the progress on solar collectors [66,86]. Large-scale concentration of solar energy can be obtained using parabolic reflectors namely, trough, tower and dish systems, the capability of which is expressed in terms of their mean flux concentration ratio (or suns) [65]. Fig. 20 shows the flow diagram of a solar-based thermochemical water-splitting process. At present, the most promising low-temperature thermochemical cycles appear to be Cu-Cl and Mg-Cl, without releasing any GHG to the atmosphere and requiring heat at least 550 °C [55–57]. The energy efficiencies and rates of hydrogen produced are found to be increasing with rise in solar light intensity [90]. It should be pointed out that, apart from the capital investment for the necessary equipment, criteria such as toxicity

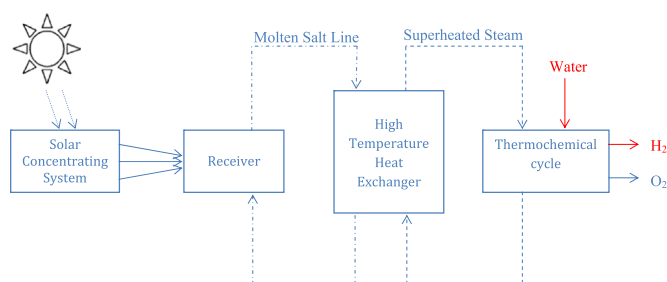


Fig. 20. Flow diagram of the solar-based thermochemical water splitting process.

of the elements involved, availability and cost of chemicals, materials separation and corrosion problems, are reflected in the H_2 production cost [81]. Hydrogen production costs by various approaches for thermochemical water-splitting are listed in Table 4.

3.2.3. Photo-electrolysis

Photolysis, in general, is effected when the energy of visible light is absorbed with the help of some photo-catalysts and is then utilized to decompose water into H_2 and O_2 [28]. In photo-electrolysis, the sunlight is absorbed through some semiconducting materials and the process of water splitting is similar to electrolysis. Particularly, if a photon with greater or equal to semiconductor's bandgap energy strikes the semiconducting surface of the anode, an electron-hole pair is generated and separated by the electric field between the semiconductor and the electrolyte. The holes remain at the anode where they split water into H^+ which in turns travel through electrolyte to the cathode and O_2 which remains back with water, while the electrons flow through an external circuit to the cathode where they interact with H^+ to form H_2 [91]. A schematic diagram of the photo-electrolysis process is presented in Fig. 21 while the energetic view of H_2 production can be summarized by Eqs. (39)–(41).

Anode:



Cathode:



• Overall:



Although the free energy required for the decomposition of water into H_2 and O_2 is only 1.23 eV, the separation of electron from the hole, without the use of any external bias potential, requires high bandgap energy and as a result the overall efficiency decreases dramatically [92]. In [93], some materials that have been investigated as electrodes in photo-electrolysis cells are listed, whereas Akikusa et al. [94] concluded that the combination of SiC and TiO_2 provides a self-driven system with suitable band

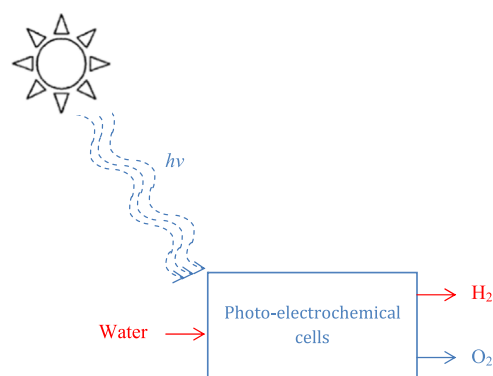


Fig. 21. Flow diagram of the photo-electrolysis process.

positions and photoconversion efficiency of only 0.06%. A recent study showed a production cost of 10.36 \$/kg of hydrogen produced [30].

4. Overall comparison

In this work, an overview of the major hydrogen production processes has been presented. Following, a comparative assessment is performed to evaluate both the technical and economic aspects, while the relating data are summarized in Tables 5 and 6 respectively.

Justifiably, SMR is currently the most cost-effective process for H_2 production followed by CG. SR possess the lowest operating temperature requiring no oxygen, followed by ATR and POX, while hydrocarbon pyrolysis provides the advantage of reduced-step and emission-free procedure, with carbon being the only byproduct that requires treatment. Referring to Table 5, these methods occur more advantageous in that, they constitute a mature and highly developed technique for H_2 generation through infrastructures that already exist. They also provide a more efficient conversion of energy (up to 85%) compared to renewable methods which makes them, in most cases, the most viable approach. By combining membrane reactors with H_2 generation from fossil fuels, further improvements occur in terms of efficiency, maximum temperature of operation and consequently capital investments. The low temperature (550 °C) achieved, could be provided from the exhaust gases of a gas turbine in a combined-cycle for both power and H_2 production or even from concentrated solar energy. In contrast, the dependence on fossil fuels in combination with CO_2 byproduct released in the atmosphere during the reforming process, are the key limitations leading most researches to alternate, renewable methods. Since fossil fuels are currently used as both the reactants and the fuel for the process, these methods are heavily dependent on their price.

Biomass represents a renewable, abundant feedstock available almost anywhere. The thermochemical pyrolysis and gasification offer an effective means of hydrogen production (efficiency in the range of 35–50%) while the fermentative processes provide the distinct advantage of simultaneous hydrogen generation and waste recycling. Both modes have a neutral effect on CO_2

Table 4
Hydrogen production costs by various approaches for thermochemical water splitting.

| Heat source | Thermochemical cycle | Maximum temperature [°C] | Overall eEfficiency [%] | Production rate [kg/day] | Hydrogen cost [\$/kg] | Refs. |
|-------------|--|--------------------------|-------------------------|--------------------------|-----------------------|----------|
| Nuclear | S-I | 850 | 45 | 800,000 | 2.45–2.63 | [39,105] |
| | Cu-Cl | 550 | 45 | 7000 | 2.17 | [106] |
| | ZnO/Zn | 1727 | 20.8 | 6000 | 7.98 | [107] |
| | Fe ₃ O ₄ /FeO | 1627 | 17.4 | 6000 | 8.40 | [107] |
| | Fe ₂ O ₃ /Fe ₃ O ₄ | 1327 | 18.6 | 6000 | 8.40 | [107] |

Table 5
Comparison of the different hydrogen production processes.

| Process | Efficiency (%) | Major advantages | Major disadvantages |
|----------------------|----------------|---|---|
| SR | 74–85 | Most developed technology, existing infrastructure. | CO ₂ byproduct, dependence on fossil fuels. |
| POX | 60–75 | Proven technology, existing infrastructure. | CO ₂ byproduct, dependence on fossil fuels. |
| ATR | 60–75 | Proven technology, existing infrastructure. | CO ₂ byproduct, dependence on fossil fuels. |
| CHs pyrolysis | – | Emission-free, reduced-step procedure. | Carbon byproduct, dependence on fossil fuels. |
| Biomass pyrolysis | 35–50 | CO ₂ -neutral, abundant and cheap feedstock. | Tar formation, varying H ₂ content due to seasonal availability and feedstock impurities. |
| Biomass gasification | – | CO ₂ -neutral, abundant and cheap feedstock. | Tar formation, varying H ₂ content due to seasonal availability and feedstock impurities. |
| Bio-photolysis | 10 | CO ₂ -consumed, O ₂ is the only byproduct, operation under mild conditions. | Requires sunlight, low H ₂ rates and yields, requirement of large reactor volume, O ₂ sensitivity, high raw material cost. |
| Dark fermentation | 60–80 | CO ₂ -neutral, simple, can produce H ₂ without light, contributes to waste recycling, no O ₂ limitation. | Fatty acids removal, low H ₂ rates and yields, low conversion efficiency, requirement of large reactor volume. |
| Photofermentation | 0.1 | CO ₂ -neutral, contributes to waste recycling, can use different organic wastes and wastewaters. | Requires sunlight, low H ₂ rates and yields, low conversion efficiency, requirement of large reactor volume, O ₂ sensitivity. |
| Electrolysis | 40–60 | No pollution with renewable sources, proven technology, existing infrastructure, abundant feedstock, O ₂ is the only byproduct, contributes to RES integration as an electricity storage option. | Low overall efficiency, high capital costs. |
| Thermolysis | 20–45 | Clean and sustainable, abundant feedstock, O ₂ is the only byproduct. | Elements toxicity, corrosive problems, high capital costs. |
| Photo-electrolysis | 0.06 | Emission-free, abundant feedstock, O ₂ is the only byproduct. | Requires sunlight, low conversion efficiency, non-effective photocatalytic material. |

concentration whereas the bio-photolysis is considered as CO₂-consumed due to the photosynthesis involved during the process. In terms of efficiency, dark fermentation could compete with all methods listed in Table 5, in contrast to bio-photolysis and photo-fermentation which require sunlight. Regarding the disadvantages, the thermochemical processes suffer from the feedstock impurities and its seasonal availability, with the consequent varying H₂ content [102,103]. On the other hand, the biological processes provide low rates and yields, requiring larger reactor volume. Consequently, biomass could contribute in large scale generation only through thermochemical pathways of pyrolysis and gasification, whereas biological processes may be used in small-scales for local H₂ production or for centralized waste recycling and treatment.

Water-splitting pathways occur clean and sustainable, producing only H₂ and O₂ from one of the most abundant raw materials in the world. Electrolysis is responsible for the emission of CO₂ only when fossil fuels are used to generate the needed electricity. From renewable energy sources, such as solar and wind, it is able to produce H₂ and improve the load factor of a plant, contributing to the increase of RES integration. According to Table 5, thermochemical cycles provide a more efficient way of H₂ production with the main limitations being the toxicity of the elements involved as well as the separation between them. Due to the lack of effective photo-catalytic materials, photo-electrolysis is the less efficient process (efficiency of only 0.06%). However, comparing all methods based on their primary energy source, solar-based processes provide the less conversion efficiency. Following the biological methods which operate under mild conditions, water-splitting methods provide moderate temperatures and conversion efficiencies when nuclear is the preferred energy source for both water electrolysis and thermochemical water splitting.

To qualitatively assess the costs derived from each hydrogen production method, variables such as energy source, feedstock and capital investment, have been included in Table 6. As byproducts, are considered only those that either infect and must be seized, or can be used from another process to reduce costs. In this context, the methods which produce H₂ from fossil fuels appear disadvantageous as the releasing CO₂ from reforming process and coal produced by hydrocarbon pyrolysis, constitute expensive procedures requiring energy-intensive steps of CCS to be addressed. As energy source, the conventional fossil fuels require

reactors that already exist and possessing acceptable capital cost. Due to the still low price of natural gas and coal, and the high efficiency they provide as a feedstock, the final hydrogen production cost from conventional technologies is quite low (< 2 \$/kg). As can be seen in Table 6, the cost per kilogram of H₂ produced including and without CCS ranges between 1.34 and 2.27 \$ (based on 2005 values) with the lowest corresponding to CG without CCS process. Further reduction in H₂ cost derived from hydrocarbon pyrolysis is expected, if a market for coal purchase would be found. Utilizing cheaper energy source and feedstock, thermochemical pyrolysis and gasification of biomass are economically viable as they provide similar to conventional technologies production costs. Biomass pyrolysis and gasification offer viable approaches with production costs in the range of 1.25–2.20 \$/kg (based on 2004 values) of H₂ produced. Although algae constitutes one of the most expensive feedstocks, biological processes offer production costs around 2 \$/kg, assuming very optimistic capital costs for photo-bioreactor of only 50 \$/m² and 135 \$/m² for direct and indirect bio-photolysis, respectively. According to a recent study performed in 2014, biochemical dark and photo-fermentation produce H₂ priced between 2.5 and 2.8 \$/kg, mainly due to the low rates and yields along with the large reactors needed.

High production cost also stems from water-splitting methods, particularly from those that use solar or wind technology to provide the needed energy. Both the high capital costs and low conversion efficiencies, lead to increased production cost which in some cases exceeds 20 \$/kg and 8 \$/kg for electrolysis and thermolysis, respectively. With a production cost higher than 10 \$/kg of H₂ and an efficiency as low as 0.06%, photo-electrolysis is by far the least cost-effective method currently available. In conclusion, according to the data listed in Tables 5 and 6 together with the above discussion relating to the key parameters outlined, carbon taxes imposition directly influence H₂ cost. Apart from this and in order for the renewable methods to become competitive in terms of cost-effectiveness, the second step should be the further research in renewable technologies and development of less expensive equipment able to produce H₂ in a more efficient way.

5. H₂ storage, transportation and utilization

Aiming to fulfill the goals of security in the energy supply system, environmental protection and economic growth of

Table 6
Summary of the different hydrogen production processes.

| Process | Energy source | Feedstock | Capital cost (M\$) | Hydrogen cost [\$/kg] | Study year dollars |
|----------------------------|----------------------------|-----------------|--------------------------|-----------------------|--------------------|
| SMR with CCS | Standard fossil fuels | Natural Gas | 226.4 | 2.27 | 2005 |
| SMR without CCS | Standard fossil fuels | Natural Gas | 180.7 | 2.08 | 2005 |
| CG with CCS | Standard fossil fuels | Coal | 545.6 | 1.63 | 2005 |
| CG without CCS | Standard fossil fuels | Coal | 435.9 | 1.34 | 2005 |
| ATR of methane with CCS | Standard fossil fuels | Natural Gas | 183.8 ^a | 1.48 | 2005 |
| Methane Pyrolysis | Internally generated steam | Natural Gas | – | 1.59–1.70 | 1992 |
| Biomass Pyrolysis | Internally generated steam | Woody Biomass | 53.4–3.1 ^b | 1.25–2.20 | 2004 |
| Biomass Gasification | Internally generated steam | Woody Biomass | 149.3–6.4 ^c | 1.77–2.05 | 2004 |
| Direct Bio-photolysis | Solar | Water+Algae | 50 \$/m ² | 2.13 | 2002 |
| Indirect Bio-photolysis | Solar | Water+Algae | 135 \$/m ² | 1.42 | 2002 |
| Dark Fermentation | – | Organic Biomass | – | 2.57 | 2014 |
| Photo-Fermentation | Solar | Organic Biomass | – | 2.83 | 2014 |
| Solar PV Electrolysis | Solar | Water | 12–54.5 | 5.78–23.27 | 2007 |
| Solar Thermal Electrolysis | Solar | Water | 421–22.1 ^d | 5.10–10.49 | 2007 |
| Wind Electrolysis | Wind | Water | 504.8–499.6 ^e | 5.89–6.03 | 2005 |
| Nuclear Electrolysis | Nuclear | Water | – | 4.15–7.00 | 2006 |
| Nuclear Thermolysis | Nuclear | Water | 39.6–2107.6 ^f | 2.17–2.63 | 2007 |
| Solar Thermolysis | Solar | Water | 5.7–16 ^g | 7.98–8.40 | 2007 |
| Photo-electrolysis | Solar | Water | – | 10.36 | 2014 |

^a Based on a 600 MW_{H₂} power plant with a capital cost of 306.35 \$/kW_{H₂}.

^b The capital cost of 53.4 M\$ corresponds to a plant capacity of 72.9 tn/day, 3.1 M\$ is referred to a 2.7 tn/day plant output.

^c The capital cost of 149.3 M\$ corresponds to a plant capacity of 139.7 tn/day, 6.4 M\$ is referred to a 2tn/day plant output.

^d The capital cost of 421 M\$ is referred to a power-tower electrolysis plant and 38.4 tn/day of H₂, 22.1 M\$ corresponds to stirling-dish technology and 1.4 tn/day.

^e The cost of 504.8 M\$ assumes the coproduction of electricity along with hydrogen whereas, 499.6 M\$ represents the cost of only hydrogen production.

^f The capital cost of 39.6 M\$ corresponds to a Cu-Cl plant capacity of 7 tn/day, 2107.6 M\$ is referred to a 583 tn/day S-I plant output.

^g The capital cost of 5.7 M\$ corresponds to a plant capacity of 1.2 tn/day, 16 M\$ is referred to a 6 tn/day plant output.

societies, the introduction of produced H₂ as a fuel and energy carrier presents, beyond the undisputed advantages, several problems in developing the required technologies for storage, transmission and utilization [23].

At ambient temperature and atmospheric pressure, 1 kg of H₂ gas occupies a volume of 11 m³. With such a low density of 0.09 kg/m³, H₂ storage has become one of the key barriers restricting its wide spread use [95]. The main storage methods enable hydrogen to be stored physically as a gas or liquid, and on the surfaces or within the solids by adsorption and absorption, respectively.

High pressure gaseous hydrogen storage is currently the most common and mature method, achieving high pressures of up to 77 MPa using standard piston-type mechanical compressors [96]. However, the work needed for the compression is much higher than 2.21kWh/kg, providing a gravimetric and volumetric density of 13 wt% and lower than 40 kg/m³, respectively [97]. Liquid hydrogen can be stored in cryogenic tanks through a double-step procedure of compression and cooling in a heat exchanger. Because of its low boiling point of –252.87 °C, the work needed is estimated to 15.2 kWh/kg, achieving 70.8 kg/m³ volumetric density at atmospheric pressure, while the gravimetric density depends on the tank size. Even with the perfect insulation, the daily boil-off losses of releasing H₂ into the atmosphere are typically rated at 0.4%, 0.2% and 0.06% for storage volumes of 50 m³, 100 m³ and 20,000 m³, respectively [96].

Solid-state storage occurs more effective at storing large amounts of hydrogen at moderate temperature and pressure. In a process of adsorption, a gas molecule interacts with several atoms at the surface of a solid where it is bonded and reversibly released when needed. Carbon nanotubes are able to store H₂ at quite low temperatures (–196.15 °C) and pressures (6 MPa), providing a gravimetric and volumetric density of 10.8 wt% and 41 kg/m³, respectively [97]. The low pressure and cost of the materials involved are key advantages over the quite low temperatures needed. Alternatively, H₂ can react at elevated temperatures with many transition metals and their alloys to form hydrides. Light

metals such as Li, Be, Na, Mg, B, and Al, form a large variety of metal-hydrogen compounds while a high volumetric density of 150 kg/m³ at ambient temperature and pressure has been achieved in Al(BH₄)₃ [96]. However, the gravimetric density is limited to less than 3 wt% and therefore, intense interest has been developed in even lighter metals, complex hydrides. Complex hydrides open a new field of hydrogen storage materials, providing gravimetric densities of up to 18 wt% for LiBH₄ [98]. The main characteristics of the five basic methods which enable reversible hydrogen storage are listed in Table 7.

There are two possible modes for H₂ transportation and distribution. The first category regards the bulk transportation storage vessel, truck trailers, railway tank cars and containers, while the second includes the pipelines [99]. The low carrying capacity along with the lack of capability to handle H₂ through the conventional means of first category, results in high delivery costs [96]. The future H₂ transport and distribution system might look like current natural gas pipelines and could be envisaged as part of a system of networks, including electricity and natural gas [100]. Consequently, significant innovations are needed as the transport losses of methane and electricity over large distances are fairly equal at 5–7%, whereas using the same pipelines for H₂ could increase to 20% [101].

Beside its use in the chemical and oil industries, H₂ can be used in internal combustion engines, fuel cells, turbines, cookers and

Table 7
The basic hydrogen storage methods.

| Storage method | ρ_m (wt%) | ρ_v (kg/m ³) | T (°C) | P (MPa) |
|--------------------------------------|----------------|-------------------------------|---------|-------------|
| High pressure gaseous H ₂ | 13 | 40 | ambient | 77 |
| Cryogenic liquid | – | 70.8 | –252.87 | atmospheric |
| Adsorbed on carbon nanotubes | 10.8 | 41 | –196.15 | 6 |
| Absorbed to form hydrides | 3 | 150 | ambient | atmospheric |
| Absorbed to form complex hydrides | 18 | 150 | > 100 | atmospheric |

gas boilers [24]. In terms of simplicity, modularity and environmental protection, fuel cells own great interest relating to power generation, heating and transportation. Polymer electrolyte fuel cells (PEMFC) will be able to provide from few kW up to hundreds of kW for power generation and CHP in residential and industry applications, and two to three times higher efficiency than those of conventional vehicles, while molten carbonate fuel cells (MCFC) and solid oxide fuel cells (SOFC) will be available for distributed generation and industrial co-generation from some hundreds of kW to tens of MW [100]. Nevertheless, as a hydrogen economy with a national distribution system is far away, the proposed solutions support to initially use local small hydrogen generators for both smaller stationary and mobile applications [101]. Regarding the hydrogen-based vehicles, the two alternatives under consideration are either direct storage of H₂ provided by refueling stations or indirect, on-board production of H₂ from methanol [22,23].

6. Conclusions

A wide variety of processes are available for H₂ production. In this work, the process descriptions along with the technical and economic aspects of 14 different production methods were discussed. SMR is currently the most cost-effective process for H₂ production followed by CG. However, alternative processes need to be developed in order to reduce the dependence on fossil fuels so that commodities being able to face the increase in hydrogen demand, at least in transportation sector, as a consequence of population increase and fossil fuels depletion in the forthcoming years. The thermochemical pyrolysis and gasification are economically viable approaches providing the highest potential to become competitive on a large scale in the near future. The near-term trends appear to be in process fuel reduction through the integration of membrane reactor and combined-cycles utilizing alternative energy sources such as gas exhaust from gas turbines and concentrated solar energy. Water-splitting methods will not become competitive, unless the carbon taxes will be imposed by governments, and research will be further developed. Apart from the research gaps in H₂ production, issues concerning storage, transportation and utilization have to be addressed. Although H₂ storage has reached a technological level, further research and development needed to improve volumetric and gravimetric density. In addition, transportation and utilization of H₂ fuel requires knowledge and standards concerning safety such as indoor and outdoor operation safety distance, flammability range, leakage sensing, refueling speed control etc. All this information is completely unfamiliar and should be notified in public. From the above discussion it is clear that further R&D relating to H₂ production and storage, together with setting of codes and standards about H₂ transportation and utilization, implies the decrease of the national dependence on fossil fuel imports so that countries to be able to produce much of their own energy through a wide variety of available processes and feedstocks, getting more hydrogen to market.

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