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Review Article

Hydrogen: Trends, production and characterization of the main process worldwide

Tatiane da Silva Veras, Thiago Simonato Mozer [1], *Danielle da Costa Rubim Messeder dos Santos* [1], *Aldara da Silva César* [*]

Universidade Federal Fluminense, Brazil

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ABSTRACT

There is a worldwide debate about which energies are more efficient and renewable energy systems. This discussion comprises hydrogen and fuel cells as potential emerging technologies. However, information about hydrogen technology remains somehow unknown to a broader public. Currently some technologies supporting hydrogen productive chain are not so competitive and this means a tight bottleneck. Expectation is that this would be the most promising innovation in a new energy system based on renewable sources. This paper reports the large range of existing processes and technological routes for the production of hydrogen in many countries. Thus, this work aims to show the current energy landscape, highlighting the hydrogen and the main characteristics of the technological routes for its production. The overview about the current situation and trends of Hydrogen Economy is presented. The prominent research on hydrogen technology, processes and their main characteristics are addressed as well. The uncertainties surrounding the implementation of hydrogen energy, based on renewable sources, require further studies regarding competitiveness.

Contents

* *Corresponding author*. Departamento de Engenharia de Agronegócios, GASA – Grupo de Análise e Sistemas Agroindustriais, Av. dos Trabalhadores, 420, Vila Santa Cecília, Volta Redonda, RJ, CEP 27255-125, Brazil.

E-mail addresses: tatiane.sveras@gmail.com (T. da Silva Veras), mozer@vm.uff.br (T.S. Mozer), daniellerubim@id.uff.br (D. da Costa Rubim Messeder dos Santos), aldaracesar@id.uff.br (A. da Silva César).

[1] Departamento de Química, R. Desembargador Ellis Hermydio Figueira, 783, Bloco C, Aterrado, Volta Redonda, RJ, CEP 27213-145, Brazil.

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Introduction

The growing energy demand causes more pollution and requires increase in energy efficiency [1]. Therefore, the emissions of greenhouse gases (GHG) and the global warming become important issues in science and global policy, accelerating the necessity for replacing fossil fuels with renewable energy sources [2,3]. Thus, energy systems are the main source of sulfur dioxide emissions (82% of total emissions) and a significant portion of carbon monoxide emissions (46% of total emissions) [4,5].

Countries with higher energy demand have high emissions of greenhouse gases (GHG), because the current economic development is based on intensive use of energy sources from fossil fuels [2]. According to the International Energy Agency (IEA), the energy sector will increase the CO_2 emissions from 50% in 2030 to 80% in 2050 [6]. This way, the environmental issues associated with the use of fossil fuels have been a concerning of the international community.

Furthermore, social and economic development indicators are directly related to high levels of per capita energy consumption [7]. Thus, modern society is characterized by a growing dependence on energy use [8,9].

Between 2000 and 2013, global energy demand grew 38% [10]. It is estimated that the world population will reach approximately 7.5 billion in 2025. Therefore, the global consumption of energy increased 50–60% compared to current consumption [11]. Environmental impacts, energy vulnerability and fossil fuels depletion led many governments to promote the use of alternative energy sources, nonpolluting and renewable [12,13]. Thus, the future of energy changed over the last decades [14,15]. The IEA reaffirmed many times the need of a revolution in the energy field, based on the implementation of low carbon technologies and encouraging governments to rethink the current energy model [12].

Hydrogen and fuel cells have been mentioned as an emerging potential technology [16] and an option for a transition in the long term to cleaner energy and transport systems [14,17]. The use of hydrogen as energy carrier and fuel cell as a technology transformed hydrogen into electricity, it was considered a break in the current energy system. Thus, the generated electricity can be used both for stationary and vehicular application [18–20], replacing the direct use of fossil fuels in the combustion engines. Many studies aim to develop energy sources to several applications, from vehicular –about 100 kW– to small mobile devices that requires few watts.

Hydrogen energy is considered a clean technology [21], the storage of hydrogen energy is an advantageous way to produce electricity using fuel cell [22]. To find an economic way to store hydrogen is the center of discussions about renewable energies [22–24]. Borohydride fuel cell have been studied [22,25–27] as an alternative way to store hydrogen. Several authors [8,28–30] have reported that hydrogen is a key component to developing a clean and sustainable energy system, although it is necessary for its production technology to be made to be economically feasible [31].

In this sense, global initiatives promoted by the International Partnership for Hydrogen and Fuel Cells in the Economy (IPHE) searched actions to contribute with the development of hydrogen as energy carrier and the transition from the current energy model to the Hydrogen Economy - expression introduced by General Motors Co. in 1970 to name a new economy based on the use of hydrogen as an energy source [32]. Thus, governments have been funding development projects and studies on the hydrogen economy for local industrial use. As a result, the use of hydrogen enables the most efficient use of energy resources of local production chains [2].

There is not enough public dissemination of information about the hydrogen technology, its advantages and negative impacts affecting the social acceptance of this technology [8]. The study, analysis and comprehension of the transition possibilities for a new energy system can generate contributions to the development and consolidation of hydrogen energy, justifying the proposed efforts in this work. The existing processes and technological routes for the production of hydrogen reveal the importance of this review. This work aims to show the current energy overview highlighting the hydrogen and the main features of the technological routes for its production.

Research on hydrogen production technologies has been well documented; however they do not cover as much of the technologies currently known. More detailed studies are needed to further enhance the development of hydrogen economy [33].

This present review allows a better understanding of hydrogen production technologies and hydrogen conversion using fuel cells, giving a broad view about this subject. This paper has four sections: the first one is this introduction; the second section provides an overview about energy in the world and the importance of hydrogen energy; the third section presents the processes, technological routes and inputs, highlighting strengths, the weaknesses of them, fuel cells types and typical characteristics. Finally, the last section presents the final remarks.

Energy overview in the world and the hydrogen potential for energy generation

The current world energy system is based on fossil fuels for stationary and vehicular energy generation [34,35]. Industry demands high energy consumption and the main energy

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inputs are: oil, natural gas and coal [36]. These inputs have displayed higher consumption rates due to their use as energy source. Fossil fuels have been supplying the society's energy demands from the 18th century until nowadays. Fossil fuels provide more than 80% of global energy. In 2014, the oil was the main source (31,1%), followed by coal (29%) and natural gas (21,5%) (Fig. 1).

However, renewable energy sources have been studied as alternatives to ensure the sustainability of modern societies, in this sense, hydrogen has emerged as a promising energy carrier.

The process works in two stages. First, carbon-rich industrial waste gases like carbon monoxide are captured and fed to specialized microbes. These microbes consume the gas and produce ethanol (i.e., alcohol), and the ethanol undergoes additional processing to be suitable for jet engines. To accomplish this, in the Pacific Northwest National Laboratory (PNNL) the specialized chemical catalyst transforms ethanol into a product that can be upgraded into a finished fuel product. The resulting fuel is functionally equivalent to petroleum-derived jet fuel—meaning it can be used in today's aircrafts without engine modification and can provide the same level of performance and safety as petroleum-derived jet fuel. In addition, this fuel emits fewer other pollutants when it is burned [37].

Throughout time, carbonaceous energy sources were progressively substituted by energy sources with low or no carbon content, increasing the amount of hydrogen in the fuels [14]. It is expected that hydrogen energy will be responsible for 90% of energy generation in 2080 [38,39]. Therefore, the economy based on hydrogen from renewable sources will bring the end the carbon energy age. In 2050, the fuels will be carbon free [40] (Fig. 2).

The hydrogen economy describes a new hydrogen economy paradigm based on hydrogen as energy carrier [41] and the fuel cells as a technology that will convert hydrogen to electricity, for stationary and vehicular applications. This expression still relates to an energy system based on hydrogen for energy use, distribution and storage, mentioned as an option to change the actual energy system [34].

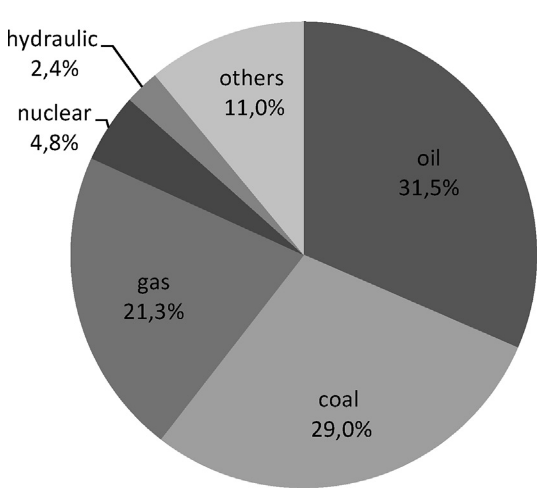

Fig. 1 – Global energy matrix in 2014 (%). Source: Adapted from Ref. [21].

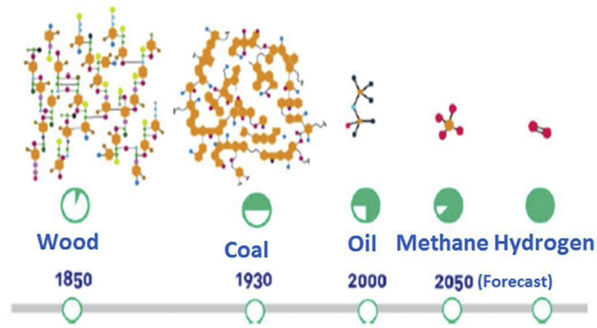

Fig. 2 – Progression in content into hydrogen fuel. Source: Adapted from Ref. [40].

The hydrogen economy still refers to an organized market, that allows its commercialization with competitive prices, quality, reliability and security of supplies, using renewable sources, available all over the world [2,42].

The hydrogen economy evolution proposed by the United States Department of Energy (DOE) [43] is shown in Fig. 3.

The use of hydrogen as energy carrier is related to an efficient use of the energies available, obtained with balanced costs and sustainable economic development [44].

Changes in the world energy system have been progressing since the era of solid fuels associated with carbon (wood biomass) to the current era based on liquid fuels from oil [45], which is usually a pollutant – and finally there are also have the gaseous fuels in the current era together with the liquid fuels. Nowadays, there is an increasing interest in using natural gas as a fuel, with the advantage over oil and coal of having high combustion efficiency and low level emission of pollutants [46]. The use of natural gas enables a reduction of global carbon emissions and less dependence on fossil fuels." [44,47] (Fig. 4).

The international incentives to a move to the hydrogen economy have been reported by many countries, signing initiatives with the IPHE and International Energy Agency (IEA) [48]. These partnerships accelerate the transition to hydrogen economy, organizing and implementing international researches of hydrogen technology and fuel cell [6]. The researches develop new technologies for hydrogen use as a fuel [2].

In order to develop the technology of hydrogen production, IPHE proposes actions to create a hydrogen economy chain worldwide, connecting governmental and private entities to invest in fields of basic and applied researches, development of products and services; inserting the government as an encourager of these projects; creating standards all over the world and reducing the cost to adapt the technology [49].

IPHE determines the major areas for transition to hydrogen economy, such as: research and development, hydrogen production and storage; regulations and standards for hydrogen, fuel cell technology and social-economic issues about hydrogen. Consequently, actions to accelerate the transition to the hydrogen economy have been created, comprising technologies related to hydrogen economy market. It is expected that these actions reduce the costs associated with the system integration all over the world and also accelerate the transition to hydrogen as energy carrier [2].

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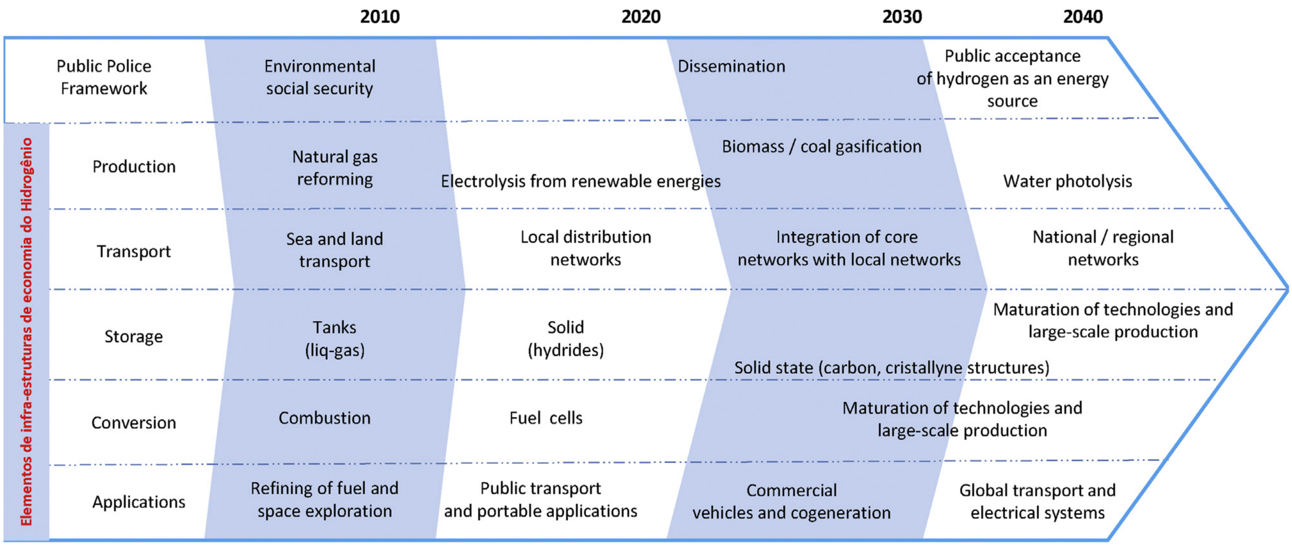

Fig. 3 – Possibilities of technological developments in the production chain to transition to HE. Source: Adapted from Ref. [18].

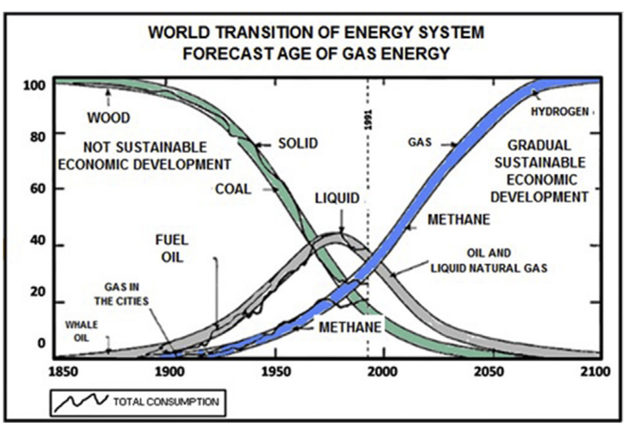

Fig. 4 – Global energy system transition from 1850 to 2150. Source: Adapted from Ref. [44].

The official documents from countries that wish to implement the hydrogen economy allow identification of the main purpose of production from different sources, its usage with low environmental impact and, to development of technologies for energy generation by hydrogen.

According to *Centro de Gestão e Estudos Estratégicos* (CGEE), the countries showing interest to implement this new economy have relatively higher energy demand and relatively higher level of greenhouse emissions [2].

The competitiveness of hydrogen as an alternative energy source depends on the efficiency and policies to support this technology, research and development, taking into account the time to commercialize [50]. These issues must provide the supply, demand and motivation of global competitiveness.

Features of hydrogen and production processes

Hydrogen can be produced from any feedstock (renewable or not) that contains the hydrogen atom (H) in its composition [51]. However, hydrogen gas (H_2) does not exist in nature in a sufficient amount, so it is an energy carrier, an energy holder.

Hydrogen is known as a fuel of the future, idealized for the next century [52]. Besides its long term potential to reduce the dependence on the petroleum oil and reduce the carbon emissions from transport sector, hydrogen also has the advantage of its high energetic yield (122 kJ/g), which is 2.75 times higher than hydrocarbon fuels [53].

Hydrogen is one of the most efficient energy fuels in energy conversion for the transportation sector [20,54]. Furthermore, hydrogen is 2.5 times more efficient than gasoline due to its specific weight (0,0899 $kgNm^{-3}$ at 0 °C and 1 atm) [55]. It is also an efficient alternative to mitigate environmental problems caused by fossil fuels in stationary applications (i.e., by GHG) or in vehicular applications (especially atmospheric pollution in big cities). Additionally, it is a sustainable way to vary the energetic system, with the warranty of secure supply, it can also be converted to electricity when necessary [35].

It is estimated that 1.0 kg of hydrogen has a storage energy greater than 2.75 kg of gasoline [56]. Therefore, 1 L of hydrogen contains the same energy of 0,27 L of gasoline [56]. The hydrogen use as a fuel is progressing and it is possible to see already prototypes of cars powered by hydrogen in the develop countries [57].

Regarding the production processes, hydrogen can be produced in two ways: in larger production units or decentralized (on site), where inputs are transported to a place near the final consumer (as a gas station) and on board hydrogen production while it is being used [29].

However, most of the manufactured hydrogen is consumed in the same place of production (as petrochemical industry) and only a small portion is used for energetic purposes. There is a great expectation of increasing the energetic utilization of hydrogen by fuel cells and reducing GHG emitions [14].

In addition, in order to be used on a large scale, researchers need to develop economic and practical means of hydrogen storage and production, mainly for energy conversion in fuel

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cells, the most advantageous way to obtain energy from hydrogen. The emissions of a fuel cell station are smaller and produce less carbon dioxide [58].

Studies with direct borohydride fuel cell (DBFC) showed advantages for hydrogen storage as: uses liquid fuel safely, has a low fuel crossover to the cathode side and has a high theoretical cell voltage (1.64 V) with a theoretical high power density (9.3 $kWh \cdot kg^{-1}$) [27].

The flexibility in planning of fuel cell results in strategical and financial benefits to producers and consumers. Energy production by fuel cells can be implemented near the consumer in order to avoid transportation expenses and energy losses in the distribution network. One fuel cell can convert more than 90% of the stored energy in a fuel to electric energy and heat.

Fuel cells can be developed to work using natural gas, gasoline, alcohol, carbohydrates and other fuels that can be obtained and transported. They are the recent technology of interest with high development potential [58,59].

This way, both hydrogen and fuel cells are identified as direct potential alternatives to substitute fossil sources and combustion engines [17,60–63].

Primary energy sources can be used in the hydrogen production processes [64,65]. It is important to notice the possibility to use several inputs and processes, making a connection among a variety of technologies [2,66] (Fig. 5).

One of the features of hydrogen is the multiplicity of sources through which it can be produced [30,67,68]. The renewable sources are biomass, sunlight, wind energy [69]) and thermal energy of the oceans. Hydrogen can be obtained from these sources through water electrolysis, a technology to dissociate water into hydrogen and oxygen [62]. Moreover, hydrogen can also store the excess of energy produced in the hydroelectric power plant to be consumed subsequently. All these possibilities allow each country to study better ways to produce hydrogen, according to its own capacity [70].

Hydrogen from renewable sources is a natural cycle with low environmental effects, high process efficiency with no exhaustion, because it depends on renewable sources only as wind energy and sun light.

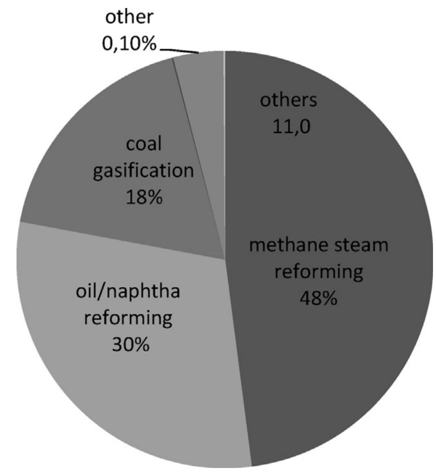

Fig. 6 – Primary energy distribution through the sources for the production of hydrogen. Source: Adapted from Ref. [71].

The actual hydrogen production represents around 2% of primary energy demand. Almost half of hydrogen used all over the world comes from steam reforming of natural gas (48%), the most economic route (from hydrocarbons) and the main production chain in the world [30]. Fig. 6 shows the main routes for hydrogen production, 96% of the production comes from fossil fuels [71].

Different technologies also can be used with different inputs to produce the H_2 molecule. The technologies available nowadays can be divided in four categories: (i) electrochemical; (ii) photobiological; (iii) photoelectrochemical and (iv) thermochemical [71]. The different processes also can be divided as: (i) thermal; (ii) electrolytic and (iii) biochemical processes [29].

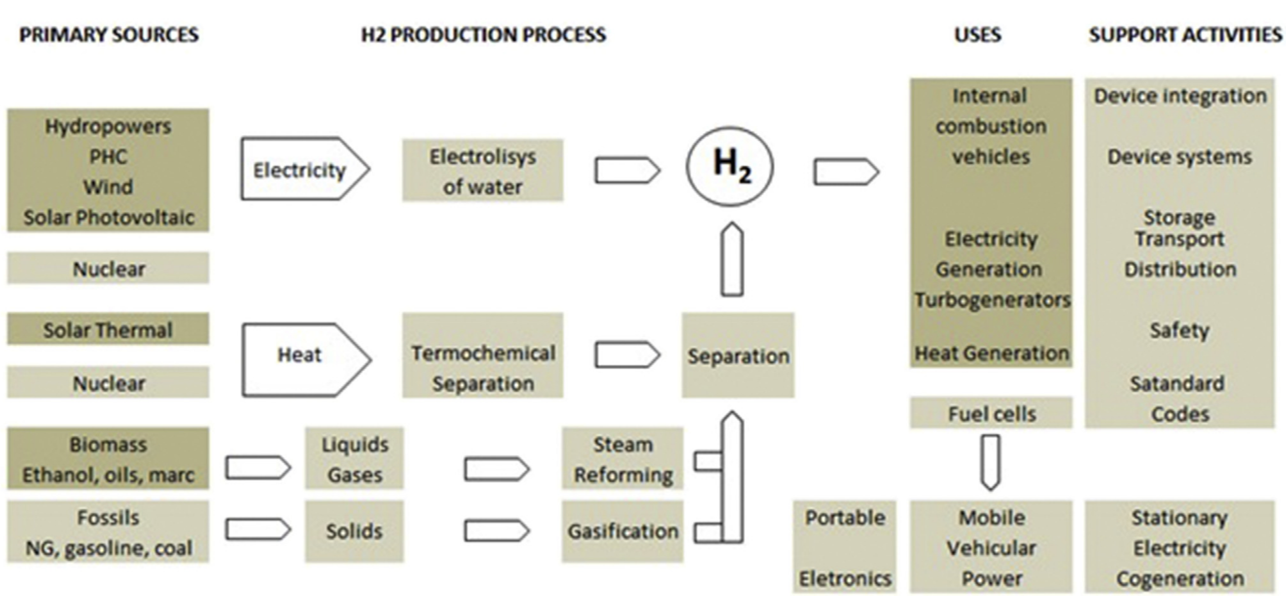

Fig. 5 – Possible routes for the production and use of hydrogen as energy carrier. Source: Adapted from Ref. [2].

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Thermal processes

Steam reforming involves reaction of a fuel with steam over a catalyst (Equation (1)) producing hydrogen and carbon monoxide (syngas), has the maximum theoretical yield of hydrogen and has been extensively studied [72–77]. It is a strongly endothermic reaction requiring external heat source [78]. Steam reforming is the most commonly used process for production of hydrogen and synthesis gas, and most widely used nickel catalysts supported on alumina in the presence or absence of promoters. This process is responsible for 48% of the world production of hydrogen [79].

$$CnHm + nH_2O \leftrightarrow (n + m/2)H_2 + nCO \quad \Delta H^{\circ} > 0 \qquad (1)$$

Table 1 – Thermal technologies and inputs applied to hydrogen as an energy carrier.

Technology	Input	Strengths	Weaknesses
Steamreforming	Natural Gas [98–102]	- established technology (main H_2 production process) - high thermal efficiency (>80%) - higher relative amount of H_2 relative to CO in the produced gas (H_2/CO = 3) - H_2 produced with 99.95% purity	- high energy consumption (endothermic reaction) - high operating costs - CO_2 emissions (due to fuel combustion to heat the vapor) - catalyst deactivation by coke deposition process
	Ethanol [103–105]	- lower reaction temperatures than natural gas - uses renewable natural resource (sugar cane→ ethanol)	- cause side reactions (decomposition, dehydrogenation and dehydration)
CO_2 Refoming [106–112]	Natural Gas	- can be deployed into existing retirement units, where there is production of CO_2 by converting it into H_2 - total operating costs and lower investment than steam reforming - lower emissions of CO_2 and CH_4 in the atmosphere - Utilization of biogas from landfills, sewage sludge digesters or anaerobic fermentation as a renewable feedstock	- lower H_2/CO ratio (produced in relation to steam reforming) H_2/CO = 1 - higher risk of deactivation of the catalyst in the steam reforming - few plants in operation
Catalytic Partial Oxidation	Natural Gas [113–115]	- does not require heating (exothermic reaction) - economically promising process for syngas production	- Ni-based catalysts can be deactivated by coking and sintering, hampering the large-scale application of partial oxidation of methane
	Ethanol [116–119]	- renewable natural resource - Is a weakly endothermic reaction compared to strongly endothermic steam reforming of ethanol	- more difficult to control the reaction due to the release of energy - lower H_2 yields - dilution of the product in case of using air as the oxidizing agent - high flammability
Autothermal reforming [68,73,78,87,88,120]	Natural Gas	- lower operating costs than other processes - most appropriate technology for GTL (gas to liquid) - increased energy use - Nearly thermodynamically neutral reaction makes it a better alternative for reforming of fuels	- has a lower H_2 yield than steam reforming
Direct conversion in non-oxidative conditions [93,95,121–123]	Natural Gas	- It is selective given its unique capability in aromatics and hydrogen forming. - consumes less energy than steam reforming - carbon produced can be gassed with water vapor producing hydrocarbon	- fast catalyst deactivation by coking
Gasification [96,97,124–126]	Biomass	- used as raw material a renewable natural resource - highly efficient process (high efficiency and high conversion) - Economically viable and environment-friendly. - Higher hydrogen yields. - Favorable alternative for large scale hydrogen production	- the gas produced must be conditioned to remove impurities and tar - high reactor cost

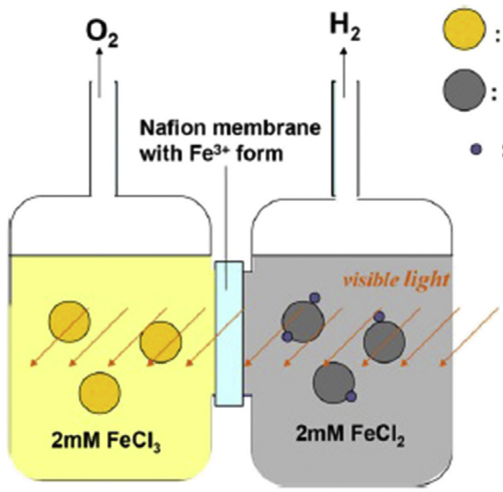

Fig. 7 – Schematic diagram of the twin-reactor system [140].

Catalytic partial oxidation involves the reaction of an oxygen lean mixture of fuel and air for incomplete combustion (Equation (2)), producing syngas. Ni, Co and Ru have been used for this reaction [80–82]. Catalytic partial oxidation involves the reaction of an oxygen lean mixture of fuel and air for incomplete combustion. The advantage is that the reaction is exothermic; however, it has the least hydrogen yield of all the reforming reaction. This reaction also has been actively studied in the last decade [73,76,83,84].

$$CnHm + n/2O_2 \leftrightarrow m/2H_2 + nCO \quad \Delta H^\circ > 0 \tag{2}$$

Autothermal reforming combines the endothermic steam reforming reaction and the exothermic partial oxidation to get a nearly thermodynamically neutral reaction (Equation (3)), producing syngas, Ni catalysts promoted with Pt, Pd, Re, Mo and Sn can be used [85]. It has a lower H_2 yield than the steam reforming, but the thermodynamic neutral nature makes it a better alternative for fuel reforming. This has been studied through various theoretical and experimental studies for comparing these reactions [68,76,86,87].

$$CnH_m + n/2O_2 + nH_2O \leftrightarrow (m/2 + n)H_2 + nCO_2 \quad \Delta H^\circ \approx 0 \tag{3}$$

For methane reforming reactions, Rh-based reforming catalyst, especially Rh/Al_2O_3, has been investigated extensively because it exhibits a higher reaction rate. But the long-time stability and the coking resistance is still a problem for the application and awaits better solutions [88].

Studies on methane conversion have explored the direct methane aromatization (DMA) [89–92]. DMA is more selective given its unique capability in forming aromatics and hydrogen [93]. Among the investigated catalysts, Mo/MFI and Mo/MWW have been the most active catalysts in alleviating the kinetic barriers in DMA reactions [94].

Methane is directly converted to benzene and hydrogen without participation of oxygen (Equation (4)) [95].

$$6CH_4 \leftrightarrow C_6H_6 + 9H_2 \tag{4}$$

Biomass can be converted into combustible gas mixture containing hydrogen by the gasification process [96], given by a simplified reaction (Equation (5)) of steam gasification:

$$\text{Biomass} + \text{Steam} \rightarrow H_2 + CO + CO_2 + CH_4 + \text{light and heavy HC} + \text{Tar} + \text{Char} \tag{5}$$

Considering the different technologies for hydrogen production from biomass, gasification has been accepted as an economically viable and environment-friendly option as well as a favorable alternative for higher hydrogen yields and large scale hydrogen production. As a result, this technology is likely to play a major role in the future need of green environment and hydrogen based energy economy [97]. Table 1 showed several thermal processes of hydrogen production, some features and differences among them were described as follows.

Electrolytic processes

Instead of fossil and biofuels, hydrogen also can be produced by water using electrochemical processes: electrolysis [127–129], photo-reduction [130] and thermolysis [76,131,132].

The electrolysis decomposes water into hydrogen and oxygen using an acid or alkaline electrolyte, the practical realization of water electrolysis has encountered major drawbacks such as its relatively low efficiency and high production cost comparing with hydrocarbon reforming [127].

Table 2 – Electrochemical technologies and inputs applied to hydrogen as an energy carrier.

Technology	Input	Strengths	Weaknesses
Electrolysis [127,133,147–149]	Water	- entirely clean processes	- high electricity consumption - Relatively low efficiency and high production cost, compared with hydrocarbon reforming.
Photo-reduction [130,136,139,150–152]	Water	- effective method for converting solar energy or sunlight into clean and renewable hydrogen fuel. - the most promising and renewable choice for the generation of hydrogen.	- toxicity of the products generated in photo arsenic electrodes. - the development of active and stable catalysts is highly challenging for the utilization of solar energy - Large over potential for H_2 evolution on TiO_2 surface, TiO_2 becomes inactive for hydrogen production
Water thermolysis [131,132,141–146,153]	Water	- single step thermal dissociation of water - very high temperatures are required	- recombination of H2 and O2 - energetically unfavorable

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Water electrolysis involves hydrogen evolution reaction on cathode and oxygen evolution reaction on anode, respectively. The reaction and standard equilibrium electrode potential (E^0) at 25 °C and 1 atm are written as Equation (6) [133]:

$$H_2O = H_2 + ½O_2 U^\theta = E_a^\theta - E_c^\theta = 1.23\ V \tag{6}$$

Water electrolysis in an alkaline electrolyte solution has an advantage in cost effectiveness over electrolysis in an acidic electrolyte, because highly concentrated hydroxide ions enable a hydrogen evolution reaction (HER) mechanism that uses non-noble metals as catalysts for both the reduction and the oxidation of water [128,129].

The photo-reduction can use solar energy associated to photocatalysts like Zinc oxide (ZnO) or titanium oxide (TiO_2) to decomposes water [134]. The emission of pollutants is lower compared to other processes, but has the highest cost. Therefore, this process is generally used to obtain high-purity hydrogen gas [135].

Some authors demonstrated the concept of water decomposition using a photo-electrochemical cell [77,134,136–138]. Fig. 7 shows a photocatalytic water splitting into hydrogen and oxygen using semiconductor catalyst, an effective method for converting solar energy or sunlight into clean and renewable hydrogen fuel, this process is the most promising and renewable choice for the generation of hydrogen [130,136,139].

Water thermolysis, also known as single step thermal dissociation of water (Equation (7)) [141]:

$$H_2O \rightarrow H_2 + 1/2O_2 \tag{7}$$

The recombination of H_2 and O_2 can be avoided by effective hydrogen separation with the use of palladium membranes [131,132].

At higher temperature levels, in the range of 2000–3000 K, a homogeneous kinetic mechanism with a few reversible elementary steps involving H_2O, OH, H, O, H_2 and O_2 is believed to govern. Different versions of the homogeneous mechanism are proposed [142,143] based on kinetic [144,145] and thermodynamic [146] data. The overall reaction proposed by Baykara can be expressed by Equation (8) [131]:

$$H_2O \rightarrow x_1H_2O + x_2OH + x_3O + x_4H + x_5O_2 + x_6H_2 \tag{8}$$

Table 2 showed several electrochemical processes of hydrogen production, some features and differences among them were described as follows.

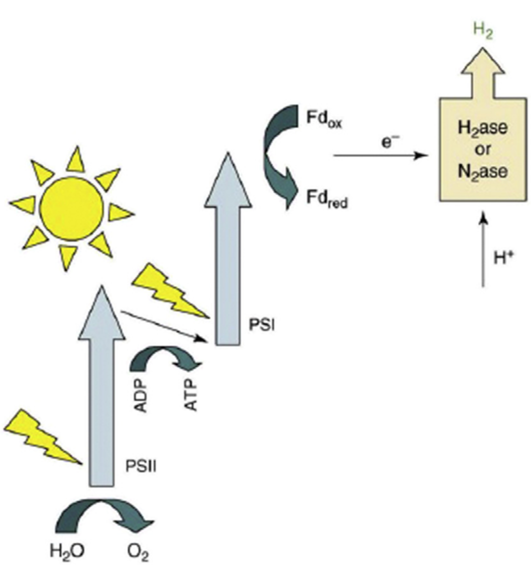

Fig. 8 – Biophotolysis of green algae or cyanobacteria [154].

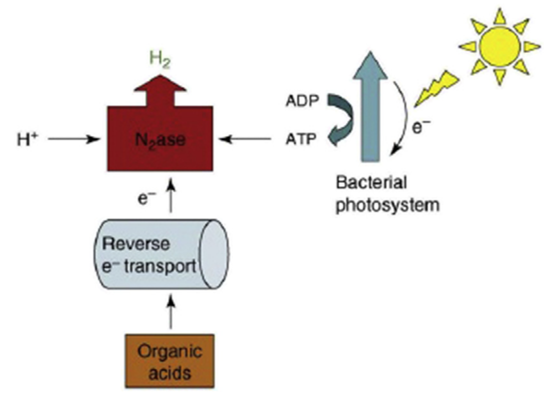

Fig. 9 – Photo-fermentation processes by photosynthetic bacteria [154].

Biological processes

Water also can be converted to hydrogen by microorganisms in biological processes [154,155] like direct biophotolysis, indirect biophotolysis and photo-fermentation.

Direct biophotolysis is a biological process that can produce hydrogen directly from water using microalgae photosynthesis system to convert solar energy into chemical energy in the form of hydrogen (Fig. 8).

The reaction of biophotolysis of green algae or cyanobacteria generally as Equation (9).

$$2H_2O + \text{solar energy} \rightarrow 2H_2 + O_2 \tag{9}$$

Indirect biophotolysis is a biological process that can produce hydrogen from water using a system of microalgae and

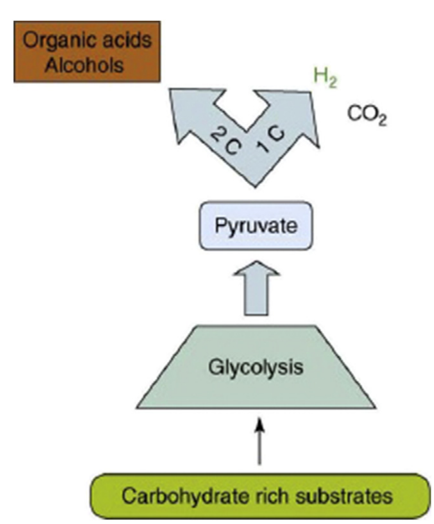

Fig. 10 – Dark fermentation [141].

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Table 3 – Biological technologies and inputs applied to hydrogen as an energy carrier.

Technology	Input	Strengths	Weaknesses
Direct Biophotolysis [29,154,156,164–166]	Water + green algae or cyanobacteria + sun light	- high theoretical efficiency - there is no requirement of adding the substrate nutrients - water is the substrate and solar energy is the source of energy. - it is not necessary to produce ATP - even in low light intensities, green algae and an aerobic conditions are still able to convert almost 22% of light energy by using the hydrogen to an electron donor in the process of fixation of CO_2	- sensitivity of hydrogenases enzymes to O2 - need lighting - inhibition by O2 - low light conversion efficiencies;
Indirect Biophotolysis [155,156,167–169]	Water + green algae or cyanobacteria + sun light	- simple mechanism and inexpensive (low cost) - microorganisms grow in environments containing simple minerals - uses water as substrate - it has the ability to fix N_2	- high energy costs - need lighting - need for ATP - high energy costs - presence of CO_2 in the gas produced
Photofermentation [154,169–171]	Water + photosynthetic bacteria + sun light	- it has no activity for O_2 evolution - ability to use a long light spectrum - ability to consume organic substrates derived from waste - can use as a substrate different wastes and effluents - ability to use a wide spectrum of light - complete conversion of organic acid wastes to H_2 and CO_2;	- low conversion efficiency of solar energy - requires anaerobic photobioreactors with large area exposed to sunlight - light is necessary - presence of CO_2 in the gas produced - high energy costs - high energy demand by nitrogenase - expensive hydrogen impermeable photobioreactors required
Dark fermentation [158,159,172–174];	organic compounds + anaerobic microorganisms	- requires no illumination - does not depend on O_2 (anaerobic process) - it produces by-products with organic acids having commercial value - wide variety of carbon sources as substrate - produces valuable metabolites as by-products - anaerobic process, no inhibition by O_2 - higher hydrogen production rate compared with other biological methods. - utilization of low-value waste the raw materials. - simple reactor technology.	- produces biogas containing H_2 and CO_2, but also CH_4, H_2S and CO - the residue of the fermentation should be treated to prevent environmental pollution - low H_2 yields - large quantities of side products formed.

Cyanobacteria photosynthesis using solar energy to split water molecules and convert solar energy into chemical energy in the form of hydrogen (Fig. 8) through several steps: (i) biomass production by photosynthesis, (ii) biomass concentration, (iii) dark aerobic fermentation produces 4 glucose mol hydrogen/mol in the algal cells, together with 2 mol of acetate, and (iv) conversion of 2 mol of acetate into hydrogen. In this process also decrease ferredoxin, hydrogenase or nitrogenase which these compounds are very sensitive to oxygen [154–156]. This process can be classified into two distinct groups, one of which is depending on the light and the other is light independent process.

Photo-fermentation is a fermentative conversion of organic subtrates by a diverse group of photosynthetic bacteria that use sun light as energy to convert organic compounds into hydrogen and CO_2 (Fig. 9) [156].

Dark fermentation is the fermentative conversion of organic substrate, including organic waste, and biomass materials to produce biohydrogen which takes place in anaerobic conditions and without the presence of light (Fig. 10). It is complex process manifested by various groups of bacteria by involving a series of biochemical reactions [76,157]. Dark hydrogen fermentation has several advantages compared with other biological methods of hydrogen production such as photosynthetic and photofermentation because of its ability to produce hydrogen continuously without the presence of light, higher hydrogen production rate, process simplicity, lower net energy input and utilization of low-value waste as raw materials [158–160]. Dark fermentation produces hydrogen from organic compounds by anaerobic microorganisms [161,162]. Dark fermentation is shown in Equation (10) [156,163]:

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$$C_{12}H_{22}O_{11} + 9H_2O \rightarrow 4CH_3COO^- + 8H^+ 4HCO_3^- + 8H_2 \quad (10)$$

Table 3 shows several biological processes of hydrogen production, some features and differences among them were described as follows.

Fuel cells

Fuel cells are electrochemical devices that produce electricity using hydrogen as fuel. The technologies differ between themselves by the electrolyte used in the cell, for their electrochemical reactions and the temperatures involved.

Fuel cells are being developed in Brazil since the late 70s, but the Brazilian government began its concrete actions in the area only in 2002. In this type of system the use of pure hydrogen has advantages such as not requiring reformers (equipment used to extract hydrogen from a source of this fuel, such as natural gas, reducing the size and cost of the system, and does not contaminate the membrane and electrodes that are sensitive to certain compounds [15].

For this reason, Brazil has a national research and development for fuel cell technology and hydrogen program (Brazilian Program for Fuel Cell Systems) identifying research groups and suggests a networking. In this way, the first Brazilian fuel cell bus was planned as an initiative of the Ministério de Minas e Energia (MME) and the Global Environment Facility (GEF) by means of the United Nations Development Program (UNDP) in 1999 [175,176].

Some companies like Electrocell, Unitech and Novocell, among others, already have products for this new technology. The Institute of Nuclear and Energy Research (IPEN) has played an important role on the national scene for the development of this technology [15,70].

Fuel cells offer much higher power generation efficiencies than conventional generation systems, based on engines and turbines, and the preferred fuel for these technologies is hydrogen. There are seven main types of fuel cell [73,177–180] as listed in Table 4, which shows typical efficiencies operating temperature, catalysts and other operation parameters.

According to the authors, the Alkaline Fuel Cell (AFC) requires an oxidant of either pure oxygen or CO_2-free air, and so has not been favored by developers for any applications other than niche markets. The Low Temperature Proton Exchange Membrane (also known as Polymer Electrolyte) fuel cell (PEMFC or PEM) has been chosen by most of the automotive companies as the power source for future vehicles. The Phosphoric Acid Fuel Cell (PAFC) is the most developed in terms of hardware and demonstrations, but has been overtaken recently by the PEM fuel cell. Current low temperature fuel cells (Polymer Electrolyte Membrane Fuel Cell, Direct Methanol Fuel Cell, Direct Ethanol Fuel Cell, Phosphoric Acid Fuel Cell) make extensive use of catalysts. Impurities may poison the catalysts reducing activity and efficiency. The high temperature fuel cells (Molten Carbonate Fuel Cell and Solide Oxide Fuel Cell) are capable of converting hydrocarbon or alcohol-derived fuels in the anode chamber by internal reforming, resulting in a higher electric efficiency [180-182].

In this sense, the hydrogen economy meets the development of fuel cell technologies, combined with its economic viability [13]. It can identify a scenario in which the hydrogen energy has good prospects of progressive increase of its use in global energy matrix.

Final considerations

From the above, it is concluded that hydrogen can be produced from non-renewable and renewable energy sources. The lowest percentage of air pollution and carbon cycle stability can be mentioned as some of the benefits of their use for the production of hydrogen.

Steam reforming, which involves the reaction of a fuel with steam over a catalyst, has the maximum theoretical yield of hydrogen and has been extensively studied. It is a strongly endothermic reaction requiring external heat source. Steam reforming is the most commonly used process for the production of hydrogen and syngas. This process is responsible for 48% of the world production of hydrogen. Catalytic partial

Table 4 – Fuel cell types and typical characteristics cell.

Fuel cell type	Operating temperature (°C)	Electrolyte	Charge carrier	Catalyst, anode	Fuel for the cell	Electrical efficiency (%)	Qualified power (kW)
Alcaline (AFC)	70–100	KOH (aqueous solution)	H^+	Ni	H_2	60–70	10–100
Proton Exchange membrane (PEM)	50–100	Perfluor-sulphonated polymer (solid)	H^+	Pt	H_2	30–50	0.1–500
Direct methanol (DMFC)	90–120	Perfluor-sulphonated polymer (solid)	H^+	Pt	Methanol	20–30	100–1000
Direct ethanol (DEFC)	90–120	Perfluor-sulphonated polymer (solid)	H^+	Pt	Ethanol	20–30	100–1000
Phosforicacid (PAFC)	150–220	Phosphoricacid (immobilizedliquid)	H^+	Pt	H_2	40–55	5–10000
Moltencarbonate (MCFC)	650–700	Alcaline carbonate (immobilizedliquid)	CO^{2-}	Ni	Reformate or CO/H_2	50–60	103–300
Solid oxide (SOFC)	800–1000	Yttria-stabilized zircônia (solid)	O^{2-}	Ni	Reformate or CO/H_2 or direct CH_4	50–60	0.5–100

Source: [180].

oxidation involves the reaction of an oxygen lean mixture of fuel and air for incomplete combustion. The advantage is that the reaction is exothermic; however, it has the least hydrogen yield of all the reforming reaction. Additionally, autothermal reforming combines the endothermic steam reforming reaction and the exothermic partial oxidation to get a nearly thermodynamically neutral reaction. It has a lower H_2 yield than the steam reforming, but the thermodynamic neutral nature makes it a better alternative for fuel reforming. This has been studied through various theoretical and experimental studies for comparing these reactions.

Instead of fossil and biofuels, hydrogen also can be produced by water using electrochemical processes. The electrolysis decomposes water into hydrogen and oxygen using an acid or alkaline electrolyte. The practical realization of water electrolysis has drawbacks such as its relatively high production cost. Biophotolysis can produce hydrogen from water using a system of microalgae and cyanobacteria photosynthesis to convert solar energy into chemical energy in the form of hydrogen.

The hydrogen production processes from biomass derivatives allow the use of low value-added products, diversifying the sources of hydrogen. These technologies, although promising, still present many technological bottlenecks. Considering the different technologies for hydrogen production from biomass, gasification has been accepted as an economically viable and environment-friendly option as well as a favorable alternative for higher hydrogen yields and large scale hydrogen production. As a result, this technology is likely to play a major role in the future need for green environment and hydrogen based energy economy.

The uncertainties surrounding the possibility of hydrogen energy, based on renewable sources, appear to be mainly due to lack of technologies that give it competitive edge over other energy competitors and the lack of economic studies on the subject. It is therefore hereby recommended that further studies, especially on competitiveness, should be carried out.

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