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Review

Use of Hydrogen as Fuel: A Trend of the 21st Century

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Abstract: The unbridled use of fossil fuels is a serious problem that has become increasingly evident over the years. As such fuels contribute considerably to environmental pollution, there is a need to find new, sustainable sources of energy with low emissions of greenhouse gases. Climate change poses a substantial challenge for the scientific community. Thus, the use of renewable energy through technologies that offer maximum efficiency with minimal pollution and carbon emissions has become a major goal. Technology related to the use of hydrogen as a fuel is one of the most promising solutions for future systems of clean energy. The aim of the present review was to provide an overview of elements related to the potential use of hydrogen as an alternative energy source, considering its specific chemical and physical characteristics as well as prospects for an increase in the participation of hydrogen fuel in the world energy matrix.

Keywords: hydrogen; fuel cell; green fuel; environmental pollution; greenhouse effect

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1. Introduction

The greenhouse effect is directly linked to energy production, which is the sector of the economy with the highest emissions of carbon dioxide (CO_2), accounting for 80% of emissions throughout the world [1]. Fossil fuels contribute to the largest percentage of the world energy matrix. These fuels are depletable and involve risks related to extraction and consumption as well as the release of gases contributing to the greenhouse effect. However, most sources of energy throughout the world are fossil fuels. The annual production demand is expected to stabilize over the long to medium term, with a reduction in the production of fluid fuels (medium-long term) and coal (short-medium term) (Figure 1) [2], following a trend in global markets in accordance with international treaties for the reduction of atmospheric pollution [1,3,4].

The growing demand for electricity had led to its production by thermoelectrical plants. However, such plants produce one of the most expensive sources of energy and are major consumers of petroleum products, underscoring the need to find renewable, economically viable alternatives [5–7]. The generation of electricity on a larger production scale with the use of diesel, B1 fuel oil or other petroleum-based fuels has driven the search for new sources of energy that are less aggressive to the environment to ensure reductions in atmospheric pollution and emission of greenhouse gases, with the additional potential of reducing the costs of energy production [6].

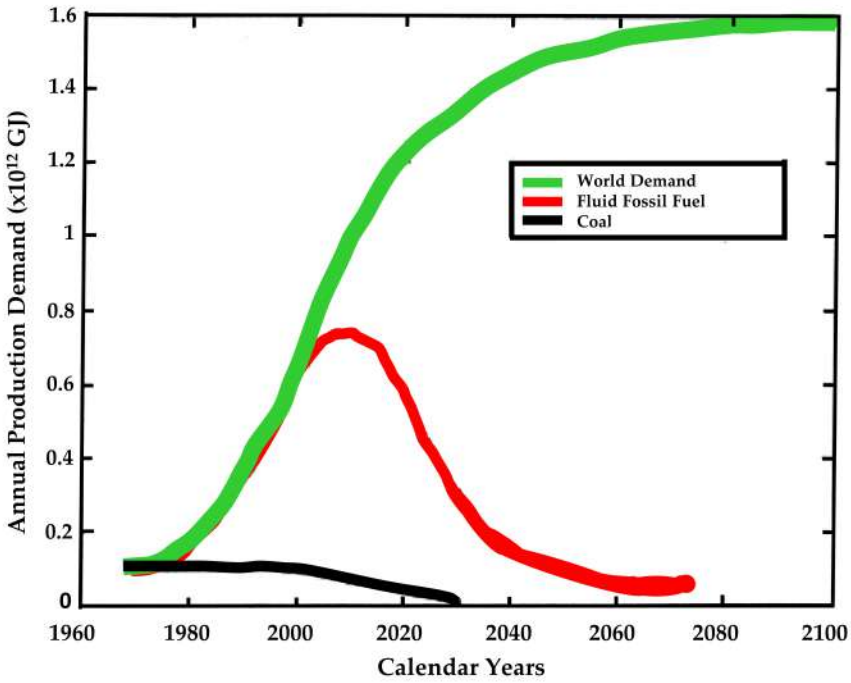

Figure 1. Estimated world production of fossil fuels. Adapted from Veziroğlu and Şahin [2].

2. Hydrogen as a Sustainable Energy Source

Hydrogen could play a crucial role in the global energy transition. This green energy is produced from renewable sources and has nearly zero carbon emissions. There is a relevant synergy between the accelerated implantation of renewable energies and the production and use of hydrogen. Plans for the use of hydrogen have been developed in Australia [8,9], Brazil [10], France [11], Germany [12,13], Japan [14,15], The Netherlands [16,17], Great Britain [18] and USA [19]. The different strategies depend on the methods of producing hydrogen and the main uses of hydrogenation in accordance with the particularities of each country [20,21].

In 2014, approximately USD $286 billion was invested in renewable energies around the world, surpassing investments in natural gas and coal [22]. Brazil was one of the developing countries that most applied capital in processes using renewable sources of energy, corresponding to an investment of approximately 73%. This generated a change in the Brazilian energy matrix, as the fossil fuels that dominated the means of production began to correspond to only 22% of the production of electric energy [23]. By increasing the use of renewable sources of energy, hydrogen began to be seen as a fuel that could replace petroleum-based products in the automobile industry. Moreover, hydrogen may replace coal as a fuel for powering turbines at thermoelectrical plants and could serve in the production of secondary energy such as solar, wind and hydroelectrical plants [24].

Hydrogen has been widely studied in innovative research analyzing its use for the purposes of energy production, proving to be a promising option as a fuel in fuel cells or as an additive to fossil fuel [24,25]. Thus, it emerges as a valid alternative, given that it is the most abundant amongst the universe's elements, and its direct combustion leads to a large quantity of energy while emitting only water vapor.

2.1. Physical Properties of Hydrogen

The hydrogen atom was discovered in 1766 by Henry Cavendish through the decomposition of water. However, it was Antoine Lavoisier who gave it its name. H (hydrogen) is widely available, as approximately 93% of existing molecules have H in their composition. As a pure chemical compound, hydrogen has a diatomic molecule (H_2), is odorless, tasteless and colorless under standard conditions of temperature (25 °C) and pressure (1 atm) and is insoluble in water. It is a flammable gas, has a high diffusion power due to having a lower density than air and becomes a liquid at −253 °C in a cryogenic storage system [4,5].

Hydrogen has several characteristics that make it a promising fuel, such as the large amount of energy released when combusted, i.e., a high calorific value [6,26] (Table 1).

Table 1. Calorific value of different fuels under standard conditions of temperature and pressure. Adapted from Zhao et al. [6] and Ortiz-Imedio et al. [26].

Fuel	Calorific Value (MJ/kg)
Hydrogen	119.93
Methane	50.02
Propane	45.60
Gasoline	44.50
Diesel	42.50
Ethanol	27.00
Methanol	18.50

Hydrogen is currently used as an alternative fuel combined with other fuels in vehicles. The growing idea of its use is associated with its higher calorific value in comparison to gasoline, as well as the reduction in the release of harmful compounds into the atmosphere when burned. The high cost of petroleum-based products has driven the market as well as the research and innovation field toward the search for different energy sources. Moreover, there is the possibility of using H_2 combined with conventional fuels in internal combustion engines (Figure 2) with no significant change in the vehicle [27–31].

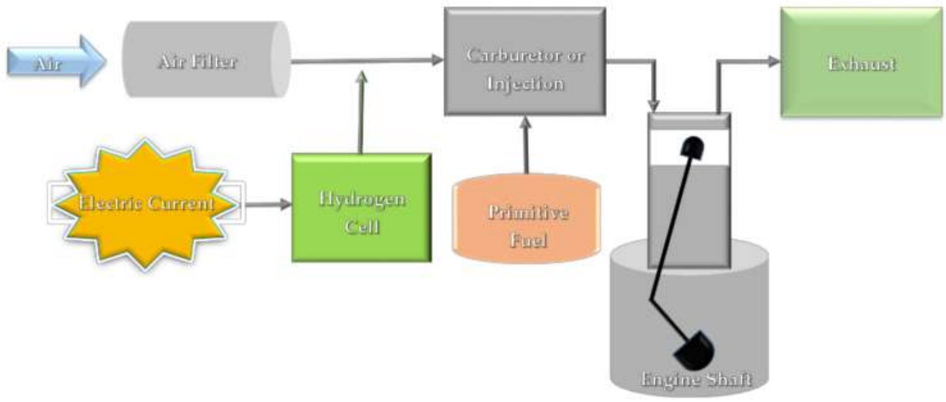

Figure 2. Schematic of hydrogen cell in an internal combustion engine. Adapted from Al-Rousan [31].

Hydrogen has the greatest quantity of energy per unit mass of all fuels, which means that 1 g of H has the same quantity of energy as 2.8 g of gasoline. When cooled until reaching its liquid state, this low molecular mass fuel occupies a volume 700 times smaller than what it occupies in the gas state. Its density (0.08967 kg/m^3) is 14.4-fold less than that of air (1.2928 kg/m^3) [4].

The hydrogen flame has a very high thermal gradient, with a much higher energy density (38 kWh/kg) compared to gasoline (14 kWh/kg). Since the energy needed to ignite an air/hydrogen blend is only 0.04 mJ, whereas that of hydrocarbons is 0.25 mJ, H_2 is extremely flammable in air (between 4% and 75% per volume of air) and, under some conditions, spontaneous combustion can occur [5].

For use by the public, hydrogen needs to have the same level of trust with no more risk than conventional fuels. The relevant physical properties for the safety of hydrogen are compared in Table 2 to those of gasoline, propane and methane (CH_4) [4,6,32,33].

Table 2. Relevant characteristics and properties for safety of different gases and hydrogen. Adapted from Zhao et al. [6] and Taghavifar et al. [33].

Data	Hydrogen	Methane	Propane	Gasoline	Unit
Lower Detonability Limit (LDL) in Air	11–18	6.3	3.1	1.1	% (*v*/*v*)
Upper Detonability Limit (UDL in Air	59	13.5	7	3.3	% (*v*/*v*)
Lower Flammable Limit (LFL) in Air	4	5.3	2.1	1.4	% (*v*/*v*)
Upper Flammable Limit (UFL) in Air	75	15	9.5	7.6	% (*v*/*v*)
Maximum Laminar Burning Velocity	3.46	0.43	0.47	-	m/s
Maximum Concentration	42.5	10.2	4.3	-	% (*v*/*v*)
Stoichiometric Laminar Burning Velocity	2.37	0.42	0.46	0.42	m/s
Stoichiometric Concentration	29.5	9.5	4.1	1.8	% (*v*/*v*)
Density (NTP)	0.084	0.65	2.01	-	kg/m^3
Ignition Limit in Air (NTP)	4.0–77.0	4.4–16.5	1.7–10.9	-	% (*v*/*v*)
Ignition Temperature	560	540	487	228–471	°C
Minimum Ignition Energy in Air	0.02	0.29	0.26	0.24	mJ
Maximum Combustion Rate in Air	3.46	0.43	0.47	-	m/s
Detonation Limits in Air	18–59	6.3–14	1.1–1.3	-	% (*v*/*v*)
Stoichiometric Rate in Air	29.5	9.5	4.0	-	% (*v*/*v*)

According to the literature, when hydrogen is used as a fossil fuel supplement, it is important to know its level of reactivity for the onset of combustion, which is where the flame develops [33,34].

Due to the growing interest in hydrogen gas, studies involving the design of novel fuel cells and the application of H_2 in internal combustion engines have been developed for direct application in the automotive industry. Some findings have shown a reduction in the consumption of fuel in gasoline engines with the introduction of H_2 in the admission system. In these studies, the authors reported that the inclusion of hydrogen in internal combustion engines can be performed without substantial changes in the design of the vehicle, resulting in an increase in the torque of the engine as well as reductions in the emission of carbon monoxide and unburned hydrocarbons along with a reduction in the specific fuel consumption [28,29,35].

Energy quantification studies on the mechanical expansion potential produced by hydrogen during its molecular transition under ignition were developed between 2009 and 2013 at the Technology Support Lab in partnership with the HOD Research and Development Company. Safety systems were developed for explosion prevention, as the flame speed of hydrogen gas in the presence of oxygen is a thousand-fold that of gasoline [36–39].

These hydrogen regulating devices in the combustion cycle of internal combustion engines result from the so-called "flashback" effect, as such devices are extremely expansive when burned. Very often, the closure time of the input value is insufficient such that a spark of burning gas returns to the feed line, traveling to the storage cylinder, or the source reaches the hydrogen generating cell, causing catastrophic effects, as occurred in research developed by the Technology Support Lab. Based on this experience, a device was developed and connected to the axial bearing of the cylinders, the purpose of which was to obtain a relation of times of exhaust and admission coordinated by a set of gears capable of injecting into a two-cycle pump the fraction of hydrogen that would subsequently be admitted at the moment of aspiration, thereby avoiding the flashback. The derivation of this technology may one day be applied to a hydrogen-assisted fuel oil injection system in future studies on the laboratory scale [40,41].

2.2. Chemical Properties of Hydrogen

From the chemical standpoint, the hydrogen atom (H) is very reactive and is therefore difficult to find in its free elemental form in nature. At common temperatures, hydrogen is not very reactive unless it has been activated in some way, while very high temperatures are required for the dissociation of the hydrogen molecule into hydrogen atoms. In nature, hydrogen is linked mainly to oxygen or carbon atoms.

Energy expenditure is required to obtain hydrogen from natural compounds. Therefore, hydrogen should be considered a carrier of energy—a means of storing and transmitting the energy from primary sources of energy. The hydrogen atom also has a strong reducing power at room temperature. For instance, it can react with numerous metal oxides or chlorides, including those of Ag, Cu, Pb, Bi and Hg, with salts, such as nitrates, nitrites, sodium cyanide and potassium cyanide, releasing free metals, and with a set of both metallic and non-metallic elements such as N, Na, K and P, producing the corresponding hydrides. With sulfur, it forms a set of hydrides, the simplest of which is H_2S [42].

H can also react with organics forming a complex product mixture. For instance, by reaction with H, ethane and butane can be formed from ethene. Hydrogen can also react violently with oxidants such as nitrous oxide, with halogens such as F_2 and Cl_2, and with unsaturated hydrocarbons such as ethyne, releasing a large amount of heat. By reactions between hydrogen and oxygen in combustion or electrochemical processes for energy generation, water vapor is formed as the reaction product. Such a reaction, which is extremely slow under environmental conditions, can be sped up with a catalyst, such as platinum, or an electrical spark. From the safety standpoint, however, it is important to evaluate the different properties of hydrogen, such as diffusion, compared to traditional fuels.

Hydrogen diffusion in the air is faster than that of other gas fuels. Its diffusion coefficient is 61 $m^2\ s^{-1}$, demonstrating a fast dispersion rate, which is the most significant issue relating to the safety of its use. Regarding the floatability (density) of hydrogen, under standard conditions, it is faster than those of methane, propane and gasoline vapor. Hydrogen and methane have some similar characteristics, such as being colorless, odorless, tasteless and non-toxic. Its flammability is proportional to its concentration and is higher than those of methane and other fuels [43,44].

The flammability limit of hydrogen-containing blends in the presence of oxidants depends on factors such energy of ignition, pressure, temperature, use of diluting agents as well as the installation, equipment or device size and configuration. Mixtures can be diluted with any one of their constituents until the concentration drops below the lower flammability limit (LFL). The flammability limit in ambient air conditions is 4–75 vol% for hydrogen, 4.3–15 vol% for methane and 1.4–7.6 vol% for gasoline. When the concentration exceeds the LFL value, a very small quantity of energy can ignite hydrogen due to its low energy of ignition (0.02 mJ). In contrast, the ignition energy of gasoline and methane are 0.24 and 0.28 mJ, respectively. These mixtures were performed using stoichiometric data. When confined, hydrogen detonates in a broad concentration range, with a higher flame speed (1.85 $m\ s^{-1}$) compared to gasoline vapor (0.42 $m\ s^{-1}$) and methane (0.38 $m\ s^{-1}$). The air-hydrogen flame is hotter than that of methane and cooler than that of gasoline under identical stoichiometric conditions (2207, 1917 and 2307 °C, respectively) [45].

3. International Standardization of Hydrogen

A survey of Brazilian norms revealed vast knowledge on the use of hydrogen as well as a set of comprehensive international standards on its safe use as a fuel. The survey was conducted to obtain knowledge on norms directed at the reduction of gas emissions, mainly responsible for the greenhouse effect and the safety in using this green alternative. We found some organizations that have performed excellent work in the attempt to maintain a world standard of procedures that facilitate the operationalization/understanding of hydrogen usage as a current and future fuel. We cite some examples below.

International Organization for Standardization (ISO) [46], represented in Brazil by the *Associação Brasileira de Normas Técnicas* (ABNT). Some of the norms related to hydrogen issued from 1999 and 2010 are ISO 13984, 13985, 14687-1, 16110-1, 16110-2, 16111, 17268, 22734-1 and 26142, ISO/TS 14687-2 and 15869, to which we can add, among others, ISO/PAS 15594, ISO/TR 15916, NBR ISO/TS 20100, ABNT/CEE-067, ISO/TC 197, IEC/T 105, ABNT/CB-003 and ABNT NBR ISO 16110.

Through its safety commission, the Fuel Cell and Hydrogen Energy Association (FCHEA) publishes a report that provides information on the development of codes and norms for fuel cells and hydrogen as well as related safety issues.

The public-private partnership Fuel Cells and Hydrogen Joint Undertaking (FCH JU) is the only company in the field that supports research, development of technologies and demonstrations in fuel cells and hydrogen energy technology in Europe. Its objective is to speed up the launch of such technologies on the market, serving as an instrument to achieve a clean energy system and representing the European Commission as well as fuel cell and hydrogen industries. FCH JU is also represented by the research community.

The International Electrotechnical Commission (IEC) is a world leader in drafting and issuing global standards for electric, electronic and related technologies, including those that involve hydrogen fuel cells for the generation of mechanical energy, citing, for example, the norm IEC/T 105 for fuel batteries. Together with ISO and the International Telecommunications Union (ITU), IEC is one of the sister organizations developing global standards and working together to ensure that international norms fit perfectly and harmonize with each other. Joint committees ensure that global norms are in line with all relevant knowledge from specialists who work in related fields. Table 3 lists some of the norms found in the literature [46,47].

Table 3. Global standardization norms of the International Organization for Standardization (ISO) and International Electrotechnical Commission (IEC) for the use of hydrogen as a fuel.

Organization	Area	Norm	Application	Source
ISO	Fuel Hydrogen quality	PAS 15594:2004-TS 15869:2009	Gaseous hydrogen (H_2) and hydrogen mixtures—fuel tanks for land vehicles	[46]
		ISO 14687-1:1999	All uses of H_2 as a fuel for road vehicles excluding proton-exchange membrane fuel cells (PEMFC)	[46,47]
		ISO 14687-2:2012	PEMFC use for road vehicles	[46,47]
		ISO 14683-3:2014	PEMFC use for stationary devices	[46]
	Safety in the use of hydrogen	ISO/TR 15916:2015	General issues on safety of H_2 powered systems	[46,47]
		ISO 16110-1:2017	Safety of H_2 generation systems integrated with fuel processing technologies	[46,47]
		ISO/TS 19883:2017	Safety of systems based on pressure swing adsorption to separate and purify H_2	[46]
		ISO 23273:2013	Safety of H_2-fueled road vehicles	[46]
	Hydrogen production and purification	ISO 22734-1:2008	Industrial/commercial uses of H_2 generation systems based on the electrolysis of water	[46]
		ISO 22734-2:2011	Residential uses of H_2 generation systems based on the electrolysis of water	[46]
	Hydrogen storage, transport and fueling	ISO 13985:2006	Liquid H_2—Land vehicle fuel tanks	[46,47]
		ISO 16111:2018	Devices to store H_2 for transport absorbed in reversible metal hydride	[46,47]
		ISO 19881:2018	Containers for gaseous H_2 as a fuel for land vehicles	[46]
		ISO 19882:2018	Pressure relief devices to be used in fuel tanks of H_2-powered vehicles	[46]
		ISO 13984:1999	Systems for liquid H_2 fueling and delivery on all types of land vehicles	[46,47]
		ISO 17268:2012	Refueling connectors for gaseous H_2 land vehicles	[46,47]
		ISO/TS 198801:2016	Fueling stations delivering gaseous H_2 to light-duty land vehicles	[46]
		ISO 19880-3:2018	High-pressure gas valves for gaseous H_2 stations	[46]

Table 3. *Cont.*

Organization	Area	Norm	Application	Source
	Testing	ISO 2626:1973	Copper—H_2 embrittlement (HE) test	[46]
		ISO 7539-11:2013	Tests for assessing metal and alloy resistance to HE and H_2-assisted cracking	[46]
		ISO 11114-4:2017	Tests for qualifying steels to be used to manufacture cylinders and valves resistant to HE	[46,47]
		ISO 15330:1999	Preloading test to detect HE by the parallel bearing surface method	[46]
		ISO 16573:2015	Method for assessing resistance of high-strength steel to HE	[46]
		ISO 17081:2014	Method to measure H_2 permeation, uptake and transport in metals and alloys electrochemically	[46]
		ISO/TR 11954:2008	Procedure to measure the maximum speed of fuel cell vehicles using compressed H_2	[46]
		ISO 15859-2:2004	Limits for the composition of H_2 for space systems as well as sampling and test requirements to verify	[46]
		ISO 23828:2013	Procedure to measure the energy consumption of fuel cell vehicles using compressed H_2	[46,47]
		ISO 16110-2:2010	Methods to assess the performance of H_2 generation systems integrated with fuel processing technologies	[46,47]
		ISO 26142:2010	H_2 detection apparatus—Stationary applications	[46]
IEC	Terminology	IEC 60050-485:2020	General terminology relating to all applications of fuel cell technologies	[46]
	Safety in the use of hydrogen	IEC 62282-3-100:2019	Safety of stationary fuel cell power systems (FCPS)	[46]
		IEC 62282-4-101:2014	Safety of FCPS intended for use in industrial electric trucks	[46]
		IEC 62282-5-100:2018	Safety of portable FCPS	[46]
		IEC 62282-6-100:2010	Safety of micro FCPS	[46]
		IEC PAS 62282-6-150:2011	Safety of micro FCPS using H_2 released by the reaction of water-reactive compounds in indirect PEMFC	[46]
	Hydrogen application	IEC 62282-2:2012	Safety in construction, operation and testing of fuel cell modules	[46]
		IEC 62282-3-300:2012	Safety in the installation of stationary FCPS	[46]
		IEC 62282-3-400:2016	Small-sized stationary FCPS with combined production of heat and power	[46]
		IEC 62282-6-300:2012	Fuel cartridge interchangeability in micro FCPS	[46]
		IEC 62282-6-400:2019	Interchangeability of power and data between micro FCPS and electronic devices	[46]
	Testing	IEC/TS 62282-3-200:2016	Methods to assess the performance of stationary FCPS	[46]
		IEC 62282-3-201:2017	Methods to assess the performance of small stationary FCPS	[46]
		IEC 62282-4-102:2017	Methods to assess the performance of FCPS for industrial electric trucks	[46]
		IEC 62282-6-200:2016	Methods to assess the performance of micro FCPS	[46]
		IEC/TS 62282-7-1:2017	Single cell performance tests for polymer electrolyte fuel cells	[46]
		IEC/TS 62282-7-2:2021	Single cell and stack performance tests for solid oxide fuel cells	[46]

4. Hydrogen Use Prospects

Environmental sustainability applied to energy generation systems and the excellent improvement in the quality of life of those who use sustainable systems constitute the driving force to provide clean, safe, reliable energy to the world [48].

Over the years and with the constant increase in population, the demand for energy around the world has increased with economic growth. During the 20th century, the human population increased six-fold, and with that, energy consumption increased 80-fold [49,50].

As the trend is toward technological improvements in the resources used for energy generation, everything indicates that efficiency will increase, causing an increase in the total consumption of this resource as follows: the increase in energy efficiency makes energy cheaper and increases economic growth. In the current situation, almost 80% of the total energy supply and almost 65% of the electricity production is dependent on fossil fuels (coal, oil and natural gas) [51]. There are several reasons to make hydrogen a fuel option, either in replacement or partial use, improving energy efficiency over fossil fuels.

One of the main reasons is its atoxicity to the environment, which means that H_2 exploitation has no environmental impact because it only produces water as a product when burned in the air. It is easily transportable via transmission lines in the form of electricity. Other reasons include its recyclability and its reasonable cost in relation to energy density. In different regions, the cost of hydrogen varies widely in the range of 0.8 to 4 USD $/kg depending on technology and raw material costs [51,52].

The growth in demand for the use of hydrogen is proportional to the objectives imposed by the policies developed by the government sectors and the implementation of the production system, facilitating communication among the parties involved in this process. In Figure 3, the possible applications and use of H_2 are illustrated. The use of H_2 in the medium- and long-term exhibits a growth trend proportional to its demand and application, making it a valuable and easily obtainable input in the future [53].

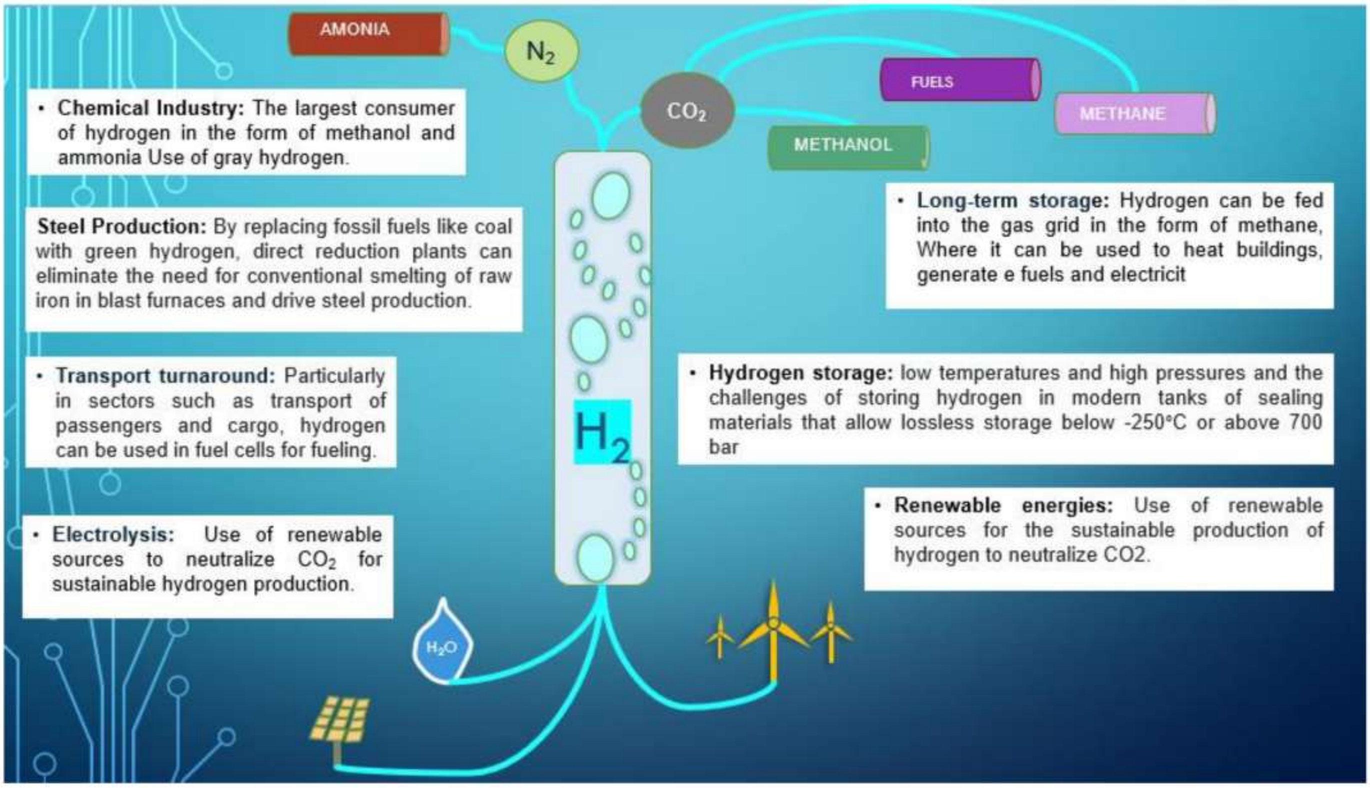

Figure 3. Possible applications and use of hydrogen.

Some long-term H_2 application scenarios are described in the literature, which report energy production ranges involving hydrogen as a fuel in giga watts (GW) and/or tera watts (TWh) per year and type of application. Three categories for future use and application of H_2 according to each demand can be cited:

- Use in existing industrial processes that use H_2 as a raw material, being characterized by a high demand for H_2 in their processes;
- Use in the transport sector, where this fuel is already used, although the current demand for refueling at H_2 fueling stations is low, indicating a greater number of fueling stations and a greater number of H_2 vehicles for this increase in use;
- Volume proportional use: volume for heating energy production through gas distribution systems by mixing in a methane or 100% H_2 gas distribution network;
- The regulatory change on the future use of H_2, however, must be regulated by each of these sectors independently and/or through a set of policy measures for the growth of demand for use and consequent production of H_2 across the globe [53].

After decades of being treated as an energy source of considerable potential for the future but with significant technological and market challenges, hydrogen has become a strategic objective of governments and companies throughout the world. The hydrogen market is expected to gain momentum from post-pandemic (COVID-19) energy policies for the economic resumption as well as to accelerate the energy transition in different countries.

In 2019, the world hydrogen market assessed its value from an economic standpoint, corresponding to a total ranging from USD $118 billion to USD $136 billion. Moreover, significant market growth is expected in the upcoming years, which could reach USD $160 billion to nearly USD $200 billion [54–56].

In 2018, the world demand for hydrogen was 115 million tons, 73 million tons of which corresponded to pure H_2. The production of ammonia for fertilizers and the refining of petroleum accounted for 96% of the demand for pure H_2. The demand for H_2 in mixtures with other gases was 42 million tons, with methanol production accounting for 29%, a direct reduction in the steel industry (DRI) accounting for 7%, and the remainder for other uses. Figure 4 shows the evolution in demand for pure H_2 and in mixtures with other gases per application [21].

To assure an economically sustainable environment, energetic systems should meet a number of social requirements with regards to accessible prices, namely, mitigation of climate change impact, reduction in hazardous pollutant emissions and a strategy for the gradual reduction in the use of a petroleum energy matrix. Failure to comply with these requirements will affect not only the economy and environment but also human health. Therefore, initiatives need to be undertaken that stimulate more effective energy exploitation with a supply proportional to the growth of carbon-free sources [56,57].

Hydrogen pipe systems stretching hundreds of kilometers are found in several countries and regions, operating with no incidents for many years. Likewise, hydrogen transportation by truck has a long history. Despite these conventional applications that have existed for decades, the use of hydrogen is quite modest. Its importance to the energy transition is likely to be accompanied by novel applications, and its supply should preferably be decarbonized. There has been a growth in residential fuel cell units worldwide, with approximately 225,000 units installed by the end of 2018. The country positioned in the leadership of these applications is Japan, accounting for approximately 98% of such units. For informative purposes, we can cite some data from the existing market according to the IEA, such as the sale, in 2018, of about 2,500,000 electric vehicles. Moreover, at the end of the same year, the global fleet of fuel cell electric vehicles reached 11.2 thousand units, and the sales reached approximately 4000 units. To put these figures into perspective, the Hydrogen Council predicts 3000 hydrogen stations by 2025, which would be enough to supply approximately two million fuel cell electric vehicles [21,58].

According to the Hydrogen Council [52], in 2020, hydrogen energy was used significantly and was able to meet 8% of the global energy demand, at a production cost close to 2.50 USD $/kg. With this, there is a forecasted reduction of H_2 production costs for the year 2030 of around 1.80 USD $/kg, thus satisfying the global energy demand by around 15%. The Hydrogen Council [52] also stated that the demand and supply of H_2

will be 10 hexa Joules (EJ) per year by the end of the year 2050, and thereafter the demand will increase by around 5–10% per year. Furthermore, H_2 would be able to meet 18% of global energy demand in the year 2050. Thus, in the future, it should become an attractive competitor in the energy system due to its low production cost, low energy density and low emissions [51,60].

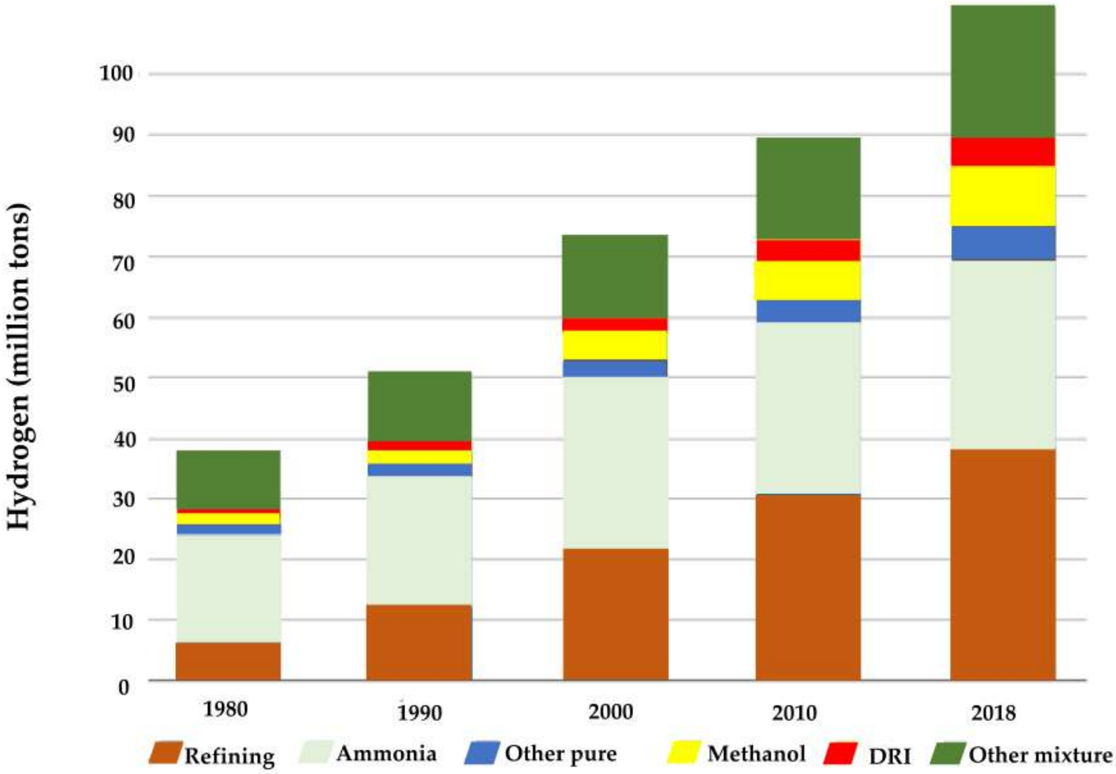

Figure 4. Hydrogen use trend in the period from 1980 to 2018. DRI: direct reduction in the steel industry. Adapted from IRENA [59].

5. Hydrogen Production

The climate is the main driver of the use of hydrogen in the energy transition. Global warming of no more than 2 °C requires around a 25% reduction in CO_2 emissions by the year 2030 in relation to 2010 levels, reaching zero by the year 2070 [61]. A reasonable change to limit global warming to less than 1.5 °C would require anthropogenic CO_2 emissions to be reduced by 45% by the year 2030 compared to the level of 2010, achieving zero two decades later. Despite these goals, CO_2 emissions related to energy have increased recently and are responsible for two-thirds of the global emissions of greenhouse gases. Thus, the energy transition is urgently required to sever the relationship between economic development and increases in carbon dioxide emissions [21,62,63].

H_2 will play a pivotal role in the emission reduction efforts in the upcoming decades. The International Renewable Energy Agency (IRENA) (REmap) indicates at 6% participation in total energy consumption by the year 2050 [21], whereas the Hydrogen Council suggests that 18% participation could be reached by the same year [64].

Currently, the annual production of H_2 is about 1.2×10^8 tons, 66.7% of which is pure H_2, while 33.3% is mixed with other gases. According to statistics from the International Energy Agency, this is equivalent to 14.4 EJ, about 4% of the total use. Most of the H_2 (95%) is produced from coal and natural gas, and the rest as a byproduct of the production of chlorine through electrolysis. Coke oven gas has a high content of H_2 as well, which is partially recovered. Although the current H_2 production from biomass is negligible, this could soon change. Most hydrogen is generated and utilized locally in industries. Ammonia synthesis and petroleum refining constitute the main focus of the market, accounting for

66.67% of the use of H_2 (Figure 4). Ammonia is utilized as a fertilizer and to produce other chemical products. In oil refineries, H_2 is used to produce transportation fuel from petroleum [65,66].

H_2 is produced in different ways according to the raw material. Moreover, the design of H_2 energy systems depends on the location, kind of demand, price of energy sources and primary energy availability. In a typical analysis on the production of hydrogen and the distribution of various raw materials, the estimated cost is based on the almost coincident energy amounts of one gallon of gasoline and one kg of H_2. The hydrogen production cost varies widely with the kind of technology and distribution channel. According to a survey performed in 2004, the total cost of one kg ranged from USD $1.91 for H_2 produced from coal and distributed through a pipeline to 6.58 for that produced through electrolysis [45,67].

6. Hydrogen Storage and Transport

Hydrogen storage is a method used to store hydrogen for later use. It is one of the fundamental barriers to its widespread use as an energy carrier. Hydrogen storage provides a clean and sustainable form of energy and has no environmental impact [68]. Possible storage methods are liquid H_2 storage, compressed gas H_2 storage and solid H_2 storage (Figure 5).

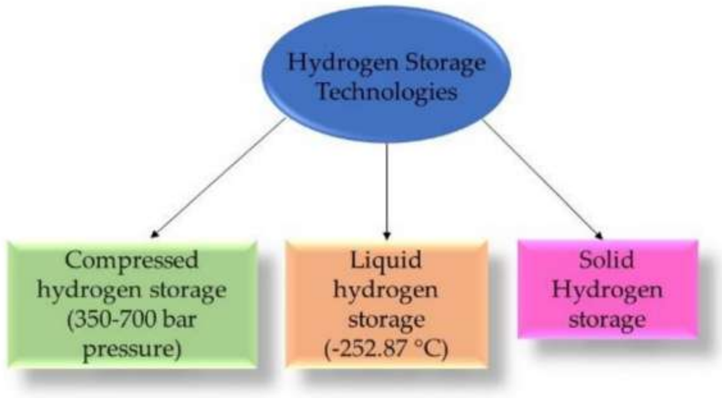

Figure 5. Hydrogen storage in the period from 1980 to 2018. Adapted from Singla et al. [68].

Hydrogen storage is very important due to its wide range of applications, ranging from stationary and portable energy to transport. However, as the ambient temperature density is low, the energy per unit volume is low as well; therefore, it is necessary to develop an improved storage method that can increase energy density.

Hydrogen can be physically stored as a gas or a liquid [69]. Physical storage means storing it in its molecular form. Options for storing H_2 in molecular form are liquid H_2 tanks and compressed gas H_2 tanks. Liquid H_2 can be stored through a compression and cooling process in tanks in cryogenic systems; the work required is predicted to be 15.2 kWh/kg, the volumetric density is 70.8 kg/m^3 and the gravity density is influenced by the tank size. Typically, a high-pressure tank (350–700 bar) is required to store H_2 as a gas [70].

Today, hydrogen is most commonly stored as a gas or liquid in tanks for small-scale mobile and stationary applications. However, the smooth functioning of large-scale and intercontinental H_2 value chains in the future will require a much broader range of storage options. At an export terminal, for example, hydrogen storage may be required for a short period before shipment [71]. Hours of hydrogen storage are required at vehicle filling stations, while days to weeks of storage would help users face possible mismatches in its supply and demand. Long-term storage options would be needed if hydrogen were to be used to meet large seasonal changes in electricity supply or heat demand. The most suitable storage method depends on the volume to be stored, the duration of storage, the discharge speed and the geographic availability of the different options. In general, however, geological storage is the best option for large-scale, long-term storage, while tanks are best suited for short-term storage [71].

Tanks that store compressed or liquefied hydrogen have high discharge rates and efficiencies of around 99%, making them suitable for applications where a local supply of fuel or raw material needs to be readily available. Hydrogen compressed at 700 bar has only 15% of the energy density of gasoline; therefore, storing the equivalent amount of energy at a vehicle filling station would require nearly seven times the space. When it comes to vehicles rather than filling stations, compressed hydrogen tanks have a higher energy density than lithium-ion batteries and therefore allow for a greater range in cars or trucks than is possible with battery electric vehicles. Research continues with the aim of finding ways to reduce the size of tanks, which would be especially useful in densely populated areas. This includes examining the scope of underground tanks that can tolerate 800 bar of pressure and thus allow for greater H_2 compression [71].

Salt caves, aquifers and depleted natural gas or oil reservoirs are possible options for long-term hydrogen storage [72,73]. They are currently used for natural gas storage and provide significant economies of scale, high efficiency (amount of injected H_2 divided by the amount that can be extracted) and low operating costs [74]. While geological storage offers good prospects for long-term and large-scale hydrogen storage, the geographic distribution, size and minimum pressure requirements make it less suitable for short-term, smaller-scale storage [73]. For these applications, tanks are the most promising option [71].

As described above, there are some disadvantages to storing hydrogen in liquid form, while the gaseous state requires large physical volume, with high cost, high energy consumption, high pressure, very low temperature and, most importantly, safety issues, which make it not viable for commercial application [51]. Therefore, due to various problems in storing H_2 in the liquid and gaseous state, its storage by chemical means has attracted the attention of scientists as it decreases essential storage pressure and increases volumetric capacity [68].

In the chemical storage method, hydrogen can be stored in solid-state materials. Although this technology is at an early stage of development, it may allow even greater densities of H_2 to be stored at atmospheric pressure [51]. In recent decades, solid-state materials have been the subject of numerous studies. Various materials have been explored in the search for a suitable material that meets the requirements established by the U.S. Department of Energy (US-DOE), such as a storage capacity of more than 8% by weight and an operating capacity of 40–85 °C [75,76]. Several materials are available for this purpose, such as sorbents, light metal hydrides and complex metal hydrides. In sorbent systems such as C-based materials and Metal Organic Frameworks, hydrogen is connected to the surface through physisorption. These systems need a very low operating temperature, which is practically unfeasible, and their storage capacity is not as good [77]; therefore, light metal hydrides and complex metal hydrides are promising methods as they require viable working temperatures and good H_2 storage capacity according to the US-DOE targets [78]. The cost of filling a 700-bar tank is much higher (USD $1.94/kg H_2) than that (USD $1.23/kg H_2) of a metal hydride tank. Thus, comparing all hydrogen, metal hydride and fuel cell electric vehicle storage technologies seem to be the most promising storage options [79]. The transport and storage of hydrogen on a large scale is a matter to be developed, and consequently, there is a lack of studies on costs. In the future, new catalysts able to increase the rate of H_2 sorption kinetics must be investigated.

Furthermore, to evaluate the economic aspects, two types of hydrogen storage systems must be considered: (i) transport applications and (ii) stationary applications. Each of them has different needs and drawbacks. The transportation sector will be the most prominent application of the H_2 economy for the foreseeable future. Hydrogen storage requirements for transport applications are more stringent than for stationary applications [51].

The requirements for the transportation sector are as follows: operating temperature reduction, low operating pressure, need for reversibility of multiple hydrogen cycles, absorption and release, fast kinetics, high gravity and volumetric H_2 densities and H_2 storage cost less than 15 pounds/kg. Currently, there is no hydrogen storage system available that could satisfy all these conditions. Stationary applications have fewer restrictions for H_2 storage materials compared to transport applications, as they can be operated at high temperatures and pressures, can occupy a large area and can have slower kinetics. However, storing H_2 for stationary use also has many challenges [51,68].

Compressed gas and liquid hydrogen storage options cannot meet most of the conditions described above. Advances in solid-state H_2 storage materials, on the other hand, can have a significant positive impact on the hydrogen economy so that its safe and efficient generation, storage and usage can meet the target of US-DOE 2020 for H_2 energy storage in terms of storage density, which has yet to be met in order to completely replace fossil-based fuels [68].

7. Green Hydrogen Production

The growing need for decarbonization of the energy system and the latest prospects for reducing the emission of greenhouse gases was confirmed by the recently concluded United Nations Conference on Climate Change 2021 (COP26) in Glasgow [67].

Green hydrogen, generated from renewable sources, is the most suitable for a completely sustainable energy transition. Many technologies are applied to obtain it, but the most applied one, obtained using renewable electricity, is the electrolysis of water. Green H_2 production by electrolysis is a route that allows the exploitation of synergies that the sector needs, thus reducing the costs of applied technology and providing flexibility to the power system. At reduced costs with the use of little technology, the production of green H_2 has been increasingly researched and produced, and with that, its production cost tends to decrease proportionally. As a result, green H_2 produced by the electrolysis of water has gained increasing attention [80].

Since green hydrogen is a renewable source of energy in the long term and can be stored, it can be used to replace hydrocarbons as fuel in the mobility of people, in the generation of thermal energy and as an ecological raw material for industrial use. However, in the long term, the most used methods to obtain it are not the most common in view of the agreed energetic and climatic targets. Nowadays, one of the important economic activities around the world is the H_2 provision to around 90% of user industries; its importance is demonstrated by the fact that in 2018 its supply exceeded 74 million tons, which corresponds to an increase in demand of over three hundred percent compared to 1975. Currently, H_2 is mainly generated by the cracking of fossil fuels, about 6% from natural gas and 2% from coal, thus being called gray hydrogen and brown hydrogen [81–84].

Green hydrogen may alternatively be generated from biomasses through gasification and pyrolysis, which, however, are still very costly [85], or, even more expensively, via electrolysis of H_2O using wind or photovoltaic energies [85,86]. An FCH study carried out on "green hydrogen" [87] recognized about ten different options to generate H_2 from renewable resources, with the use of biogas being the least expensive and the most promising, since it is primarily made up of CH_4 as raw material for its production, as well as carbon dioxide. Although it is similar to the steam conversion process, it should be used in smaller quantities compared to existing biogas production units, being able to produce about 0.25 $Nm^3 \cdot s^{-1}$ of CH_4, compared with 25 to 30 $Nm^3 \cdot s^{-1}$ when utilized on a large scale. In 2014, Europe had more than 17 thousand biogas plants, with the production of more than 8000 MW [88]. The following year, the EU produced 15.6 Mt of primary energy from biogas plants, with an annual increase of > 5% over the previous decade [89].

However, Germany and Italy have about 75% of small and medium-sized anaerobic biodigesters with up to 1 MW of energy, where raw materials for biogas production are leaves, crop residues and animal manure, while the UK mainly produces biogas from plants installed in larger landfills. Other works have already demonstrated how this technological process is economically viable to produce hydrogen [90]. Furthermore, as biogas is similar in composition to natural gas, it does not require significant changes in the systemic steam reforming process. Steam or autothermal reformers have conventional fuel processors, composed of 1 or 2 stages for changing the water gas to increase the hydrogen concentration in the reformed stream, as well as a pressure swing adsorber to separate and purify H_2. Alternative, unconventional techniques used to produce hydrogen from CH_4 include solar or thermal plasma reforming as well as catalytic splitting [87,91,92]. H_2 can also be generated via steam reforming of biogas over a wide temperature range (from 600 to 1000 °C), a region of endergonic reversible reactions that often involve events of combined catalysis.

Either process may be carried out at low or barometric pressure in a fixed tube or fluidized bed reactor [91,93,94]. The main difference between CH_4 and biogas steam reforming is the presence of CO_2 in the composition of the latter gas, which makes the unit highly sensitive to C formation under the operating conditions due to its consequent deposition in both the support and the catalyst. Carbon deposition can be prevented, in the latter case, by feeding the system with excess steam, which can then be recovered at the outlet by means of condensation [95].

Most of the studies carried out on the production of green H_2 from biogas describe experiments in which synthetic mixtures of carbon dioxide and methane were used to simulate biogas composition, while only a few of them use actual biogas produced by anaerobic digestion of waste biomass [96,97].

Most full-scale anaerobic digesters operate at mesophilic (24 to 45 °C) or thermophilic (45 to 65 °C) temperatures, while it is difficult to find psychrophilic applications [98–101]. However, cold-tolerant bacteria, often having enzymes with moderate to low optimal temperature, are of commercial interest due to the possibility of their use at low temperatures and to the thermal stability of their enzymes. Some studies described the possibility of H_2 production at relatively low temperatures (e.g., 4 to 9 °C) [102]. Given the above, this technology can be considered a promising method for the production of H_2 even in very cold climates [103].

Another sustainable way to produce hydrogen is based on the use of microalgae, which have two important natural catalysts: photosystem II and hydrogenase used to split water and combine protons and electrons to generate H_2, respectively. About 20 years ago, the production of H_2 was aimed at photobiological production using the sulfur protocol, which represented an important advance in this field of biotechnology. However, considering that this strategy was not economically viable, further studies were conducted with different strains of microalgae capable of producing a sustainable amount of H_2 without nutrient starvation [104]. The most promising approach has been the "two-stage process" of photosynthesis (stage 1) and H_2 production (stage 2). In this process, the oxygen and hydrogen production reactions are separated [105]. Several microalgal species have been studied for this purpose, especially *Chlamydomonas reinhardtii*, *Chlorella vulgaris* and *Chlorella pyrenoidosa* [104]. Among them, *C. reinhardtii* is a model microorganism recognized as an efficient H_2 producer, thanks to a hydrogenase with an activity 10 to 100 times greater than that of other species [106].

The production of H_2 requires the optimization of several parameters such as the selection of the microalgal strain, growth medium, pH, temperature, light, chlorophyll concentration and photobioreactor [107,108]. Many works describe the production of H_2 by many strains of microalgae using sulfur-, phosphorus- or nitrogen-poor medium [109,110]. Under these conditions, however, the production of H_2 only lasts a few days, as the depletion of the macro/micronutrient compromises cell viability, which is the main disadvantage of processes carried out under nutrient deprivation conditions. Moreover, H_2 production by microalgae requires anaerobic conditions due to the sensitivity of the hydrogenase to O_2 [111], which represents a major problem. Therefore, many studies on oxygen suppression have been conducted to improve H_2 yield. Microalgal genetic and metabolic engineering, nutrient stress optimization of light conditions and elimination of concurrent pathways by electrons are examples of applications to improve such a process [104].

8. International Hydrogen Market

The international hydrogen market also merits attention, although it represents less than 10% of the total H_2 market in economic value. According to data from the Observatory of Economic Complexity, the international H_2 trade moved approximately USD $11.75 billion in 2017. The major exporters were the USA (USD $2.22 billion), China (USD $1.75 billion), Germany (USD $1.33 billion), South Korea (USD $1.29 billion) and Norway (USD $580 million), while the largest importers were China (USD $2.78 billion), Japan (USD $1.71 billion), Germany (USD $921 million), South Korea (USD $789 million) and other Asian countries (USD $800 million). The participation of Brazil was USD $335 million in exportation and USD $61 million in importation [54,63,65].

H_2 promises to be a novel raw material, demonstrating that it can be bought and sold. New perspectives for natural gas producers, including Canada, Iran, Norway, Qatar, Russia and USA, arise from the possibility of converting green H_2 into synthetic natural gas (utilizing carbon dioxide from burning biomass or contained in the air) and sending it to the market (through the current infrastructure) as well as converting natural gas into low-carbon H_2 (through steam methane reforming and carbon capture and storage). As H_2 can be cheaply produced in remote desertic areas and easily reach markets, it can also be seen as a novel economic opportunity in regions such as the Middle East and North Africa. Finally, the conversion to the H_2 economy would also offer new economic perspectives for countries that strongly depend on fossil fuel imports like Argentina, Australia, Chile and China.

9. Conclusions and Prospects

The study of hydrogen enables the identification of the main drivers for the establishment of new technologies related to the generation of clean energy. Such aspects are clearly related to the economy and the characteristics of hydrogen as an energy vector, which include production from diverse sources and use with very low environmental impact. The main countries that have demonstrated interest in the implantation of this new source of energy are those with the highest energy demands and, consequently, the highest levels of greenhouse gas emissions. The economy of hydrogen is also a solution for the issue of energy security caused by the huge dependence of these countries on imported fossil fuels and is a strategic option in countries that have other sources of energy.

Important elements of the hydrogen economy include its production, delivery, storage, conversion and application. Various methods can be used to produce H_2, such as partial oxidation of hydrocarbons, steam methane reforming, coal gasification, biomass gasification, pyrolysis, electrolysis and the thermochemical method. Electrolysis and solar energy technologies are the most promising methods from an environmental point of view. On the other hand, hydrogen storage methods need more research and development. Hydrogen is difficult to store and transport, which is different from other energies such as electricity or batteries. Storage of hydrogen requires special care as it is highly combustible and can be easily oxidized in containers and pipelines. As discussed throughout this review, hydrogen can be stored as a gas, liquid or solid-state material, the latter being the most promising and acceptable way. In this sense, the production of hydrogen through the electrolysis of water and its storage in ionic form (electrochemical storage of hydrogen) can be suggested as a safer and more viable path, demonstrating that hybrid systems that include combinations of renewable sources and fuel cells can meet the energy requirement in the future. Modern processes for maintaining gasification, absorbing carbon dioxide and developing new, efficient and economical electrochemical processes are needed during the transition period to the hydrogen market. An economic analysis of the hydrogen-obtaining chain clearly demonstrates that the hydrogen production cost is the most important factor when compared to other factors such as utilization and storage costs. Therefore, by choosing more promising and sustainable production and storage methods, the dominant importance of fossil fuels in energy systems can be reduced for the world to finally enter the hydrogen era. Finally, it is important to emphasize that confidence is key to increasing the use of fuel cells and other hydrogen-based technologies. This boost in community trust could be significantly enhanced through increased product publicity, marketing and the development of educational projects that allow hydrogen to be accepted as a fuel.

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