

A Review of History, Production and Storage of Hydrogen

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Received 17 February 2021; Accepted 4 August 2021

Abstract

The need to reduce fossil fuel consumption has created opportunities for alternative fuels, including the migration of hydrogen as an unconventional alternative fuel. This alternative has more significant environmental and energy benefits due to the acquisition of raw materials and the integration of renewable energy sources. The research presents a review of historical evolution, a bibliometric analysis, and the processes used to produce and store this molecule. The POx and pyrolysis processes have the highest amount of research. At the same time, electrolysis is the process that has had the most significant growth, and research indicates that they allow greater sustainability due to the integration of renewable energies. Research trends indicate studies for integrating renewable energy resources and materials to improve chemical properties to increase capacity storage and decrease the risks due to high volatility.

Keywords: Renewable Energy, Hydrogen Production, Hydrogen Storage.

1. Introduction

Fuel demand is continuously growing [1], and fluctuations in hydrocarbons' prices generate financial imbalances due to high prices [2]. The countries must develop plans for the implementation of renewable energy sources (RES) [3]–[5] as a substitute for conventional thermal generation and power distribution networks; according to Nigam et al., this relationship often exceeds 20% [6].

To reduce fuels in mobility, the government applies plans like the use of biofuels [7], the electrification of the vehicle fleet [8], improve the efficiency in combustion processes [9], and the use of other fuels [10]–[12], like as the hydrogen. In electrical energy production through thermal generation, installing hybrid systems for combustion [13] reduces fossil fuels. In the case of nuclear energy, the remaining energy produces hydrogen [13]. This fuel can be stored and used at high electricity prices [13], thus obtaining a lower environmental impact than conventional fuels [14].

Hydrogen is a candidate to be an alternative fuel used to generate electricity [15], [16] through fuel cells [17], [18], which convert chemical energy to electrical energy using an electrochemical process [19]. This alternative has become necessary due to the possibility of using renewable energy for its production [19]; previously, it was not viable due to its high energy costs [20].

The growth of net installed electricity generation capacity (NIEGC) with renewable energy resources invites us to study alternatives to produce hydrogen. This research identifies the knowledge gaps within each area, which focused on focused research and innovation aimed at sustainable development of

hydrogen technologies; these results may be the basis for developing strategies, strengthening, and infrastructure development to produce hydrogen as an alternative fuel.

2. Methodology

The research presents a bibliographic review on technological developments around hydrogen. It begins with a compilation of research that has marked technological development to date. According to the bibliographic production indexed in the Scopus database, a bibliometric analysis is carried out to identify the behavior of the research and the countries that make the most significant efforts. It presents the technologies used for the production of hydrogen and ends with a comparison of each technology. Finally, it presents the storage technologies and associated hazards.

3. Results

3.1 Hydrogen as fuel

Hydrogen is a colorless gas, odorless, and harmless; it is the most abundant element in the universe. It is the fuel of the stars [21]. Hydrogen is 14.4 times even lighter than air and condenses at -252.77 °C [22], [23]. When burned, this gas produces much higher energies than other fuels. Unlike these, its harmful combustion emissions turn out to be negligible [23], [24].

Hydrogen is called an "energy vector" [25] because it is not found in its pure state in nature but rather is found in substances such as water, biomass, which includes plants and animals [26]. Thus, hydrogen should not be exploited like coal or oil but produced through chemical compounds [23], [27].

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doi:10.25103/jestr.145.14

Pure hydrogen can be produced from other compounds that contain this element [26]; each production method requires an energy source such as thermal energy and photocatalytic energy, energy for the breakdown of chemical bonds [28], [29]. Some natural resources, like water, biomass, and hydrocarbons, can produce hydrogen [30].

In 1541 T. Von Hohenheim artificially produced hydrogen by reacting metals with strong acids, although he did not know this molecule [31]. Hydrogen in the gaseous state was recognized and described in 1766 by Henry Cavendish as a "flammable gas" [22]. In 1800 William Nicholson and Anthony Carlisle discovered electrolysis. In this process, water molecules are broken down into hydrogen and oxygen using an electrical current [32].

In 1839 William Grove built the first fuel cell, which directly transformed chemical energy into electrical energy [33], [34]. In 1920 Rudolf Erren used hydrogen as fuel in an automobile [35]; by 1958, Francis Bacon T successfully built the first fuel cell. The fuel is used as an energy supply method by the National Aeronautics and Space Administration [15], [36].

In the 1990s, Germany and the company Solar-Wasserstoff-Bayern built a photovoltaic solar power generation plant capable of producing 371 kWp; the energy was used to produce hydrogen electrolysis [37]. In 1999, the Shell company opened the first service stations to sell hydrogen in Munich and Hamburg [38]. In 2003, DaimlerChrysler Corporation, Ford Motor Company, General Motors Corporation (GM), and the US government made joint and developed technology to reduce oil consumption and minimize vehicles' emissions [39]. One of the proposed alternatives was to create electric vehicles powered by fuel cells [19], [39].

Initiatives in countries like Belgium with 3MOTION, a proposal to invest in Fuel Cell Buses (FCB), and achieve the emission reduction [40], Australia built a wind power plant to produce hydrogen through electrolysis [41], Germany developed a train to use hydrogen using fuel cells [42];. At the same time, the Uruguayan government, the state oil company ANCAP and the National Administration of Power Plants and Electric Transmissions (UTE) began the pilot project called "Verne" to produce hydrogen and use it as gas fuel in vehicles [43]. USA has 80 power plants using fuel cells, with around 190 MW [43]; Red Lion Energy Center is the largest capacity with 27 MW and is located in Delaware [44]. These projects encourage governments to implement and adopt technologies that use hydrogen to reduce the environmental impact.

3.2. Bibliometric analysis

The methodology analyzed 15.543 documents obtained through the search in the Scopus database. Using the keywords "Hydrogen & Fuel & Type Technology" this input allowed us to analyze the temporal evolution of the subject between 2010 and 2020. Figure 1 presents a classification of the processes. Figure 2 shows the number of publications associated with the different methods. Finally, figure 3 illustrates the percentage relation of the annual publications according to the process.

Figure 2 presents a constant growth in research production on hydrogen, where the years 2019 and 2020 had the highest growth. Figure 3 shows the percentage behavior of the publications, more than 50% of annual investigations are in Catalytic Reforming and Catalytic POx technologies. Non-Catalytic POx investigations had a decrease in both

percentage and quantity. On the other hand, the Electrolysis had an increase, mainly in Anaerobic.

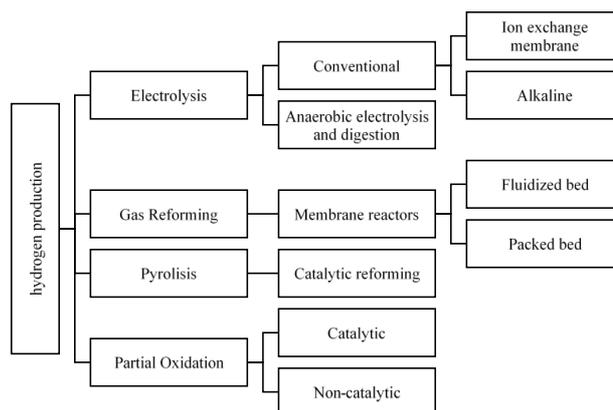


Fig. 1. Classification of hydrogen production processes.

The top five countries with the highest contribution are China with 4.354, the USA with 2.062, Spain with 920, the UK with 791, Japan with 601, and Germany with 599 publications; this amount represents 54% of publications indexed in Scopus. Figure 4 presents publications from these five countries from 2010 to 2020 according to the contributions.

China has the highest contribution; initially, it has a substantial participation in the Non-Catalytic POx processes. Then, they increased their investigations in the Catalytic Reforming and Catalytic POX processes. Finally, for 2018, the studies in Anaerobic processes increased. However, the behavior of the other countries is similar. The significant difference is the percentage of research carried out on Electrolysis, mainly on Ion Exchange Membrane and Anaerobic technologies.

3.3. Technologies for hydrogen production

Research on hydrogen production is geared for power generation [45] and a substitute for fossil fuels [17], [46], [47]. This section presents hydrogen production and obtention [46], [48]; it identified the production mechanisms, chemical reactions, process efficiency, and by-products.

3.3.1. Electrolysis

Electrolysis is a process by which a breakdown of the water molecule is generated (H_2O) by the action of electric current flow, generated from sources such as solar or nuclear [30] [49]. In environmental conditions ($25^{\circ}C$ y $1\ atm$), a chemical reaction occurs $2H_2O \rightarrow 2H_2 + O_2$. If the electrolysis is carried out at low temperatures, there is an increase in the consumption of electrical energy [50] and generates greater inefficiency in the process [30]; for high temperatures, the energy consumption increases, but the efficiency is considered acceptable [30].

Huang et al. [51] y Li et al. [52] present the use of electrolysis and anaerobic digestion to produce hydrogen through a negative pressure control chamber and food waste. The results show that by using only anaerobic digestion, it obtains $49,39\ ml\ H_2\ g^{-1}$ in production and combining the two teams is obtained $H_2\ g^{-1}$ [51]. Figure 4 shows the process assembly; Through an anion exchange membrane and a DC source connection, a reaction will be generated where the water circulates in the membrane and hydrogen and hydroxyl ions are formed [32].

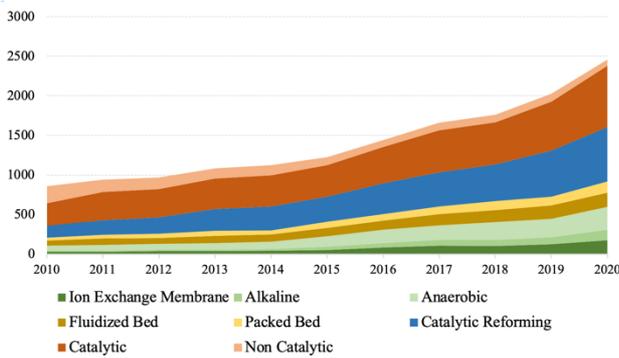


Fig. 2. Publications made during 2010-2020 according to the technology used.

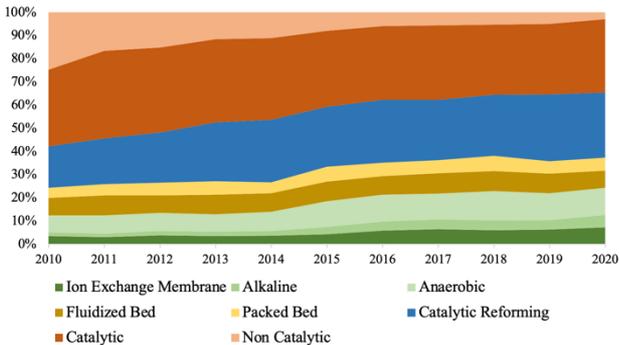


Fig. 3. Percentage behavior of the publications made during 2010-2020.

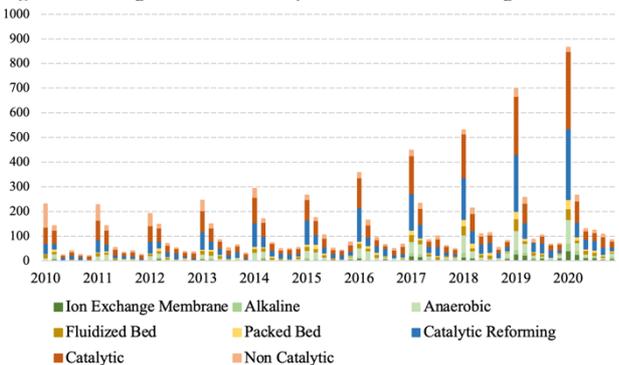


Fig. 3. The behavior of the publications of the countries China, USA, Spain, UK, Japan, and Germany.

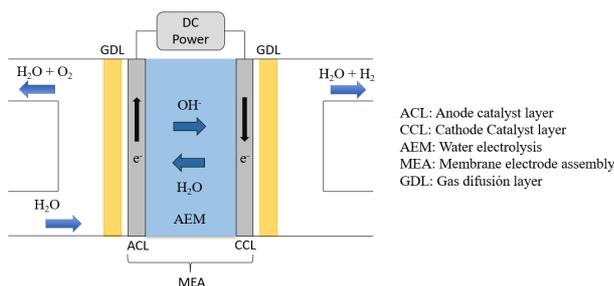


Fig. 4. Electrolysis process.

3.3.2. Fuel cells

The fuel cell is an energy conversion system that converts chemical energy into electrical energy [33], [34]; they transform hydrogen or any energy source containing hydrogen [53] into electrical and thermal energy when fuel and oxidant are supplied [54]. Figure 5 presents the process; it begins with the entry of chemical energy as a fuel, combustion, and a hydrolysis process for hydrogen production are carried out; finally, this passes to the fuel cell to generate electrical energy [34].

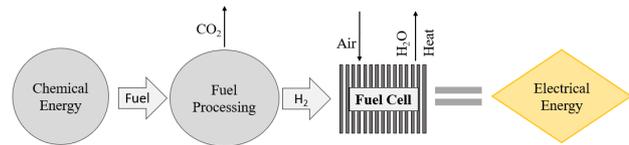


Fig. 5. Fuel cell operating diagram.

They have advantages such as high electrical efficiency, high temperature of the heat source, high energy density, among others [55]. The reaction in the anode electrode is $2H_2 \rightarrow 4H^+ + 4e^-$ and the cathode electrode is $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$, on both sides of the membrane are proton exchange, the final reaction is $2H_2 + O_2 \rightarrow 2H_2O + Energy$, the products are water and energy as the heat and the electricity [56].

There are a variety of types of fuel cells [54], [57]; the Alkaline Fuel Cell (AFC) operates at temperatures below $120^\circ C$ and uses 35-50% concentrated potassium hydroxide (KOH) electrolyte [58]. The electrodes are platinum/palladium for the anodes and gold/platinum for the cathodes [59]. The fuel must be pure hydrogen; CO_2 can form potassium carbonate due to KOH and reduce efficiency. The Polymer Electrolyte Fuel Cell (PEFC) operates at temperatures below $100^\circ C$ to obtain good efficiency. It uses a hydrated perfluorinated sulfonic acid polymeric membrane to improve the conduction of protons [60], [61]. Platinum supported on carbon is commonly used as a catalyst or bifunctional metal electrocatalyzers based on platinum and a metallic element such as ruthenium. They require hydrogen of high purity, and another fuel must go through a previous reforming process [60]–[62].

The Phosphoric Acid Fuel Cell (PAFC) operates at temperatures between $150-250^\circ C$; the electrodes are platinum supported on carbon and concentrated phosphoric acid as electrolyte [63]; it has a tolerance to pollutants generated in the reforming process.

Molten Carbonate Fuel Cell (MCFC) operates at temperatures above $650^\circ C$; it uses as electrodes nickel doped with chromium or aluminum for the anode, lithium nickel oxide for the cathode. The electrolyte is a molten salt of alkali carbonates (Li, Na, K) retained in a lithium aluminate matrix [64], [65]. It can be fed directly with a hydrocarbon without needing the previous step of transforming it into hydrogen [66]–[68]. Direct Carbon Fuel Cell (DCFC) is a variation [69], which uses a carbon-rich material as a fuel such as biomass or coal, to convert directly into electrical energy [70], [71].

The Solid Oxide Fuel Cell (SOFC) operates at temperatures between $900-1000^\circ C$; it uses as electrodes a mixture of ceramic and metal, Ni/ZrO₂ at the lanthanum manganite doped with strontium or selenium at the cathode. The electrolyte is a non-porous metal oxide used by an excellent ionic conductor, such as zirconium oxide stabilized with yttrium oxide [72]. Like MCFC, they can use the waste heat generated in the fuel reforming process [73]. The current challenge is to lower the operating temperature in the range of $600-800^\circ C$ [74].

3.3.3. Natural gas steam reforming

Kalamaras et al. indicate that 50% of global hydrogen demand occurs through steam reforming natural gas [75]. In the United States, 95% of production is done by this method [76]. This technology is the cheapest [77], uses natural gas, mainly methane [78]; it is an endothermic process because it exposes natural gas to steam with high temperatures [19]. The reactor

uses Palladium and Gold's membrane to obtain high purity hydrogen [78]. Figure 6 presents the process and reactions.

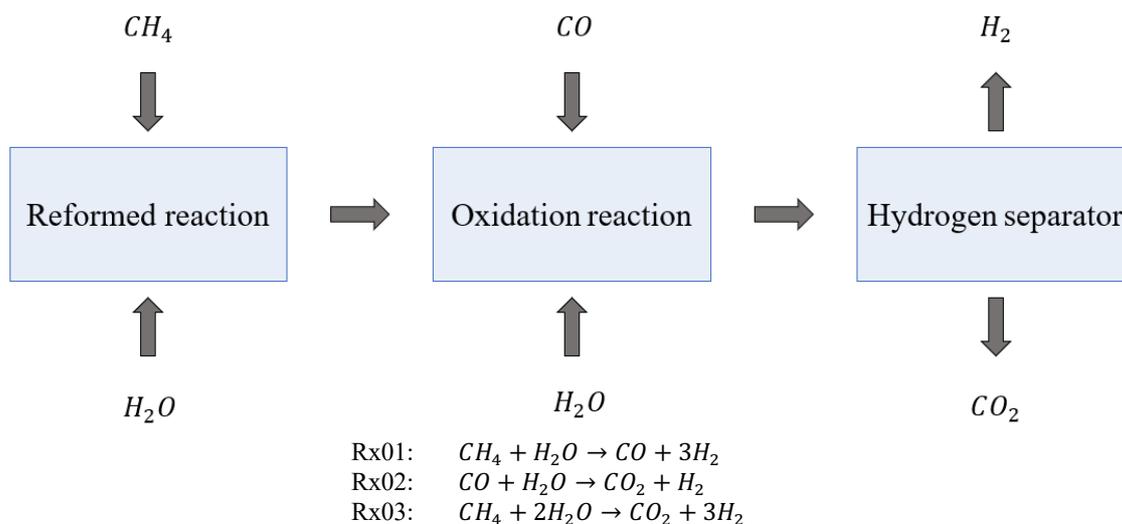


Fig. 6. Natural gas steam reforming process.

The reforming process has two reactions, one of reforming and the other of oxidation, finally, the hydrogen (H_2) is separated [26]. Catalysts such as nickel–boron–alumina xerogel improve the efficiency of the reaction. [79], the monolithic catalyst FeCrAlloy coated with ruthenium (Ru) [80], among other things.

Methane is one of the most critical raw materials for hydrogen production under this method [81]. However, biomass is investigated as a surrogate due to its environmental effects and cost reduction [82]. Recently, reforming technology has improved the production of hydrogen to purified hydrogen [83]. Iulianelli and Basile propose that hydrogen perm-selective membrane be incorporated into a reactor, improving the chemical reaction and obtaining purified H_2 in a single reactor [84]. This membrane must be permeable and thermally stable using palladium, palladium

alloys, and an inorganic membrane such as niobium and tantalum.

3.3.4. Pyrolysis

The pyrolysis consists of the decomposition of solid organic material in the absence of oxygen and high temperatures [85], [86]; through the application of heat temperature of $500^\circ C$ is reached for biomass and $1.200^\circ C$ for coal [87]. Figure 7 presents the chemical reaction; the results depend on raw material, temperature, pressure, and process time [88]; gaseous products such as hydrogen (H_2), carbon monoxide (CO) and carbon dioxide (CO_2), liquids such as hydrocarbons and solids such as carbonaceous residues and coke are obtained [19].

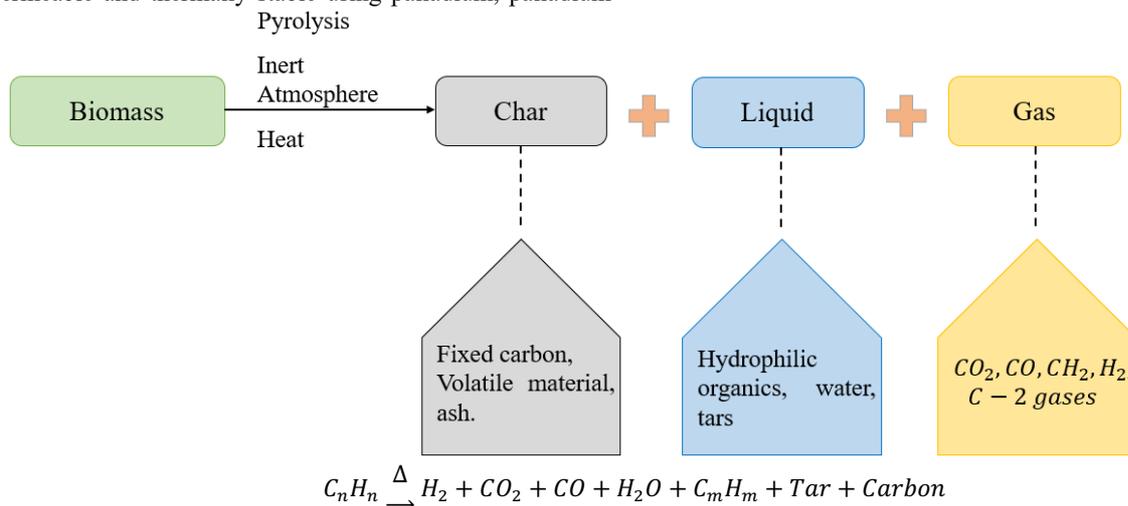


Fig. 7. Pyrolysis process in biomass.

The pyrolysis requires high temperatures. Performance depends on reactor technology, process temperature, and the raw material or biomass used [89], [90]. To improve the technical and economic efficiency of the process, Tahmasebi et al. [91], Niu et al. [92], and Ye et al. [93] performed lignite pyrolysis with pressurized and restricted flow conditions,

where high purity nitrogen is used as the scavenging gas. Lignite, due to its energy potential and current reserves [94], turns out to be a valuable source for the production of (CO_2H_2), (CO), (CH_4), (C_2H_6), and (H_2); Tahmasebi et al. evidenced by increasing the temperature and pressure of the process, increasing the concentration of hydrogen [91].

Setiabudi et al. [95] y Bizkarra et al. [96] carried out a double process; they start pyrolysis to biomass. The liquid or oil by-product applies a steam reforming process, using catalysts such as acetic acid, ethanol, and phenol. Yang et al. present the extraction of hydrogen in waste from palm oil, obtaining gases such as H_2 , CO , CO_2 , CH_4 , and traces of C_2H_4 and C_2H_6 [88], its process grinds, dries, and heats the waste to a temperature between 500 and 900 °C in the reactor. Side reactions can occur within the reactor, increasing or decreasing other gases other than hydrogen [97]. Pyrolysis with the waste manages to generate H_2 and CO up to 70% of the volume of the gas produced, however, when the maximum temperature of 900 °C is reached, it is possible to obtain CO_2 and CH_4 [88], [98]; Yang et al. indicated that if the resistance of the waste decreases the production of H_2 y CO and will decrease [88].

3.3.5. Partial Oxidation

Partial oxidation (POX) consists of incomplete oxidation of a hydrocarbon [99], where carbon is oxidized, up to carbon monoxide (CO), and releases hydrogen (H_2). It is an exothermic reaction with a standard enthalpy of -36 kJ/mol, allowing to do without external burners [30], allowing reactors to be more compact, reduces energy cost to 10-15% and capital investment to 25-30% [100]. POX processes preferentially use methane [101].

In the presence of catalysts, the reaction reaches temperatures above 800°C [19]; if there is a high presence of carbon monoxide, it can generate the deposition of charcoal and cause the inhibition of the catalysts [19]; Nickel (Ni) is used as a catalyst, and its activity and durability depend on the size of the Ni core [101]. Without the presence of catalysts, the temperature rises between 1.300 and 1.500°C [102]. Figure 8 presents the POX process and reaction.

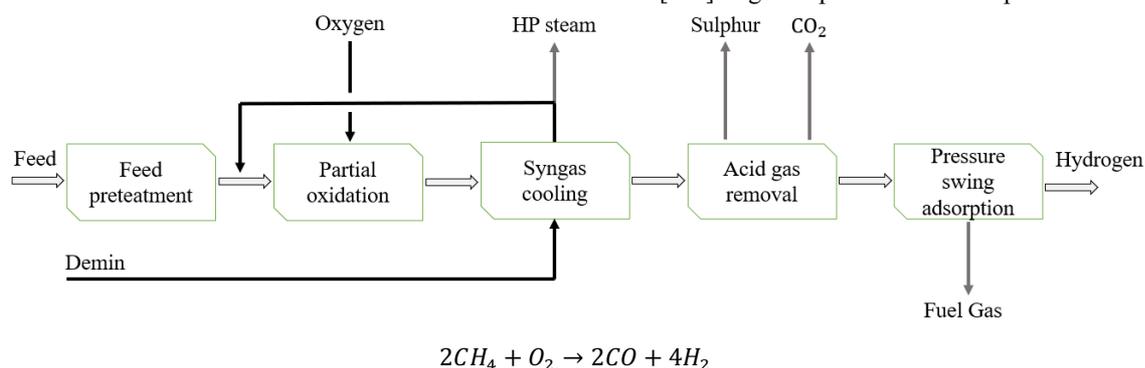


Fig. 8. The partial oxidation process of methane.

The partial oxidation process begins with the entry and preheating of a hydrocarbon and oxygen, an oxidation reaction is carried out, and obtained a synthesis gas; this will be recirculated to extract steam and remove acids such as CO_2 and sulfides. Finally, adsorption is carried out by the pressure oscillation (pressure swing adsorption) to extract the hydrogen.

There is a process derived from this methodology called partial catalytic oxidation. (CPOX), uses natural gas or other hydrocarbon and a catalyst from the conventional POX process. It produces synthesis gas rich in hydrogen and

methanol, which can be used in the Fischer-Tropsch process to obtain valuable products [103].

3.4. Technological comparison

Hydrogen is a possible candidate to replace fossil fuels [14], [15]. However, its final price limits its competitiveness due to the costs associated with storage and transportation [20]. Having an efficient production process and by-products that deliver added value will help improve their competitiveness; Table 1 presents a comparative summary of the technologies presented.

Table 1. Technological comparison.

Technique	Raw material	Efficiency	By-products	Cost	Applications	Comments
Electrolysis	Water. Acid and alkaline solutions	50% - 70%	-	\$2.77/KgH ₂ . [104]	Use unconventional energies (wind, solar) for the production of hydrogen with a fuel approach. [105][106]	Efficiency depends on operating temperature. The cost depends on how the electrical energy production is.
Fuel cells	Metals	30% - 60%	Water, Heat.	€1200–2000 [107]	They are used as central or distributed generation, even as APU (Auxiliary Power Unit) in vehicles and portable applications. [54]	Efficiency depends on operating temperature and technology. Versatile applications. It produces few vibrations in its operation. Therefore, they are

Gas steam reformed	CH_4	70% - 85%	CO_2	\$0.75 - 0.77/KgH ₂ . [108]	Nickel-based catalysts using alumina pellets as supports for the production of hydrogen through methane steam reforming. [109] Reactors produce hydrogen from plastic waste through catalytic reforming. [111]	silent and do not produce NOx. Cost-efficient technology.
Pyrolysis	Coal biomass	64% - 73%	Tar, Coal, Water.	\$1.25 - 2.20 /KgH ₂ . [110]	Efficiency improvement through Ni/Al ₂ O ₃ -SiC catalyst for hydrogen production, through partial oxidation.[113], [114]	Efficiency depends on operating temperature and pressure. Wide range of raw materials.
Partial oxidation (POX)	CH_4	60% - 75%	CO_2	\$1.48 /KgH ₂ . [112]		The catalyst influences energy consumption. Compact reactors. It requires high temperatures.

Table 1 presents critical elements to have a competitive process, such as the required raw materials, the process's efficiency, by-products with commercial value, and flexibility in operation. Strengthening each of the elements or finding alternatives will improve reliability and decrease operating costs (OPEX). They propose having security or low acquisition prices of raw materials, reducing energy consumption, and using low-cost energy or renewable energies to avoid using the grid.

The cost of hydrogen production is affected by the raw material prices and the necessary infrastructure. Photovoltaic electrolysis is the most expensive, and its cost is more than \$5/KgH₂ compared to other energy supplies [115]. The fuel cell can use different fuels, such as methanol, ethanol, and natural gas, having these different applications. However, fuel cell manufacturing costs are not directly related to hydrogen but are related to operating costs [116].

3.5. Hydrogen Storage

The storage factor is one of the most complex because it is a highly volatile element in its pure state. [117]. Compared to other fuels, hydrogen has low activation energy [118]; therefore, it does not require much energy to start combustion. This factor generates a benefit in the combustion processes and electrochemical processes [119], [120]. However, it is an excellent security inconvenience due to the risk of combustion [121]. Hydrogen has the particularity of being colorless and odorless [118]; this makes leak detection difficult, and detection equipment is required.

The hydrogen liquefaction process is currently used to decrease the occupied volume. Going from a gaseous to a liquid state [122]–[124], it cools down to temperatures below -1000°F [125], making it difficult to change its state and direct storage. Hydrogen has a low energy density [19], lower than fossil fuels requiring large storage systems slower than fossil fuels requiring larger storage systems [126]. The storage system requires a high storage pressure to avoid inconveniences, the use of materials that attract a large number of hydrogen molecules, or a shallow storage temperature [127].

These technologies are divided into two main groups, which are physical storage and material-based storage. The second group is subdivided into two main groups of sorption, chemistry, and physics. [128]. Physical sorption also called physisorption, is when a sorbate makes contact with a solid's surface, known as the sorbent [129]. Chemisorption, or chemical sorption, is that reaction between a sorbate and a sorbent, whose results are variations in the chemical form of sorbate [130]. Figure 9 presents the classification of the technologies used for the storage of hydrogen.

One of the main challenges when evaluating hydrogen as an alternative fuel is its storage and transportation [131], [132]. Therefore, storage is one of the leading research objects. Furthermore, hydrogen is one of the possible alternative candidates to face progressive energy demand [133]–[135]. Therefore, hydrogen storage in materials has recently been studied [135]; this type of storage is carried out through physical and chemical adsorption and reactions [136].

Compressed Gas

One standard method to store hydrogen is through gas compression, using gas cylinders with maximum capacities of 20MPa [137]. Four cylinders commonly provide compressed air storage; Type I cylinder presents limitations in storage efficiency, having pressure restrictions between 20 and 30 MPa. The type II container has an envelope fundamentally of fiber resin [138]. Finally, the type III and type IV containers are alloys of plastic fibers and embedded carbons. The main difference is that Type III uses metal, and Type IV uses polymers [139].

Liquid Gas

Hydrogen liquefaction is an alternative, in the liquid state has a density of nearly 71 g/L at its boiling point of 20°K. It has a low boiling point. Therefore, it requires a refrigeration system that consumes 30% of its total energy [140], [141]. Therefore, it is necessary to use cryogenic pressure vessels. However, this technology becomes ineffective as hydrogen boils are

present, in addition to the high use of energy to carry out the hydrogen liquefaction process [142]–[144].

Cryo-compressed

The storage of hydrogen through Cryo-compressed containers (CcH_2) has excellent potential for fuel cell vehicles due to its high density and thermal resistance [145], [146]. Cryo-compressed storage makes use of liquefied hydrogen and compressed hydrogen gas storage systems [147]. This type of storage can minimize the loss of boiling from hydrogen storage. Generally, the container is made of metal wrapped in carbon fiber (Type III) [148]. At the same time, it conserves a higher energy density of the system [148]. Furthermore, this method allows storage at cryogenic temperatures at temperatures of 20K and high pressures of at least 30Mpa, all this at room temperature [149].

Ammonia

Ammonia is a liquid hydrogen storage carrier [150]; this method mixes it with water to store hydrogen in liquid form at ambient temperature and pressure. It provides high

densities and reduces the few cryogenic limitations [151], [152]. Furthermore, by reforming ammonia, hydrogen can be produced without generating harmful by-products [128]. The development of catalysts would allow achieving an efficient conversion to hydrogen from ammonia. The temperature is an essential factor. The ruthenium-based catalyst requires temperatures higher than 450°C [153].

Formic Acid

Formic acid is a promising material for hydrogen storage [154], [155]. It is a light organic molecule capable of storing liquid hydrogen at room temperature [156]. In addition, its liquid state is more compact and safer than hydrogen in gas [157]. Using formic acid as a molecule that stores hydrogen requires catalysts that promote the reaction [158]. During the reaction, hydrogen is produced free of CO. The co-produced CO₂ can be hydrogenated again to formic acid [159]. Hydrogen produced in this way is beneficial for fuel cell applications [155], [160].

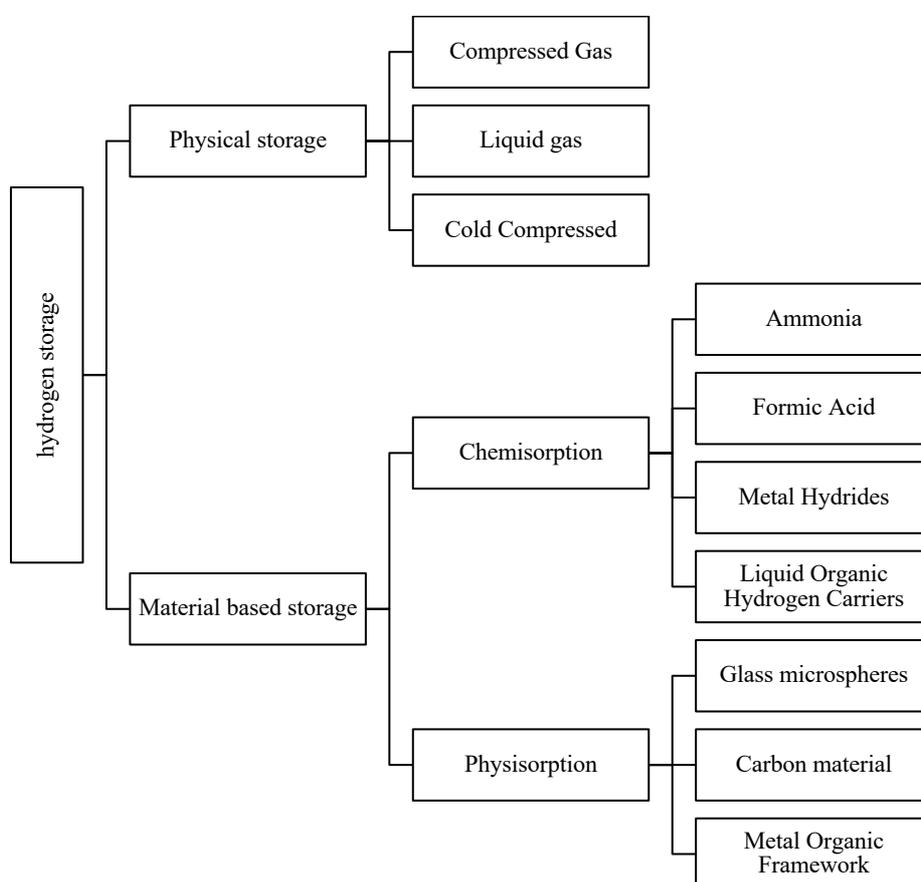


Fig. 9. Storage hydrogen classification.

Metal Hydrides

Metal hydrides have a high hydrogen storage capacity, abundance and are lightweight. As a result, it is considered a promising alternative in medium and small-scale applications [135], [161], mainly in applications between 0.01 and 30 Nm_3H_2 [162]–[165]. This storage type uses reversible hydrogen reactions with metals, intermetallic compounds, and alloys [166]–[168].

The choice of metal hydride materials needs two critical criteria. First, the formation and decomposition processes

must have the capacity to be reversible. Second, the material used must have a high reversible hydrogen storage capacity under operating conditions [169].

The storage can be in carbonaceous materials [170], metals and alloys [171], [172], borohydrides [173], and materials formed by boron nitride [174], [175]. The last one has demonstrated significant results in terms of performance. Finally, the kinetic adsorption and desorption of hydrogen is an additional property that MH materials must carry out the storage and compression of hydrogen [176], [177].

Liquid Organic Hydrogen Carriers

Liquid Organic Hydrogen Carriers (LOHC) are liquid with low melting. The hydrogenated and dehydrogenated process needs the presence of a catalyst [178]–[181]. The LOHC hydrogenation is an exothermic reaction; it produces heat with a temperature between 150°C to 170°C, this energy is used [182]. The operating pressure depends on the exothermic hydrogenation and endothermic dehydrogenation method. However, both processes can be carried out at the same temperature level [183], [184]. Furthermore, hydrogen LOHC compared to molecular hydrogen has a marked increase in volumetric energy density. Thus, facilitating its storage under environmental conditions, with minimal energy losses during transport [185].

Glass Microspheres

There are several well-established methods to produce hollow glass microspheres (HGMs) [186], [187]. This material has advantages such as high efficiency, safety, lightweight, low density, nontoxic, low production cost [188]. Additionally, they are strong materials due to their small diameters and can contain hydrogen pressures of up to 150 MPa [189]. The filling process in the HGMs is initially carried out with hydrogen at high pressure with approximate levels of 350-700 bars at a temperature of 300 ° C; then, a rapid cooling process is carried out at room temperature [190]. Finally, to achieve a controlled release of hydrogen, they are reheated to 200-300 ° C [191].

Carbon Material

Hydrogen can be stored in solid form by combining different materials through physisorption and/or chemisorption [192]. It can be stored in its solid form with different carbon materials [193]. Carbon materials retain a high hydrogen storage capacity due to their large porous microstructures with High Specific Surface Area (SSA) and low mass density [194].

Carbon-based storage uses activated carbon (AC), graphite, fullerene, and carbon nanostructures. Activated carbon is a form of processed carbon that includes amorphous carbon and graphite crystallites. Hydrogen adsorption in these materials is strongly dependent on SSA and pore volume [195]. Graphite is one of the four sp^2 ordered carbon allotropes. Hydrogen is stored in its molecular form through adsorption by Van der Waals forces. From this element arise the porous graphite nanofibers (PGNF) that present an SSA of $1400 \text{ m}^2\text{G}^{-1}$ and a total pore volume of $2 \text{ cm}^3\text{G}^{-1}$ [196], [197].

Fullerene is carbon molecules with a rolled layer of graphene. They can take the form of spheres, ellipsoids, or tubes. They are formed when carbon vaporizes, mixes with inert gas, and slowly condenses [196], [198]. Nanostructures are classified into Carbon NanoTubes (CNT) and carbon nanofibers (CNF). CNT is formed when metallic catalysts are included in the fullerene process with multiple graphene sheets [199]. CNF is graphite platelets, and they are formed in the application of hydrocarbons using nickel catalysts and iron-based alloys [200].

Metal-Organic Framework

Metal-organic frameworks (MOF), also known as porous coordination polymers (PCP), are porous materials built from metal-containing nodes and are also organic linkers [201]. MOFs have ultra-high porosity and huge internal surfaces, which extend beyond $6.000 \text{ m}^2/\text{g}$ [202]. Together with the

extraordinary degree of variability for both the organic and inorganic components of their structures, they are attractive for storing gases such as hydrogen and methane [203].

3.6. Hazard and safety of hydrogen

Hydrogen is odorless, colorless, and nontoxic [203]–[205]. Its density is $0.0899 \text{ kg}/\text{m}^3$, and the boiling point is 20.39K [206], [207]. Hydrogen has a minimum ignition energy (0.017mJ) and a high heat of combustion of approximately $142 \text{ kJ}/\text{gH}_2$ [208].

One of the most significant risks when using hydrogen is its excellent permeability through different materials, leading to different unique methods for specific applications [153]. As has already been discussed in this document, hydrogen has good combustible and explosive properties. For this reason, it is essential to maintain specific safety parameters and continuous control when having any application related to this element [209]. An important aspect is to maintain good explosion ventilation in the work building [210].

Cao *et al.* propose a spherical ventilation system [211], which considers flame propagation, effects of temperature, and pressure in the ventilation. It evaluates the danger from the explosion ventilation based on the effects of temperature and pressure. In addition, another significant factor has a good ignition and explosion suppression system in the event of faults [211]–[213].

Another fault that can occur is filtration through containers or pipes due to its small molecular size [214]. Consequently, hydrogen sensors are essential for continuous monitoring and detection of leaks during transport, storage, and any application [215].

Lee *et al.* present a chemochromic sensor used to detect hydrogen leaks at room temperature through electrostatic spray deposition of a solution of Pd and W_3O_3 . The sensor presented has a response time of 15s, when hydrogen levels decrease by 1% at room temperature. In the same way, the sensor can be reversible, allowing it to return to normal when being in contact with the air again [216]. Semiconductor gas-hydrogen sensors, based on metallic oxides, have been implemented to a great extent to detect hydrogen gas [217].

Zhou *et al.* present a sensor for the detection of hydrogen in the gaseous state. It is highly sensitive and manufactured using microelectromechanical systems [218]. The sensor has a quartz resonator, with an operating frequency of 165MHz, accompanied by a 200nm palladium film. The sensor operates wirelessly, exciting and detecting the resonator's vibration, and uses non-contacting antennas. Research results show that the sensor has a high level of sensitivity, allowing it to detect leaks even with humidity in the air at room temperature.

Concerning security, Tolia *et al.* simulate the hydrogen release diffusion behavior and identify the minimum safety distances; that must implement to minimize the adverse effects in cases of an explosion at hydrogen stations [219].

4. Discussion

Hydrogen requires improved production, storage, and end-use to improve process efficiency and sustainability and design economically viable business models. The cost of hydrogen storage systems is higher than that of petroleum fuel storage; the most significant challenges are increasing the efficiency, durability, and cost of materials and components.

Technologies for hydrogen storage are under investigation, and compressed storage is the most developed.

However, metal hydrides are a potential alternative due to their absorption and kinetic properties.

On the other hand, fuel cell systems are the most versatile technology, but they must be cost-effective. The most critical challenges are reducing costs and improving durability; The research seeks to identify and develop new materials to reduce costs and extend the component's useful life.

5. Conclusion

The work presented an evolution of hydrogen research as an alternative to fossil fuels; it described and compared the technologies used to produce hydrogen. Finally, it presented the storage technologies, the review allowed for the identification of challenges.

The production and storage of hydrogen require high energy consumption for the chemical thermodynamic processes involved due to exothermic reactions. The review introduced hydrogen as an alternative fuel, which has improved its viability due to the integration of renewable energy; storage could be used when there is a shortage of energy to meet the demand. The hydrogen's simplicity and

nature are significant drawbacks due to its high reactivity and the risks associated with its volatility. It is changed to a liquid state in storage to reduce the risk.

The cost reduction in the production, storage and transport chain is related to the raw material and energy source used, renewable energies being an attractive method due to sustainability. Transportation remains a critical point due to the high risks. Hydrogen has gained acceptance for use in automobiles, using fuel cell technology, where storage is its most significant challenge due to the amount that can be stored. Like fossil fuels, infrastructure and investments are required to make commercialization viable.

Research suggests that the process's economic and energy efficiency needs to improve, integrate renewable energies, use raw materials with lower economic/energy value, and give economic value to the by-products of the processes used. The most significant challenges are the business models and the material sciences of the materials and components.

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