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Review Article

Green hydrogen: a state-of-the-art review of generation technologies for the decarbonisation of the energy sector

Hidrógeno verde: revisión del estado del arte de las tecnologías de generación para la descarbonización del sector energético

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Abstract

The Growing concern about environmental problems and the depletion of fossil fuels has generated interest in the development of technologies that allow us to produce electricity without having to pollute the environment. Hydrogen has become the main candidate to replace fossil fuels in the last decades, having the possibility to be used as a primary fuel to be burned in combustion engines, or as an energy vector for the production of energy by means of fuel cells, becoming an attractive fuel due to its high energy density and that does not emit any type of pollution. Currently, hydrogen is not produced for energy purposes, but for industrial purposes, so the objective of this article is to learn about the predominant forms of hydrogen production, which use fossil fuels as raw materials, and to study the new technologies developed to obtain decarbonised hydrogen intended for the energy sector, investigating known technologies such as electrolysis, getting to compare the functioning of the existing types of electrolysis and describing other novel forms such as those that make up the production of biological hydrogen or bio-hydrogen, getting to analyse different research with the aim of presenting the results in fermentative methods, the use of microalgae and the microbial electrolysis cell, explaining the main challenges and analysing the characteristics and the research status into these forms of production.

Resumen

La creciente preocupación por los problemas ambientales y el agotamiento de los combustibles fósiles ha generado un interés hacia el desarrollo de tecnologías que nos permitan producir electricidad sin necesidad de contaminar el medio ambiente. El hidrógeno en las últimas décadas se ha convertido en el principal candidato para reemplazar a los combustibles fósiles, teniendo la posibilidad de poder utilizarse como combustible primario para quemarse en motores de combustión, o como vector energético para la producción de energía por medio de las pilas de combustible, convirtiéndose en un combustible atractivo por su alta densidad energética y que no emite ningún tipo de contaminación. En la actualidad, el hidrógeno no se produce con fines energéticos, sino industriales, por ello, el propósito de este artículo es conocer las formas predominantes de producción de hidrógeno, que usan combustibles fósiles como materia prima y estudiar las nuevas tecnologías desarrolladas para obtener hidrógeno descarbonizado destinado al sector energético, investigando tecnologías conocidas como la electrólisis llegando a comparar el funcionamiento de los tipos de electrólisis existentes y describir otras formas novedosas como las que componen la producción de hidrógeno biológico o bio-hidrógeno, llegando a analizar diversas investigaciones con el objetivo de exponer los resultados en los métodos fermentativos, el uso de microalgas y la celda de electrólisis microbiana, exponiendo los principales desafíos y analizando las características y el estado de investigación de estas formas de producción.

Keywords: hydrogen production, green hydrogen, bio-hydrogen, water electrolysis, alternative energies, dark fermentation, photofermentation, biophotolysis, fossil fuels.

Palabras clave: producción de hidrógeno, hidrógeno verde, Biohidrógeno, electrólisis del agua, energías alternativas, fermentación oscura, fotofermentación, biofotólisis, combustibles fósiles.

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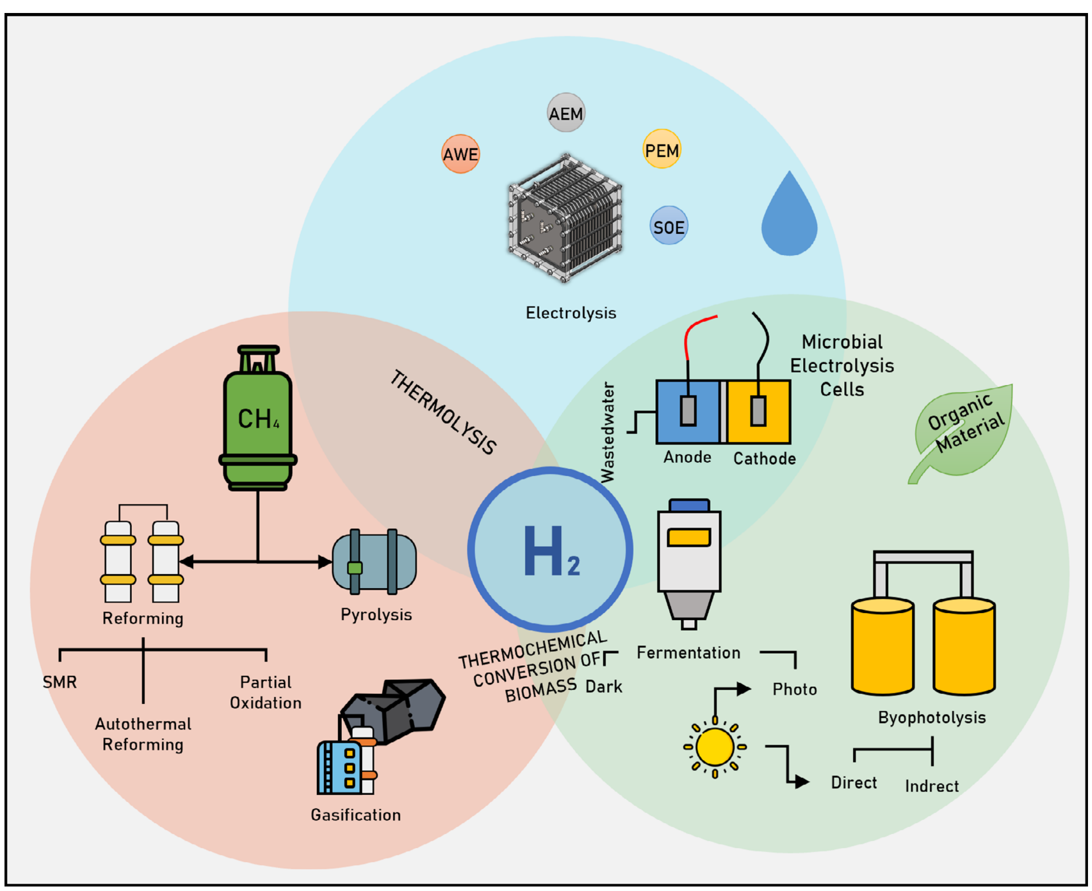
Why was it conducted?:
The manuscript is intended to address and explore the various hydrogen generation routes and technologies that have evolved up to the present day. Its central objective is to provide a comprehensive overview of the current status and trends in the development of efficient and clean hydrogen production technologies, especially in the context of the energy transition towards more sustainable sources. This approach is justified by the need to find energy alternatives that reduce greenhouse gas emissions, given that current energy production, based on fossil fuels, is a major contributor to greenhouse gas emissions. Furthermore, the manuscript seeks to examine both established and emerging technologies, with a special emphasis on green hydrogen production, to help mitigate climate change and move towards a cleaner and more sustainable energy matrix.

What were the most relevant results?
The most relevant results indicate that hydrogen is positioned as an energy matrix with great potential to replace fossil fuels. Current research focuses on electrolysis and biohydrogen production as the main mechanisms for obtaining hydrogen without environmental pollution. Different methods have been identified in the biohydrogen field, adapted to different microorganisms and feedstocks. Specific challenges include the design of suitable reactors, the need for glucose-rich substrates and the control of bacterial growth for fermentative processes, as well as the exploration of genetic engineering solutions for biophotolysis.

What do these results contribute?
These results provide a clear direction for energy research by identifying electrolysis and biohydrogen production as key technologies for clean hydrogen generation, underlining the importance of further developing these solutions to reduce dependence on fossil fuels. Furthermore, by analysing the technical challenges in biohydrogen production, such as reactor design and limitations in biophotolysis, they provide a basis for focusing research on improving the efficiency of these processes. They also highlight the need to develop adequate infrastructure for hydrogen storage, transport and distribution, which is crucial for its integration into existing energy systems. Taken together, these findings not only drive the development of more sustainable technologies, but also guide the formulation of energy policies that promote the transition to a hydrogen economy.

Graphical Abstract



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Introduction

The current energy demand is mostly satisfied through the use of resources such as natural gas, coal and oil. This form of energy production is responsible for a considerable amount of greenhouse gas (GHG) propagation, representing 66,667% of global emissions, as reported by the United States Environmental Protection Agency (EPA) (1). Just during 2021, the release of carbon dioxide (CO_2) linked to power generation showed an increase by 6%, reaching a record of 36.3 billion tonnes (2,3). This increase is largely due to population growth and the constant exploitation of fossil fuels, which has resulted in a 68% increase in CO_2 and anthropogenic carbon concentrations in the atmosphere (4).

For these reasons, efforts have been made to find other ways to generate energy with zero carbon emissions, an energy resource that has had some relevance in recent decades has been hydrogen, its importance is given by the ability of the element to store energy in relation to its mass, which is estimated to be around the 143MJ/Kg (5–7), this energy density is the highest among known fuels. Another important factor is the versatility of this element to generate clean energy, either by burning it directly (8) or by using it as a fuel or producing energy using fuel cells to produce electricity (9), this element is considered environmentally friendly when generating energy, however, its carbon neutrality is based on the way in which the hydrogen is produced (10).

For many years, hydrogen has played a crucial role in the industrial sector, especially for synthesising ammonia and in the manufacture of fertilisers (11), driving the development of specialised technologies for its separation from fossil resources, the development of these technologies being due to the fact that hydrogen is not isolated in nature (12). Over the years, different procedures have been explored to obtain hydrogen isolated from these compounds, based on the type of raw material used: fossil resources such as oil, coal and natural gas, or renewable resources such as water and biomass (13,14).

In Latin America, there has been a growing interest in hydrogen production and storage at the global level. This is partly due to the fact that several countries in the region have a low cost of clean energy as a result of the energy transition towards a cleaner energy matrix, such as Brazil and Colombia, which generate a significant proportion of their energy through hydroelectric sources. (15–17). In addition, there has been interest in building green hydrogen production plants in the region, an industry that could generate multiple benefits, including job creation, increased affordability of energy services for sectors that do not yet have them, climate change mitigation and poverty reduction (18). Among the countries in the region, Chile has developed a greater emphasis with two projects under development, countries like Colombia are in a state of analysis for the development of a roadmap and in Costa Rica an alliance between public and private companies has been consolidated with the aim of generating supply and demand for this resource (18–20).

The main objective of this research is to address the different hydrogen generation routes that have evolved up to the present day. On the one hand, the consolidated technologies for hydrogen production at industrial level will be reviewed. On the other hand, emerging technologies that allow hydrogen to be generated in a sustainable way, without producing environmental pollution, will be explored, with the main emphasis on understanding the operation of technologies to produce green hydrogen. In order to develop this objective, different research articles will be examined that present experimental results of the various technological alternatives for hydrogen production. In this way, the study wants to provide a comprehensive overview of the current status and trends in the development of efficient and clean technologies for hydrogen generation, in order to contribute to the energy transition towards more sustainable sources.

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Methodology

In this section we will detail the process we carried out to perform the bibliographical tracking, which was crucial on identifying relevant studies for our state-of-the-art article. The bibliographic sources selected for data collection are the following: Scopus, Science Direct, Google Scholar, Web of Science, Springer Link,Taylor & Francis.

These platforms greatly facilitate the filtering of research articles, allowing us to limit the search to review and research articles, as well as by year. We developed search equations employing Boolean operators (AND, OR, NOT), using the following keywords: "Hydrogen production" "Fuel cells" "Green hydrogen" "Technologies for hydrogen production" "Electrolyzers" "Electrolytic cells" "Biohydrogen" "Pyrolysis" "Natural gas" "Gasification" "Autothermal reforming" Thermochemical.

The use of these equations allowed us to significantly reduce the number of documents retrieved, limiting it to less than 50 per search equation. This strategy streamlines the review process and ensures a more accurate selection of relevant documents. Regarding the inclusion criteria, we prioritized documents from the last 10 years and in English language. Initially, we included a large number of review articles to obtain an overview of all production technologies. Subsequently, we focused our attention on individual investigations of each technology, with the objective of going deeper operational aspects, efficiency, advantages and disadvantages of each one, this approach allowed us to obtain a detailed and complete knowledge of each technology considered. Thus, the research structure was organized according to the different hydrogen production technologies, such as electrolysis, gasification and biological production, among others, allowing a systematic analysis of the various approaches and focus used in each area, as well as the identification of emerging trends and promising areas of research.

Hydrogen generation technologies

Over the years, global demand for hydrogen has experienced a remarkable increase, driving a significant increase in hydrogen production. According to recent data, global hydrogen production will amount to 90 million tonnes (Mt) in 2020 (21), while by 2021, this figure rise to 94 million tonnes (22). In addition, over the course of 2022, total hydrogen production will increase by a further 11.1 million tonnes per year. (23). It's important to highlight that, most of this growing hydrogen production continues to rely exclusively on fossil resources resulting in the release of approximately 900 Mt CO_2 (22,24).

In general, these technologies are classified using a colour coding system, in order to facilitate the distinction and description of the various production processes (25,26). Figure 1 shows the colour coding of hydrogen, with their respective production processes and the raw materials most commonly used in the generation of hydrogen, these are classified into different categories according to the production processes used, which results in a wide range of colours that reflect their origin and environmental impact, which are, grey hydrogen, blue hydrogen and green hydrogen are the main variants, each with their particularities (27,28).

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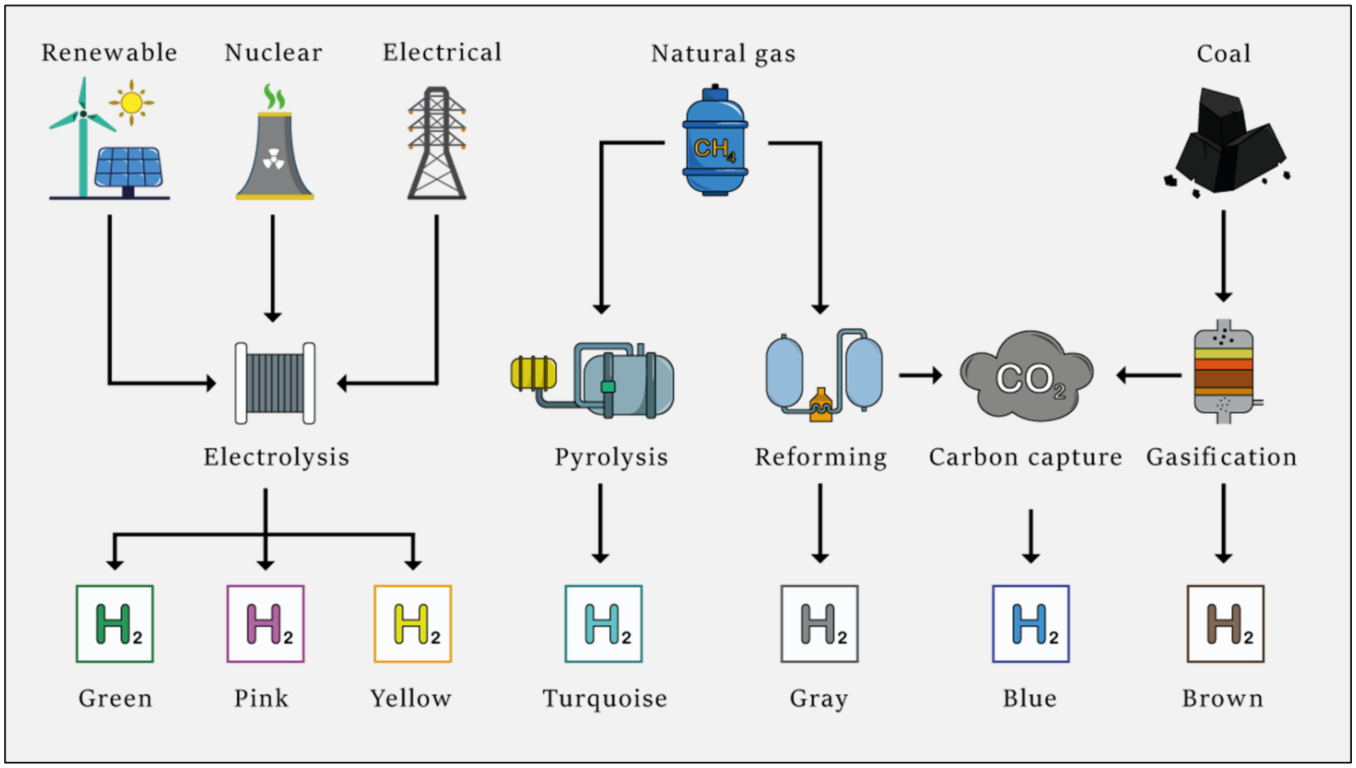

Figure 1. Categorisation of hydrogen according to production methods. **Source:** Authors.

Firstly, grey hydrogen is obtained by reforming hydrocarbons, especially methane, through thermochemical processes (29), being the cheapest method, but with high CO_2 emissions (9,5 $KgCO_2/KgH_2$). Blue hydrogen incorporates carbon capture and storage technologies to mitigate emissions, reducing them to between $KgCO_2/KgH_2$, although it still relies on non-renewable resources (30). In contrast, green hydrogen is produced by electrochemical processes, such as the electrolytic dissociation of water, using electricity from sustainable sources such as wind, solar or hydroelectric power, with low emissions (31,32) (8,2 $KgCO_2/KgH_2$ in Colombia) (33). This colour classification allows the identification of the origin and environmental footprint of each type of hydrogen, encouraging informed decisions and a more sustainable approach to energy management (34,35).

Production from fossil fuels

So far, hydrogen production has been mostly linked to the use of fossil fuels as the main raw material, which are mainly composed of hydrocarbons characterised by large amounts of hydrogen and carbon in their molecular structure, the physical state at room temperature of these fuels (coal, oil and natural gas) varies depending on the amount of carbon present (36). The procedures for obtaining hydrogen focus on the decomposition of the bonds between hydrogen and carbon in these hydrocarbons, representing one of the most widely used methods for the production of hydrogen from fossil fuels today (37).

Hydrocarbon reforming

Currently, the predominant technological route for hydrogen generation on a global scale is hydrocarbon reforming, mainly methane, accounting for about 48% of total production (38). In this field, three different approaches have been established: steam reforming (39), partial oxidation and autothermal reforming (40),(41).

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Firstly, steam methane reforming (SMR) involves reacting methane with steam at temperatures in the range of 700 and 1000°C and moderate pressures between 3 and 25 bar (40–42), where this reaction takes place in the presence of a metal catalyst composed mainly of nickel. The endothermic reaction is presented in Equation 1, separating and recombining the methane molecules (CH4) and water (H2O), to generate carbon monoxide and hydrogen (43).

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \text{Ec. (1)}$$

Subsequently, using the gas-water shifting technique, convert CO to CO_2 and release more hydrogen, as shown in Equation 2 (44), this reaction is considered exothermic because it has a standard enthalpy reaction of -41,17 kJ/mol, but this heat release is not adequate to maintain the temperature required in the reforming reaction, and some of the natural gas is used as fuel to meet the temperature demand.

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \text{Ec. (2)}$$

Subsequently, the aim is to purify the hydrogen by separating the CO_2 and other pollutant gases, finally obtaining high purity hydrogen (44). Although this process is considered the cheapest option, the hydrogen produced is categorised as “grey hydrogen” because of its high direct CO2 emissions, producing 9,5 $KgCO_2/KgH_2$ (37,39), it is feasible to implement carbon capture and storage (CCS) systems that enable the cost-effective and low-emission production of short-term hydrogen called “blue hydrogen” (45).

Another process used in hydrocarbon reforming is partial oxidation, this process consists of the incomplete oxidation of the hydrocarbon by oxidising the carbon and leaving the hydrogen free, as can be seen in equation 3, the process consists of injecting a stream of air or oxygen into a reactor containing the hydrocarbon (37), where only carbon is oxidised leaving CO and releasing H_2.

$$CH_4 + \tfrac{1}{2} O_2 \rightarrow CO_2 + 2H_2 + (\text{calor}) \quad \text{Ec. (3)}$$

The CO produced is subjected to water and gas displacement to obtain additional hydrogen, as in equation 2 (46); in addition, the reaction rate exceeds that of steam reforming, and this makes it possible to use a reactor of smaller dimensions (47), a remarkable aspect is its ability to handle the presence of sulphur in the feedstock without the need for catalysts, although in cases of low sulphur concentration in the feedstock, catalysts can be used to reduce the reaction temperature and facilitate thermal control of the process (44).

Finally, autothermal reforming is presented, this process combines partial oxidation and SMR in a single reactor to optimise the thermal equilibrium, taking advantage of the energy generated by the partial oxidation to drive the SMR reactions (48). In this process, oxygen and water vapour are introduced into the reactor simultaneously, allowing precise temperature control by adjusting the air to fuel ratio, the energy efficiency of this process is relatively high as it demands less energy than steam reforming, but with a lower efficiency than SMR, although higher than partial oxidation (42,49,50).

Pyrolysis of hydrocarbons

The pyrolysis process is a thermochemical reaction involving the thermal decomposition of hydrocarbon molecules by the application of heat in an oxygen-depleted environment, getting hydrogen and carbon as expressed in equation 4 (45,51). The products derived

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from this transformation are affected by various elements, such as the type of fuel used, the pressure and temperature conditions during operation, as well as the time the material spends in the processing unit (42).

$$C_nH_m \rightarrow nC + ½\, mH_2 \quad \text{Ec. (4)}$$

During this procedure, hydrocarbon molecules, such as methane (CH_4), ethane (C_2H_6), propane (C_3H_8), among others, which are found in fossil fuels, are subjected to high temperatures, generally in the range of 700 to 900°C (52), as thermochemical separation occurs from heavy residual fractions with boiling points above 350 °C, it makes sense that hydrogen production is carried out in two steps, hydro-gasification as described in equation 5, where methane is subjected to hydrogen-rich gas and water vapour to convert it into syngas (53).

$$C_nH_m + (2n - m/2)\, H_2 \rightarrow nCH_4 \quad \text{Ec. (5)}$$

This leads to the breaking of the chemical bonds connecting carbon and hydrogen atoms, resulting in hydrogen and solid carbon in the form of coke as in equation 6 (50).

$$CH4 \rightarrow C + 2H_2 \quad \text{Ec. (6)}$$

The hydrogen produced can be separated and purified much like the last two phases of the SMR, on the other hand, the solid carbon or coke that is formed can be gasify with steam to produce more hydrogen, making use of the displacement reaction as in equation 7.

$$C + 2H_2O \rightarrow CO + H_2 \quad \text{Ec. (7)}$$

The pyrolysis process is notable for its ability to prevent the generation of carbon dioxide (CO2), making it a low-emission technology for the production of hydrogen from fossil fuels (49). Although this process requires higher temperatures in contrast to SMR, it has the advantage of dispensing with expensive catalysts (52).

Coal gasification

Gasification consists of converting a solid material into combustible gas by means of a thermochemical process that makes it possible to obtain synthesis gas from materials such as biomass or coal (54). Synthesis gas consists of carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), methane (CH_4), these gases can be used as fuel on their own, or can be separated to produce different chemical products (51).

Gasification is carried out in a special reactor, known as a gasifier, in which feed materials are heated to high temperatures ranging from 700 to 1500°C, usually in an oxygen deficient environment limited to 10 to 50% of stoichiometric (55). This process allows the feedstock to be thermally decomposed and converted into gas, instead of being burnt completely as in conventional combustion (56,57).

Gasification is presented as an alternative to conventional coal combustion, offering notable advantages such as higher efficiency for power generation and a significant reduction of GHGs (58). However, it should be noted that this process still involves considerable costs and requires specialised equipment, which restricts its application on a large scale (50).

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Production from renewable resources

Conventional hydrogen production from fossil fuels, although efficient, generates high CO_2 emissions. (59). However, cleaner technologies have been developed that make use of renewable energy resources such as sunlight, electricity and biochemical processes (60). These production routes, which include electrolysis of water, photolysis with direct solar energy and biomass conversion through biological and thermochemical processes, allow clean hydrogen to be obtained using raw materials such as water and biomass. (61,62). This approach not only reduces pollutant emissions, but also contributes to the transition towards a more sustainable and environmentally friendly energy matrix (63).

Water division

Water splitting emerges as an extremely important production route, since it has been consolidated in the production of hydrogen, based on breaking down water molecules through specialised water splitting processes such as electrolysis, thermolysis and photolysis (62,63).

Thermolysis

Linares and Moratilla define thermolysis as “the extraction of hydrogen from the molecule that contains it through the application of heat; we speak of thermolysis when the heat comes from an external source”.(64), these authors call thermolysis, “when the heat comes from an external source”. For water splitting to occur, it is necessary to bring the Gibbs free energy (ΔG) to zero, which is necessary for the decomposition of water to take place. However, the main limitation of this way of producing hydrogen lies in reaching the required level of Gibbs free energy, for which temperatures around 2500 K are necessary (65). The thermodynamic properties of water decomposition reactions under standard conditions hinder the efficient realization of direct thermal synthesis at lower temperatures (66).

Electrolysis

Electrolysis is based on the splitting of a chemical compound into its most basic components by the use of electric current, the basic reaction of electrolysis is found in equation 7. Lladó & Jubbert. (67), explain how the combination of Gibbs free energy and thermal energy satisfies the theoretical energy demand, which is responsible for the dissociation of the water molecule. Also, the theoretical voltage that must be applied for water splitting to occur is 1.23V as explained by Fabregas & Huertas. (65), this value is obtained by linking the free energy to the concept of useful work, applying the first law of thermodynamics (65,67,68) .

$$H_2O + \text{Electricidad } (237{,}2 \text{ kJ} \cdot \text{mol}^{-1}) + \text{Calor } (48{,}6 \text{ kJ} \cdot \text{mol}^{-1}) \rightarrow H_2 + \tfrac{1}{2} O_2 \quad \text{Ec. 8}$$

It should be noted that this technology has been developed and used on a commercial scale (10,69), its constant development has allowed the introduction of four types of electrolysis, which are differentiated by their operating parameters and materials of construction, where (i) alkaline water electrolysis, (ii) anion exchange membrane (AEM) water electrolysis, (iii) proton exchange membrane (PEM) water electrolysis and (iv) sodium oxide water electrolysis, where the operating principles are the same for each of the cases

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(62), table 1 shows the different existing technologies, their operating conditions and the advantages and disadvantages they present.

Table 1. Performance of different electrolysis technologies.

Type of electrolysis	Electrolyte	Temperature (°C)	Voltage (V)	Current density (A/m²)	Catalyst	Efficiency	Ref.
Alkaline (AWE)	KOH, NaOH	60 - 80	1,4 - 3	0,2 – 0,8	Nickel, iron and cobalt	50% – 71%	(69–71)
Anion Exchange (AEM)	DVB polymeric support with KOH/NaOH 1 M	20 - 80	1,4 – 2	0,2 – 2	Noble metals such as platinum	57% - 59%	(62)
Proton Exchange (PEM)	Polymer solid electrolyte (PFSA)	60 – 80	1,4 – 2,5	1,4 – 2,5	Noble metals such as platinum	50% - 83%	(72–74)
Solid Oxide (SOE)	Yttria-stabilised zirconia (YSZ)	800 - 1000	1 – 1,5	1 – 1,5	Noble metals	89% (Laboratory)	(75,76)

Current research on water electrolysis has focused on increasing the efficiency of the process, which is hampered by poor kinetics due to the transfer of four electrons in the oxygen evolution reaction (OER), which is slower than the hydrogen evolution reaction (HER), which needs only two electrons (77). Song et al., provides a comprehensive review of advances in the synthesis, catalytic mechanisms and applications of oxygen evolution catalysts (OER), highlighting the need for efficient and low-cost catalysts. Several types of promising catalysts are explored, including transition metal hydroxides and oxides, transition metal phosphates, complex metal composites and metal-organic materials (MOFs), while highlighting the importance of understanding and optimising the reactivity, stability and scalability of these catalysts through various characterisation techniques, continued research into the development of economical and efficient electrocatalysts is essential to achieve an affordable and sustainable water electrolysis process, as well as for the large-scale production of hydrogen and the efficient conversion of solar energy into chemical fuels (78).

For these reasons, the field of electrolysis has remained focused on the development of low-cost electrocatalytic materials, which allow for increased energy efficiency, safety, durability, operability, portability and high installation and operating costs (68). Angeles-Olvera et al. (79), carried out a review of nickel-based electrocatalysts as an abundant metal on earth, where they point out that it is key to elucidate the reaction mechanisms and the role of heteroatoms, defects, dopants and nanostructures, and it is also important to design synthesis and characterisation techniques that are accessible at an industrial level.

Chen et al., (80) extends this perspective by examining various renewable energy sources, such as urea, hydrazine and biomass, for the sustainable production of hydrogen through water electrolysis. The advantages of urea oxidation reactions in alkaline media, the advantageous use of hydrazine as an environmentally friendly and economical fuel, and the possibility of harnessing biomass with pre-treatment strategies are explored. Overall, the article highlights the importance of diversifying renewable energy sources, offering

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opportunities for more efficient and economical technologies that reduce dependence on fossil fuels and mitigate environmental impact.

On the other hand, the article written by Liu (78), addresses the need to develop affordable electrocatalysts for hydrogen production through proton exchange water electrolysis (PEMWE), presenting alternatives not based on platinum group metals (PGMs), platinum, palladium, rhodium, rhodium, ruthenium, iridium and gold, looking for to replace them with carbon and boron nitride-based compounds. This research highlights the importance of addressing challenges in the design of non-PGM based catalysts, proposing solutions such as atomic layer deposition and the injection moulding technique. Finally, the economic analysis suggests cost efficiency in the medium and long term with the implementation of these catalysts.

In the same way, Angeles-Olvera et al., (79) provide a detailed review on the use of nickel catalysts for water electrolysis, highlighting the importance of developing sustainable and affordable electrocatalysts. Specific types of nickel catalysts are discussed, such as nanotubes, aerosols, alloys and nanoparticles, which have demonstrated efficiency and stability. The article emphasises the need to determine the catalytic activity under standard conditions to compare and evaluate the efficiency of these materials.

Biomass production

Biomass has attracted a lot of attention in hydrogen production because it is a feedstock that can be obtained from biological resources and generating itself naturally, in that way, biomass becomes a renewable resource that can be produced in a sustainable way (81). A crucial aspect is the possibility of using thermochemical processes to extract hydrogen from fossil fuels; however, using biomass has the advantage of significantly lower environmental impact (61). Likewise, hydrogen production can also be carried out by biological processes, which offer a number of benefits. However, it is essential to optimise these processes and improve energy efficiency to maximise their potential (82).

In contrast to the previously described methods, biological approaches allow the use of various types of organic waste, thanks to the activity of different groups of microorganisms. Figure 2 shows all the production processes for producing hydrogen by means of microorganisms, this form of production makes it possible to reduce CO_2 emissions, in addition to the efficient elimination of a large amount of waste and residual biomass.

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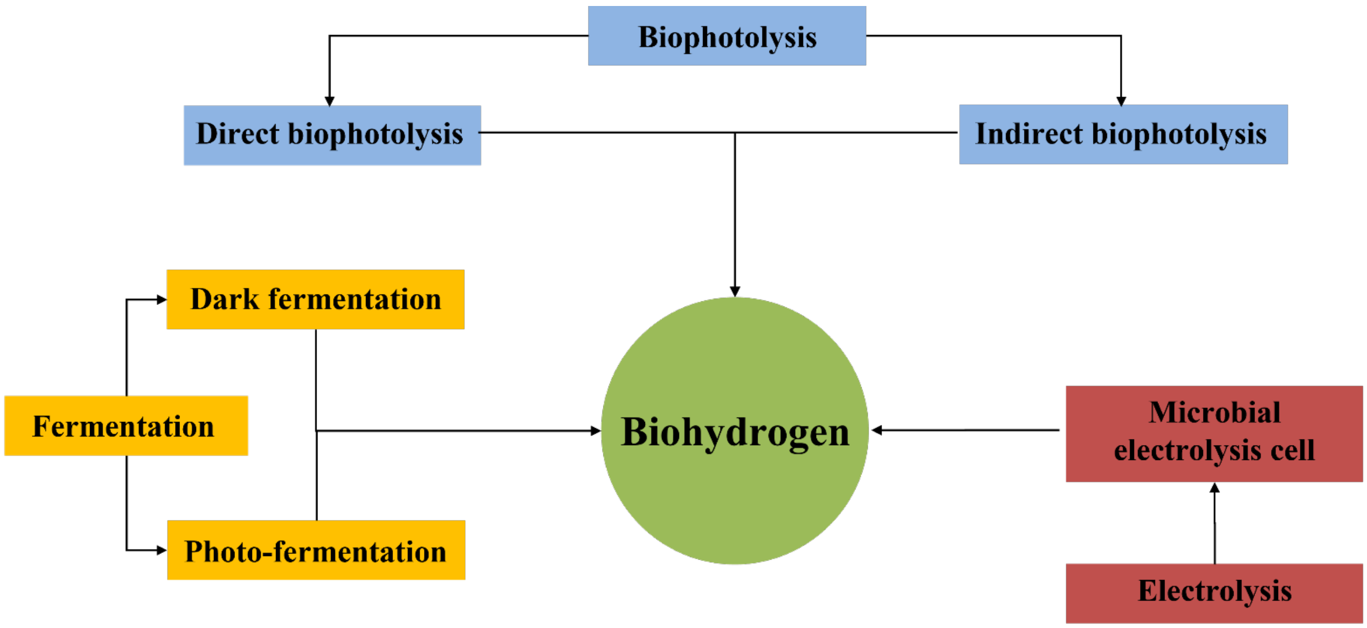

Figure 2. Various biological hydrogen production processes. **Source** (6)

Fermentation

In general, fermentation processes use microorganisms to produce alcohols, acetone, H_2 and CO_2 from organic substrates, depending on the type of microorganism, the type of fermentation, as there are groups of bacteria that carry out fermentation in the absence of light, this variety of bacteria gives rise to two types of fermentation, dark fermentation (DF) and photofermentation. table 2 shows experimental research on the production of hydrogen by means of these fermentation processes (83).

Table 2. Experimental investigations on hydrogen production by fermentative processes with respect to different substrates, pH and microorganism.

Microorganism	Process	Substrate	Substrate	pH	Production	Ref.
Mixed saccharolytic crops	Dark Fermentation	Distillery waste water (DWW)	40g/L	6,5	0,8-1,6 L H_2/L	(84)
Rhodobacter sphaeroides B-3059	Photofermentation	Distillery waste water (DWW)	40g/L	7	17,6 L H_2/L	
Rhodospirillum rubrum, Rhodobacter capsulatus and Rhodopseudomonas palustris	Photofermentation	Potato starch	Not specified	6 - 7 - 8	45mL/L*h	(85)
Photosynthetic bacteria HAU-M1	Photofermentation	Alfalfa	31,23g/L	6,95	12,5mL/h	(86)
Rhodobacter sphaeroides 158 DSM	Photofermentation	Brewery wastewater pretreated with banana peel	50% treated	Not specified	408,33 ml/h	(87)
Mixed bacterial cultures	Dark Fermentation	Food waste	10g/L	7 ± 3	74,91ml/g	(88)

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Mixed crops	Dark Fermentation	Hydrolysed sugar beet pulp	Not specified	5,5	36dm³/Kg	(89)
Bacterial strain TERI S7	Dark Fermentation	▪ Xylose ▪ Glucose ▪ Sucrose ▪ Sucrose ▪ Maize syrup solution ▪ Soluble starch	10g/L	7	▪ 1899 ± 15 ml/L ▪1725 ± 37 ml/L ▪ 1651 ± 43 ml/L ▪ 1581 ± 63 ml/L ▪ 1416 ± 41 ml/L	(90)
Mixed crop obtained from a water treatment plant	Dark Fermentation	Hydrolysed wheat residue	15g/L	5,0 - 6,0	Not specified	(91)

Firstly, dark fractionation (DF) decomposes biomass-based substrates or wastewater from industrial processes using groups of anaerobic bacteria in a light-free environment, which use sugars as an energy source, however, this form of production presents several challenges, Ren et al. (92), explains that the main challenges are in the construction of the bioreactor, the selection of the glucose-rich substrate and the inhibition of the substrate, it is also necessary to control the growth rate of the bacteria, as Wheelock Gutiérrez explains (49), since low production is related to a high proportion of acids and short-chain alcohols, causing pH reduction affecting the activity of the hydrogen-synthesising microorganism.

Photofermentation, on the other hand, employs photosynthetic bacteria that use light energy as a source of electrons under conditions of nitrogen and oxygen deficiency. In this process, these bacteria take the necessary carbon and electrons from the organic matter present in the substrate (49); an anaerobic medium is necessary, because H2 formation is due to the enzyme nitrogenase, fixing nitrogen and releasing hydrogen in the process, however, nitrogenase is inhibited in the presence of oxygen (93). Photofermentation presents a number of challenges, including bioreactor design, light availability, controlling variables such as substrate concentration, bioreactor pH, temperature and light penetration, all of them make photofermentation a complex process to operate with high hydrogen production costs (6,61,81,94).

Biophotolysis

Biophotolysis is a biological process that involves the use of light and organisms such as photosynthetic bacteria, microalgae and cyanobacteria, using the natural photosynthesis of these plants to break down the water molecule into hydrogen and oxygen by the action of two enzymes that are key to biophotolysis, hydrogenase and nitrogenase.(82,93,95). On the one hand, hydrogenase is responsible for the production of hydrogen from water, while nitrogenase is responsible for facilitating the fixation of atmospheric nitrogen, which can improve the yield of the process by providing essential nutrients for the micro-organisms, but these enzymes act differently for direct and indirect biophotolysis (81,96,97).

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Regarding the function of enzymes in each of the following, Nagarajan et al., (98), in his article explains, "direct biophotolysis occurs when photosynthetic electrons derived from water splitting are transferred via PS II, PS I and ferredoxin to hydrogenase under anaerobic conditions". As for indirect biophotolysis, Nagarajan et al. state that an external source of electrons required for hydrogenase action is obtained from "fermentative metabolism of stored carbohydrate reserves occurring under dark conditions" (98).

On the other hand, Kosourov et al., (99) explains that hydrogenase is involved in the reduction of electrons to hydrogen, harnessing the energy generated by photosynthesis and electron flow, making use of hydrogenase production to convert protons to hydrogen; for indirect biophotolysis, Kosourov et al. explain that the enzyme nitrogenase plays a crucial role in providing reducing agents derived from nitrogen fixation, which can be used as substrates in hydrogen generation.

In spite of the research that has been developed to understand the functioning of this process, there have also been several studies focused on the optimisation of the biophotolysis process, in table 3, some of them concentrate their efforts on the design of photobioreactors, also in the area of cellular genetics and experimentation with different types of microorganisms.

Table 3. Research in different areas of biophotolysis

Authors	Outline of the document	Reference
Schumann et al.	They focus on the use of hydrogenases to catalyse hydrogen production, emphasising hydrogenases as superior catalysts due to their higher catalytic rates and more efficient energy utilisation.	(95)
Kosourov er al.	It presents advances in the understanding of hydrogen metabolism and its impact on cellular bioenergetics, opening up possibilities for the development of hydrogen-producing cell factories with improved performance, as well as exploring the use of synthesised hydrogenase.	(99)
Kamshybayeva et al.	It studies the sensitivity of enzymes to oxygen and electron competition in different metabolic pathways, focusing on the limitations of hydrogen production at the industrial level, also using advances in genetic engineering and biotechnology, it explores solutions to enhance hydrogen production in cyanobacteria.	(100)
Kossalbayev et al.	Describes in detail the design features of photobioreactors and the conditions necessary to grow cyanobacteria optimally.	(101)
Bozieva et al.	Research on the possibility of hydrogen production by means of biophotolysis in different species of cyanobacteria. The strains Cyanobacterium sp., Dolichospermum sp. and Sodalinema gerasimenkoae IPPAS B-353 are studied, showing that the most efficient strains are Dolichospermum sp. under light anaerobic conditions and Sodalinema gerasimenkoae IPPAS B-353 in the dark.	(102)

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Microbial electrolysis cell

The microbial electrolysis cell (MEC) is related to the traditional electrolysis already described in previous sections, with the difference that it combines electrochemistry with bacterial metabolism (103), the organic material present in the anode chamber is degraded by the action of microorganisms, particularly an exoelectrogenic species, with the help of a small amount of electrostatic charge, the organic material is degraded producing electrons, CO_2 and protons.(+H) (103), where protons pass through the proton exchange membrane (PEM) into the cathodic chamber by the action of "hydrogenotrophic methanogenic micro-organisms and a small potential difference" (104) the reduction reaction takes place by pairing protons (+H) with electrons resulting in the production of hydrogen.

Interest in this form of hydrogen production has led to various designs for the configuration of MCE reactors. Murugaiyan et al,(105), conducted research focused on the study of different reactor configurations, together with the materials required for their construction. Jensen et al., (106) conducted a complete review focused on hydrogen production using (MEC), where an important point of this document is also the configurations and design of the reactors, giving importance to the anode and cathode materials; in table 4 there are different investigations making use of microbial electrolysis, testing different types of configurations, substrates, membranes, etc.

Table 4. Hydrogen production rate with respect to various substrates, materials and reactor type.

Reactor type	Anode	Cathode	Membrane	Substrate	Inoculum	Production rate	Ref.
Dual chamber	Metal oxide and graphene	nickel foam (NF)	Nafion	Waste water from the sugar industry (SWW)	Not specified	4,38 ± 0,11 mmol/L/D	(107)
Single chamber	Carbon fabric	molybdenum phosphide (MoP)	MEC without membrane	Acetate and glucose	Not specified	39,8 ± 1,9 L/L/D	(108)
Double chamber	graphite felt 5 mm thick	stainless steel mesh electrodes	Cation exchange membrane	Pig slurry	digestate from a local sewage treatment plant	0,2 LH^2/L^{-day}	(109)
Double chamber	Biochar	Grafito	Cation exchange membrane (CMI-7000)	synthetic water	Hoeflea sp. and Aquiflexum sp	0,89 ± 0,10 m^3 /day*m^3	(110)
Single chamber	carbon felt	Carbon paper cathode Nano-$Mg(OH)_2$/Gr	Non-specific	phosphate buffer	bacteria solution MFC	0,63 ± 0,11 m^3/ day*m^3	(111)

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Conclusions

The development and utilisation of hydrogen energy has become a relevant direction in the field of modern energy research, positioning itself as an energy matrix with great potential to replace fossil fuels in the future. Current research is focused on advancing various mechanisms for the production of hydrogen without environmental pollution.

On the one hand, electrolysis is at the forefront, a form of production that appears to be the main source of clean hydrogen when implemented with renewable energy sources. On the other hand, there are the various processes that include biohydrogen production. The last one is characterised by the use of renewable resources such as water and biomass, paving a way towards cleaner and more sustainable hydrogen production. Within the field of biohydrogen, different methods have been found to suit the microorganisms and the type of feedstock used. With the development of this research, we can analyse each of these different methods and what are the main challenges to be overcome in order to achieve competitive efficiency compared to traditional industrial production processes. Regarding fermentation processes, the challenges to be overcome focus on the design and construction of suitable reactors, the need for a substrate rich in glucose and the control of the bacterial growth rate. In biophotolysis, solutions must be explored in conjunction with genetic engineering to overcome the limitations of industrial production.

In addition, it is crucial to continue researching and developing more efficient and scalable technologies for hydrogen production from renewable sources in order to reduce dependence on fossil fuels and mitigate environmental impact. Furthermore, challenges such as hydrogen storage, transport and distribution, as well as the integration of these technologies into existing energy systems must be addressed for a sustainable energy transition.

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