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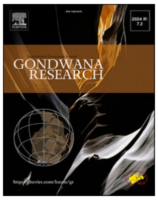

GR Focus Review

Hydrogen-powered future: Catalyzing energy transition, industry decarbonization and sustainable economic development: A review

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ABSTRACT

Hydrogen, particularly in renewable forms like green hydrogen and biohydrogen, is critical for decarbonization and sustainable development. This review provides a comprehensive overview of the multifaceted role of hydrogen and its versatility in industrial applications, energy storage, and transportation while addressing its potential to mitigate greenhouse gas emissions. The PRISMA methodology was applied, systematically analyzing over 25,000 publications and reports from 2017 to 2024, focusing on cutting-edge production methods like electrolysis and biomass conversion. Hydrogen production processes are explored, including water electrolysis, a clean method powered by renewable energy, and biohydrogen routes utilizing biomass and organic waste through thermochemical and biological conversions. These innovations align with global decarbonization targets, reducing emissions in hard-to-abate sectors like steel and aviation. The study also highlights hydrogen's evolving global market, with investments exceeding USD 680 billion and expanding project portfolios in Europe, North America, and Asia. Green finance, via tools like green bonds and sustainability-linked loans, is identified as essential for scaling hydrogen technologies. By integrating environmental, social, and governance (ESG) principles, hydrogen projects ensure socio-economic benefits, including job creation and reduced reliance on fossil fuels. Moreover, hydrogen is projected to reduce CO2 emissions by 6.5% by 2050, making it a key element in climate strategies. In conclusion, this study offers a thorough overview of hydrogen's role in achieving net-zero emissions. Its findings highlight the important interplay between technological innovation, market dynamics, and sustainable finance, providing actionable insights to aid in policy formulation and strategic decision-making. By harnessing hydrogen's potential, society can advance the energy transition and promote a resilient, low-carbon future.

1. Introduction

Climate change generates severe negative impacts on the world, both biophysical and economic, resulting in floods, the melting of the polar caps and rising sea levels, droughts, deforestation and increase in anthropogenic pressure, where the main driving force for behind these events are greenhouse gases (GHG). Population, economic growth and technological advances have recently been recognized as the main drivers of growing global energy demand, raising concerns about environmental sustainability, energy security and energy equity. Considering these serious situations, a set of international initiatives have been put forth in an effort to mitigate the effects of this phenomenon, the most important of which was the Paris Agreement adopted in December of 2015. According to this agreement, signatory countries committed themselves to maintaining the average global temperature less than 2 °C above preindustrial levels (Fernández-González et al., 2022; Karaca and Dincer, 2023; Ding et al., 2024).

Given the numerous challenges we face today, it is crucial to evaluate

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how renewable energy systems can contribute to sustainable development by producing carbon-free products like hydrogen (H_2). This clean energy source is gaining attention as a potential replacement for fossil fuels because it is abundant, nontoxic, and sustainable. Hydrogen has the highest energy content per unit of mass, with an upper calorific value of 141.9 MJ/kg and a lower calorific value of 119.9 MJ/kg, making it more efficient than any other fuel (Agaton et al., 2022; Dehane et al., 2022; Iacobuţă et al., 2022; Hossain et al., 2023).

The core concept underlying hydrogen production involves the need for both a feedstock source from which hydrogen is derived and an energy source to enable the extraction process. A wide variety of energy sources can produce hydrogen, using different technologies that lead to different levels of CO_2 emissions. H_2 produced from renewable sources, such as water and biomass, is an alternative to that generated from nonrenewable sources, such as natural gas, oil and coal, with a high carbon footprint. Renewable hydrogen includes green hydrogen and biohydrogen, which have different color codes, depending on the raw materials and energy sources used for production. Different technologies, such as thermochemical (e.g. biomass gasification), photocatalytic, biological and electrical (e.g. water electrolysis) methods, can be used for the production of H_2 (Kourougianni et al., 2024; Martínez et al., 2023; Alsaba et al., 2023; Yuan et al., 2023).

The main sources of raw materials for global hydrogen production are natural gas, crude oil, coal and water for electrolysis processes, which correspond to approximately 49 %, 29 %, 18 % and 4 %, respectively. This distribution highlights a significant dependence on fossil fuels. However, technological advances have enabled production through more renewable methods. Moreover, as the cost of renewable sources diminishes, the cost of production will also diminish, making hydrogen more accessible. H_2 can assist in reducing the dependence of a country on foreign oil imports and can strengthen local job markets, and the use of H_2 enables participation in the imminent global energy shift and the economic opportunities such a shift offers (Avargani et al., 2022; Riera et al., 2023; Hermesmann and Müller, 2022; Harichandan et al., 2023).

The significance of renewable hydrogen, especially that considered as green H_2, in the global energy landscape, lies in its potential to address several critical challenges faced by the world today, such as climate change, energy security, and sustainable development. Recognized for its capacity to generate clean energy, enable efficient energy storage, and facilitate seamless energy delivery, hydrogen offers a promising alternative to conventional energy systems due to its high energy density and clean combustion properties. When burned, hydrogen (H2) produces only water vapor. Its high energy content makes it a versatile solution for various applications, including transportation, industrial processes, and as a source of heating and power generation. Notably, producing hydrogen from renewable sources aligns perfectly with carbon neutrality goals. This approach provides a strategic way to enhance energy storage, stabilize the grid, and reduce carbon emissions, especially in sectors where electrification has been challenging. These changes also help improve air quality and public health. Additionally, the advancement and implementation of hydrogen technologies can drive innovation, foster economic growth, and create new employment opportunities (Marouani et al., 2023; Evro et al., 2024; Hassan et al., 2024).

Initiatives and innovations in the hydrogen industry are being driven by the current technological, economic, and political landscape. The decarbonization targets established in the Paris Agreement (2015) and emphasized at COP26 highlight the necessity for technological solutions to reduce emissions in sectors reliant on fossil fuels, such as transportation and energy-intensive industries. Additionally, new drivers have emerged, including the United Nations-led Net Zero Banking Alliance, which sets guidelines for the availability of credits based on investors' commitments to addressing the climate and carbon emissions of each financed project (Akhtar et al., 2023; O'Rourke et al., 2023; Rossi et al., 2023; Cavalcanti, et al., 2024).

This review article investigates the diverse role of renewable hydrogen in achieving net-zero emissions and driving the global energy transition. An overview of this fuel is provided, in addition to presenting the potential of hydrogen as a clean energy source, focusing on promising production methods, applications, and its ability to reduce greenhouse gas emissions. The article also explores the expanding hydrogen market and its significance within the hydrogen economy, highlighting its alignment with global climate objectives and sustainable development goals, in addition to green finance and aspects related to environmental, social, and governance (ESG) principles. In doing so, the study offers key insights into how renewable hydrogen can support the transition to a low-carbon economy and contribute to global sustainability.

2. Methodology

Literature reviews are crucial in synthesizing past research findings to effectively utilize the existing knowledge base and formulate future research perspectives, aiming to update knowledge on a specific research topic or a given fundamental question (Manrique-Escobar et al., 2022). The PRISMA methodology was used to construct the article in question, as it is a widely used approach to conduct systematic reviews and *meta*-analyses in a rigorous and transparent manner (Page et al., 2021; Silva et al., 2024). This approach allows for the use of keywords to clearly define the scope and limitations of the study. Through the four procedures of identification, screening, eligibility, and inclusion, PRISMA assists the author in finding the appropriate literature in accordance with the study's objectives (Albhirat et al., 2024).

Thus, the analysis comprised 25,733 publications, from articles and book chapters from databases such as ScienceDirect and Google Scholar. In addition, reports provided by international agencies such as the International Energy Agency, Hydrogen Council and International Renewable Energy Agency were also incorporated into the article. This review focused on studies published from 2017 to 2024, intending to present a multiple and updated view on hydrogen, as an important player for a sustainable energy transition. The main keywords used were hydrogen production, green hydrogen, biohydrogen, and decarbonization. The criteria defined for the inclusion of the literature were based on the robustness of each journal through experimental articles and reviews, book chapters, and relevant reports, and all should be open access. All duplicates and literature not relevant to the study were excluded, such as low-quality studies, articles in languages other than English, and materials with discussions different from the scope of the research; in addition, non-open access documents or with some types of restriction were also discarded. Therefore, after applying the criteria described above, 177 publications were reached for the construction of the review article. To better represent the ideas about the methodology, a PRISMA flow diagram was constructed, as shown in Fig. 1.

3. Overview of hydrogen

Hydrogen is the most abundantly available element on Earth and is mainly found chemically linked to water and hydrocarbons. However, its availability in the form of a stable diatomic molecule is very limited (less than 1 %). H_2 has the potential to function as a highly effective next-generation fuel, characterized by its zero emissions and elevated calorific value per unit of mass (Kumar et al., 2022).

The physical state of H_2 depends on certain pressure and temperature conditions, as shown in the diagram of hydrogen phases in Fig. 2. At low temperatures, H_2 is a solid, with density of 70.6 kg/m^3 at 11.15 K (−262 °C). At high temperatures, H_2 is a gas with low density, such as 0.08989 kg/m^3 at 273.15 K (0 °C) and 1 bar. The diagram also shows a region of liquid H_2 (solid line), the triple point (21.2 K) and critical point (32 K) (Massarweh et al., 2023).

Hydrogen diffuses through the air more rapidly than other gaseous fuels. Its molecular diffusion coefficient in air are in the range from

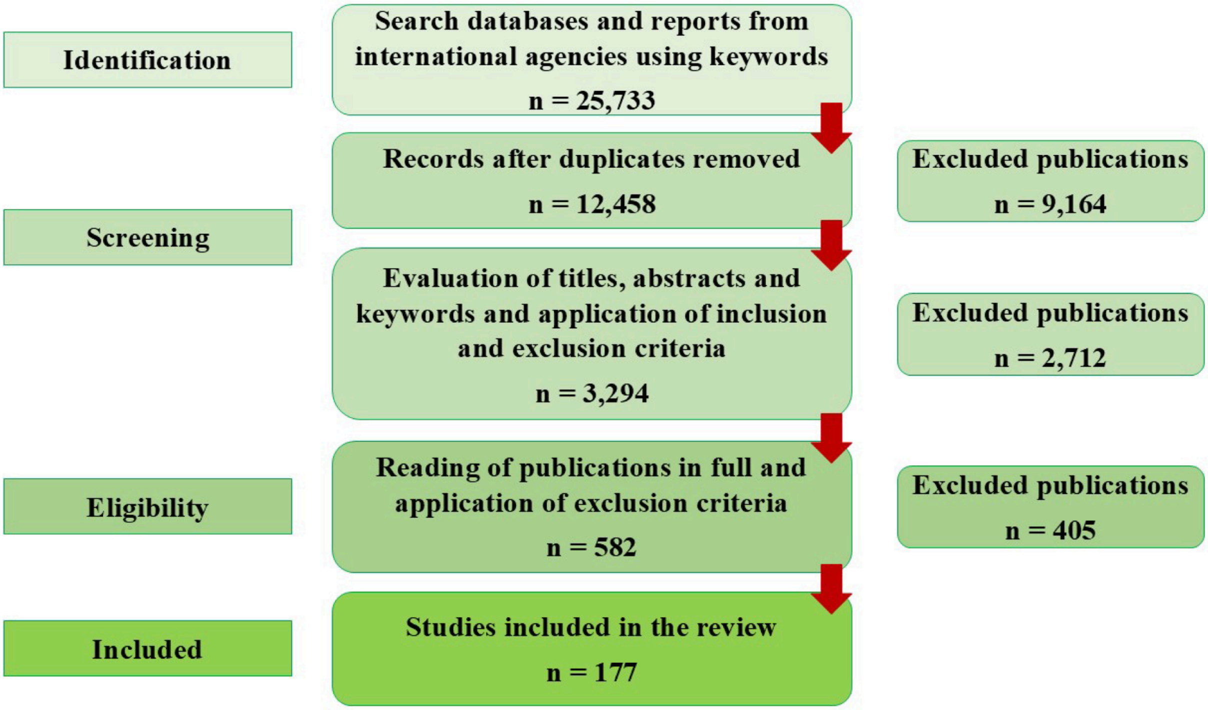


Fig. 1. PRISMA flow diagram for the literature review.

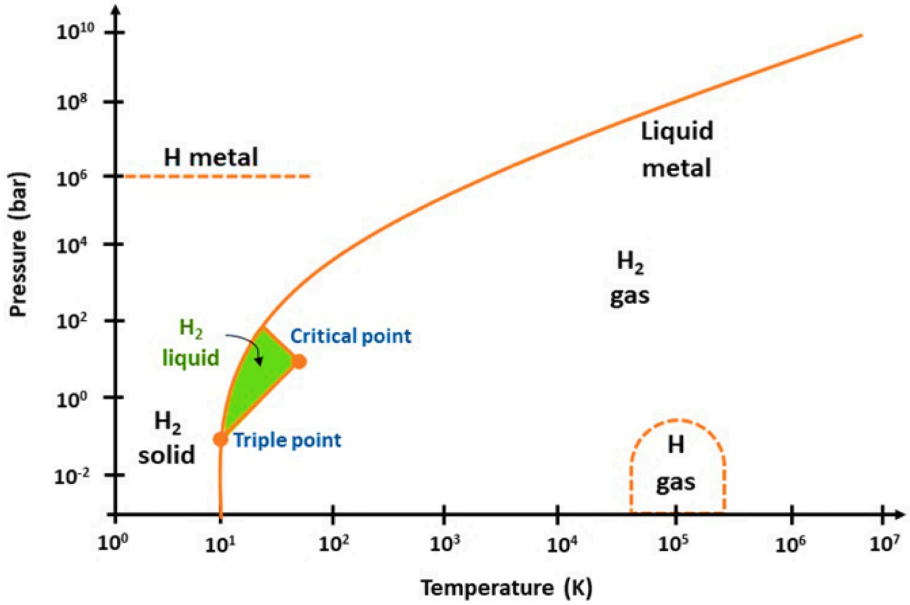


Fig. 2. Diagram of hydrogen phases.

0.756 to 1.604 x 10^{-4} m^2/s, while the diffusion coefficients of hydrogen in pure water range from 3.9 to 6.1 x 10^{-9} m^2/s, the rapid dispersion rate of hydrogen represents a critical safety concern associated with its utilization. In terms of buoyancy (density), hydrogen exhibits a higher dispersion velocity compared to methane, propane, and gasoline vapors under standard conditions. Hydrogen and methane possess several analogous characteristics, including being colorless, odorless, tasteless, and non-toxic. The flammability of hydrogen is directly proportional to its concentration, and it is notably greater than that of methane and other conventional fuels (Farias et al., 2022; Strauch et al., 2023).

The global hydrogen market is undergoing notable expansion, fueled by the worldwide effort to achieve decarbonization and the growing acknowledgment of hydrogen as a crucial component in the shift toward clean energy. Several countries and industries are investing heavily in hydrogen technologies, fostering innovation and collaboration. The hydrogen market encompasses a diverse range of production methods, including electrolysis, steam methane reforming and biomass gasification. Demand for hydrogen spans multiple sectors, including transportation, industrial applications and power generation, reflecting its versatile role in facilitating a transition to cleaner energy systems. The hydrogen market size was beyond US$ 183 billion in 2022 and it is expected to grow by 5.5 % from 2023 to 2032. The growth drivers are mainly; a) emerging new government policies and regulations; b) major progress in production and storage technologies; c) significant increase in private investments with government incentives; and d) increasing focus on net-zero emissions by 2050 (Global Market Insights, 2023).

In the global search for energy in a carbon neutral world for the year 2050, the International Renewable Energy Agency estimates that hydrogen will account for 6 %, whereas the Hydrogen Council estimates that this proportion could reach 18 %. Moreover, 16 % of electricity production could be destined for hydrogen generation by 2050 (Li et al., 2023; Webb et al., 2023).

3.1. *Applications of H_2*

Hydrogen is gaining prominence in industrial and commercial applications, and has numerous favorable attributes, such as general storage capacity, efficiency, renewability, cleanness, massive distribution, high conversion, zero emissions, versatility and rapid recovery, making it an excellent choice as a source and raw material for the production of heat and different types of energy and chemical products. Thus, H_2 has been considered the most ecological and promising energy source of the 21st Century and fundamental for numerous industrial applications (Qazi, 2022; Zhang et al., 2024). Fig. 3 displays some of the main applications of hydrogen.

Hydrogen is a basic substance widely used in industry, especially in the production and processing of chemical products (such as ammonia and methanol) as well as petrochemical refining, such as hydrotreatments, hydrogenation of unsaturated hydrocarbons, hydrodesulfurization, etc.). H_2 can be used as a reducing agent for metal processing (steel and aluminum) and glass fabrication, and the production of hydrochloric acid. This element also has applications in the food industry (hydrogenation of oils or fats for the production of margarine) and analytical chemistry (e.g., atomic absorption spectroscopy and gas chromatography). Other applications include use as fuel for vehicles and H_2 and O_2 mixtures as propellants in the aerospace sector. Hydrogen can also be used for the generation of electricity in fuel cells by way of electrochemical reactions. The energy of H_2 currently has broader applications in the storage and supply of energy and has considerable potential in hybrid energy systems. In such systems, hydrogen is mainly used for energy storage and the joint supply of thermal energy (Abdalla et al., 2018; Acar and Dincer, 2018; Pan et al., 2020; Rasul et al., 2022; Lanjekar and Panwar, 2024).

3.2. *Classifications of H_2*

Hydrogen can be generated from various primary energy sources. The production method and the type of energy utilized can lead to significant variations in both the cost of hydrogen and its associated emissions. This variability is why hydrogen generation technologies are commonly categorized using a color code (Ajanovic et al., 2022). Fig. 4 illustrates the different classifications of hydrogen by color.

3.2.1. *Green hydrogen*

Green hydrogen is produced using renewable energy sources, including wind, solar, biomass, and other environmentally friendly sources. The most adequate well-developed technology is based on the electrochemical separation of water (electrolysis), as illustrated in Fig. 5. In this process, water is dissociated into hydrogen and oxygen by utilizing electrical energy. When hydrogen is generated through this method, it is regarded as a source of clean and renewable energy, producing no CO_2 emissions. Consequently, the broader definition of green hydrogen is inherently linked to the absence of carbon dioxide emissions throughout its production process (Fig. 6) (Zhou et al., 2022; Squadrito et al., 2023).

The production of green hydrogen does not emit greenhouse gases, thereby contributing to reaching the climate goals established by the 2015 Paris Agreement. As emissions are difficult to eliminate in certain parts of the economy, direct electrification, renewable energy and energy efficiency can significantly minimize emissions from the production of electricity as well as some forms of transportation, such as long-distance travel, maritime transport and aviation, and the production of cement and steel, the decarbonization of which is challenging because these processes require energy dense fuels or intense heat. Hydrogen is highly abundant, widely available and can be carried from one place to another or used where it is produced. Green hydrogen also has the unique benefit of being able to be produced wherever there is water and energy to produce more electricity and heat (International Energy Agency, 2021; Jayaprabakar et al., 2024; Hassan et al., 2024).

Policy makers are working on plans and implementing programs to

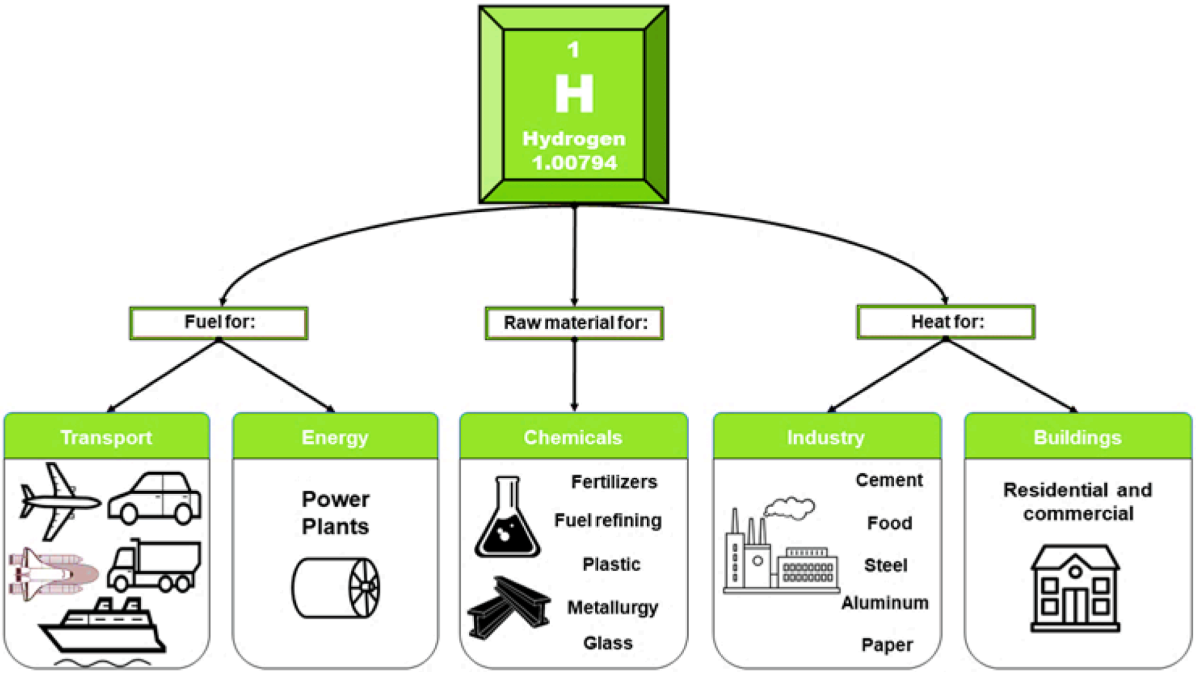
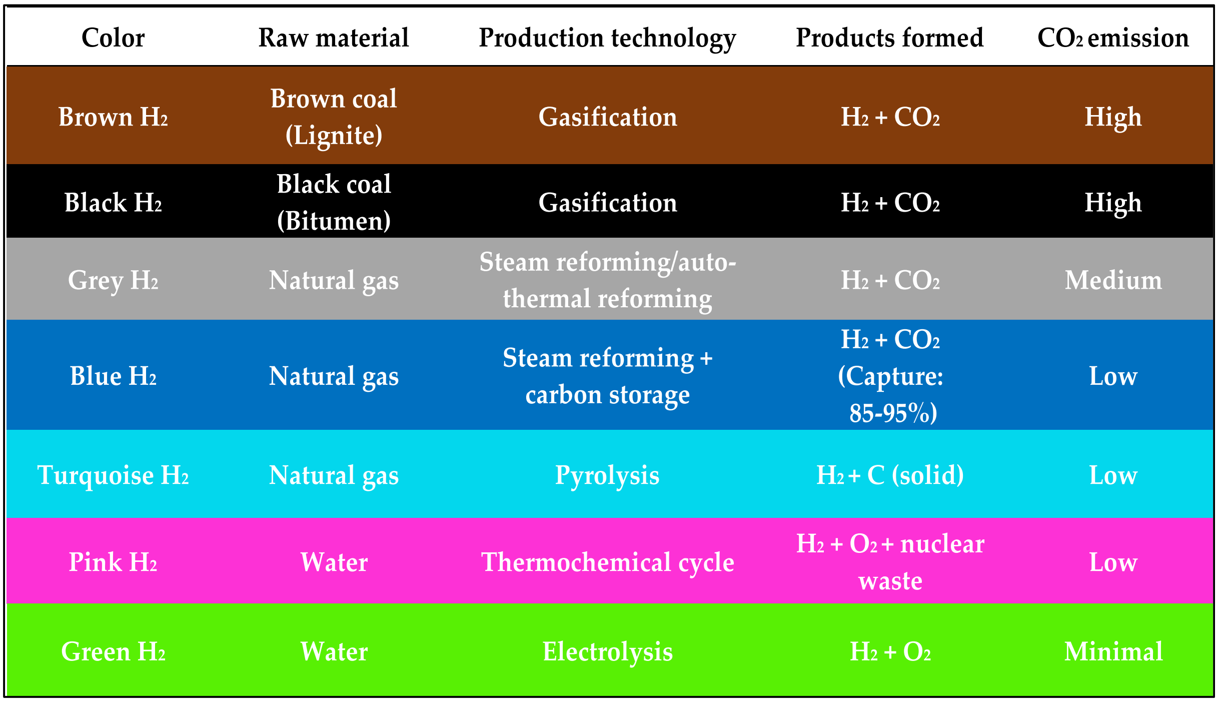


Fig. 3. Main applications of hydrogen.



Color	Raw material	Production technology	Products formed	CO_2 emission
Brown H_2	Brown coal (Lignite)	Gasification	$H_2 + CO_2$	High
Black H_2	Black coal (Bitumen)	Gasification	$H_2 + CO_2$	High
Grey H_2	Natural gas	Steam reforming/auto-thermal reforming	$H_2 + CO_2$	Medium
Blue H_2	Natural gas	Steam reforming + carbon storage	$H_2 + CO_2$ (Capture: 85-95%)	Low
Turquoise H_2	Natural gas	Pyrolysis	H_2 + C (solid)	Low
Pink H_2	Water	Thermochemical cycle	$H_2 + O_2$ + nuclear waste	Low
Green H_2	Water	Electrolysis	$H_2 + O_2$	Minimal

Fig. 4. The main colors codes used for classifications of hydrogen. and
Adapted from Kumar and Lim (2022), Huang et al. (2023)Incer-Valverde et al. (2023).

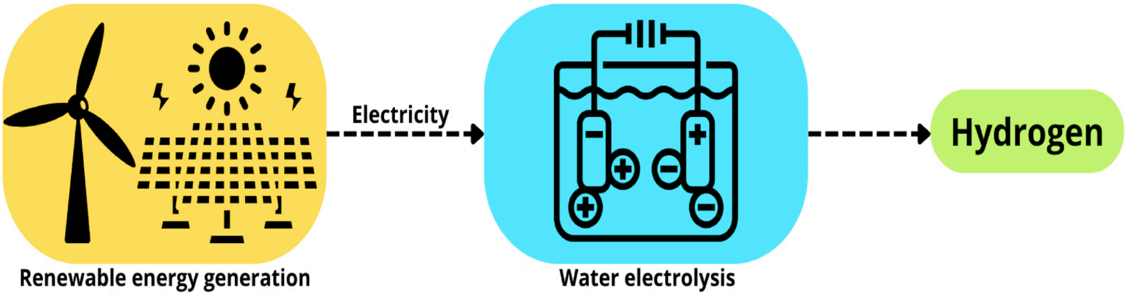


Fig. 5. Green hydrogen production system via water electrolysis by electricity from renewable energy systems.

support the development of the green hydrogen economy. Companies are also assessing the impact of green hydrogen on their businesses and identifying potential business opportunities. An economy based on green hydrogen sees hydrogen as the key to enabling a society with 100 % renewable energy. Green hydrogen energy serves as a natural alternative to fossil fuel-based energy and boosts a country's long-term energy security (Wappler et al., 2022; Raman et al., 2022).

4. Electrolysis

The electrolysis of water is an ascending reaction, as demonstrated by the positive Gibbs free energy value. The reaction normally passes through a substantial kinetic barrier. When combined with renewable energy sources, it is considered environmentally correct, sustainable and a long-term solution for energy production. The process of water splitting comprises two distinct half-reactions: the hydrogen evolution reaction, which occurs at the cathode, and the oxygen evolution reaction, which takes place at the anode (Panigrahy et al., 2022; Li et al., 2022). The general reaction of water electrolysis is represented by Equation (1) (Risco-Bravo et al., 2024):

$$H_2O(l) + Energy \rightarrow H_2(g) + \frac{1}{2}O_2(g) \tag{1}$$

The thermodynamic properties of the system determine the voltage required to trigger this electrochemical process. Since water electrolysis is endothermic, it requires energy input in the form of enthalpy change (ΔH), the energy required to break the bonds in water molecules. Part of the energy demand for the electrolysis process can be met through a change in Gibbs free energy (ΔG), which must be supplied as electrical energy to the electrodes. The other part is supplied by the heat produced during the reaction (Q). The latter is the result of the product of the process temperature (T) and the entropy change (ΔS) (Sebbahi et al., 2024). Given these approaches, Equation (2) correlates the above-mentioned variables (Cruz et al., 2023).

$$\Delta H = \Delta G + Q = \Delta G + T.\Delta S \tag{2}$$

An equilibrium cell voltage, or "electromotive force," or E°, must be applied to produce hydrogen (and oxygen) via the electrolysis of water. Thus, assuming that there is no cell current between the two distinct electrode reactions and that reversibility is established, the open-cell potential, also known as the equilibrium cell voltage, is defined as the equilibrium potential difference between the respective anode and cathode, as expressed by Equation (3) (Elmaihy et al., 2024).

$$E^{\circ} = E^{\circ}_{Anode} - E^{\circ}_{Cathode} \tag{3}$$

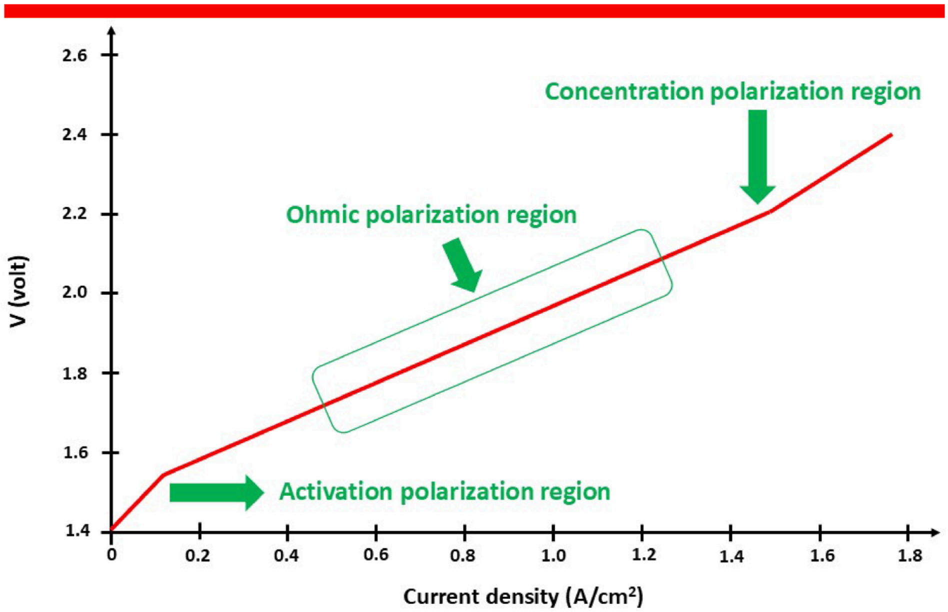


Fig. 6. Example of polarization curves.

Reversible voltage (E_{rev}) is a reversible cell voltage that shows the minimum amount required to start the electrolyzer operation and is determined by ΔG. If the thermal energy (T.ΔS) is supplied by electricity, the minimum voltage to start the electrolysis is called thermoneutral voltage (E_{tn}). Since the total energy required is the same as the enthalpy oscillates (ΔH) during the ideal process, Etn is equal to the enthalpy voltage. The calculation formulas of E_{rev} and E_{tn} are described as Equation (4) and Equation (5), respectively (Firtina-Ertis, 2022).

$$E_{rev} = \frac{\Delta G}{nF} \tag{4}$$

$$E_{tn} = \frac{\Delta H}{nF} \tag{5}$$

where n is the number of electrons to produce one mole of hydrogen (n = 2) and F is Faraday's constant, which shows the electric charge per mole of electrons (96.485C.mol^{-1}) (Rodriguez-Castillo et al., 2023). At standard pressure and temperature conditions, $\Delta G^{\circ} = 237.21$ kJ.mol^{-1} and $\Delta H^{\circ} = 285.84$ kJ.mol^{-1}, where the reversible and thermoneutral voltage are$E_{rev} = 1.23$ V and$E_{tn} = 1.48$ V (Tello et al., 2024).

A voltage higher than the standard theoretical thermodynamic potential (the potential difference between the experimental and theoretical value is called overpotential) is required to drive the electrochemical water-splitting reaction satisfactorily. There are different types of overpotential in electrolysis, such as: activation, ohmic, and concentration overpotential. The kinetics of the electrode at the reaction site determines the overpotential caused by the activation energy required for charge transfer, known as the activation overpotential (η_{activ}). The concentration overpotential (η_{conc}) is caused by a rapid reduction in concentration at the interfaces due to the variation in concentration between ions in the bulk of the solution and at the electrode surface. While the ohmic overpotential (η_{ohm}) is caused by the resistance of the electrolyte and electrodes to the transport of ions and electrons. (Raveendran et al., 2023; Aralekallu et al., 2024). Equation (6) describes the calculation of the overpotential required to perform electrolysis (He et al., 2023).

$$\eta = \eta_{activ} + \eta_{conc} + \eta_{ohm} \tag{6}$$

Therefore, the total voltage of an electrolytic cell can be described according to Equation (7) (Muthiah et al., 2024).

$$V_{cell} = E_{rev} + E_{tn} + \eta \tag{7}$$

Voltage efficiency (η_V) compares the thermoneutral voltage (E_{tn}) with the actual supplied voltage (V_{cell}), indicating the amount of heat loss in the electrolyzer system. According to Equation (8) (Niblett et al., 2024).

$$\eta_V = \frac{E_{tn}}{V_{celula}} \tag{8}$$

Regarding electrochemical analysis, the reversible (theoretical) potential of the cell is given by the Nernst equation, according to Equation (9) (Jang et al., 2022).

$$E_{rev} = E^{\circ}_{rev} + \frac{RT}{2F} ln\left[\frac{P_{H_2}P_{O_2}^{0.5}}{\alpha_{H_2O}}\right] \tag{9}$$

where E°_{rev} is the standard cell potential (approximately 1.23 V at 25 °C), R is the gas constant, T is the absolute temperature in Kelvin, is the Faraday constant, P_{H_2} and P_{O_2} are the partial pressures of hydrogen and oxygen gases, respectively, and α_{H_2O} is the activity of water (generally considered to be 1 for pure liquid water) (Hu et al., 2022).

The development of improved water electrolysis systems still occurs mainly empirically, by making newly formulated electrodes, membranes, and membrane-electrode assemblies. These components are then combined in an electrochemical cell and their performance is evaluated by measuring polarization curves. In electrochemistry, polarization refers to the difference between the applied voltage and the ideal thermodynamic potential of an electrochemical cell, and indicates the energy losses that occur in electrolytic systems due to various internal resistances (de Groot and Vermeulen, 2024). Fig. 5 represents the polarization curves that are determined by the increase in voltage as a function of current density.

The initial increase step is attributed to the barrier to electron transfer reactions occurring at the electrodes. This is known as the "activation polarization region". As the load resistance decreases further (i.e., with increasing current density), there is a range where the voltage increases almost linearly with the current. This is known as the "ohmic polarization region", where the current is limited by the internal resistance to ion flow. With further increase in current, a threshold value is reached where the mass transfer of reactants to the electrode/electrolyte interface limits the reaction. This is known as the "concentration polarization region". Cells that exhibit nonlinear behavior at higher currents exhibit polarization, and the degree of polarization is given by an overvoltage, or overpotential, which represents the difference between the theoretical and effective potential required (Esposito et al., 2022).

In an acidic medium, water is oxidized at the anode to form molecular oxygen, resulting in the production of protons. These generated protons are then transported to the cathode, where they undergo reduction to produce molecular hydrogen. In contrast, under alkaline conditions, hydroxide anions produced from water at the cathode serve as the primary electrochemical charge carriers. Oxidation of hydroxyl ions at the anode produces O_2 and electrons, which are then used to generate H_2 at the cathode. Electrochemical reactions take place at the boundary between the electrode surface and the electrolyte, with the rate of gas evolution being directly proportional to the current flowing through the electrical circuit, in accordance with Faraday's law of electrolysis (Tüysüz, 2024).

Based on the operating conditions and type of electrolytes, the electrolysis of water is classified into three main types: alkaline electrolysis, with OH^- ions as the charge carrier; proton exchange membrane electrolysis, with H^+ as the charge carrier; and solid oxide electrolysis, with O^{2-} as the charge carrier (Gerloff, 2021; Wang et al., 2022). Fig. 7 displays the main electrolyzing models for water electrolysis.

4.1. Alkaline electrolysis

Alkaline electrolysis is a mature separation process and is based on the water division method, which uses electricity to split water into its two main components: hydrogen (H_2) and hydroxyl ions (OH^-). H_2 is formed on the negative electrode (cathode) and the OH^- ions are transferred to the positive electrode (anode) (Daoudi and Bounahmidi, 2024).

Non-noble metals are generally used for the electrodes, such as nickel with an electrocatalytic coating, which has a relatively lower cost and longer useful life. Nickel is a transition metal that is plentiful on Earth and exhibits significant catalytic activity in both the hydrogen evolution reaction and the oxygen evolution reaction (Liu et al., 2023; Zamanizadeh et al., 2023). Stainless steel electrodes are also widely used in alkaline electrolysis due to their high corrosion resistance in alkaline environments, high conductivity, and mechanical strength, and because they are highly affordable (Barauskienė et al., 2023; Esfandiari et al., 2024; Ning et al., 2024).

The electrolytes commonly utilized in alkaline water electrolysis consist of sodium hydroxide (NaOH) and potassium hydroxide (KOH). These alkaline solutions provide the necessary hydroxide ions (OH^-) for the electrochemical reactions taking place at the electrodes during the water dissociation process. The primary role of the electrolyte is to act as a medium for the transport of ionic charges, thereby facilitating the decomposition of water into hydrogen and oxygen. Among the two compounds, KOH is most frequently used in industrial alkaline water electrolysis systems due to its greater solubility and greater resistance to corrosion compared to NaOH (Palhares et al., 2018; Gambou et al., 2022).

Liquid electrolytes have good ionic conductivity and when a direct electrical current is applied, electrons flow into the electrolyte solution from the negative terminal, cathode of the energy source, where they are attracted by hydrogen ions in the water, producing H_2 (Equation (10). To sustain equilibrium within the electrolyzer, the hydroxide ions produced from the cathodic reaction migrate toward the anode surface. At this location, they undergo oxidation, releasing electrons that return to the positive terminal of the energy source, thereby generating O_2 (Equation (11) (Brauns and Turek, 2020; Figueiredo et al., 2023).

$$\text{Cathodic reaction}: 4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \tag{10}$$

$$\text{Anodic reaction}: 4OH^- \rightarrow 2H_2O + O_2 + 4e^- \tag{11}$$

Alkaline water electrolysis is a mature technology with a high technology readiness level (TRL), and its electrolyzers have been used for many years worldwide and are known for their durability, cost-effectiveness, and reliability, making them suitable for large-scale industrial applications (Malik et al., 2023; Schneider et al., 2024).

4.2. Proton exchange membrane electrolysis (PEM)

PEM electrolysis is based on a solid polymer electrolytic membrane (generally Nafion) that is permeable to protons (H^+) and separates the cell into an anode and a cathodic compartment. The membrane is coated with a layer of catalyzer on both sides, forming what is known as a membrane electrode assembly. Highly pure water enters the cell by the side of the anode, is distributed through integrated flow fields on the bipolar plate throughout the entire cross-section of the cell and diffuses through a porous transport layer to the anodic catalytic layer, where it is converted into molecular oxygen and protons (Equation (12). The protons permeate the membrane together with the water molecules due to

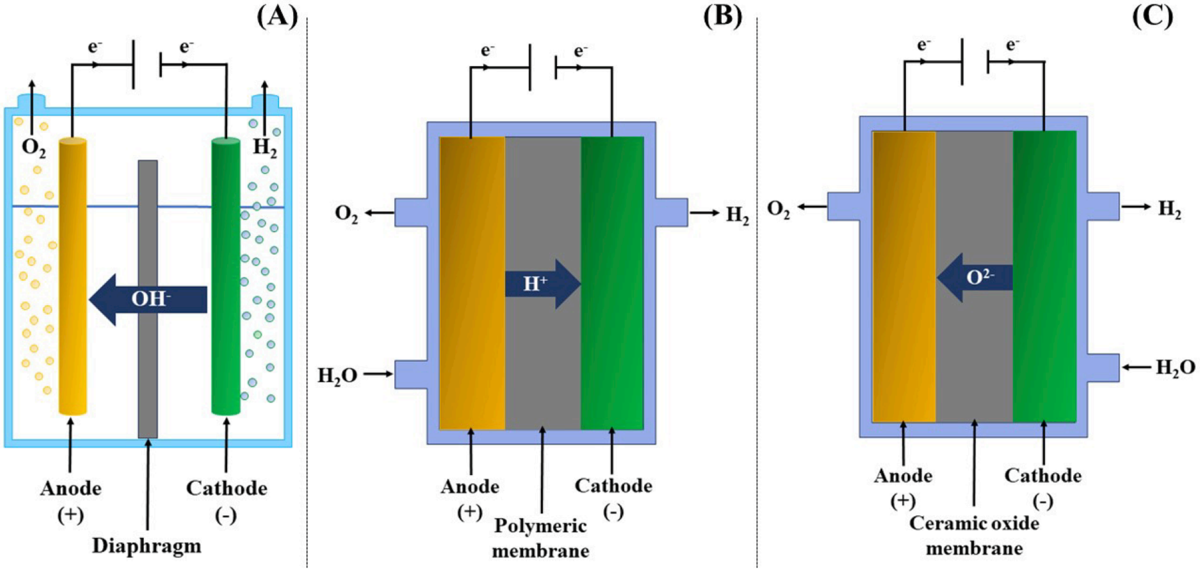


Fig. 7. Main electrolyzing models: (A) Alkaline, (B) Proton exchange membrane, (C) Solid oxide.

electroosmotic drag. On the side of the cathode, the protons are reduced to molecular hydrogen (Equation (13) (Aldakheel et al., 2022; Hemauer et al., 2023).

$$\text{Anodic reaction}: H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^- \tag{12}$$

$$\text{Cathodic reaction}: 2H^+ + 2e^- \rightarrow H_2 \tag{13}$$

Proton exchange membrane electrolysis is one of the most promising technologies that uses continuous current energy from renewable energy sources, such as solar, wind and biomass, to split water and generate hydrogen and oxygen gases. This is a compact, highly efficient system with high current density operation and easy maintenance (Kang et al., 2022; Ozdemir et al., 2023).

4.3. Solid oxide electrolysis (SOEC)

A SOEC electrolyzer consists of a negative fuel electrode (usually made of Yttrium-stabilized Nickel-Zirconia (YSZ)), a positive oxygen electrode (usually made of Strontium-doped Lanthanum Manganite (LSM)-YSZ), and an electrolyte (generally from YSZ) which has a high ionic conductivity at high temperatures in addition to its electron insulating property. During operation, high-temperature steam is introduced to the cathode side, where it undergoes reduction to yield hydrogen and oxygen ions at the catalyst interface. The oxygen ions are subsequently conveyed through the electrolyte via phase potential to the anode side, where they are oxidized to produce oxygen molecules. The underlying phenomena are typically intricate, encompassing aspects such as reaction kinetics, thermodynamics, operating conditions, and material characteristics (Ruiz Diaz and Wang, 2024). Equations (14) and (15), below, present the reactions that occur in solid oxide electrolysis (Biswas et al., 2023).

$$\text{Cathodic reaction}: H_2O + 2e^- \rightarrow H_2 + O^{2-} \tag{14}$$

$$\text{Anodic reaction}: O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^- \tag{15}$$

The solid oxide electrolyzer cell is a technology in development. Solid oxide electrolysis uses thermal energy and electricity for operation. This feature causes industrial waste heat, cheap energy compared to electricity, to provide part of the required electrolysis energy. This innovative technology uses conductive ceramics instead of traditional metal-based catalysts, offering a promising method for hydrogen production in commercial applications. Unlike other electrolysis technologies, SOECs function at high pressures and temperatures, increasing the thermodynamic efficiency of the water splitting reaction (Nejadian et al., 2023; Lahrichi et al., 2024).

The state in which the heat from internal losses just balances the heat sink maintained by the endothermic reaction marks a special operating condition, the so-called thermoneutral point. Operating SOECs at the thermoneutral point or voltage (1.29 V) means that no external heating or cooling is required, which not only allows very high system efficiencies but also avoids balancing the plant components for heating and cooling. When operated above the thermoneutral voltage, excess heat is generated, which requires external cooling and thus reduces efficiency. Conversely, when operating below the thermoneutral voltage, the SOEC is cooling and heat must be supplied from external sources to maintain the operating temperature (Mueller et al., 2024).

Table 1 displays specifications to enable comparisons of the alkaline, proton exchange membrane and solid oxide electrolytic processes.

Table 1
Comparison of operational conditions for electrolysis of water: alkaline, PEM and SOEC.

Specifications	Alkaline electrolysis	PEM	SOEC
Operating Temperature (°C)	60–100	70–90	> 500
Operating Pressure (bar)	2–30	15–30	< 30
Voltage (V)	1.8–2.4	1.4–2.5	0.95–1.3
Electrolyte	KOH/NaOH	Solid polymer (perfluorosulfonic acid)	Yttrium Stabilized Zirconia (YSZ)
Charge carrier	OH^-	H^+	O^{2-}
Purity of gas (%)	99.5–99.9998	99.9–99.999	99.9
Energy efficiency (%)	62–84	67–82	81–100
Cold start-up time (min)	15	<15	>60
Lifetime (h)	<90,000	50,000–80,000	20,000

Adapted from Kumar and Lim (2022), Tian et al. (2022); El-Shafie (2023), Arsad et al. (2023), Al-Douri and Groth (2024), Awad et al. (2024) Daoudi and Bounahmidi (2024).

5. Routes for production of biohydrogen (bio-H_2) from biomass and solid waste

The term ’biomass’ applies to any living or recently dead material derived from the direct or indirect photosynthesis of plants or animals; this does not include coal, oil or the fossilized remains of organisms. Its composition depends on its origins, such as agriculture, forestry and urban waste, which are composed of a variety of different materials, such as wood, crop residues, sawdust, manure, paper scraps, domestic waste, wastewater, etc. Biomass is also the most abundant material on the planet, with 550 to 560 billion tons of carbon. Annually, over 100 billion tons of biomass are generated globally, with projections indicating that biomass could potentially supply 3000 TWh of electricity by 2050. This shift is anticipated to result in a reduction of approximately 1.3 billion tons of CO_2 emissions each year (Antar et al., 2021; Pocha et al., 2023).

Biomass is widely acknowledged as a significant renewable and sustainable energy supply that may be used to replace fossil fuels. Due to its rapid production, harvesting and regeneration, biomass can be converted into heat and electricity as well as chemicals and fuels, etc. Estimated that by 2050, biomass will be the source of more than 25 % of the world’s primary energy, when considering the use of forest, urban wastes and the cultivation of perennial energy crops. Bioelectricity and biohydrogen (bio-H_2) can be obtained from sources of biomass by way of bioelectrochemical systems (Amjith and Bavanish, 2022; Agrawal et al., 2024; Sridevi et al., 2024). Fig. 8 displays global production capacity of the main types of biomass.

Bio-H_2 is a form of H_2 produced from biological sources, such as biomass, organic waste and algae, and can be produced indefinitely provided that there is a supply of biomass or organic waste. One of the primary benefits of bio-H_2 as an energy source is its renewability, distinguishing it from fossil fuels, which are limited in supply and will ultimately be exhausted. Furthermore, the generation of bio-H_2 does not emit CO_2 or other greenhouse gases, rendering it a more environmentally friendly alternative to fossil fuels. Additionally, bio-H_2 offers considerable versatility, as it can serve as a fuel for transportation, electricity generation, and the synthesis of chemical products, among other applications. The main routes for the production of biohydrogen are classified into two categories: thermochemical or biological conversion (Machineni et al., 2023; Rizvi et al., 2023; Zainal et al., 2024). Fig. 9 illustrates the main biomass conversion routes for the production of Bio-H_2.

5.1. Thermochemical conversion

The term “thermochemical conversion” refers to the thermal degradation of organic molecules. These decomposition processes take place at elevated temperatures and result in alterations to the chemical

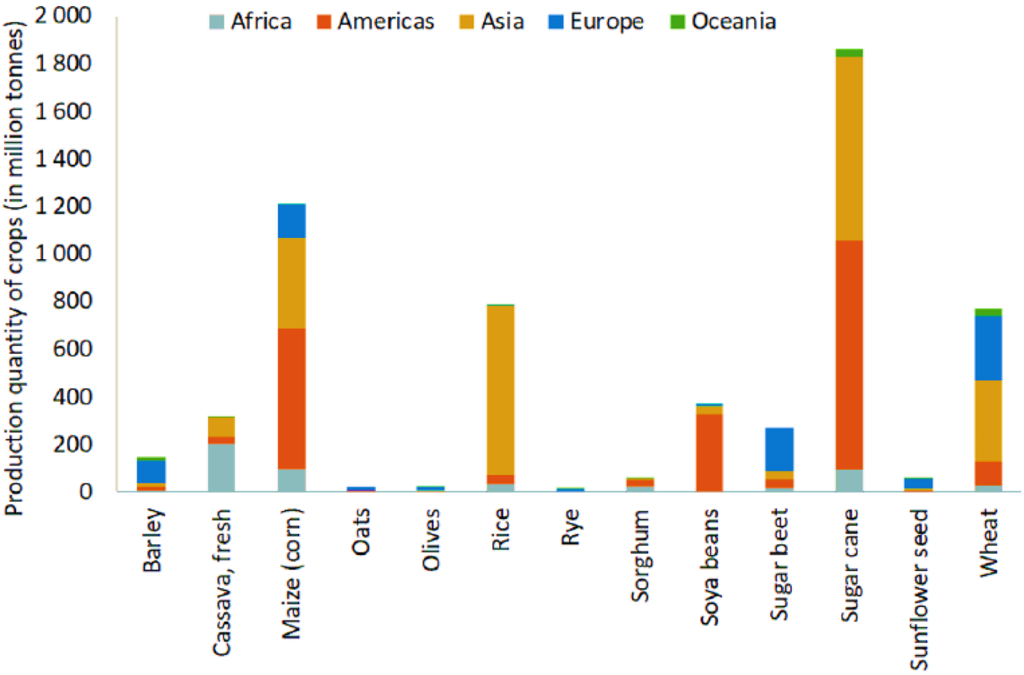


Fig. 8. Quantity of production of the main agricultural crops by continent in 2021.
Adapted from World Bioenergy Association (2023).

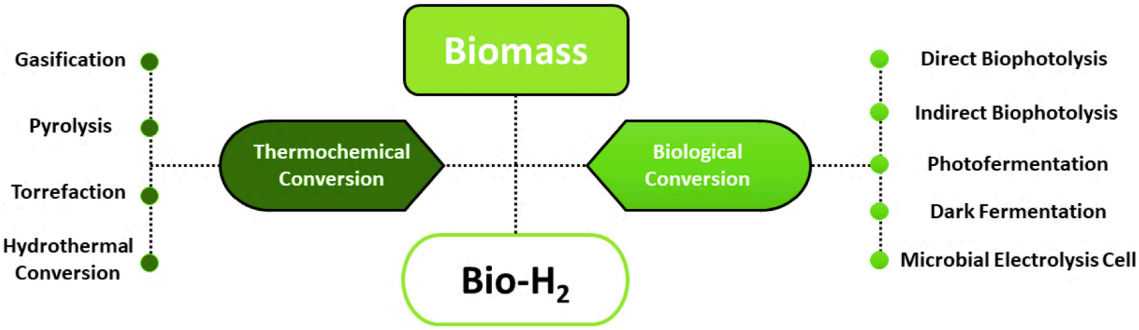


Fig. 9. Main biomass conversion routes for production of Bio-H_2.

structure of the materials involved. The most prevalent thermochemical conversion methods include gasification, pyrolysis, torrefaction, and hydrothermal conversion (Krishnan et al., 2022; Jeon et al., 2023; Yao et al., 2023).

5.1.1. *Gasification*

Gasification is a thermochemical process by which biomass or organic solid waste is treated at a high temperature (700–1200 °C) in a gasifier with different media (oxygen, steam, air, CO_2, etc.). Four different stages are generally involved in the gasification process: drying of the raw material, pyrolysis (decomposition), oxidation (combustion) and reduction (gasification). The main product of the gasification process is a combustible mixture of gases known as synthesis gas (syngas), which can then be used as fuel or substrate in boiler combustion, fuel cells and the synthesis of chemical products through Fischer-Tropsch processes (Murugesan et al., 2022).

Conventional gasification processes produce syngas that consists of small quantities of hydrogen. The concentration of hydrogen can by increased by a water–gas shift reaction system, followed by conventional gasification reactors. The gasification of biomass is a well-established technology that can produce H_2-rich syngas through controlled partial (sub-stoichiometric) oxidation methods in the presence of gasifying agents (air, oxygen and steam). Equations (16) and (17) describe a simple reaction for biomass gasification (Ghodke et al., 2023).

$$C_xH_yO_z(biomass) + O_2 + H_2O \rightarrow CO + CO_2 + H_2 + otherspecies \quad (16)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (17)$$

The production of hydrogen from biomass and solid waste by gasification requires an additional process of cleaning and purification of the gas before the product can be used. The gas hydrogen product goes through a cleaning and purification process of a contaminant, whereas CO is subsequently reactive with the water vapor by the steam reforming process to produce CO_2 and hydrogen (water–gas shift reaction). One of the challenging issues in gasification is the formation of tar, which can form a tar aerosol that is unfavorable to the subsequent steam reforming and use of hydrogen. Tar formation can be minimized by altering the gasifying project or employing additive/catalysts. Another useful byproduct of coal can be transformed into gas using a gasifying agent to enhance the gasification reaction (Aziz et al., 2021). Among the different types of gasification technologies and processes, the most common are a fixed bed gasifier, fluidized bed gasifier, drag bed gasifier and plasma gasifier (Midilli et al., 2021).

5.1.2. *Pyrolysis*

Pyrolysis is a process by which solid waste, such as biomass, is decomposed in the absence of O_2, which is normally achieved in the temperature range of 400 to 650 °C at a pressure of 0.1 to 0.5 MPa. Pyrolysis generates gas, liquid and solid products, but the proportions of each phase depend on the operating conditions. The temperature of the process, residence time and residence time of the steam are the main factors that affect the proportions of the end products in each phase of the process (Shahabuddin et al., 2020; Hosseinzadeh et al., 2022; Sivaranjani et al., 2023). The pyrolysis reaction is described in Equation (18) (Liu et al., 2020):

$$Biomass + heat \rightarrow H_2 + CO_2 + CO + CH_4 + others \tag{18}$$

Pyrolysis is categorized into three main types depending on the heating rate and residence time of the raw material in the reactor: slow, fast and flash. With slow pyrolysis, the temperature of the process ranges from 300 to 700 °C and the particle size of the biomass ranges from 5 to 50 mm. In fast pyrolysis, the organic matter is treated thermically in the absence of oxygen at about 600 to 650 °C, with high heating rates up to 1000 °C/s and a residence time between 0.5 and 10 s. Flash pyrolysis is conducted at temperatures close to 1000 °C, with heating rates higher than 700 °C/s and with a biomass residence time less than 0.5 s. Other technologies include microwave pyrolysis, catalytic pyrolysis, hydrated pyrolysis and hydropyrolysis (Hu and Gholizadeh, 2019; Al-Rumaihi et al., 2022).

The raw material converted through pyrolysis mainly generates three products: liquid (bio-oil), solid (biocoal) and gas (pyrolytic gas), the proportions of which depend on the variables of the process. If the pyrolysis process is operated at low temperatures and with a long gas retention time (slow pyrolysis), biocoal is the primary product. An increase in temperature promotes the conversion of the substrate into pyrolytic gas However, a longer steam retention time and lower heating rate lead to a lower proportion of bio-oil. In contrast, high temperatures and heating rates and short gas retention time (fast and flash pyrolysis) promote the production of bio-oil (Andreides et al., 2022).

5.1.3. *Torrefaction*

This process is performed in the absence of oxygen in a temperature range of 200 to 320 °C at atmospheric pressure with a residence time of 15 to 60 min and is similar to pyrolysis. The loss of mass occurs when water, volatile organic components and non-condensable gases evaporate during torrefaction. Once equilibrium is reached, the process returns to its original state. Particle size and shape, surface area, hydrogen, nitrogen, oxygen content, high hydrogen volume, carbon content, hydrogen-carbon ratio and oxygen-carbon ratio are some of the variables that can be altered. Torrefaction is divided into two categories: dry and wet. The dry torrefaction process is a thermochemical technique conducted at temperatures between 200 and 300 °C, typically in an inert atmosphere for a duration of 30 to 60 min. In contrast, wet torrefaction utilizes subcritical water within a temperature range of 180 to 260 °C and pressures reaching up to 5 MPa. Wet torrefaction is often favored over dry torrefaction for various reasons, including its non-toxic nature and the requirement for a relatively straightforward chemical reactor (Kota et al., 2022; Nazos et al., 2022; Khan et al., 2023; Saravanakumar et al., 2023).

5.1.4. *Hydrothermal conversion*

Hydrodynamic conversion is a promising option that uses the high moisture content inherent to biomass to its benefit. The process occurs at high temperatures and pressure above saturation, which causes reactions that alter the physicochemical properties of the raw materials of the biomass in hot compressed water to produce biocoal, bio-crude oil and/or synthesis gas as well as aggregated value chemical products (ethanol, acetone, acetic acid, etc.). This makes hydrothermal conversion a potentially viable, scalable, energy-efficient thermochemical route for biomass conversion. The three main types of hydrothermal processes are dependent on the operating temperature and desired product: hydrothermal carbonization, hydrothermal liquefaction and hydrothermal gasification (Güleç et al., 2022; Lisbona et al., 2023).

Hydrothermal carbonization is a thermochemical process that involves the conversion of raw materials in hot water (subcritical) to form solid (biocoal), liquid (dissolved organic matter or residual water) and gas fractions. The process occurs through dehydration, polymerization and carbonization reactions. Hydrothermal carbonization uses different types of biomass as raw material, even those with a high moisture content (70–90 %), without the need for pre-drying. The process is also conducted at milder temperatures (170 to 250 °C) and pressure of 2 to 10 MPa, thus consuming less energy than pyrolysis. Moreover, hydrothermal carbonization has enormous resource recovery potential. Other advantages include lower carbon emissions, the non-use of strong chemical products and a significant reduction in the volume of the raw material (Nguyen et al., 2023; Antero et al., 2020; Shen, 2020; Zhi et al., 2023).

Hydrothermal liquefaction is the conversion of biomass into small oily liquid organic molecules through polymerization, decomposition, rearrangement and decarboxylation reactions at high temperatures (250 to 370 °C) and pressure up to 35 MPa. Hydrothermal liquefaction is the most adequate conversion process for biomass with a high moisture content, such as “black liquor” from cellulose factories, wastewater sludge, food scraps and recently harvested algae. This process is normally performed in the presence of hot compressed water, water and alcohol mixture or other organic solvents in a discontinuous high-pressure reactor or continuous reactor, eliminating the drying step of the wet raw material, with a resultant reduction in energy consumption and greater economic benefits (Yuan et al., 2023; Wu et al., 2022).

Hydrothermal gasification is a biomass conversion process that occurs at pressures of approximately 30 MPa and temperatures that can reach 750 °C, using subcritical or supercritical water as the reaction medium to generate hydrogen-rich syngas and other compounds. The reactions are endothermal processes in which the necessary energy is furnished by an external source through the heating of the gasification unit. Depending on the reaction temperature, hydrothermal gasification processes are divided into three subcategories: aqueous phase reforming (215 to 265 °C), the main products of which are H_2 and CO_2; near-critical catalyzed gasification (350 to 400 °C), the main product of which is CH_4; and supercritical water gasification ($>$ 374 °C), temperatures higher than 500 °C are normally employed to obtain H_2. Hydrothermal gasification is an effective method for converting biomass with a high-water content into gas. Under high pressures, the water in the biomass serves as a green solvent, catalyst and reaction medium for the simultaneous enhancement of mass transfer and reaction rates (Correa and Kruse, 2018; Okolie et al., 2021; Shahbeik et al., 2022; Hussin et al., 2023).

5.2. *Biological conversion*

Biological conversion routes represent alternative methods for hydrogen production that can be conducted at ambient temperature and pressure. These processes rely on the ability of microorganisms to transform organic substrates and water into hydrogen through the catalytic functions of two primary enzymes: hydrogenase and nitrogenase. Various substrates can be employed, and the methods differ based on the particular microorganism utilized for hydrogen generation. The most prevalent biological conversion techniques for hydrogen production include biophotolysis (both direct and indirect), fermentation (which encompasses photo-fermentation and dark fermentation), and microbial electrolysis cells. Biological methods are often favored over thermochemical approaches due to their lower energy requirements, cost-effectiveness, and greater ecological sustainability (Buffi et al., 2022; Badawi et al., 2023; Goria et al., 2024).

5.2.1. Direct and indirect biophotolysis

Biophotolyiss is a process that uses light energy (solar and artificial) to produce bio-H_2 from water molecules through the photosynthesis of photoautotrophic organisms. This process occurs mainly in green algae and cyanobacteria, with nitrogenase or hydrogenase as the main biohydrogen-producing enzyme. Biophotolysis is classified as direct or indirect (Feng et al., 2023; Suresh et al., 2023).

With direct biophotolysis, water is used as a reagent in the presence of sunlight to convert solar energy into chemical energy. Different photosynthetic microorganisms (cyanobacteria, green algae, etc.) reduce ferredoxin, transporting electrons to hydrogenase, absorbing light and reducing water molecules. Hydrogenase produces hydrogen by reducing proteins and then oxidating water. The availability of ATP and $NADP^+$ is also related to direct biophotolysis. The biophotolytic reaction is often catalyzed by several nitrogenase or hydrogenase enzymes (Ahmed et al., 2022). The photosynthetic and biochemical reaction of H_2 production during direct photolysis is described in Equations (19) and (20) (Javed et al., 2022):

$$2H_2O + sunlight \rightarrow 4H^+ + O_2 + 4e^- \tag{19}$$

$$4H^+ + 4e^- + hydrogenaseenxyme \rightarrow 2H_2\uparrow \tag{20}$$

Indirect biophotolysis for the generation of hydrogen involves two steps. Microalgae first transform solar energy into chemical energy in the form of lipids, carbohydrates and other organic compounds to increase the quantity of endogenous substrate, generating oxygen as a byproduct. In the second step, the metabolism uses fixed carbon in the form of carbohydrates to produce a large quantity of electrons. The electron transport chain stops functioning when the oxygen is depleted, creating an anaerobic environment and the oxygen-sensitive hydrogenase enzyme is activated. The free electrons are then transported to photosystem I, ferredoxin and hydrogenase, which use the electrons to generate hydrogen. The reactions are represented by Equations (21) and (22) (Woon et al., 2023; Zhang et al., 2023).

$$\text{Aerobic reaction}: 6H_2O + 6CO_2 + sunlight \rightarrow C_6H_{12}O_6 + 6O_2 \tag{21}$$

$$\text{Anaerobic reaction}: C_6H_{12}O_6 + 6H_2O + sunlight \rightarrow 6CO_2 + 12\,H_2 \tag{22}$$

5.2.2. Photo-fermentation

Photo-fermentation takes place in anoxic or anaerobic environments and entails the fermentative transformation of organic substrates into smaller molecules, including H_2 and CO_2, facilitated by photosynthetic bacteria such as green sulfur bacteria, purple sulfur bacteria, and purple non-sulfur bacteria. The latter group is particularly promising and is the most widely utilized for biological hydrogen production. These microorganisms harness light as their energy source while utilizing organic matter as the carbon and electron source (Sagir et al., 2021; Putatunda et al., 2023).

Photo-fermentation hydrogen is obtained by the nitrogenase of photosynthetic bacteria coupled to photosynthetic phosphorylation, as these bacteria have a photosystem that is not strong enough to decompose water molecules directly. The electrons of the oxidation reaction of organic substances are transported through electron transporters to pump protons through the cell membrane to produce adenosine triphosphate (ATP). Next, part of the electrons used are sent to ferredoxin, which directs the electrons to the nitrogenase with the ATP formed to produce hydrogen under nitrogen-poor conditions (NH^{4+}). The action of nitrogenase in the presence of nitrogen indicates that one hydrogen molecule can be generated per N_2 molecule, as seen in Equation (23). In contrast, four hydrogen molecules are produced in the absence of molecular nitrogen, as seen in Equation (24) (Zhang et al., 2017; Zhang et al., 2022).

$$N_2 + 8e^- + 8H^+ + 16ATP \rightarrow H_2 + 2NH_3 + 16ADP + 16P_i \tag{23}$$

$$8e^- + 8H^+ + 16ATP \rightarrow 4H_2 + 16ADP + 16P_i \tag{24}$$

5.2.3. Dark fermentation

Dark fermentation (DF) requires no light to produce H_2. This process is performed by obligate or facultative anaerobic fermentative bacteria, such as *Clostridia, Escherichia coli, Enterobacter, Citrobacter, Alcaligenes* and strains of *Bacillus*. In some cases, algae rich in carbohydrates are also used. Additionally, this method can be executed using mixed cultures. The theoretical yield of H_2 from DF can be estimated based on the metabolic pathways of the microorganisms employed and the concentration of sugars present in the fermentation medium (Ferraren-De Cagalitan and Abundo, 2021; Sivaramakrishnan et al., 2021).

DF is a process that requires minimal process conditions, which reduces the need for nutrients and energy and diminishes the formation of sludge. The carbohydrates are obtained from different sources, such as agriculture, paper, urban solid waste and the food industry, and are used for conversion into hydrogen, carbon dioxide and volatile fatty acids. Moreover, this method serves as an effective approach for the elimination and management of nutrient-rich organic waste (Yaashikaa et al., 2022).

The production of biohydrogen depends on essential enzymes (hydrogenases), although the enzymatic complex of nitrogenase also has hydrogenase activity. Hydrogenases catalyze hydrogen molecules into protons and electrons and participate in two main DF pathways. The first pathway is the acetate pathway, which theoretically yields 4 mol of H_2 for every mole of glucose consumed. The second pathway is the butyrate pathway, which generates 2 mol of H_2 per mole of glucose. In the initial stages of the DF process, nicotinamide adenine dinucleotide + hydrogen (NADH) is formed by the oxidation of organic substrates in pyruvate and can be used by microbial species that have NADH- ferredoxin oxidoreductase, producing reduced ferredoxin. Pyruvate is then transformed into acetyl-CoA and formate via the action of pyruvate formate-lyase, or alternatively into acetyl-CoA and reduced ferredoxin through the activity of pyruvate-ferredoxin oxidoreductase, both of which result in the production of H_2. In fermentative bacteria, there is a significant accumulation of NADH during the glycolysis of glucose, attributed to the restricted capacity of the electron transport chain. The $NADH/NAD^+$ ratio is normally maintained through the oxidation of NADH and H^+ in NAD^+ during the acidogenesis phase. The insufficient oxidation of NADH leads to an accumulation of both NADH and H^+. To restore normal metabolic functions, fermentative bacteria strive to oxidize the surplus NADH by producing hydrogen. Additionally, acidogenic bacteria can convert propionic acid, butyric acid, ethanol, and other organic compounds into acetic acid and hydrogen during the process known as acetogenesis (Yang and Wang, 2019; D' Silva et al., 2023).

Equation (25) represents the DF process with acetic acid as the byproduct and Equation (26) represents the DF process with butyric acid as the byproduct. As can be seen, the theoretical maximum yield of Bio-H_2 (for glucose) is 4 mol of hydrogen/mol of glucose and can be achieved through the acetate pathway (Angeriz-Campoy et al., 2023; Talapko et al., 2023).

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \tag{25}$$

$$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2 \tag{26}$$

Fundamental environmental factors, such as temperature and pH, should be closely monitored and managed to ensure the generation of efficient, effective fuel. DF can be conducted at temperatures between 25 and 80 °C or higher temperatures ($>$ 80 °C) for the production of Bio-H_2. Bacteria that produce hydrogen by DF include mesophilic (25–40 °C), thermophilic (40–65 °C), extreme thermophilic (65–80 °C) and hyperthermophilic ($>$ 80 °C) species. DF methods work better at temperatures between 35 and 55 °C. The development of harmful bacteria is also inhibited by large temperature variations during fermentation. Thermodynamically, DF at higher temperatures is considered favorable to the generation of hydrogen, because the increase in temperature increases entropy, making fermentation highly vigorous (Ahmad et al., 2024; Rathi et al., 2024).

In DF, operational pH exerts an influence on metabolic pathways, the structure of the microbial community and the distribution of the product. In most studies, greater enzymatic efficacy and better microbial growth have been achieved under ideal pH conditions. When operational pH varies above or below ideal values, a substantial decrease in the production of Bio-H_2 occurs. In many studies, ideal pH is reported to be between 5.5 and 6.5. Fermentation using mixed cultures requires low pH, which inhibits methanogenic microbes that consume H_2. Hydraulic retention time in another important factor and is defined as the average time that the soluble component remains in the reactor. This variable affects the use of H_2 by hydrogen-consuming microbes, such as methanogenic species and homoacetogens, as well as the bioconversion rate of organic matter into bio-H_2 and organic acids. A wide hydraulic retention time range has been reported during the production of bio-H_2 using dark fermentation, ranging from 0.5 h to several days (Arun et al., 2022).

5.2.4. *Microbial electrolysis cells*

The idea of microbial electrolysis cells (MECs) was originally introduced in 2005. This environmentally friendly technology utilizes electrochemically active microorganisms to oxidize organic matter, facilitating the release of protons and electrons at the anode. The electrons flow to the cathode through the external electrical circuit and the protons pass through the separating membrane to the cathode and combine in the absence of oxygen to produce hydrogen. MECs are based on electrohydrogenesis, which is an electron release process by microorganisms to combine with protons, forming hydrogen gas as the product. Under tension applied to MECs, electroactive microorganisms use organic materials to produce CO_2, H^+ and electrons (Rousseau et al., 2020; Gautam et al., 2023).

Theoretically, an MEC requires minor external voltage of > 0.2 V to drive the process. Moreover, the biological energy of organic matter in wastewater can be converted into chemical energy, which further reduces energy consumption. The reduced energy requirement is due to microbial metabolism's efficiency, which surpasses that of the abiotic hydrogen evolution reaction (Park et al., 2022; Xu et al., 2023). The degradation of the substrate on the anode and the hydrogen evolution reaction on the cathode in MECs is described according to Equations (27) and (28) below (Rani et al., 2022):

$$\text{Anode}: C_2H_4O_2 + 2H_2O \rightarrow 2CO_2 + 6O_2 + 8e^- + 8H^+ \tag{27}$$

$$\text{Cathode}: 8e^- + 8H^+ \rightarrow 4H_2 \tag{28}$$

The components of MECs (biocatalyser, electrode materials, external potential, type of substrate, organic load rates and membrane) play a significant role in the performance and can function effectively with pure strains, cocultures and mixed strains with different substrates, such as cellulose, glucose, volatile carboxylates, ethanol, and lactic acid acetate, and produce H_2 ranging from 70 % to 90 %. Biohydrogen production through MECs is considered a low-carbon process, as CO_2 emissions are relatively low compared to other H_2 production methods and treated as biogenic carbon emissions, which are not seen as an additional burden for the environment (Lee et al., 2022).

6. Global market of H_2

By May 2024, the global industry reported the initiation of 1,572 clean hydrogen projects. Of these, 1,125 projects have a planned commercial operations date (COD) by 2030, representing an estimated investment of approximately USD 680 billion in hydrogen value chains. Notably, giga-scale projects comprise more than half of the total investment, exceeding USD 380 billion. Growth is evident across most regions in terms of both investment volume and the number of projects, although the pace of growth has slowed compared to previous years. Europe continues to lead with the largest number of projects, totaling 617, followed by North America with 280 projects. In terms of total investment, Europe also holds the highest amount, with USD 199 billion in announced investments. Latin America ranks second with USD 107 billion, while North America comes in third with USD 96 billion. North America also records the highest absolute growth in announced investments, with an increase of USD 28 billion. Regarding relative growth, Japan and South Korea exhibit the highest increases, with investments growing by approximately 130 %, while India shows a 110 % increase. The rest of Asia follows closely, with a growth rate of 75 %. In contrast, Africa is expected to experience a decline in investment through 2030, with a projected total of USD 11 billion. This decline is attributed to the rescheduling of major projects across multiple phases, with some phases, including a USD 7 billion mega-project, being shifted to post-2030 (Hydrogen Council, 2024).

In 2022, hydrogen ranked as the 236th most traded product, with a total trade value of US$18.5 billion. Between 2021 and 2022, hydrogen exports increased 35.4 %, from US$ 13.6 billion to US$ 18.5 billion. Hydrogen sales accounted for approximately 0.078 % of total world sales. The main exporters of hydrogen were China (US$ 3.34 billion), Germany (US$ 2.43 billion), the United States (US$ 2.35 billion), Norway (US$ 1.01 billion) and Malasia (US$ 1 billion), while the main exporters China (US$ 3.46 billion), Japan (US$ 1.98 billion), Germany (US$ 1.73 billion), South Korea (US$ 1.51 billion) and the United States (US$ 1.18 billion). Export and import figures in Brazil were US$ 935 million and US$ 105 million, respectively (OEC, 2023).

The clean hydrogen industry faces some adversities. Costs and cost expectations have increased substantially, especially in the case of renewable hydrogen. The estimated levelized cost of producing renewable hydrogen (LCOH) in the near term is anticipated to fall between approximately 4.5 and 6.5 US$/kg, reflecting an increase of roughly 30 % to 65 %. This rise in costs can be attributed to several factors, including increased labor and material expenses, heightened costs associated with constructing electrolyzer plants, a 3 to 5 percentage point rise in capital costs, and an over 30 % increase in renewable energy costs. The hydrogen sector is experiencing these cost escalations, which are also being observed across various other industries. Despite these short-term cost pressures, it is anticipated that unsubsidized renewable LCOH could decrease to a range of 2.5 to 4.0 US$/kg by the end of the decade, contingent upon regional conditions. Furthermore, it is projected that prices may further decline to between 1 and 2 US$/kg by 2050. The anticipated reduction in the levelized cost of renewable hydrogen (LCOH) in the near term will necessitate the normalization of capital expenditures (capex) associated with renewable energy, a decrease in financing costs, and a swift expansion of global electrolyzer production capacity. Notwithstanding the recent rise in costs, projections indicate that electrolyzer expenses could decrease by as much as 45 % by 2030 and 70 % by 2050, relative to 2023 levels. While an increase in global electrolyzer production may facilitate a more pronounced decline in system costs prior to 2030, ongoing advancements and continuous learning within the sector could further contribute to reductions in costs by 2050 (Hydrogen Council, 2023).

One of the biggest cost factors for the production of green hydrogen is renewable electricity, but this has been becoming cheaper with each passing year. The leveled cost of energy (LCOE) is the ratio between the total cost of a project and the generation of electricity over its lifetime and was conceived to assess and compare the relative cost of energy produced by different sources. In 2022, the LCOE was 0.049 US$/kWh for photovoltaic solar energy, 0.033 US$/kWh (onshore) and 0.081 US $/kWh (offshore) for wind energy, 0.061 US$/kWh for bioenergy (that obtained from biomass), 0.056 US$/kWh for geothermal energy and 0.061 US$/kWh for hydroelectric energy. Combining the cost of electricity, an aggressive implantation of elecrolyser could make green H_2 cheaper than low-carbon alternatives in markets with low electrolyser costs prior to the year 2040 (International Renewable Energy Agency, 2021; International Renewable Energy Agency, 2022).

The reduction in the final H_2 production cost also depends on the conformation of the system (production scale, useful life and utilization factor), which are important variables for the dilution of capital costs, as well as operating flexibility, which would enable variations in the energy input and quantity of H_2 production. Moreover, increases in the annual hours of operation and useful life are expected (Castro et al., 2023).

The need to support technologies with higher technology readiness levels for the rapid uptake of hydrogen in diverse applications is driven by the objective of transitioning to a more sustainable and low-carbon system. Technologies with higher TRLs are more refined and have undergone rigorous testing and validation, and result in economies of scale, optimized designs and improved manufacturing processes (Boretti, 2023). The level of maturity of technologies related to low-carbon hydrogen are being well developed and innovation continues to make great advances, as shown in Fig. 10.

In each stage of the low-emission hydrogen supply chain, different technologies with varying TRLs can be found. For example, in the hydrogen production process via water electrolysis, two key technologies stand out: alkaline electrolysis and proton exchange membrane (PEM) electrolysis. Additionally, hydrogen can also be produced from biomass, utilizing biological methods such as water photolysis, photo-fermentation, or dark fermentation, among others, as well as chemical methods like biomass gasification or pyrolysis reforming (Rey et al., 2023).

7. Potential mitigation of greenhouse gas emissions by hydrogen

Climate change is a critical issue throughout the world that has raised awareness regarding the need for the management of greenhouse gas emissions and is the result of the burning of fossil fuels (manufacturing, electricity generation, transportation and heating homes/businesses), forestry and agriculture (livestock farming, fertilizers, deforestation and the lumber industry) and waste elimination (landfills and incineration). These factors have led to the deaths of individuals due to environmental disasters and favors the occurrence of diseases, especially those transmitted by mosquitos (malaria, yellow fever and dengue). All of this diminishes the possibility of achieving a sustainable society with a healthy environment for present and future generations (Kongboon et al., 2022; Requia et al., 2018).

Carbon dioxide (CO_2) accounts for 80 % greenhouse gases and methane (CH_4), nitrogen oxides (NO_x) and fluorinated gases account for approximately 20 %. These gases naturally trap heat on the planet and are emitted mainly by the combustion of fossil fuels, such as crude oil and coal, mining activities and diverse manufacturing industries, such as the cement industry (Ntuli et al., 2022). Fig. 11 displays the increase in greenhouse gas emissions and consequent changes in temperature in the world over a period of time.

Decarbonization of the energy system has attracted considerable interest because it could diminish the dependence on fossil fuels, reduce negative environmental impacts and accelerate the search for new energy sources. Indeed, some of these goals were established in the 2015 Paris Agreement to achieve zero CO_2 emissions (carbon neutral), with 70–85 % of all global electricity production from renewable energies. Thus, hydrogen – especially that classified as green hydrogen – has been

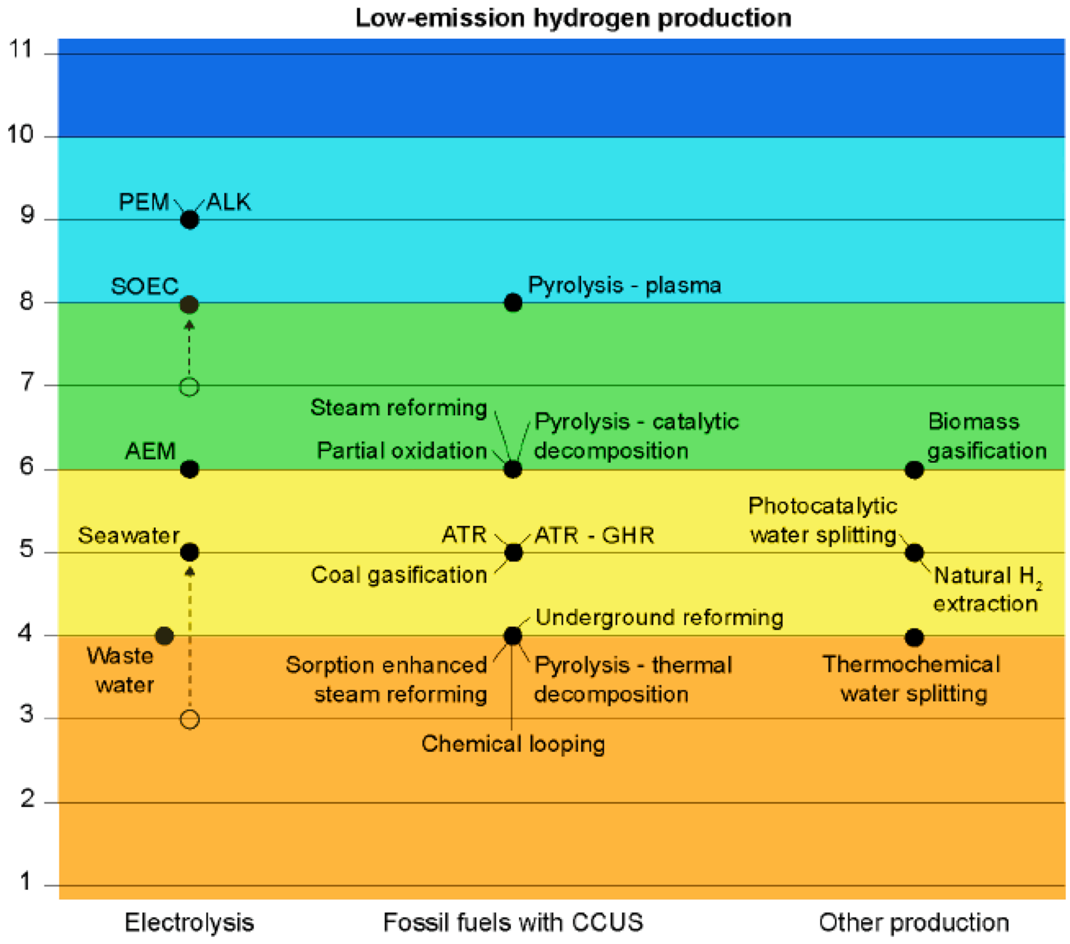


Fig. 10. Technology readiness levels of low-emission production hydrogen. Adapted from International Energy Agency (2023).

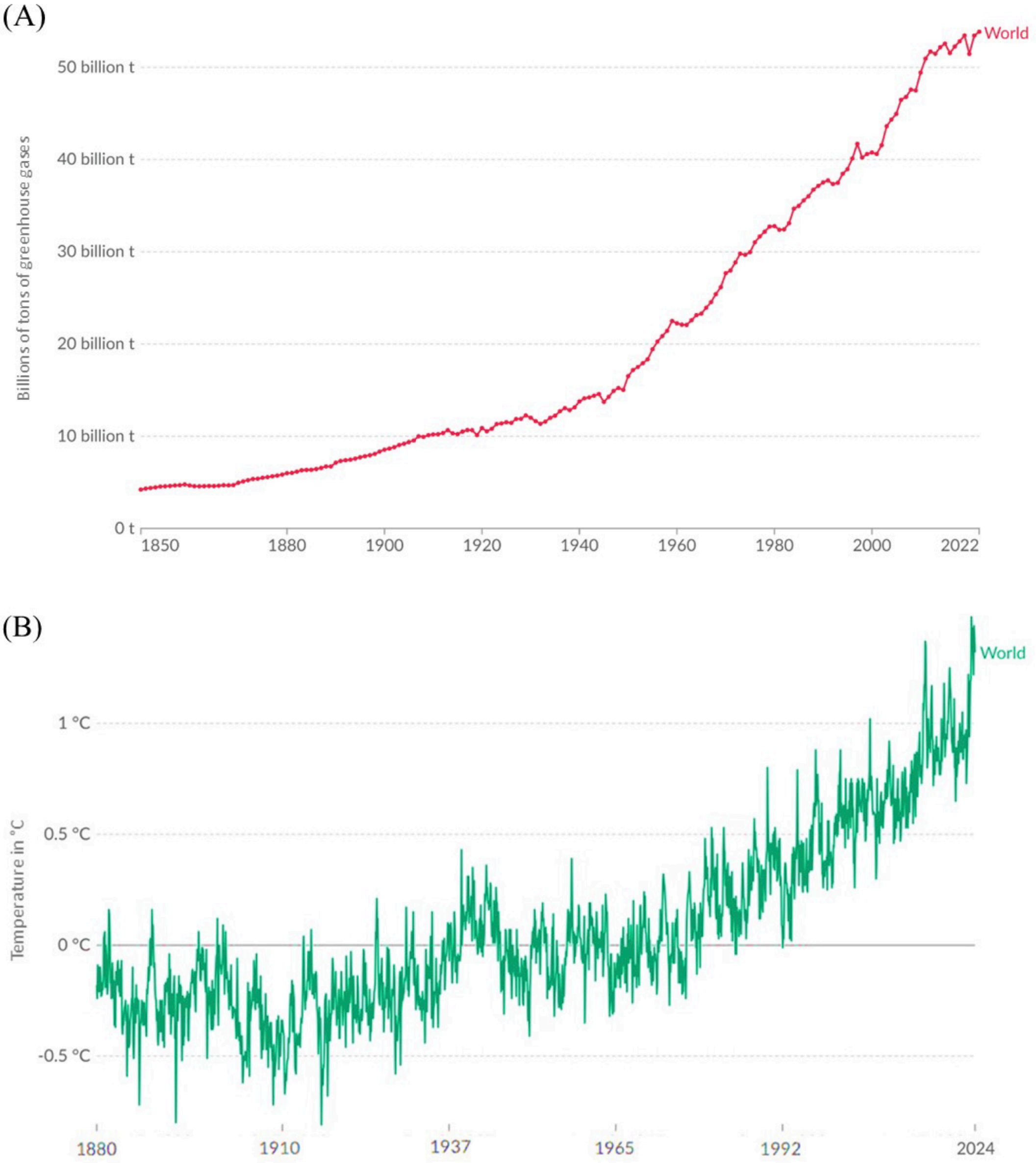


Fig. 11. (A) Increase in global greenhouse gas emissions and (B) global change in temperature. Adapted from Our World in Data (2024).

increasingly considered a viable option for clean and sustainable energy in national and international strategies for application in different sectors (Lee et al., 2021; Noussan et al., 2021; Brito et al., 2023; Hoang et al., 2023).

To ensure a smooth transition to cleaner, more ecological options, effective mitigation strategies should be adopted as soon as possible. Hydrogen, as a fuel, possesses a gravimetric energy density that is 2.5 to 3.0 times greater than that of the most commonly utilized fossil fuels. Furthermore, green hydrogen is anticipated to play a significant role in the future in achieving approximately 6.5 % of the total cumulative reductions in CO_2 emissions by 2050. Its considerable potential for decarbonization has fostered broad acceptance of hydrogen as a feasible energy carrier (Galitskaya and Zhdaneev, 2022; Raman et al., 2022; Akhtar et al., 2023; Harichandan et al., 2023; Meda et al., 2023). Fig. 12 presents the estimate in a planned energy scenario for reducing annual carbon dioxide emissions and 1.5 °C scenario where emissions would reduce around 34 $GtCO_2$ in 2050, and how this emissions abatement would happen in the 1.5 °C scenario for the same year.

Technologies and deployment plans for the production, supply and use of hydrogen must be closely examined to ensure that greenhouse gas reduction and energy security objectives will be achieved. Life cycle analysis (LCA) is a commonly utilized method for evaluating the environmental impacts linked to a product or process. This approach considers direct emissions resulting from various process activities, such as those from the combustion of natural gas on-site. Furthermore, LCA accounts for “upstream” emissions associated with supporting operations, such as those from power generation and fuel supply chains. It also assesses “downstream” emissions, which pertain to the emissions produced during the transportation of the product to its final usage (Frank et al., 2021). Fig. 13 illustrates a life cycle analysis of the primary hydrogen production processes.

As the world undergoes an energy transition away from fossil fuels and in the pursuit of a more sustainable, low-carbon future, hydrogen is an important element emerging as a key player in solving these global problems. H_2 can play some crucial roles in ensuring energy security and decarbonization of the main sectors of the economy, for example: a) if used as an energy source, it can allow the efficient and large-scale integration of renewable energies; b) if used as the backbone of the energy system, it can distribute energy between sectors and regions and act as a buffer to increase the resilience of the system; c) for end uses, it

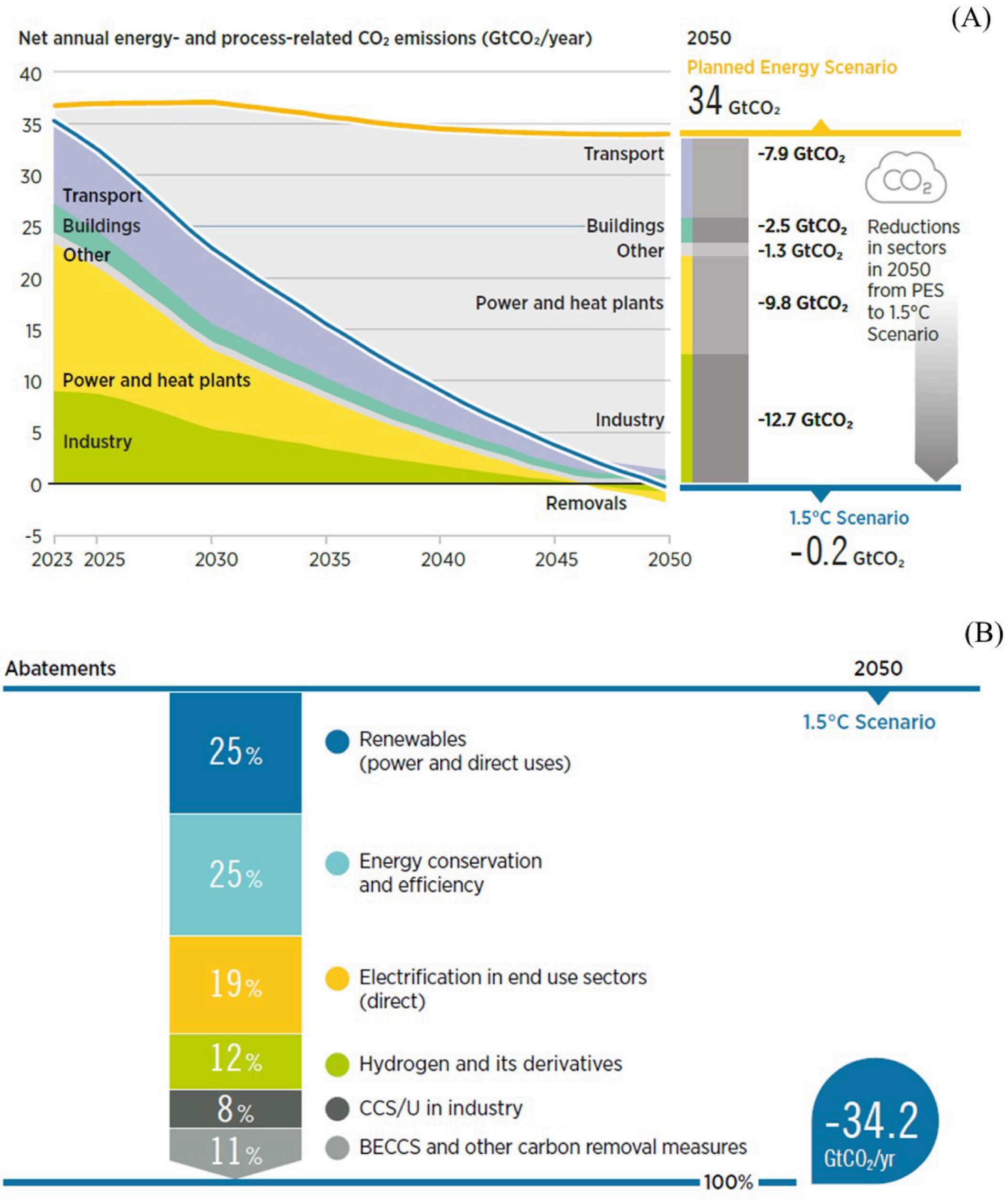


Fig. 12. (A) Estimated trends in global CO_2 emissions, assessing the period 2023–2050, observing the Planned Energy Scenario (PES) and 1.5 °C Scenario and (B) the reduction of carbon dioxide emissions projected under the 1.5 °C Scenario by 2050. Adapted from International Renewable Energy Agency (2023). * CCS/U = Carbon Capture and Storage/Utilization; BECCS = Bioenergy with Carbon Capture and Storage.

can help decarbonize transportation, decarbonize industry energy use, serve as a feedstock using captured carbon, and help decarbonize building heating (Hydrogen Council, 2017; Blay-Roger et al., 2024; Hassan et al., 2024).

8. Hydrogen, green finance and environmental, social and governance (ESG)

The transition to a low-carbon economy requires substantial financial investments, and green finance has emerged as a crucial enabler in this process. A green finance policy consists of a set of principles that guide the acquisition and use of funding for environmentally friendly activities, the development of green finance instruments, and the operations of various stakeholders in the green finance sector. These guidelines dictate how financial investments are directed toward environmentally sustainable projects and sustainable development goals.

By channeling capital toward eco-friendly initiatives, green finance facilitates the scaling of renewable hydrogen technologies, which are essential for meeting global decarbonization targets. Financial instruments such as green bonds, sustainability-linked loans, and carbon credit mechanisms play a vital role in alleviating the high upfront costs associated with hydrogen infrastructure and production facilities. These tools help reduce investment risks, foster innovation, and encourage both public and private stakeholders to prioritize renewable hydrogen as a clean energy source (Falcone et al., 2018; Falcone and Sica, 2019; Ozili, 2023).

Renewable hydrogen, including green hydrogen derived from renewable electricity and biohydrogen produced from organic waste, aligns closely with the principles of environmental, social, and governance (ESG) frameworks, and can help achieve several United Nations (UN) Sustainable Development Goals (SDGs), such as SDG 7 (Affordable

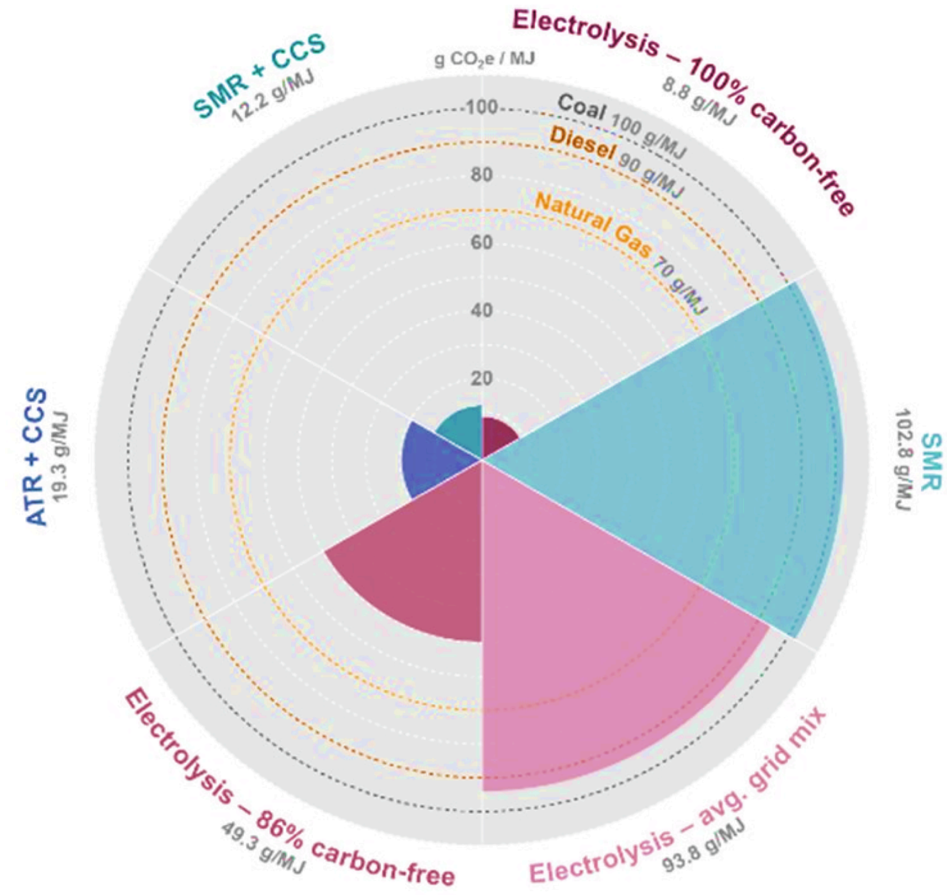


Fig. 13. Average life cycle carbon intensities of main hydrogen production methods. Adapted from Carbon Solutions (2022). *SMR= Steam Methane Reforming; ATR = Autothermal Reforming; CCS= Carbon Capture and Storage.

and Clean Energy), SDG 13 (Climate Action) and SDG 17 (Partnerships for the Goals). These frameworks emphasize not only environmental stewardship but also social responsibility and governance transparency, ensuring that hydrogen investments deliver broad societal benefits. For example, H_2 projects adhering to ESG criteria can enhance energy access in underserved regions, reduce reliance on fossil fuels, and create new employment opportunities in clean energy industries. Moreover, the adoption of ESG principles by financial institutions and corporations ensures that renewable hydrogen development is pursued in an equitable and sustainable manner, balancing economic growth with environmental protection (Zavarkó, 2023; Koneczna and Cader, 2024; Pak and Lee, 2024; Tillu et al., 2024; Zainal et al., 2024).

The integration of green finance, renewable hydrogen initiatives, and ESG principles creates a powerful synergy to address the climate crisis and promote sustainable development. By incorporating ESG considerations into investment decisions, stakeholders can ensure long-term resilience and align with global climate goals, such as the Paris Agreement (2015) and the Sustainable Development Goals. Mobilizing green finance for hydrogen technologies not only accelerates the deployment of these solutions but also reinforces the role of hydrogen as a transformative energy source in achieving net-zero emissions. This comprehensive approach, which combines financial innovation, technological advancement, and strong governance, is essential for unlocking the full potential of hydrogen in the global energy transition (Taghizadeh-Hesary et al., 2022; Fu et al., 2023; Udeagha and Muchapondwa, 2023; Fu et al., 2024; Martins et al., 2024).

9. Conclusion

Besides fostering the discussion on the serious global climate challenges caused by greenhouse gas emissions, this review emphasizes the potential of renewable hydrogen as a cornerstone for global decarbonization. Significant investments in hydrogen-related technologies and infrastructure are increasing globally, supported by declining renewable energy costs that enhance the competitiveness of renewable hydrogen against other hydrogen types and fossil fuels, making it a long-term and economically viable alternative.

Green hydrogen and biohydrogen represent complementary pathways toward a sustainable energy future, each with unique contributions to decarbonization. While green hydrogen leverages renewable energy sources for electrolysis, biohydrogen offers a biologically driven approach utilizing organic waste, enhancing circular economy principles. Their synergy, combined with strategic investments and innovation, underscores hydrogen's pivotal role in achieving global energy and climate goals.

Moreover, the integration of green finance plays a pivotal role in scaling the hydrogen economy by enabling capital mobilization for research, production, and distribution. Financial mechanisms, such as green bonds and public–private co-financing schemes, mitigate investment risks and ensure alignment with ESG principles. Whether in the form of pure gas or as derived molecules (ammonia, methanol, and synthetic fuels for aviation), hydrogen can lead to a significant reduction in greenhouse gas emissions in industries for which such reduction is currently difficult to achieve, such as the chemical, metallurgic and heavy transportation industries, and can assist in ensuring flexibility and stability with regards to solar and wind energy systems.

Therefore, as the global community intensifies efforts to limit warming to below 1.5 °C, renewable hydrogen stands out as a transformative solution for achieving net-zero emissions and fostering a sustainable energy transition. By leveraging technological innovation, strategic investments, and robust financial frameworks, the hydrogen economy can address the pressing challenges of energy security and climate change while creating new opportunities for economic growth and industrial transformation. The coordinated actions of governments, private sectors, and financial institutions will be pivotal in unlocking the full potential of this clean energy source, marking a significant step toward a resilient and low-carbon global future.

CRediT authorship contribution statement

Bruno Augusto Cabral Roque: Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Matheus Henrique Castanha Cavalcanti:** Conceptualization, Formal analysis, Investigation, Methodology. **Pedro Pinto Ferreira Brasileiro:** Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Paulo Henrique Ramalho Pereira Gama:** Data curation, Investigation, Methodology. **Valdemir Alexandre dos Santos:** Validation, Supervision, Project administration, Conceptualization. **Attilio Converti:** Writing – review & editing, Visualization, Validation, Conceptualization. **Mohand Benachour:** Visualization, Validation, Supervision, Project administration, Funding acquisition, Conceptualization. **Leonie Asfora Sarubbo:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Data curation, Conceptualization.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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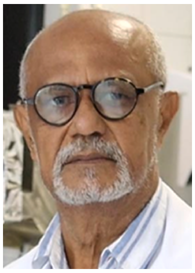

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