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Transforming biomass into sustainable biohydrogen: an in-depth analysis

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Hydrogen is considered one of the most effective alternative fuels in the journey toward achieving zero greenhouse gases in the future. Currently, it remains predominantly sourced from non-renewable energy resources, such as fossil fuels. Unfortunately, a significant concern regarding our dependence on these exhausted resources is their profound adverse effects on our environment. We view the development of a proposed biomass-to-sustainable hydrogen strategy as an attractive opportunity to produce a sustainable strategic hydrogen source. To achieve large-scale commercial adoption of biohydrogen, it is essential to optimize a range of operating parameters. In this context, machine learning is essential for achieving such results alongside physicochemical, biological, and electrochemical methods. These advanced techniques enable researchers to optimize processes, predict outcomes, and enhance the efficiency of experiments. By integrating machine learning with traditional methods, scientists can uncover insights that were previously unattainable. This review explores the recent advancements in thermochemical, biological, and electrochemical methods for generating biohydrogen from biomass. Advanced methodologies and thermochemical processes, like thermal plasma, are crucial for gasifying materials, modelling processes, treating sewage sludge, and enhancing hydrogen production by capturing and using CO_2. These methods have shown significant promise in increasing the efficiency and sustainability of biohydrogen production. By leveraging innovative techniques, researchers aim to optimize the conversion processes and enhance the overall yield of hydrogen, contributing to cleaner energy solutions. It highlights the use of machine learning in operational analysis, emphasizing its ability to capture complex relationships between operational and performance factors. The authors have thoroughly examined the applications, obstacles, and sustainability of biohydrogen. The authors have outlined the forthcoming perspectives and challenges. These findings provide a comprehensive understanding of the current state of biohydrogen research and its future potential. By articulating these insights, the authors contribute valuable knowledge to the ongoing discourse in this field. Ultimately, the authors have articulated their findings.

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Sustainability spotlight

Biohydrogen is rapidly emerging as a practical substitute for conventional fossil fuels, thanks to its impressive energy yield, carbon neutrality, and sustainable characteristics. It can be produced from various biomass sources, including agricultural residues, lignocellulosic waste, food waste, forestry byproducts, and energy crops. The suggested method for turning biomass into sustainable biohydrogen is nearing realization, using a mix of thermochemical, thermal plasma and biological processes along with advanced technology to improve efficiency and sustainability. Machine learning is crucial for optimizing operating parameters in biohydrogen, alongside physicochemical, biological, and electrochemical methods. Recent advancements in producing hydrogen from biomass show the promise of a circular bioeconomy, which connects current industries in a way that is sustainable for the economy, the environment, and society.

1. Introduction

Researchers are currently exploring renewable resources as potential sources of clean energy that could substitute fossil fuels. The primary influences contributing to this situation include increasing concerns about climate change, rising energy costs, and health issues linked to airborne pollutants.[1] Shuttleworth *et al.*[2] indicate that contemporary biomass conversion fulfils merely 10% of global energy requirements, while fossil fuels such as coal, natural gas, and oil account for the remaining 90%. Given the significance of energy in a nation's economy, many countries are diligently exploring reliable approaches to generate alternative fuels.[3] Some alternative fuels have an energy density comparable to that of fossil fuels, positioning them as potential substitutes to mitigate

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concerns related to carbon footprints.[4,5] Biofuels obtained from biomass demonstrate potential for addressing expected future energy shortages.[6]

Contemporary biomass-derived biofuels are carbon-neutral and renewable. Biomass-derived biofuels, unlike fossil fuels, originate from newly planted plants and do not increase atmospheric CO_2 concentrations. This contrasts with fossil fuels, which emit carbon dioxide that has been sequestered for millions of years.[7] Consequently, biofuels present a promising alternative to fossil fuels to mitigate greenhouse gas emissions and tackle climate change. A variety of biomass sources, such as agricultural residues, forestry byproducts, and energy crops, can generate biofuels derived from biomass.[8] This suggests that local manufacturing can produce them, thereby decreasing dependence on imported fossil fuels and enhancing energy independence. Nonetheless, a key challenge in the production of ethanol from biomass is the conversion of the substrate into simpler and more fundamental components.

Hydrogen has surfaced as a compelling alternative fuel, attributed to its exceptional energy density relative to other biofuels, which is approximately 140 MJ kg^{-1}. It can be quickly produced and moved and can be directly used in cells to produce energy.[9–12] However, restrictions across the entire process on a large scale obstruct the benefits.[13] Consequently, researchers are currently exploring numerous approaches to enhance the process. The availability of organic substrates allows for the optimization of process parameters, thereby enhancing the rate of hydrogen production. Furthermore, we can utilize biological techniques and genetic modification to boost hydrogen production. Scholars such as Nath and Das,[14] Sivagurunathan *et al.*,[13] and Zhao *et al.*[15] have explored this topic extensively. In comparison to various biofuels, biohydrogen stands out due to its lack of carbon emissions and its impressive energy density. Improving biohydrogen production presents challenges due to the complex nature of biohydrogen generation systems.

Recently, advancements in nanotechnologies have emerged for application in the agriculture, food, pharmaceutical, and energy industries.[16–18] Nanomaterials improve many biological processes by changing the growth of microbes, the movement of electrons inside cells, and the way metalloenzymes interact with each other. All of these changes affect the production of hydrogen.[19] Therefore, the use of nanomaterials could significantly improve the production of biohydrogen.[20] Nanoparticles improve the efficiency of electron transfer processes involving microorganisms, electrodes, or other electron acceptors. This enhances the efficiency of biohydrogen production.[21] Nanoparticles have attracted considerable interest as possible additives for improving biohydrogen production. A number of investigations have shown the effectiveness of this method.[12]

The production of biohydrogen has garnered significant attention in recent reviews.[22–33] To highlight a few, Eloffy's[22] review discusses patented methods for hydrogen production from biomass, including thermochemical, biological, and electrochemical approaches. Ahmed *et al.*[23] provide a comprehensive overview of key elements involved in creating economical hydrogen production technologies for long-term sustainability. Samrot *et al.*[24] analyse various sources used in biohydrogen production, their production pathways, and their applications in electricity generation. Habashy *et al.*[25] evaluate the potential of utilizing food waste for biohydrogen generation through microbial agents, while Yun's[26] review explores fermentation methods for generating H_2, focusing on dark fermentation. The review highlights the economic viability of this method and introduces strategies for enhancing H_2 yield and waste removal efficiency. Ubando *et al.*[34] give a thorough look at the different types of biomass feedstocks and processing technologies used to make biohydrogen. They also talk about how current industries could be added to a model for a circular bioeconomy.

Machine learning has shown significant potential in biohydrogen production, enabling large-scale analysis of large datasets and identifying significant patterns.[33,35,36] Kumar Sharma and Pandey[37,38] used machine learning to study biohydrogen generation, predicting metabolic pathways and energy production capabilities of various strains. These data facilitated the identification of the most appropriate microbial strains for biohydrogen generation and enhanced genetic engineering methodologies. Alagumalai *et al.*[36] provided an extensive review on the generation of biohydrogen through the application of machine learning techniques, highlighting the potential of machine learning in improving biohydrogen production efficiency.

The reviews presented above concentrate on a particular facet of biohydrogen generation from biomass waste, which is a generally singular domain of knowledge. A complete look at the newest advancements in biohydrogen production from biomass waste requires a careful approach that takes into account all relevant factors simultaneously. This review explores the use of biomass-derived feedstocks, including food and agricultural waste, in biohydrogen production. It explores thermochemical, biological, and electrochemical processes using advanced technologies. The combination of advanced methods and thermochemical processes, such as thermal plasma, is discussed in detail because it is important for turning materials into gas, modelling processes, treating sewage sludge, and improving hydrogen production by capturing and using CO_2. The study emphasizes the interconnectedness of these techniques and the importance of machine learning models in biohydrogen generation. The integration of biomass-derived feedstocks in hydrogen production is crucial for sustainability, as it ensures economic viability, environmental friendliness, and social significance. Addressing current challenges and utilizing advanced technologies can enhance cleaner energy solutions. Authors also discuss the future implications.

In the subsequent sections, we discuss biohydrogen as a viable long-term solution in Section 2, while Section 3 focuses on biomass-based feedstocks. Section 4 addresses various advanced technologies for H_2 generation. Section 5 highlights the perspectives of machine learning in the context of biohydrogen production. Section 6 looks at how biohydrogen can be used, the challenges it faces, and a detailed look at its sustainability in terms of economic feasibility, environmental safety, and social value. Sections 7 and 8 address future perspectives and challenges, and conclusions, respectively.

2. Biohydrogen: a sustainable and renewable energy solution

The concept of "biohydrogen" refers to the production of dihydrogen gas (H_2) by various microorganisms, including bacteria, archaea, and algae. Biohydrogen can be made in a number of biological ways, such as bio photolysis,[39] fermentation with bacteria that make hydrogen,[40] and microbial electrolysis cells.[41] Biowaste-based approaches offer a more economical alternative to other energy-producing systems while ensuring zero pollutant emissions. Biohydrogen emerges as a promising alternative to carbon-based fuels, demonstrating potential as an environmentally friendly energy carrier.[42,43]

Climate change is considered a paramount concern of our era; hence, it is unsurprising that one of the Sustainable Development Goals (SDGs) emphasizes 'immediate action to address climate change and its effects'. People view hydrogen as a potential source of clean energy and fuel. We can generate biohydrogen from renewable feedstocks in a sustainable and environmentally friendly manner. Biohydrogen can significantly contribute to reducing greenhouse gas (GHG) emissions. This can be achieved by converting waste, a carbon-neutral resource, into biohydrogen.[44,45] Within the framework of the European Green Deal, the EU prioritizes the hydrogen economy.

Furthermore, biohydrogen possesses numerous characteristics that render it more advantageous compared to other biofuels currently in production. The characteristics encompass increased gravimetric density, diminished emissions, and enhanced efficiency in the conversion of raw materials (*i.e.*, the feedstock) to energy.[46] Renewable hydrogen fuel-cell vehicles, recognized as life-cycle carbon-free alternatives for the transportation sector, are converted directly into fuel cells instead of undergoing combustion.[25] Furthermore, hydrogen demonstrates a high level of efficiency as an alternative fuel source in comparison to other fuel types. The highest energy content per unit weight is 34 kcal per g H_2, in contrast to petroleum, paraffin, coal, castor oil, and wood, which exhibit energy contents ranging from 10.3 to 8.4 kcal g^{-1}, 10.3 to 9.8 kcal g^{-1}, 7.8 kcal g^{-1}, 9.4 kcal g^{-1}, and 4.2 kcal g^{-1}, respectively.[47] In comparison to hydrocarbon fuel, hydrogen exhibits a 2.75-fold greater energy content, positioning it as a highly suitable energy source.[48]

Fig. 1 presents a streamlined flow diagram illustrating the biohydrogen cycle utilizing biomass as a feedstock. The initial phase involves the generation of biomass sources, including agricultural waste or food waste. The subsequent phase involves transforming the biomass source into waste. We then transport the biomass waste to the designated conversion locations. After specific processing, we convert this biomass into biohydrogen and subsequently store it. The generated and stored biohydrogen is subsequently provided to the consumer *via* distribution stations. The distribution stations facilitate consumption by end users for various applications. Condensation and precipitation processes ultimately regenerate biomass sources. This cyclical approach not only supports sustainable energy production but also minimizes waste and promotes environmental stewardship. By efficiently reusing biomass, we can significantly reduce our carbon footprint and enhance energy security for future generations.

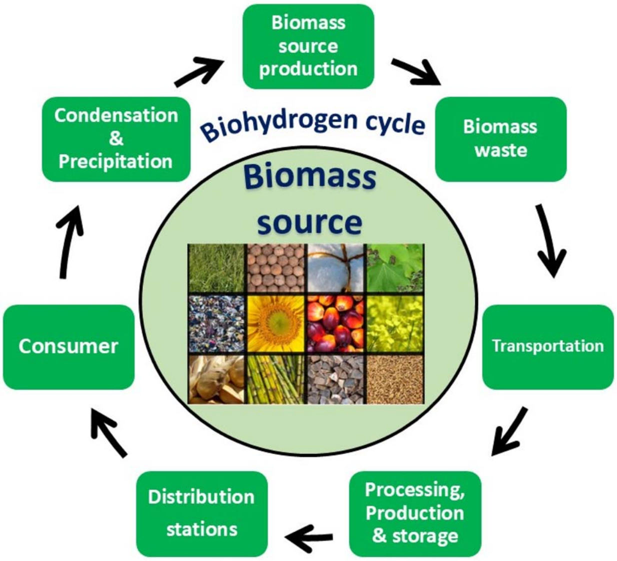

Fig. 1 Biohydrogen cycle: biomass progresses through multiple phases to generate biohydrogen, starting with biomass cultivation and concluding with its ultimate application by the consumer; adapted from ref. 25.

The ongoing global crisis regarding climate change presents an opportunity to maximize the advantages of hydrogen through the development of cost-effective and efficient hydrogen production technologies. A biological approach from bio renewable sources can achieve commercial-scale hydrogen production, serving as an alternative to physicochemical methods.[49] This method typically generates hydrogen, known as biohydrogen.[50] Biohydrogen production can occur through direct or indirect bio photolysis, photofermentation, dark fermentation, or a combination of these methods.[51] Biological processes facilitated by microbes exhibit considerable advantages in terms of their operational temperature and pressure, as well as the ability of microorganisms to exploit a wide variety of substrates. Consequently, this method proves to be more practical and pertinent for (bio)hydrogen production, as the associated costs are significantly lower compared to traditional physicochemical processes.[52,53] The different types of substrates, how they are pretreated, the design of the bioreactor, the catalysts used, the process of separating hydrogen from the gaseous mixture, the risks that come with it, and the fact that it is stored are some of the other important things that limit biohydrogen production.[54] The production of hydrogen through physicochemical processes necessitates elevated temperatures ranging from 150 to 850 °C and involves intricate machinery, leading to increased energy consumption and, consequently, higher operational expenses.

3. Biohydrogen: feedstocks from biomass

The increasing use and demand for biofuels has sparked significant interest in a biomass-based economy. Plants, animals, and microorganisms provide biomass, a highly appealing and viable renewable resource for biofuel production. The potential of these carbon-based feedstocks to substitute existing fossil-fuel energy systems and the petrochemical products needed for diverse industrial applications is significant.[55] The chosen sources for hydrogen gas generation ought to be economical and biodegradable, featuring a high carbohydrate content along with simple sugars like glucose, lactose, and sucrose. These components serve as dependable biodegradable substrates for biohydrogen production.[56] Through biophotolysis, cyanobacteria, microalgae, and photosynthetic anoxygenic bacteria break down water to produce biohydrogen. This process is very helpful because it makes use of important natural resources like water and sunlight.[57] These microorganisms provide electrons as an alternative source for survival under minimal optimal conditions or to prevent the reduction of the electron transport chain, functioning as a safety mechanism. In addition to these biochemical reactions,[58] the nitrogenase enzyme can also make hydrogen gas during nitrogen fixation. This is an important part of how blue-green algae form heterocysts. The primary biomass feedstocks utilized for biohydrogen production include various organic materials such as agricultural residues, municipal solid waste, industrial waste, food waste, and energy crops. We choose these feedstocks for their abundance and their capacity to produce hydrogen through anaerobic digestion and gasification processes. Here, we are highlighting mainly two feedstocks, such as agricultural waste (primarily lignocellulose) and food waste.

3.1. Agricultural waste

Numerous studies have focused on finding alternative sources of green, clean, and renewable energy in the past ten years. However, while the production of biofuels from food sources such as corn and sugar has emerged as a viable alternative, it has unintentionally increased food prices, resulting in a global food crisis. Consequently, the production of biofuels from agricultural waste has garnered significant interest in recent times. The generation of hydrogen gas from agricultural waste, composed of lignocellulosic material, plays a significant role in the global energy conversion process.[59] We can convert significant amounts of hemicellulose and cellulose in agricultural waste into mono- or disaccharides. This material can be used in both direct and indirect dark fermentation, photofermentation, and biophotolysis.[60]

The composition of agricultural waste typically includes cellulose, hemicellulose, lipids, lignin, proteins, simple sugars, starches, hydrocarbons, ash, water, and various other compounds.[61] Typically, these materials comprise 30–50% cellulose, 20–30% hemicellulose, and 5–40% lignin, although this composition can differ based on their source. Because lignocellulose has a lot of different parts and is naturally stable, it is challenging to turn it into certain products without using high temperatures and pressures.[62,63] Direct liquefaction of agricultural waste with high water content proves to be significantly more economical, as it eliminates the necessity for drying or pretreatment.[64] Lignocellulosic materials constitute the majority of agricultural waste and are the most significant. These materials, which include residues from crops such as corn stalks and sugarcane bagasse, can be valuable resources for producing biofuels and other bioproducts.[24] By converting lignocellulosic waste into biohydrogen, we can reduce environmental impact while promoting sustainable agricultural practices.

3.1.1. Lignocellulose waste. Lignocellulosic biomass stands out as a highly promising feedstock for the production of eco-friendly biofuels, biochemicals, and carbon-neutral biomaterials.[65] Woody plants are a renewable source of highly abundant terrestrial biomass. It comprises non-edible plant materials, ensuring that it does not compete with food crops or agricultural land use. Agricultural and forestry residues primarily provide lignocellulosic feedstocks (LCFs), with various industrial and municipal waste presenting additional potential sources.[66]

Various forms of LCFs display distinct characteristics in terms of appearance and strength; however, they primarily consist of three fundamental components that account for about 90% of their dry weight. The composition includes homopolymeric cellulose (35–55 wt%), heteropolymeric hemicellulose (20–40 wt%), and lignin (10–25 wt%) as illustrated in Fig. 2.[67] Specific bonding interactions connect the lignocellulosic polymers, creating a mesh-like network. This network affects the physical properties and strength of different LCFs.[68] Cellulose is the main part. It is a crystalline polysaccharide that holds D-glucose subunits together with hydrogen bonds, van der Waals forces, and 1,4 glycosidic bonds. This organic polymer is among the most plentiful on the planet and constitutes the fundamental building block of plant cell walls. Inter- and intramolecular hydrogen bonds hold the long, straight polymeric chains of cellulose together. This makes it easier for either crystalline or amorphous structures to form. Another type of polysaccharide is hemicellulose. It is made up of different sugar acids, hexoses, and pentoses that are linked by weaker α- and β-glycosidic bonds. The make-up of this complex carbohydrate is different in hardwood and softwood structures. It is crucial for connecting the cellulosic microfibrils and lignin. The final component that completes the structure of LCF is lignin – a complex heteropolymer made up of phenylpropanoid subunits interconnected by aryl-ether (C–O–C) and carbon–carbon (C–C) bonds in varying amounts. The composition consists of three monolignol monomers: *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. When these parts come together, they make lignin precursors. These precursors then make the *p*-hydroxyphenyl, guaiacyl, and syringyl units that make up the phenylpropane subunits. This is because lignin has a branched, polymeric, and cross-linked structure that makes the whole lignocellulosic polymer rigid and impermeable. This makes it difficult to separate cellulose and hemicellulose for making fermentable sugars.[69–71]

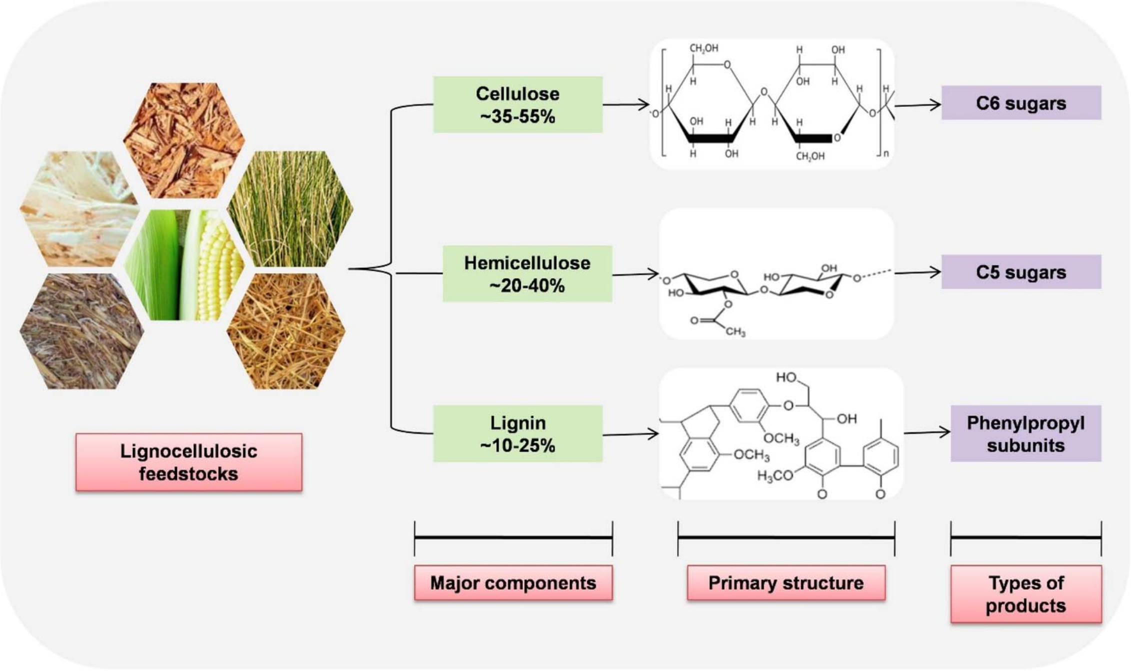

Fig. 2 Elements of lignocellulosic feedstocks and the principal categories of products produced by hydrolysis. Reproduced from ref. 67 with permission from Elsevier, copyright 2022.

Recently, researchers have utilized LCFs for biohydrogen production due to their significant carbohydrate content, specifically cellulose and hemicellulose. The prevalent LCFs utilized include corncobs, corn stover, corn stalk, switchgrass, rice straw, sugarcane bagasse, and wheat straw.[69,71] Nonetheless, the intricate nature of the LCFs hinders the effective use of lignocellulosic materials, rendering the production of $BioH_2$ unfeasible. So, scientists have come up with a number of physical, chemical, and biological pretreatment methods to break down or get rid of the lignin polymer and make cellulose and hemicellulose easier for bacteria to digest during fermentation. Physical pretreatment operations incur significant costs and demand substantial energy input, while chemical methods involve hazardous substances and generate toxic byproducts that adversely affect the environment. On the other hand, the biological pretreatment process employs microorganisms and enzymes to break down lignin, making it more effective while using less energy. This method has proven to be cost-effective, offering a broad spectrum of applications and achieving a higher yield of the final product.[72] Naturally occurring microorganisms get rid of the lignin polymer, which makes it easier to make lignocellulosic $BioH_2$ after the right fermentation reactions and helps make a number of value-added products.

Because of its efficiency, biohydrogen production from lignocellulosic waste has gained significant interest. Research has shown that different types of lignocellulosic substrates work well and have positive effects. Biohydrogen production from lignocellulosic biomass has been made better by dark fermentation, pre-treatment, hydrolysis, and the use of different microbial cultures.[73] This has led to higher biohydrogen yields and production rates. Taguchi *et al.*[74] used *Clostridium* sp. strain no. 2 from termites and oat-spelt xylan to make biohydrogen at a rate of 18.6 mmol g^{-1} of substrate. Taguchi *et al.*[75] used the same *Clostridium* sp. to break down cellulose and found that it used 0.92 mmol of glucose per hour and made 4.1 mmol of hydrogen per hour. The rise in cellulose concentration from 12.5 g L^{-1} to 50 g L^{-1} resulted in a decline in yield from 2.18 mmol g^{-1} of cellulose to 0.42 mmol g^{-1} of cellulose. They also found that high temperatures facilitated significant conversion of cellulose into hydrogen, yielding 43 mL of hydrogen per gram of cellulose at 37 °C and 69 mL at 55 °C, resulting in a total production of 567 mL of hydrogen from 1 g of cellulose.[76] Samrot *et al.*[24] and Saha *et al.*[67] recently provided a comprehensive review on LCFs as a promising resource for biohydrogen production. Fig. 3 and Table 1 illustrate the process of converting lignocellulosic biomass into biohydrogen. They also list the different types of lignocellulose biomass and how much hydrogen they produce.

Recently, Swami *et al.*[90] investigated the potential use of ionic liquids and other green solvents in the pretreatment of lignocellulosic biomass. The paper gives a thorough look at how ionic liquids can be used to prepare lignocellulosic biomass for use. Ionic liquid pretreatment differs from conventional procedures as it is recyclable and reusable, among other advantages. They look at a number of important factors that affect how biomass dissolves and talk about the hazardous properties of ionic liquids.

3.1.2. Influence of agricultural waste characteristics on energy production. Different techniques, including combustion, gasification, and anaerobic digestion, can convert agricultural waste—such as crop residues, animal manure, and

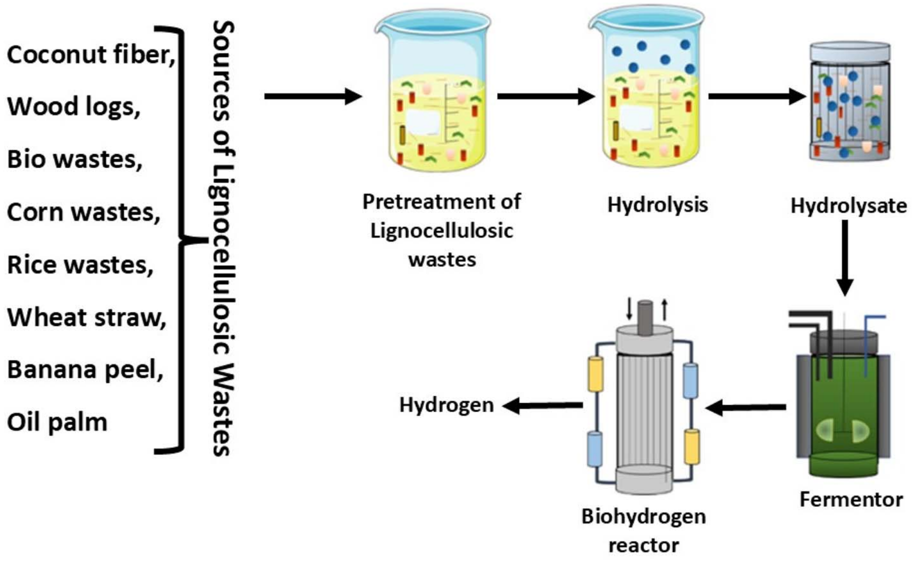

Fig. 3 Generation of biohydrogen from lignocellulosic waste materials adapted from ref. 24.

Table 1 Lignocellulosic biomass, its structure, and hydrogen generation

Lignocellulose biomass (LCB)	Monomer structure	Structure of LCB	H_2 generation	Ref.
Beer less	Not mentioned	Not mentioned	68.6 mL g^{-1} of total volatile solids	77
Corn stover	1.5 g/L-xylose 10 g/L-glucose 0.2 g/L-arabinose	37.6% cellulose, 21.5% hemicellulose and 19.1%-lignin	12.9 mmol L^{-1} in an hour	78
Grass	Not mentioned	Not mentioned	4.9 mol g^{-1} of total solid	79
Soy bean straw	3.6% of total reducing sugars	39.6% cellulose, 4.6% hemicellulose and 23.4% lignin	60.2 mL g^{-1} of dry straw	80
Wheat bran	Not mentioned	8.27% cellulose, 33.7%-hemicellulose	128.2 mL g^{-1} of total volatile solid	81
Wheat straw	Xylose, arabinose, and glucose	35–39% cellulose, 22–30% hemicellulose and 12–16% lignin	5.78 mmol mLg^{-1}	82 and 83
Banana peel	Pectic acids, monosaccharides, and flavonoids	30–38% cellulose, 15–21% hemicellulose and 7–16% lignin	32.71 mmol g^{-1}	84 and 85
Oil palm	Esterified glycerol, fatty acids	32.58% cellulose, 8.37% hemicellulose and 20.13% lignin	118.1 mmol mL^{-1}	86 and 87
Rice straw	Arabinose, arabinan, glucose, xylan, and the alcohols, *etc.*	32–47% cellulose, 19–27% hemicellulose and 5–26% lignin	24.63 mmol g^{-1}	88 and 89

food processing waste—into a source of energy. The properties of agricultural waste can affect the feasibility and effectiveness of energy extraction in both positive manner and negative manner.[91] Table 2 provides a comprehensive summary of the beneficial impacts, limits, and critical applications of agricultural waste. The characteristics of agricultural waste are illustrated, highlighting their potential influence on the effectiveness and efficiency of energy production processes. In the process of determining the most effective technology and extraction method for energy production, it is crucial to consider the unique properties of the agricultural waste feedstock.

3.2. Food waste

The issue of food waste (FW) is a global concern. Promoting a sustainable circular economy is essential, as it has the potential to boost revenue, improve food security, and provide energy in the world's most disadvantaged nations. FW has a profound impact on food quality, food supply stability, and

Table 2 Analysing the positive and negative effects caused by agricultural waste[91]

Beneficial impacts	Limitations	Applications	Ref.
Enhanced energy density: greater efficiency in agricultural waste production can be achieved by optimizing energy extraction from crop residues like wheat straw, which are rich in energy	Minimal energy content: agricultural waste with low energy content, such as grass or low-quality wood, may not be suitable for gasification or direct combustion	Electrode materials in energy storage devices	92
Enhanced volatility: agricultural waste, including sawdust and wood chips, can be efficiently gasified or combusted to generate energy	Increased ash levels: agricultural waste, including rice husk, can cause corrosion and deposition in gasification and combustion apparatus, potentially reducing energy extraction effectiveness	Extensive uses in sustainable water remediation technology, activated carbon manufacturing, oil–water separation, and the construction of high-performance composites	93
Elevated moisture levels: agricultural waste, including animal manure and food processing byproducts, can be processed through anaerobic methods to produce biogas, a valuable energy source or vehicle fuel	Elevated nitrogen levels: the combustion of agricultural waste rich in nitrogen, like animal dung, can lead to the emission of nitrogen oxides into the atmosphere, causing air pollution	Biogas fuel generation	94

economic growth advancement. Nonetheless, the use of FW can contribute positively to the conservation of the organic ecosystem.[95] Moreover, there is a notable rise in global energy consumption that aligns with the growth of population and economy.[96] Biohydrogen production from renewable materials like food processing and agricultural waste is a creative way to meet the world's growing energy needs and replace fossil fuels while also addressing the problems that come with managing solid waste in cities.[96] Anaerobic digestion processes commonly use FW as the starting material for energy generation because of its reliable physical, biological, and chemical properties. There are a lot of these things in the water, with a COD range of 19 to 346 g L^{-1}, a carbohydrate content of 25.5 to 143 g L^{-1}, and a carbon to nitrogen (C : N) ratio of 14 to 37.[97] The physicochemical characteristics of FW can influence hydrogen production and quantity. Adjustable variables include the pretreatment conditions of FW (chemical, enzymatic, or physical methods), pH, temperature, and hydrogen partial pressure.[98] To improve biohydrogen production on an industrial scale, it is also important to think about things like the particle size, moisture content, nutritional value, volatile solid composition, and biodegradability of FW.[99]

Researchers are currently conducting a variety of investigations into biohydrogen synthesis from food waste. These investigations utilize mixed cultures comprising compost, manure, and anaerobic sludge. Researchers are performing experiments on semi-continuous, continuous, and batch bioreactors. The study demonstrates that bacteria pollute naturally occurring freshwater that contains a lot of carbon. This makes it a useful raw material for making biohydrogen in places that aren't clean[100] The use of a pure culture inoculum to convert food waste into biohydrogen, as well as the maintenance of the culture's purity during prolonged reactor operation, remains uncertain.[100]

4. Biohydrogen: generation routes from biomass feedstock

Various methods are available for generating H_2 from biomass-derived materials. The leading techniques for generating H_2 from biomass currently encompass thermochemical, biological, and electrochemical processes (Fig. 4). These processes leverage different mechanisms to convert biomass into hydrogen, each with its advantages and challenges. For instance, thermochemical methods often require high temperatures, while biological processes typically operate under milder conditions but may take longer to yield results. While the challenges of scaling up biological and electrochemical hydrogen production result in limited hydrogen yields,[101] there is a growing interest in thermochemical hydrogen generation.[102] Thermochemical hydrogen generation offers several advantages, including higher efficiency and the ability to utilize a wider variety of feedstocks. As research progresses, innovations in this area may lead to more sustainable and economically viable methods for hydrogen production from biomass. In the following subsection, we will explore in detail the recent advancements achieved in the processes of biohydrogen production from biomass feedstocks.

4.1. Routes of thermochemical generation

Thermochemical transformation stands as the leading method for producing H_2 from biomass. Within the realm of commercialization, these processes face numerous challenges. Comparable techniques utilized in the domain of biofuels, including bio-methane and SMR, have resulted in the development of this technology.[103] This technology, while promising, requires further advancements in efficiency and scalability to become commercially viable. Additionally, addressing the economic feasibility and environmental impacts of these

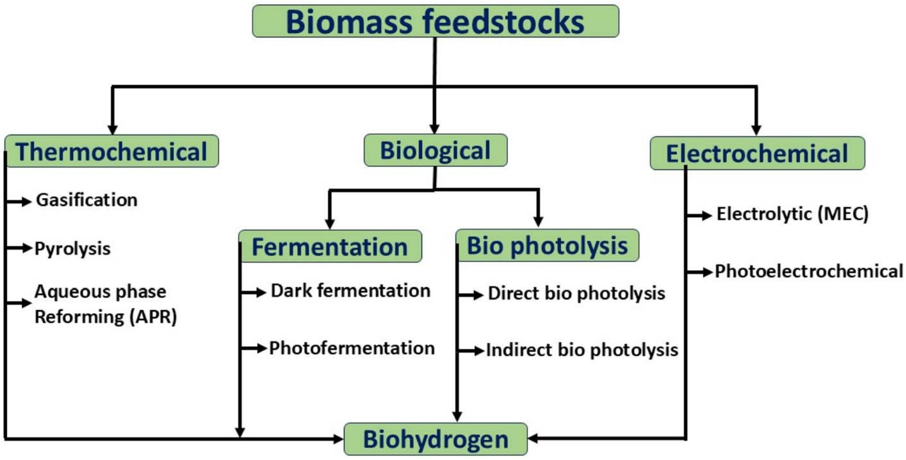

Fig. 4 The primary routes for the generation of biohydrogen derived from biomass.

processes will be crucial for their widespread adoption in the energy sector. We will discuss the three essential thermochemical techniques in detail below: gasification, pyrolysis, and aqueous phase reforming. The application of advanced methodologies in conjunction with thermochemical processes, such as thermal plasma, is of significant importance. We have looked into how thermal plasma helps gasify materials, how to model this process, how to treat sewage sludge using thermal plasma, and how to enhance hydrogen production by capturing and using CO_2.

4.1.1. Gasification: thermal plasma-assisted gasification. Gasification is a thermochemical process that converts biomass into gaseous fuels through partial oxidation and reduction reactions at elevated temperatures. The process produces syngas, consisting of H_2, N_2, CO, CH_4, and CO_2, which includes various combustible gases, inert components, tar, char, dust, and additional impurities.[22] This process does not immediately liberate the energy within the biomass; instead, it converts it into the bond energies of lighter fuels. The valorisation of organic waste streams, including biomass and hazardous waste, is increasingly utilizing modern thermal plasma technology.[104] This technology offers high temperatures and energy fluxes, efficient destruction, high-quality syngas and slag production, and environmental sustainability and operational oversight.[105]

Bioenergy with carbon capture and storage (BECCS) combines CO_2 sorption with thermal plasma-assisted gasification to pull carbon dioxide out of the air where it is. We can achieve this by introducing sorbents into steam reformers[106] or water gas shift reactors.[107] The sorbent, like calcium oxide or magnesium oxide, adsorbs CO_2, enhancing hydrogen production. We decarbonize the sorbent carbonate to restore its functionality and release a concentrated stream of CO_2. The main idea behind sorption-enhanced gasification is to trap CO_2 inside the reactor.[104] This changes the balance according to Le Chatelier's principle, which leads to more hydrogen being made.[108] Carbon capture reactions[104] transpire at lower temperatures to adsorb CO_2, generating carbonates and heat emissions. Decarbonation processes regenerate the sorbent with concentrated CO_2 release. The CO_2 stream can be used for chemical synthesis or geological storage. Fig. 5 schematically

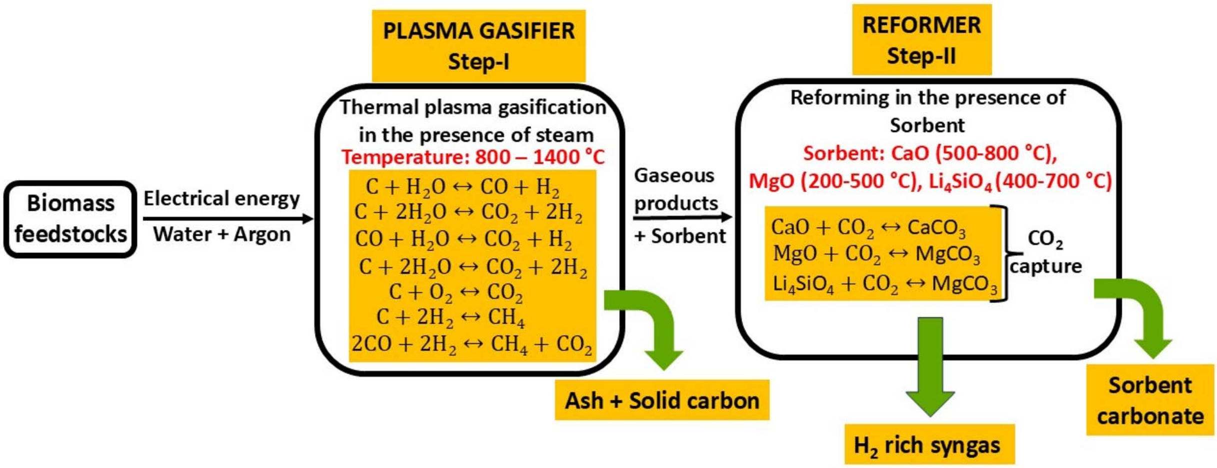

Fig. 5 Diagram depicting the suggested two-step process for sorption-enhanced gasification that includes CO_2 collection and the generation of clean energy adapted from ref. 104.

depicts the whole process of thermal plasma-assisted gasification, which occurs in two steps.

4.1.1.1 Thermal plasma-assisted gasification modelling. Assumptions of the model:[104,109] (i) all state variables within the reforming and gasifier reactors were constant: (ii) the particle size distribution of the feedstock had no effect on the gasification reactor's performance;[110] (iii) both reactors were run under isothermal conditions at 1 bar; (iv) pyrolysis occurred quickly, producing hydrogen, carbon monoxide, carbon dioxide, and methane as the cardinal gases;[111] (v) pyrolysis took place before reforming reactions and char gasification; (vi) ash was regarded as a non-reactive solid; (viii) the enthalpy of formation, specific heat capacity, and density were computed using the HCOALGEN and DCOALIGT property methods in the Aspen Plus environment; (ix) the catalytic activities of the used sorbents (CaO, MgO, and Li_4SiO_4) were not taken into consideration; (x) the catalytic activity of thermal plasma was not taken into consideration.

The gasification of biomass and waste involves many interconnected phases, including drying, pyrolysis, partial oxidation, and gasification. Heterogeneous partial oxidation of char, along with gas-phase processes and tar cracking reactions, follows the devolatilization of feedstock. Tar cracking may be succinctly shown as:[112]

$$pC_nH_x \leftrightarrow qC_mH_y + rH_2 \quad (1)$$

where C_nH_x denotes tar and C_mH_y signifies a lighter hydrocarbon. The model is succinctly described as follows:[104] the modelling framework for refuse-derived fuel (RDF) included different steps, like making thermal plasma, breaking down the feedstock, volatile reactions, gasification, reforming, improving CO_2 absorption, and separating the solids from the gases. The model compound moved at a speed of 100 kg h^{-1}, and three sorbents were used: CaO, MgO, and Li_4SiO_4. The gasification temperature, reforming temperature, steam-to-feedstock ratio (S/F), and sorbent-to-feedstock ratio (SOR/F) were adjusted to affect syngas component distribution, hydrogen production, dry gas yield, lower heating value, and optimal working conditions. Water and argon were delivered to the plasma torch at consistent rates, and water was added to the gasifier at different rates to achieve the right S/F ratio. The sorbent was also delivered to the reformer at different rates to achieve corresponding SOR/F ratios.

The thermal plasma was produced in the Direct Current (DC) Plasma Torch, where power, argon, and water were supplied. The heater functioned as the plasma torch, providing thermal plasma input to the gasifier. The feedstock (RDF) was heated in the heater before being introduced to the pyrolyzer. The Aspen block RYield functioned as the pyrolyzer because of its capacity to calculate yields from complicated feedstocks, including non-conventional resources such as biomass, trash, and coal. The reaction is presumed to have occurred in the pyrolyzer as given below:[113]

$$C_xH_yO_z \rightarrow H_2 + CO + CO_2(g) + HC(g) + Tar(l) + Char(s) \quad (2)$$

where $C_xH_yO_z$ represents the biomass or organic waste, and HC denotes the hydrocarbons.

A calculator block was used to calculate the yields based on the literature pertaining to the RYield reactor.[111] The temperature-dependent empirical connections accurately predicted the yields. The pyrolyzer's products were introduced to the gasifier in conjunction with water for steam gasification. As a gasifier, the RGibbs reactor worked by minimizing Gibbs free energy so that phase and equilibrium calculations could be done and the final yields after gasification could be found.

The gasifier sent its gaseous byproducts to the reformer, which made it possible for reactions to happen that involved reforming, carbonation, and decarbonation. Solid products, including carbon and ash, were isolated using a filter. The RGibbs reactor was used as the reformer, ensuring sorbent regeneration. The reformer always got a new sorbent at different feed rates, and the products were filtered to separate the gases and solids. A comprehensive examination of this subject may be found elsewhere.[98]

4.1.1.2 Thermal plasma processing of sewage sludge: experimental studies. Researchers are looking into a new thermochemical method that uses high-temperature thermal plasma to break down organic waste streams like sludge into syngas and slag/ash that can be used to get nutrients and make other useful products.[114,115] This method aligns with clean energy and circular economy principles, as it can provide substantial heat fluxes at extreme temperatures with reactive species.[116] Using thermal plasma to turn solid waste into gas is also useful for storing energy when combined with renewable energy sources. This is because syngas can store energy when the output is high and send it to the grid when the demand is high.[117]

An overview of the experimental procedures for treating sewage sludge (SS) is as follows:[114] the SS was turned into gas in a thermal plasma reactor that could hold 300 L on the outside and 220 L on the inside. It also had a ceramic liner that was about 0.4 m thick to keep the heat inside. An argon–water stabilized DC plasma torch with variable arc power (maximum 150 kWe) produced thermal plasma. Water and argon stabilize the arc to inhibit cathode oxidation. Water is introduced tangentially to the arc chamber, creating a vortex that envelops the electric arc. A portion of the water evaporates and becomes ionized, while the remainder is recirculated to the water management system, therefore lowering the temperature of the plasma torch. A revolving copper disk, cooled by water, functions as the anode. The disc's rotation significantly mitigates anode deterioration. The arc power was modified between 120 and 80 kW throughout all experimental runs to maintain a consistent average temperature of 1200 °C in the reactor, depending on energy needs.

The generated plasma exhibited the following characteristics: (i) a bulk temperature ranging from 17 000 to 18 000 °C near the plasma torch outlet, leading to a wall temperature of 1200 °C in the reactor;[115] (ii) a very low mass flow rate of Ar and H_2O through the plasma torch; (iii) a high ratio of net arc power to plasma mass flow rate at 200 MJ kg^{-1}; (iv) negligible syngas dilution by plasma gas; and (v) negligible generation of tars.

The plasma torch was affixed to the upper section of the reactor, accompanied by a water-cooled jacket and a hopper for feeding stainless steel. After the reactor's top was opened, the gas was collected for mass spectrometry and Fourier-transform infrared spectroscopy. The water spray system directed the gas to a quenching chamber, reducing its temperature to 300–500 °C. After that, the mixture was sent to a ceramic filter that was very good at separating solids, like solid carbon and fly ash, from the gas (>99%). Finally, a flare safely ignited the gas. It's important to note that adding a water ejector between the filter chamber and gas burner made it easier for the reactor to work at a pressure of several hundred Pa below atmospheric pressure. Multiple thermocouples were strategically placed at various locations to enhance understanding of the temperature distribution within the reactor, at the gas outlet, following gas quenching, and within the filter. A more thorough analysis of this topic may be found elsewhere.[114,115]

4.1.1.3 Enhanced hydrogen production with CO_2-sorption under CCUS. Because of the current climate change scenarios caused by rising greenhouse gas emissions, rising energy needs, and plans to capture CO_2, we need to switch to a clean and efficient fuel source right away. Hydrogen possesses an impressive energy content of 120 MJ kg^{-1}, nearly three times that of gasoline when compared on a mass basis, making it a potential candidate in this context. Hydrogen serves multiple purposes, including power generation and chemical synthesis, and it is also applicable in fuel cell-driven electric vehicles. It's important to note that electrolysis and photolysis can directly make pure hydrogen. Other methods, such as steam reforming, partial oxidation, and auto-thermal reforming, produce hydrogen-rich gas mixtures that need to be concentrated and cleaned up further.[118]

One potential approach involves integrating the previously discussed processes with *in situ* CO_2 capture using solid sorbents during reforming, which would subsequently improve H_2 production in the syngas.[119] We refer to this concept as sorption enhanced reforming, or SorE. This process offers the versatility to utilize a diverse range of feedstocks, including biomass, waste materials, and natural gas.[118] It is important to recognize that hydrogen-rich syngas requires additional processing to achieve pure hydrogen. Researchers have recently extensively investigated this route using a variety of sorbents and a range of feedstocks. This technology makes it possible to capture CO_2 before it burns in carbon capture and storage (CCS) systems.[118] It also makes high-purity hydrogen to meet the world's energy needs.

The main reason for making different sorbents is to capture as much carbon dioxide as possible, taking into account the sorption conditions, such as whether they happen after or before combustion. Traditionally, zeolites and activated carbons were the initial sorbents utilized. Recently, many new sorbents have been created, some of which are based on metals (like calcium and magnesium), others on alkali ceramics (AC), and still others on metal–organic frameworks (MOFs).[118] These are all meant to improve how well they absorb CO_2 and how long they last. You can test how well solid sorbents capture CO_2 by looking at their selectivity, their ability to regenerate, and their ability to take in carbon dioxide, which are shown in eqn (3)–(5):[120,121]

$$\text{Selectivity} = S = \left(\frac{x_1}{x_2}\right) \Big/ \left(\frac{y_1}{y_2}\right) \tag{3}$$

$$\text{Regenerability} = (R\%)\left(\frac{\Delta A_{CO_2}}{\Delta A^{sor}_{CO_2}}\right) \times 100 \tag{4}$$

$$CO_{2\,\text{capacity}} = \Delta A_{CO_2} = \Delta A^{sor}_{CO_2} - \Delta A^{desor}_{CO_2} = CO_{2\,LSP} - CO_{2\,LDP} \tag{5}$$

LSP = loading at sorption pressure; LDP = loading at desorption pressure. In this context, CO_2 sorption capacity is denoted as $A^{sor}_{CO_2}$, A^{sor}_1 represents the adsorbed CO_2, and A^{sor}_2 signifies the adsorbed CH_4 (or N_2). The variable x_1 indicates the CO_2 mole fraction in the adsorbed phase, while x_2 denotes the CH_4 (or N_2) mole fraction in the adsorbed phase. Furthermore, y_1 refers to the CO_2 mole fraction in the gas phase, and y_2 corresponds to the CH_4 (or N_2) mole fraction in the gas phase. A more comprehensive examination of this subject is available elsewhere.[118]

4.1.2. Pyrolysis. Pyrolysis is a thermochemical process that converts biomass into hydrogen (Fig. 6),[122] similar to gasification but operating at lower temperatures and without an oxidizing agent.[123] It typically occurs within a temperature range of 400 to 800 °C and can involve pressures reaching up to 5 bar. Pyrolysis' primary goal is to produce bio-oil, but it can also generate H_2 through flashing or rapid pyrolysis at high temperatures with a suitable residence time.[124] Three types of pyrolysis exist: conventional (or slow), rapid, and flash pyrolysis.[125] Conventional pyrolysis occurs at temperatures below 450 °C, resulting in charcoal. Fast pyrolysis produces up to 75 wt% bio-oil at medium temperatures (450–600 °C), using a high heating rate and brief residence time. Flash pyrolysis, similar to rapid pyrolysis, occurs at higher temperatures and heating rates, optimizing gas production.[126] However, lower operational temperatures from rapid and flash pyrolysis result in lower gas yields compared to gasification.[127,128]

Fast pyrolysis is a process that transforms various types of biomass into solid char, liquid oil, and volatile gas, even without air or oxygen. This process generates pyrolytic gas, which is then cooled and condensed to produce bio-oil, a dark brown liquid with a high heating value.[129] We can categorize bio-oils into two groups: those that dissolve in water and those that don't. The insoluble portion transforms into platform molecules such as benzene, toluene, and xylenes (BTX), or olefins suitable for use in adhesives.[130] Bio-oil is used as fuel in engines, boilers, and combined heat and power (CHP) facilities. The optimal yield occurs at 500 °C, with a 2-second residence period and high heating rate.[131] The biomass must be desiccated to less than 10% and pulverized into tiny particles for maximum production and improved bio-oil quality. Bio-oil typically contains 15 to 30 wt% water, making it suitable for combustion engines. However, the carboxylic acid in bio-oil significantly influences its pH, making it caustic and

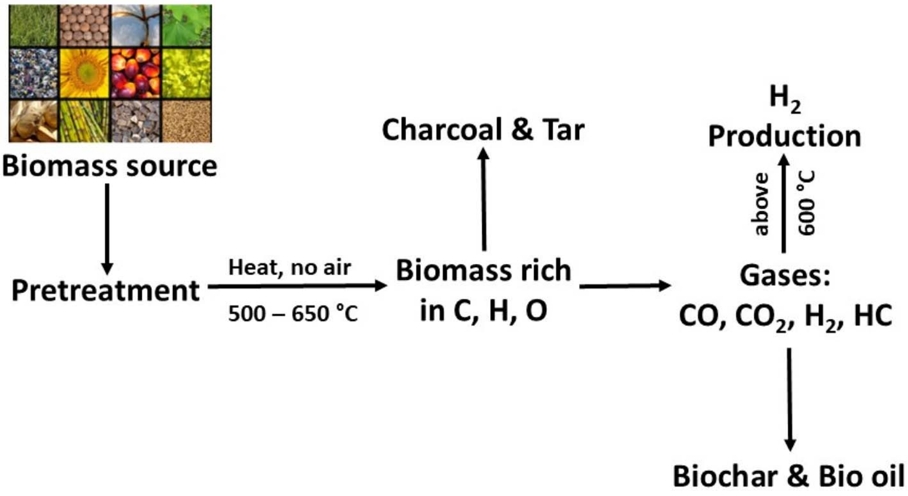

Fig. 6 A simplified diagrammatic representation of the pyrolysis operation adapted from ref. 122.

requiring additional upgrading before it can be used as fuel in the transportation sector.[132]

Chandran *et al.*[133] looked at how temperature affected the bio-oil yield from *Prosopis juliflora* biomass and how well it worked as a blending agent. Borges *et al.*[134] found that using wood sawdust and corn stove feedstock in microwave-assisted pyrolysis led to the highest bio-oil output of 65% at 480 °C and 64% at 490 °C. Chen *et al.*[135] used a fixed bed reactor to study how temperature and the amount of catalyst affect the fast pyrolysis of cotton stalk. The study found that the proportion of ketone in bio-oil increased with CaO use as a catalyst. However, bio-oil output was superior between 500 and 600 °C, regardless of biomass species and reactors used.

The pyrolysis process entails breaking down cellulose into smaller particles and converting them into gaseous products. Increasing the temperature, heating rate, and residence time can accelerate the pyrolysis process. Fast pyrolysis yields higher output than slow pyrolysis,[136] with lignin being the most stable fraction. We noted that initial H_2 emissions for all species in pyrolysis experiments involving pine, cottonwood, and rice straw began at 400 °C and peaked between 650 and 750 °C. However, variations in biomass composition resulted in rice straw exhibiting a higher release rate compared to pine, while cottonwood showed the lowest rate.[137] Solar pyrolysis can achieve extremely high temperatures, reaching up to 2000 °C, which has been shown to enhance gas yield.[138] Hot radio-frequency plasma pyrolysis has successfully explored a temperature range of 900–2000 °C, resulting in high syngas productivity.[138] Phenolic compounds facilitate the complete breakdown of unstable compounds at pyrolysis temperatures exceeding 700 °C.[139]

Phuet Prasertcharoensuk *et al.*[140] noted that there were no significant yield changes when the pyrolysis temperature was increased from 600 to 700 °C; however, they did document a 23% increase in gas yield when the temperature was raised to 800 °C. The observed trend was linked to the total release of volatiles in the temperature range exceeding 700 °C, along with their subsequent cracking and dry reforming at elevated temperatures. Their observations indicated a clear upward trend in CO and the H_2/CO ratio, alongside a downward trend in CO_2 content. This was explained by the ongoing consumption of the released CO_2 in the Boudouard reaction, which is enhanced above 700 °C, as well as the dry reforming of light hydrocarbons, which is facilitated above 640 °C to generate additional H_2 and CO.[140] Al Arni *et al.*'s[141] study on sugarcane slow pyrolysis found that the yield of syngas increased, with hydrogen content notably rising from 7% to 28.8% as the temperature elevated from 773 K to 953 K. This enhancement was attributed to the promotion of tar cracking reactions, which led to an increase in gaseous products at the expense of heavier hydrocarbons, according to the study. CO and CO_2 gases were initially prevalent due to the more straightforward decomposition of hemicellulose and cellulose. However, their levels decreased beyond 400 °C, at which point the gradual decomposition of lignin began to contribute to the release of H_2 and methane.[141] They did an inline pyrolysis-catalytic SR experiment on pyrolysates made from sawdust using 10 wt% Ni/Al_2O_3.[136] As the temperature rose, gas production and H_2 yield increased, with the highest H_2 content found between 600 and 700 °C.[136]

Pyrolysis, a process involving heating and decomposition of materials, significantly impacts gas yield. Raising heating rates can increase gas yield but may decrease oil and char yield.[22,141] Research shows that a limited range of heating rates, specifically from 5 to 20 °C min^{-1}, has a negligible impact on gas yield. A higher rate, exceeding 30 °C min^{-1}, significantly influences results.[136] For instance, in refuse-derived fuel pyrolysis, gas yield rose from 14 to 47% when the heating rate was elevated from 5 to 350 °C min^{-1}.[136] However, this led to a decrease in bio-oil yield and a gradual decline in solid content.

A slow pyrolysis process with a long residence time can help with re-polymerization, making char and turning liquids or tar into more gas.[141] Excessive residence time increases reduce H_2 production by accelerating the thermal cracking of heavier hydrocarbons and releasing more gas. However, different reactions use up H_2, forming other gases like carbon oxides and methane.[142] Pyrolysis-steam reforming is an innovative two-stage thermochemical approach that has gained significant interest.[143] The catalysts used are the same ones used in the cracking phases of gasification, and carbon deposition renders them inactive. A phase of catalyst regeneration makes it easier for coke to be burned and turned into CO_2, which clears out active sites.[144] Global H_2 yields are comparable to those achieved through gasification *via* steam reforming, falling between 70% and 80%.[145] Table 3 summarizes some notable instances using thermal plasma, microwave, and vacuum pyrolysis methods.

4.1.2.1 Steam thermal plasma assisted pyrolysis. Thermal plasma-assisted pyrolysis is a sophisticated method for industrial hydrogen production. The process employs methane to produce hydrogen as per eqn (6):[158]

$$CH_4 \rightarrow 2H_2 + C \tag{6}$$

where C represents carbon black. To comprehend methane pyrolysis, it is customary to concentrate on the generation of H_2 and carbon black, as shown in eqn (6). This method produces what's known as turquoise hydrogen. We can classify methane pyrolysis methods into three primary categories: thermal, catalytic, and plasma.[158] However, the plasma techniques represent the most advanced technology. For thermal and catalytic processes, heating and cooling must be done slowly and carefully, and reactors must work for long periods of time. On the other hand, one can turn off plasma reactors at any time without any negative effects.[158] This aligns well with time-dependent renewable energy sources derived from solar or wind energy. The best thing about using thermal plasma for pyrolysis of methane is that it creates high-quality carbon products along with hydrogen. These include carbon black, carbon nanotubes, graphene nanosheets, and other structures made of carbon that can have their properties changed.[146] Thermal plasma generators use a lot of energy, but the process settings can be changed to get high-purity hydrogen and high-quality carbon products.

Recently, Mašláni *et al.*[146] investigated the pyrolysis of methane using thermal steam plasma to produce hydrogen and carbon black. The study analysed methane pyrolysis for hydrogen and solid carbon production using the PlasGas plasma reactor. The reactor uses a DC plasma torch with a water vortex to generate steam plasma. They analysed the gas composition for various input methane flow rates. They found that the optimal flow rate for methane conversion was 200 slm to 300 slm, leading to high conversions of 75% and 80%. The output was a blend of hydrogen, methane, and solid carbon. The energy excess for the reaction was 16 kW for 100 slm and 4 kW for 200 slm. The solid carbon produced was made of spherical particles. The study found that oxygen addition enhances methane conversion but reduces the available energy produced.

Mašláni *et al.*[149] also looked into how simulated natural gas (NG) breaks down in a steam thermal plasma torch reactor. The study found that the optimal input flow rate of 100 slm for NG was the highest, resulting in a mixture of hydrogen and solid carbon. However, at higher flow rates, a significant amount of unconverted methane was observed in the output gas. The specific energy requirement for the produced hydrogen was more favourable for 500 slm of NG. The study also found that the composition of natural gas significantly influences the pyrolysis process. Higher amounts of hydrocarbons made the methane conversion less effective and reduced the amount of energy needed compared to pyrolysis of pure methane.

4.1.3. Aqueous phase reforming (APR). APR is a thermochemical way to turn biomass into hydrogen, mostly by changing compounds that contain oxygen into hydrogen.[159–161] The process involves the hydrolysis of cellulose and hemicellulose, resulting in the production of monomers that serve as feedstock.[162] The reaction mechanism resembles that of SR,

Table 3 Overview of some notable research using thermal plasma, microwave, and vacuum pyrolysis techniques

Thermal plasma	Microwave	Vacuum pyrolysis
(i) Methane pyrolysis using thermal steam plasma to produce carbon black and hydrogen[146]	(i) Microwave-heated pyrolysis of used motor oil to produce hydrogen and light hydrocarbons as a possible gaseous fuel[147]	(i) Optimization of parameters and economic evaluation of vacuum-promoted methane pyrolysis for hydrogen generation with carbon separation[148]
(ii) Effects of natural gas composition on the generation of solid carbon and hydrogen during steam thermal plasma assisted pyrolysis[149]	(ii) Rubber waste degradation using microwave-induced catalytic pyrolysis to produce hydrogen-enriched syngas[150]	(ii) *Ex situ* catalytic fast pyrolysis of non-thermal plasma-pretreated HDPE using 1Fe1Ni/γ-Al_2O_3 catalyst to increase hydrogen generation[151]
(iii) Possibility of combining thermochemical technology with anaerobic digestion to maximize waste[152]	(iii) Production of hydrogen using microwave plasma aided by the conversion of a CO_2–CH_4 combination[153]	(iii) An experimental and theoretical investigation into the method of producing hydrogen by the catalytic fast co-pyrolysis of cotton stalks and polypropylene[154]
(iv) RDF was pyrolyzed and gasified with the use of thermal plasma using sequestered CO_2 as a gasifying agent[115]	(iv) Using microwave-driven methane pyrolysis to produce hydrogen without CO_2 (ref. 155)	(iv) Utilizing vacuum pyrolysis to produce carbon black and hydrogen from used lubricant[156]
(v) Combining CCUS and thermal plasma to valorise sewage sludge[114]	(v) Microwaves' significance in the production and storage of green hydrogen[157]	

relying on C–C bond cleavage to generate H_2. The selection of a metal-based catalyst is significantly determined by the stability of the M–C bond and the M–O bond, which facilitate the C–O cleavage pathway.[22] Metal catalysts are prohibitively expensive for large-scale development.

The APR's selectivity is influenced by the feedstock biomass and process parameters.[163,164] We prefer basic and neutral supports over overly acidic ones due to their higher selectivity for H_2 and lower selectivity for alkanes.[165] The conversion of intricate oxygenated compounds, like carbohydrates, presents challenges due to their lower H_2 yield.[166] The thermal homogeneous degradation of carbohydrates results in a significant amount of coke, which inhibits the catalyst and competes with the reforming reactions. APR is an innovative hydrogen production method that offers lower reaction temperature and higher efficiency compared to traditional methods like steam reforming and autothermal reforming. It initially uses subcritical water, reducing energy consumption and enhancing overall energy efficiency, despite lower hydrogen yield.[167]

In the APR process, different kinds of catalysts are used to make green hydrogen from biomass derivatives. These include alloy oxides, composite active metals, feedstocks, and more.[167] For example, Al_2O_3–MgO support makes it easier for Ni particles to spread out, leading to an improvement in H selectivity (increasing from 61% to 76%) and glycerol conversion (rising from 67% to 92%).[168] Using coprecipitation and calcination, Mg and Al can make layered double oxide (LDO) and layered double hydroxides (LDHs). The 19.5 Ni/Mg_3Al-LDO catalyst achieved a remarkable turnover frequency of 99 $\text{mol}_{H_2}\ \text{mol}_{Ni}^{-1}\ h^{-1}$ for the APR of cellulose using LDO's fundamental sites.[169] Mao *et al.* looked at how the activity and structure of different perovskite structures changed.[170] They discovered that during APR, Pt/$LaNiO_3$ can change into Pt–NiO_x/$LaCO_3OH$, which makes the Pt sites and O–H groups stand out more. The H_2 yield for the APR of glycerol goes from 37% to 56% when Ce is added to the Pt/Al_2O_3 catalyst.[171] The WGS also works 2 to 10 times better.[172] The high reactivity of Pt–O–Ce is responsible for this improvement.[173] Bimetallic catalysts can enhance catalyst performance by increasing their reactivity and stability.[174] For example, incorporating copper into Ni/Al_2O_3 enhances the H_2 production rate from 180 to 353 $\text{mmol}_{H_2}\ g_{cat}^{-1}\ \text{min}^{-1}$ during the aqueous phase reforming of glycerol.[175] Researchers noted similar synergistic effects when they incorporated Co, Fe, and Ce into a Ni-based catalyst.[176,177] Non-noble metals like Fe, Co, Ni, and Cu have been added to Pt/γ-Al_2O_3 to make the catalyst more affordable.[178] Adding active metals to a metal oxide catalyst can help by providing more surface area, making oxygen atoms more reactive, and changing the interaction between different metals.[167] Pendem *et al.*[179] reported that K doping stabilizes more $^{\bullet}OH$ on the surface of the Pt/Al_2O_3 catalyst. The increased presence of $^{\bullet}OH$ facilitated the reforming of $^{\bullet}CO$ intermediates on Pt nanoparticles, leading to enhanced H_2 generation at low temperatures.

Transition metal carbides, like molybdenum carbide (Mo_2C), are commonly used as hydrogen generator catalysts because they are excellent at absorbing both hydrogen and oxygen.[180] Yao *et al.* investigated these two structural types in the WGS process, revealing that Au/α-MoC exhibited much more reactivity than Au/β-Mo_2C.[181] DFT simulations showed that varying Mo/C ratios on the Mo_xC surface resulted in the preferential formation of CO from the HOCO intermediate on the C-rich α-MoC catalyst, while CH_4 was mostly produced on β-Mo_2C.[182] Ni/α-MoC showed exceptional activity, exceeding the Cu and Co catalysts by almost five times (7.09 *versus* 1.81 and 1.40 $\mu\text{mol}_{H_2}\ g_{cat}^{-1}\ s^{-1}$).[183] The most hydrogen can be made by a single-atom MoC catalyst, but active metals on the support surface tend to stick together, which makes the catalyst lose its effectiveness quickly. A catalyst with isolated Pt atoms (Pt_1) and Pt clusters (Pt_n) was designed to address this issue.[184] At a Pt loading of 2 wt%, both Pt_1 and Pt_n were detectable concurrently, but only Pt_1 was identified at lower loadings. Over 263 hours, the 2 wt% ($Pt_1 - Pt_n$)/MoC catalyst retained 56% of its activity and made 4 300 000 mol H_2 per mol Pt.

Adding nitrogen to carbon-based substrates can make surface functionalization easier. For example, Pt–Ru/N-doped mesoporous carbons (NMCs) are better at converting glycerol to hydrogen than undoped mesoporous carbons (MCs).[185] Nitrogen doping makes the substance more basic, so it adds three new places for basic molecules to stick: graphitic, pyridinic, and pyrrolic sites.[167] This makes the material more active. The nitrogen in the carbon framework functions as an anchoring point for metal nanoparticles, preventing metal sintering and improving stability. Comparable enhancements were also observed in the doping of nitrogen with Pt Mn/platelet carbon nanofibers[186] and Fe–Cu/graphene[187] for the anodic partial oxidation of ethylene glycol and methanol. Jiang *et al.* elucidated the more particular interaction between Pt and C–N using electrochemical infrared (IR) spectroscopy and DFT computations.[188]

The approach to include additional elements into the support to enhance the interaction between the active metal and the support may be a potential avenue for future development.[167] Because of the effects on the environment, making more base-free catalysts is necessary to fix problems that happen after wastewater treatment. At the same time, some ways of making catalysts use dangerous chemicals (like organic metal salts and N/P heterocycles) that need to be changed for safer ones. Additionally, we may use some biomass materials as catalyst building blocks. For example, 3D-hydrochar made from sawdust is very stable and can produce hydrogen.[189] Simultaneously, biochar generated from these biomasses may promote carbon sequestration from the atmosphere, signifying environmental advantages.[190] The approach to include additional elements into the support to enhance the interaction between the active metal and the support may be a potential avenue for future development. The next lines of research should focus on improving catalytic systems by making them more efficient, stable, and environmentally friendly while also learning more about how reactions work.[167]

4.2. Biological generation routes

Levin's study[191] on biological hydrogen production underscores its crucial importance in the development of future biorefinery systems. Originating in the mid-1970s in response to oil-related challenges, the initiative is considered boundless and sustainable for the environment. Biological hydrogen is generated through various techniques, including fermentation, biophotolysis, enzymatic processes, and microbial electrolysis. Fermentation is categorized into two distinct types: dark fermentation and photofermentation, the latter of which harnesses solar energy. Biophotolysis can be classified into two distinct forms: direct and indirect. These methods are dealt with in subsequent subsections in detail. The application of these techniques plays a significant role in generating renewable and carbon-neutral hydrogen.

4.2.1. Fermentation. Shanmugam, Zhang, Srivastava, Sherpa, and Rai have been working on the development of biohydrogen, a cost-effective method for converting complex organic feedstock into easily fermentable glucose.[192–196] Lignocellulosic materials, made up of cellulose, hemicellulose, and lignin, require careful preparation before use. Hydrolytic enzymes are essential for decomposing complex carbohydrate polymers into basic sugars, but resistant lignin components can hinder their effectiveness. Researchers have studied enzymes that can degrade lignin and convert hemicellulose and cellulose molecules into easily digestible sugars during the pretreatment stage.

Shanmugam, Zhang, and Rai[192,193,196] have talked about how important it is to stick enzymes to nano supports before treating biomass to make biohydrogen. Nanomaterials, with their large surface area and diverse chemical and physical characteristics, are ideal for bonding hydrolytic enzymes, enhancing the effectiveness of the pretreatment process. We can recover and reuse the nano-immobilized bioactive compounds, making this method cost-effective. Recent research has shown that putting lignocellulose-degrading enzymes on nano supports can make biohydrogen production better. Several studies have shown this.

4.2.1.1 Dark fermentation. The process known as dark fermentation involves the decomposition of organic molecules in the absence of oxygen, resulting in the production of biohydrogen. According to Kim *et al.*,[197] the method involves the utilization of microorganisms, more especially bacteria, in order to degrade the organic matter and produce hydrogen as a secondary result. Dark fermentation is a method that is well-known for its capacity to rapidly produce energy from a wide range of renewable materials. Additionally, experts recognize this method for its high efficiency in generating hydrogen. According to Azwar *et al.*,[198] this technique is an environmentally beneficial and cost-effective method of operation because it does not require the use of light energy. Strict anaerobic organisms convert pyruvate into acetyl coenzyme A (acetyl-CoA) and carbon dioxide (CO_2), leading to the production of reduced ferredoxin (Fd_{red}). According to Jiménez-Llanos *et al.*[199] and Salakkam *et al.*,[200] oxygen exposure causes the Fd_{red} to undergo oxidation, leading to the formation of hydrogen gas. Faculty anaerobes convert pyruvate into acetyl-CoA through the metabolic process. The formate hydrocarbon lyase enzyme also speeds up the next step, which is the transformation of formate into hydrogen. Fig. 7 (ref. 201) provides a detailed illustration of the dark fermentation process, which produces biohydrogen from biomass. This method involves the participation of various microorganisms in the transformation of biochemical materials, such as polysaccharides or complex sugars, into products like biohydrogen. The illustrations provided by eqn (7)–(9) (ref. 202) support this concept.

$$C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CH_3COOH + 2CO_2 \tag{7}$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2H_2 + 2CH_3CH_2OH + 2CO_2 \tag{8}$$

$$C_6H_{12}O_6 \rightarrow 2H_2 + CH_3CH_2CH_2COOH + 2CO_2 \tag{9}$$

Eqn (10) and (11) illustrate the roles of oxidized ferredoxin ($Fd_{(ox)}$) and reduced ferredoxin ($Fd_{(red)}$), with pyruvate-formate lyase (PFL) and pyruvate-ferredoxin oxidoreductase (PFOR) serving as the two enzymes that facilitate the metabolism of pyruvates.[203]

$$\text{PFL: pyruvate} + C_OA \rightarrow \text{acetyl-}C_OA + \text{formate} \tag{10}$$

$$\text{PFOR: pyrruvate} + C_OA + 2Fd_{(OX)} \rightarrow \text{acetyl-}C_OA + CO_2 + 2Fd_{(red)} \tag{11}$$

Tian, Yang, Wegelius, and Dinesh[204–207] have all contributed to the advancement of dark fermentation, a method that offers numerous benefits, such as continuous biohydrogen production without light, enhanced generation efficiency, and improved biohydrogen yield. This approach uses a combination of organic and inorganic waste feedstocks, reducing energy consumption and utilizing resilient enzymes for hydrogen production. The metabolic processes of dark fermentation also don't make or use oxygen, which means that both Fe–Fe and Ni–

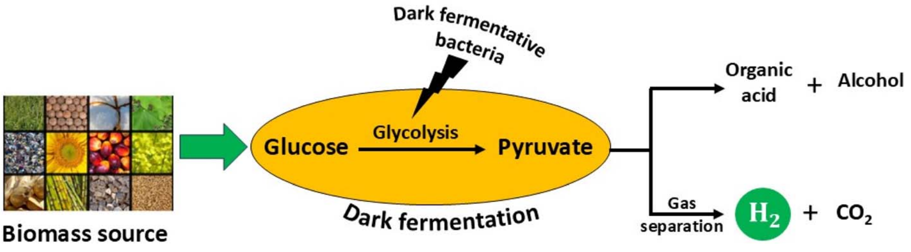

Fig. 7 A one-step approach using dark fermentation bacteria to produce biohydrogen; adapted from ref. 201.

Table 4 Dark fermentation has been employed to generate hydrogen from biomass and organic solid waste materials[22]

Biomass	Type of reactor	Pretreatment	pH, temp. (°C)	H_2 yield	Ref.
Rice waste	Anaerobic bioreactor	Thermal	5.5, 55	40 mL H_2 per g VS	208
Kitchen waste	Inclined plug-flow	Inoculum; thermal	5.5	72 mLH_2 per VS	209
Corn stover	Glass reactor (batch)	Inoculum	6.5, 35	36.1 mL H_2 per g biomass	210
Rice waste	Anaerobic bioreactor	Thermal	5.5, 55	40 mL H_2 per g VS	208
Duckweed	Serum bottle (batch)	Inoculum; thermal; acid-alkaline	7.0, 35	169.3 mL H_2 per g	211
Empty fruit bunch	Batch reactor	Inoculum; thermal	7.0, 35	287.0 mL H_2 per g biomass	212
Grass waste	Glass bottle (batch)	Inoculum; ionizing radiation, acid or both combined	7.0, 37	68.0 mL H_2 per g biomass	213

Fe hydrogenases can be used. Different forms of dark fermentation, such as mixed-type fermentation and three specific types like butyrate, propionate, and ethanol, produce varying quantities of hydrogen. Factors affecting hydrogen production in dark fermentation include feedstocks, microbial community, reactor architecture, hydraulic retention time, pH, and temperature. A multitude of studies has documented the utilization of biomass and organic solid waste for hydrogen generation, as shown in Table 4.

4.2.1.2 Photofermentation. In anaerobic environments, purple non-sulphur photosynthetic bacteria engage in photofermentation, a process that converts organic waste into hydrogen and carbon dioxide. The bacteria utilize light for its energy potential and metabolize organic acids. People often use *Rhodospirillum*, *Rhodopseudomonas*, and other purple, non-sulfur photosynthetic bacteria.[214–216] The purple bacteria discussed utilize an electron transit mechanism, which operates in reverse to reduce ferredoxin during their photosynthesis, independent of sulfur. Organisms are capable of generating ATP and high-energy electrons through the use of light energy. After that, nitrogenase helps turn H^+ into H_2 through enzymes, using ATP and reducing ferredoxin to do so. In the absence of detectable nitrogen, hydrogen production can still occur through the activity of nitrogenase. Eqn (12) (ref. 217) illustrates that photofermentation processes utilize sunlight to convert carbon sources, including basic carbohydrates and various types of volatile fats, into hydrogen and carbon dioxide. Fig. 8 (ref. 201) depicts the process of producing biohydrogen from biomass *via* photofermentation in a single step.

$$C_6H_{12}O_6 + 6H_2O + \text{sunlight} \rightarrow 12H_2 + 6CO_2 \tag{12}$$

Furthermore, photosynthetic bacteria do not possess the requisite energy to break down water molecules. However, in the absence of oxygen, they can utilize simple organic acids as electron donors. Photofermentation utilizes nitrogenase enzymes to produce biohydrogen. As stated in eqn (13), the process of nitrogen fixation by nitrogenases results in the production of two moles of ammonia and one mole of hydrogen from one mole of nitrogen.[217] Eqn (14) (ref. 217) indicates a higher production of hydrogen in the absence of nitrogen.

$$N_2 + 8H^+ + 8e^- + 16ATP \rightarrow 2NH_3 + 16ADP + 16P_i \tag{13}$$

$$8H^+ + 8e^- + 16ATP \rightarrow 4H_2 + 16ADP + 16P_i \tag{14}$$

A variety of factors can affect the efficiency and yield of photofermentation. The factors encompass waste diversity, ammonia production, culture media, light efficiency, intensity, and wavelength. Certain photosynthetic bacteria can produce ammonia, which can inhibit enzymatic activity. Consequently, it is essential to remove ammonia to enhance hydrogen production from the carbohydrate and sugar substrates present in the medium. Mirza and his colleagues conducted a study[218] which demonstrated that purple non-sulphur bacteria (PNSB) capable of photosynthesis can halt the production of polyhydroxyalkanoate (PHA) while simultaneously producing more hydrogen from organic waste.

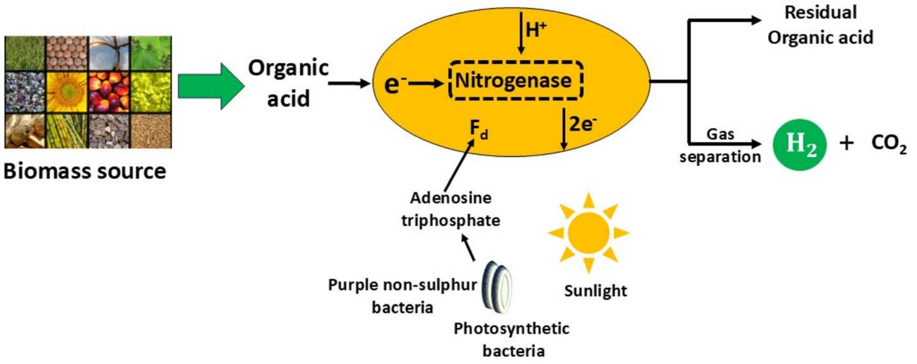

Fig. 8 Employing purple non-sulphur photosynthetic bacteria in a streamlined process for photo fermentative biohydrogen generation from biomass adapted from ref. 201.

4.2.2. Biophotolysis. During the biophotolysis process, photosystem II utilizes solar energy to dissociate water into oxygen, energy, and a reducing agent. This chemical facilitates hydrogen production by decreasing protons through the action of nitrogenases or hydrogenase enzymes. Electrons obtained from the dissociation of water traverse the electron transport chain, which comprises photosystem I (PSI) and photosystem II (PSII). Afterwards, the electrons produce adenosine triphosphate (ATP) and reduce the ferredoxin molecule. These molecules participate in various metabolic activities to produce hydrogen.[219,220] We classify the biophotolysis process into two categories: indirect biophotolysis and direct biophotolysis. Indirect biophotolysis releases electrons when endogenous substrates break down. On the other hand, water splitting in photosystem II releases electrons for direct biophotolysis.[219] Fig. 9 illustrates the mechanisms of direct and indirect biophotolysis processes for the generation of biohydrogen from biomass.[22]

4.2.2.1 Direct biophotolysis. During direct biophotolysis, sunlight serves as an energy source to facilitate the splitting of water molecules in PSII. Following the transfer of residual electrons to photosystem I, the hydrogenase facilitates the production of hydrogen while avoiding the emission of harmful greenhouse gases. The procedure concurrently discharges oxygen into the atmosphere.[199] The reaction for this procedure is described as follows:[22,221]

$$2H_2O + \text{light energy} \rightarrow 2H_2 + O_2 \tag{15}$$

PSII oxidizes water molecules in the direct biophotolysis pathway, producing electrons as a result. PSII utilizes the photons absorbed from sunlight to energize the electrons. The energized electrons subsequently traverse the electron transport chain. Ferredoxin (Fd) and PSI facilitate the movement of electrons. $NADP^+$ undergoes reduction to form nicotinamide NADPH, facilitated by plastoquinol generated *via* electron transfer. Oxidizing water replaces electrons to produce O_2 and H^+. The electrons obtained from water play a crucial role in photosynthesis through the function of photosystem II. The generation of ATP *via* ATP synthase requires the establishment of a proton gradient. The protons function as the final acceptors for the electrons in the chloroplasts of the algae. This process yields hydrogen and oxygen gases concurrently.[222]

Researchers recognize green microalgae as the only microorganisms capable of direct biophotolysis without oxygen, which facilitates the production of biohydrogen through water splitting. We classify green microalgae and cyanobacteria as "oxygenic photosynthetic microorganisms" due to their ability to absorb sunlight, break down water molecules, and convert them into chemical energy.[219] Water-plastoquinone oxidoreductase (PQOR), specifically PSII, energizes electrons in the presence of sunlight, transferring them to PSI and subsequently to Fd.[223] The enzyme Fd-oxidoreductase turns protons (H^+) into hydrogen molecules (H_2) by reducing Fd. This reduced Fd then gives an electron to [FeFe]-hydrogenase. This ultimately results in the production of O_2 at PSI.

Fd reduction in PSI:

$$2H^+ + 2Fd_{(red)} \leftrightarrow H_2 + 2Fd_{(ox)} \tag{16}$$

The process of hydrogen production under sunlight conditions is illustrated according to eqn (15) mentioned above.

The method of direct biophotolysis represents a sustainable approach. The potential is significant, given that the primary reactants, like water, sunlight, and CO_2, are readily accessible resources. Furthermore, it transforms solar energy into chemical energy to generate hydrogen and oxygen.[199] Nonetheless, the pathway must address numerous challenges in order to establish itself as a viable and effective option for biohydrogen production. A significant drawback of this pathway is that it inhibits hydrogen production resulting from the buildup of oxygen.[219] Additional limitations consist of the potential

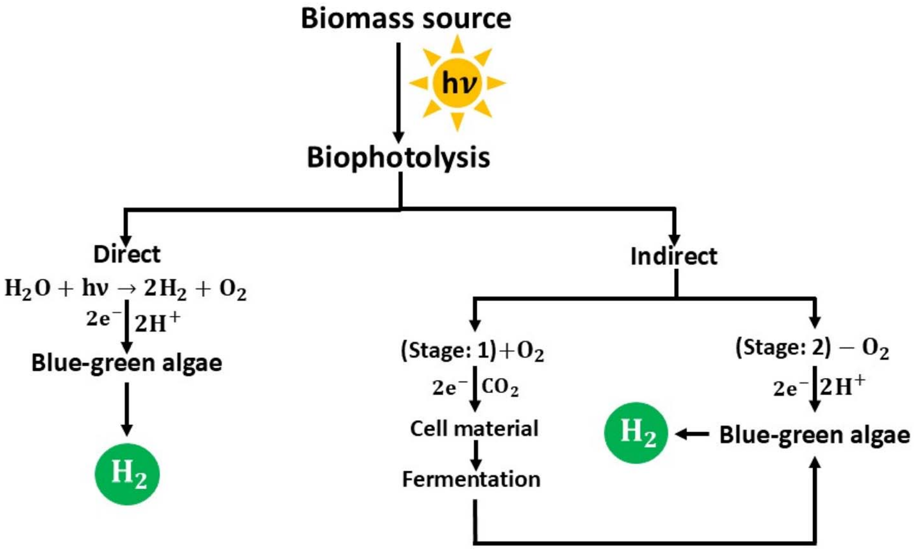

Fig. 9 Diagrammatic illustration of the biological process of biophotolysis adapted from ref. 22.

hazards associated with oxygen usage, the necessity for elevated light intensity, and the low photochemical efficiency.[221] Extensive cultivation of algae is essential to harness adequate sunlight for generating sufficient free energy (ΔG = +237 kJ mol^{-1}). Additional obstacles encompass the processing and concentration of cell biomass, respiration, and the ratio of photosynthetic capacity.[199,219]

4.2.2.2 Indirect biophotolysis. Microalgae do indirect biophotolysis in anoxic environments. Under these circumstances, microalgae can generate biohydrogen *via* fermentation or respiration. The indirect method is discontinuous, as the restitution of the light period induces photosynthetic growth and inhibits H_2ase.[224] Indirect biophotolysis has two parts.[220] The first part uses a small, sealed photobioreactor to turn oxygen and carbon dioxide into chemical energy in the form of carbohydrates and lipids. The second part uses the same photobioreactor for CO_2 synthesis, but this part often breaks down when there is no light.[220]

When there isn't sufficient oxygen, the breakdown of the natural substrate creates electrons for a non-photochemical reduction. This stops the initial electron transport chain during the anaerobic phase. Afterwards, [FeFe]-hydrogenases receive the electron and generate biohydrogen.[225] We first tested the method of making hydrogen through biological photolysis on the cyanobacteria *Plectonema boryanum*, which is a non-heterocystous microalga. These algae went through regular cycles of "aerobic light-driven CO_2 fixation and O_2".[220] Sharma and Arya[226] outline the responses to this procedure below:

$$6H_2O + 6CO_2 + \text{light energy} \rightarrow C_6H_{12}O_6 + 6O_2 \tag{17}$$

$$C_6H_{12}O_6 + 6H_2O + \text{light energy} \rightarrow 12H_2 + 6CO_2 \tag{18}$$

Researchers like Sengmee *et al.*,[227] Lam *et al.*,[228] and Acar and Dincer[229] have looked into how to make biohydrogen using oleaginous microalgae. This is a way to deal with oxygen sensitivity by temporarily separating the reactions that create oxygen and hydrogen. During the aerobic phase, microalgae transform light energy and carbon dioxide into chemical energy, producing lipids, carbohydrates, and various biomolecules. Under anaerobic conditions, the activation of oxygen-sensitive hydrogenase is essential for biohydrogen production. Sengmee *et al.*[227] evaluated various oleaginous microalgae for their capacity to produce hydrogen using crude glycerol as an economical source of external carbon. All microalgae thrived on crude glycerol and had a substantial lipid content exceeding 20%. However, only *Chlorella* sp. demonstrated the capability to generate significant amounts of hydrogen under anaerobic conditions. Under the best conditions, 11.65 ± 0.65 mL L^{-1} of hydrogen was produced in the bioreactor and 10.31 ± 0.05 mL L^{-1} in the serum bottle. The harvested microalgal biomass exhibited a lipid content exceeding 40%. More research into how oleaginous microalgae can produce both biohydrogen and lipids could make the process of making biofuel from microalgae much more sustainable. Table 5 summarizes the biological processes already addressed, highlighting their potential advantages and limitations for biohydrogen production.

4.2.3. Coupling of biochemical and thermochemical pathways. Using a circular economy to combine many technologies for processing waste may not only help each other out, but it may also help make processes more efficient and make better use of resources. Combining thermal processes like pyrolysis, gasification, and hydrothermal carbonization (HTC) with anaerobic digestion (AD) could lead to a better and more environmentally friendly way to treat waste.[152] Biological processes, like anaerobic digestion, and thermochemical methods, like pyrolysis, work well together. Anaerobic digestion is better for wet waste, while pyrolysis or gasification is better for lignocellulosic waste.[152] These factors have drawn researchers worldwide to investigate the integration of AD with thermochemical processes. In 2014, the SUPERGEN Bioenergy Hub saw that combining pyrolysis with AD could make it easier to get more energy and products from municipal solid waste (MSW).[235]

Waste materials, particularly biomass, have the potential to meet global energy demands, but a reliable process design is necessary for efficient waste-to-energy conversion.[152] Process integration is an efficient method that optimizes process efficiency by increasing product production while minimizing costs.[236] It is a powerful tool in process design research to enhance current processes and create new ones. Future research will explore waste use through revolutionary biological and/or thermochemical methods.[152] Currently, biofuel production *via* anaerobic digestion-derived digestate is limited to bioethanol and biogas. However, alternative biological mechanisms like dark fermentation and microbial fuel cells are being explored.[237–239] Zhong *et al.*[238] did a study on how to make biodiesel by mixing aerobic fungal fermentation with anaerobic digestion for biogas and lipids. Hoffman *et al.*[240] created a model for an integrated process by combining anaerobic digestion (AD) and hydrothermal liquefaction (HTL). The HTL process turned digestate from AD into bio-crude. The biorefinery idea is a complicated but long-lasting way to turn organic waste into biofuel streams and combined heat and power (CHP). According to the authors, adding a diesel-quality fuel output to the process would make the final product much more valuable than it would be in a normal anaerobic digestion facility. To build an integrated process for waste valorisation using anaerobic digestion and thermochemical processes, a shift in perspective is essential.

Over the past two decades, studies have shown that integrating thermochemical processes with anaerobic digestion can improve energy recovery, process efficiency, and digestate quality. Six coupling types have been assessed, and these have yielded numerous advantages, including improved energy recovery, enhanced process efficiency, and reduced greenhouse gas emissions.[152] Particularly char, the products made from these combined methods are better at immobilizing heavy metals and nutritional elements. Each separate process is important to the whole system because it speeds up the breakdown of waste, makes energy recovery better, and fixes

Table 5 Overview of biological processes, including their potential benefits and constraints for biohydrogen generation

S. no.	Processes	Benefits	Limitations	Ref.	Applications (hydrogen economy)[230,231]
1	Dark fermentation	(i) Efficient management of solid waste disposal (ii) Essential process requirements (iii) Monophasic biohydrogen generation using carbohydrate substrates	(i) Prevention of methanogenesis (bacterial activity) (ii) Necessitate the purification of hydrogen gas (iii) Generation of CO_2 as a by-product	232	(i) Transportation sector
2	Photofermentation	(i) Employ light energy *in lieu* of carbohydrates (ii) Elevated hydrogen yield (iii) Highlight conversion efficiency	(i) The intricacies of kinetic reactions remain poorly understood (ii) Production is slow compared to dark fermentation	233	(ii) Residential and commercial zones (iii) Hydrogen utilization as an industrial fuel (iv) Biofuel
3	Direct biophotolysis	(i) Sustained hydrogen generation (ii) A more efficient approach to the generation of hydrogen	(i) Suboptimal efficiency (ii) Hydrogen accumulation resulting from the buildup of O_2 (iii) High-intensity illumination is necessary	234	
4	Indirect biophotolysis	(i) Facile separation of H_2 from O_2 during synthesis (ii) A comparatively less amount of light is necessary (just during the first phase)	(i) Significant capital expenditure (ii) Suboptimal efficiency (iii) Safety issues with O_2 and H_2 (iv) Generation of CO_2 as a by-product	232 and 234	

problems. A more thorough analysis of this topic may be found elsewhere.[152]

4.3. Electrochemical methods

4.3.1. Electrolysis. The microbial electrolytic cell (MEC) presents a novel approach for achieving sustainable biohydrogen production from diverse renewable biomass energy sources while reducing energy demands.[219] Microbes oxidize substrates (biomass) on the anode side of the microbial electrolysis process, which results in the production of carbon dioxide, protons, and electrons. Protons join with electrons at the cathode *via* the proton conducting membrane (electrolyte) and the external circuit, creating hydrogen.[241,242] Still, it's important to remember that this electrolytic process doesn't happen on its own; it needs a voltage supply from outside the microbial cell to create biohydrogen at the cathode.[22,243,244] The implementation of MEC represents a hybrid system that significantly improves biohydrogen production compared to fermentation methods. The process of producing biohydrogen becomes more efficient when both photosynthetic and non-photosynthetic microorganisms are added to a biomass source, such as wastewater, in an electrolytic cell.[219] Fig. 10 illustrates the fundamental configurations for MEC. The reactions taking place at the electrodes are described as follows:[241]

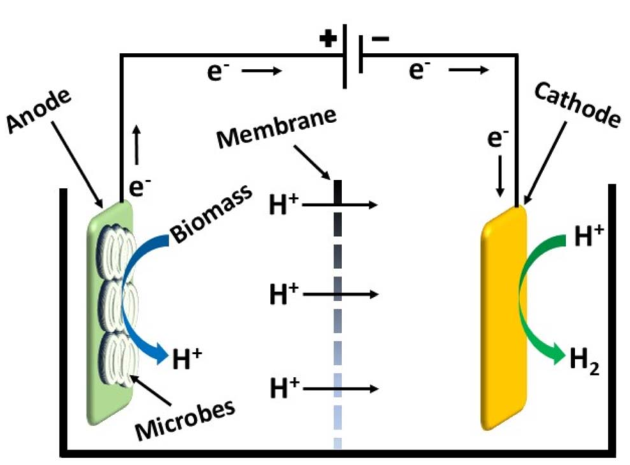

Fig. 10 Diagrammatic representation for a microbial electrochemical cell (MEC).

$$\text{At anode: } CH_3COO^- + 4H_2O \rightarrow 2HCO^{3-} + 9H^+ + 8e^- \quad (19)$$

$$\text{At cathode: } 8H^+ + 8e^- \rightarrow 4H_2 \quad (20)$$

$$\text{Overall cell reaction: } CH_3COO^- + 4H_2O \rightarrow 2HCO^{3-} + H^+ + 4H_2 \quad (21)$$

MECs represent an innovative biochemical approach for generating H_2 from biomass in a more environmentally friendly manner. A power supply connects an anode and a cathode electrode in an anaerobic environment, forming the MECs.[245] MECs resemble microbial fuel cells (MFCs) in that they share comparable electrode configurations and reaction setups. The main differences between MECs and MFC systems are that the cathode in MECs doesn't need air and the end products are different.[246] MFCs generate electricity directly, whereas MECs produce bio-H_2 outside the cathode.[247] The microbial reactions occurring on the anode in the MEC scheme play a crucial role in the H_2 generation process.[247] An electrochemically active bacterium (EAB) is a microorganism capable of generating electricity, which colonizes the anode surface and interacts with organic waste materials. The generation of H_2 in the MEC system requires an initial voltage to initiate the reaction, typically ranging from 0.2 to 0.8 V.[248] The voltage remains significantly below the 1.2 V required for water electrolysis.[242]

MEC systems have advantages for biohydrogen production since they can produce 12 moles of H_2 per mole of glucose compared to conventional fermentation methods.[219] Jayabalan *et al.*[249] used the NiO/rGO nanocomposite in a study that showed it could make hydrogen at a rate of 4.38 ± 0.11 mmol per L per day, get hydrogen back from water at the cathode (20.8%), and work at 65.6% coulombically. This demonstrates that MEC systems can achieve efficiencies of 2.68 times and 1.19 times greater than uncoated Ni-foam and Co_3O_4/rGO, respectively. However, enhancing energy recovery from industrial effluents, along with technological advancements and concurrent treatment processes, is crucial for the long-term sustainability of biohydrogen production. The generation of H_2 from various biomass sources *via* MECs is illustrated in Table 6.

4.3.2. Photoelectrochemical (PEC). The photoelectrochemical (PEC) cell is a new way to turn organic waste into biohydrogen that lasts. It achieves this by utilizing light to facilitate synergistic microbial conversion. In the PEC, active microorganisms electrochemically generate electrons from organic substances on the microbial or bioanode. The PEC comprises semiconductors (electrodes) partitioned by a membrane within an electrolyte. The photoelectrochemical process directly employs semiconductors and sunlight to dissociate water into hydrogen and oxygen. In the photoelectrochemical process, the oxidation of water molecules produces oxygen, while the reduction of biohydrogen at the other electrode produces hydrogen.[257] This technology possesses significant potential for biohydrogen production with negligible environmental impact.

Table 6 The generation of hydrogen from various biomass sources utilizing microbial electrolysis cells (MECs)[22]

Kind of biomass	Anode	Cathode	E_{app} (V), volume (mL)	Kind of MEC	Mode of operation	H_2 generation	Ref.
Cellobiose	Graphite fiber brush	Pt/carbon cloth	0.5, 28	Single chamber	Fed-batch	0.96 L per L per day	250
Lignocellulose	Graphite fiber brush	Pt/carbon cloth	0.5, 28	Single chamber	Fed-batch	1.00 L per L per day	250
Cornstalk fermentation effluent	Graphite felts	Carbon cloth coated with Pt and Nafion	0.8, 64	Single chamber	Batch mode	3.43 m^3 per m^3 per day	251
Rice straw	Carbon cloth	Pt/carbon cloth	0.8, 358	Dual chamber	Fed-batch	2.46 mmol per L per day	252
Rice straw	Carbon cloth	Carbon cloth impregnated with Pt	0.8, 360	Dual chamber	Fed-batch	1.95 mmol	253
Vegetable waste	Carbon cloth	Carbon cloth impregnated with Pt	0.8, 360	Dual chamber	Fed-batch	2.31 mmol	253
1 : 1 mixture of rice straw and vegetable waste	Carbon cloth	Carbon cloth impregnated with Pt	0.8, 360	Dual chamber	Fed-batch	2.56 mmol	253
Galactose	Carbon cloth	Carbon cloth containing 0.5 mg cm^2 Pt	0.7, 17	Single chamber	Batch mode	0.07 m^3 per m^3 per day	254
Cellobiose	Carbon cloth	Carbon cloth containing 0.5 mg cm^2 Pt	0.7, 17	Single chamber	Batch mode	0.09 m^3 per m^3 per day	254
Palm oil mill effluent (acetate and butyrate)	Graphite fibre	Felt carbon cloth	0.7, 600	Single chamber	Batch mode	7.81 L per L per -day	255
Fermented corn stover	Carbon felt	Pt deposited carbon disk with a stainless-steel wire mesh	0.2 *versus* Ag/AgCl, 16	Dual chamber	Continuous-fed	20.1 L per L per day	256

Table 7 Pros and cons of fundamental biohydrogen generation methods[219]

Innovation routes	Benefits	Drawbacks
Photofermentation	(i) Photosynthetic bacteria are capable of utilizing different forms of spectral energy	(i) The efficacy of light conversion is diminished
	(ii) Analyse a range of materials	(ii) Biohydrogen generation by photosynthetic bacteria is currently minimal
	(iii) Capable of processing dark fermentation effluent	(iii) Variability in light distribution and metabolic transition from biohydrogen production to polyhydroxybutyrate synthesis
	(iv) Bioremediation	
Dark fermentation	(i) The method generates multiple metabolites as by-products and utilizes different substrates	(i) This method yields a limited quantity of H_2, rendering it thermodynamically disadvantageous
	(ii) Integrate diverse materials	(ii) The presence of oxygen hinders the process of biohydrogen production
	(iii) Method that operates independent of light	(iii) Limited biohydrogen generation
	(iv) No limitations regarding oxygen availability	
	(v) Bioremediation	
Direct biophotolysis	(i) A comprehensive method for generating H_2 using water and sunlight	(i) O_2 and intense light act as a barrier during this procedure
	(ii) Involves straightforward production	(ii) It is not possible to achieve separate high purity streams of O_2 and H_2
	(iii) Basic substrate of H_2O	
	(iv) Carbon dioxide intake	
Indirect biophotolysis	(i) Hydrogen production from water utilizing blue-green algae	(i) The uptake of hydrogenate is diminished
	(ii) Isolation of O_2 production from the generation of H_2 a necessity	(ii) The absorption of hydrogenates can be eliminated
	(iii) Nitrogen fixation potential from atmospheric sources	(iii) The hydrogenase enzyme produces CO_2 and yields a minimal amount of H_2
	(iv) Translation of metabolite by-products to H_2	
MEC	(i) A technique that generates power in a more environmentally sustainable manner, free from pollution	(i) Solar systems can provide an improved solution; however, they are costlier
	(ii) Bioremediation	(ii) The capital expenditure is relatively elevated
	(iii) Elevated elimination of chemical oxygen demand (COD)	(iii) Loss of hydrogen and its purity
	(iv) Capable of processing black fermentation discharge	(iv) Experiences challenges related to scalability, power sources, stability, and operational modes
	(v) Elevated hydrogen recovery	
	(vi) Significant breakdown of substrate	

Researchers have conducted limited studies on solar microbial photoelectrochemical systems that use photobioanodes, which combine biological and solar energy at a single electrode. Using a two-sided photobioanode made of biocarbon material and a photocatalyst (α-Fe_2O_3) made biofilm formation a lot better. This improved the flow of electrons outside of cells and increased the amount of exoelectrogens.[258] Recently, Pophali *et al.*[259] used a metal-free carbon film containing CeO_2–rGO as a photobioanode, achieving a hydrogen evolution rate of 5 m^3 per m^3 per day while simultaneously treating wastewater. Zhu *et al.*[260] demonstrated that the use of a photoanode consisting of hematite nanowires and engineered exoelectrogens enhanced the output power and photocurrents in the presence of visible light. Nonetheless, this technique requires further investigation to achieve a sustainable level of biohydrogen production. Table 7 provides a succinct summary of biological and electrochemical biohydrogen production processes, together with their associated benefits and drawbacks.

5. Biohydrogen production: machine learning (ML) perspectives

5.1. Machine learning models

Machine learning models have been utilized to improve understanding and optimize the biohydrogen production process. A proficient approach to leveraging machine learning in biohydrogen production includes the use of data mining and predictive modelling to identify the critical factors influencing biohydrogen generation.[201] The analysis of data gathered from various tests performed on the production process facilitates the achievement of this objective. Utilizing this information, it is possible to develop predictive models to identify the variables that lead to enhanced production yields and ascertain the elements that require modification to optimize the process. Reinforcement learning techniques can serve as an alternative approach for applying machine learning in the realm of biohydrogen production.[261] By engaging in a systematic approach of experimentation and refinement, these algorithms can identify the optimal conditions for biohydrogen synthesis.

Artificial neural networks (ANN) are intricate machine learning models utilized for pattern recognition in data and predictive analysis.[262] Researchers have used ANN models to find the best parameter combinations for maximum yield in biohydrogen production processes.[263–271] These models have demonstrated significant potential in optimizing various bioprocess parameters, leading to improved efficiency and output. As a result, the application of ANNs in biohydrogen production continues to grow, paving the way for more sustainable energy solutions. Furthermore, combining ANNs with other advanced technologies like genetic algorithms and fuzzy logic systems improves them at handling complicated bioprocess factors. This combination enhances prediction accuracy and helps make quick decisions in biohydrogen production, leading to a stronger energy system.[268–271] Moreover, as research progresses, the integration of these sophisticated methodologies is expected to unlock new avenues for innovation in renewable energy. By harnessing the power of data-driven approaches, the biohydrogen sector can achieve unprecedented levels of efficiency and sustainability, ultimately contributing to a greener future. Fig. 11 depicts the predictive efficacy of the ANN algorithms for biohydrogen production, as indicated by the coefficient (R^2).

Fig. 11 illustrates that most ANN models achieve prediction accuracy values exceeding 0.90, with several instances reaching as high as 0.99, which signifies remarkable prediction accuracy. Monroy *et al.*[272] utilized an ANN model to model the generation of biohydrogen through photofermentation. They conducted controlled, indoor experiments at a temperature of 30 °C, examining various light intensities, metals, and initial pH. The framework was validated through cross-validation with data from indoor photofermentation. The chosen design showed the highest level of similarity between the artificial neural network model and the actual biohydrogen production process. The model successfully predicted biohydrogen generation by aligning the anticipated kinetics with the results obtained from tests. Tests conducted on an external fermentation process under different light intensities confirmed the effectiveness and applicability of the ANN-based framework. In a separate study, researchers Prakasham and colleagues[273] used neural network models and genetic algorithms to improve biohydrogen generation efficiency. The study found that a neural network with a topology of 4-10-1 had strong performance, with 10 neurons in the hidden layer. The network achieved a prediction accuracy of 99.99%, with a mean absolute percentage error of 3×10^{-10}, 3.4×10^{-8}, and a mean square error of 9×10^{-8}, indicating high precision in predictions.

Wang *et al.*[274] utilized a multilayer perceptron artificial neural network (MLPANN) and microbial kinetics of the Levenberg–Marquardt algorithm (MKLMA) models to investigate biohydrogen production during dark fermentation. They used the MLPANN and MKLMA models to simulate key metabolite kinetics during dark fermentation. The team used a 24-hour fermentation period to construct the MLPANN and a response surface model to analyse the electron-equivalent balance. The study suggested a new way to look at process parameters and how they affect the main substances that are made during dark fermentation to make biohydrogen. The MLPANN and response surface models let us do statistical analysis from the point of view of electron-equivalent balance, which gave us a full picture of how biohydrogen is made. Mahmoodi-Eshkaftaki *et al.*[275] developed a deep neural network model to optimize biogas production by analysing the influence of volatile fatty acids. The network demonstrated superior predictive capacity for assessing the impact of time on biogas implications compared to regression models. The study aimed to optimize biohydrogen

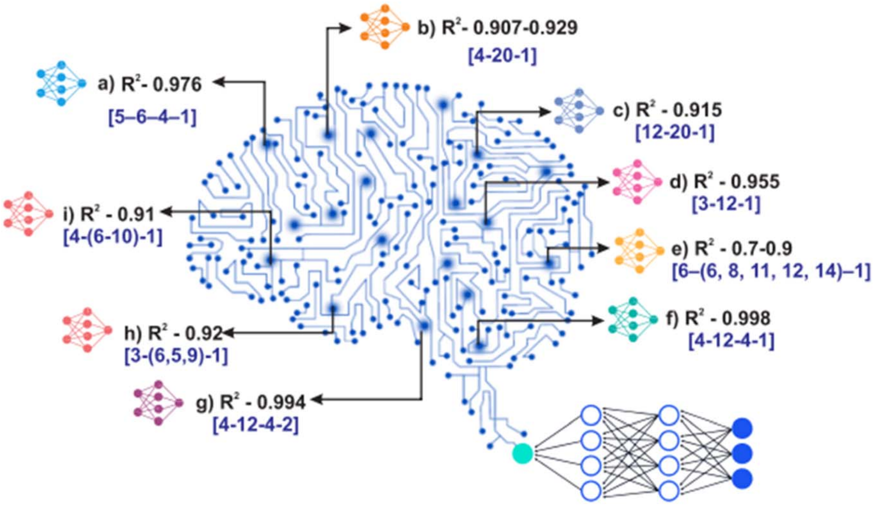

Fig. 11 Prediction accuracy of biohydrogen generation *via* artificial neural network (ANN) algorithms: (a) Research by Nasr *et al.*,[265] (b) Sridevi *et al.*,[266] (c) Nikhil *et al.*,[264] (d) Rosales-Colunga *et al.*,[263] (e) Sewsynker *et al.*,[268] (f) Mullai *et al.*,[271] (g) Yogeswari *et al.*,[270] (h) Ghasemian *et al.*,[269] and (i) Whiteman and Gueguim Kana.[267] The value within the square brackets denotes the ANN topology. The neurons of the hidden layer are denoted by the middle number or numbers, whilst the parameters of the input and output layers are indicated by the first and final numbers, respectively.

production and enhance efficiency in time-dependent situations with limited data, demonstrating the potential of deep neural networks in predicting biogas production outcomes.

Recently, researchers evaluated various machine learning techniques, including neural networks, using mean square error and R^2 to identify the most reliable models for modelling the biohydrogen process. The grid search optimization and permutation variable importance analysis revealed that the gradient boosting machine, support vector machine, random forest, and AdaBoost models excelled in identifying the crucial components of the biohydrogen generation process. These models are good at guessing how hydrogen is made because they have high R^2 values (0.89, 0.89, 0.9, and 0.89) and low mean square error values (0.015, 0.015, 0.016, and 0.015) for the gradient boosting machines, support vector machine, random forest, and AdaBoost models.[276]

5.2. Biohydrogen generation optimization using machine learning

Machine learning algorithms have shown their capacity to manage extensive datasets while necessitating less comprehensive understanding of the system and exhibiting the ability to adjust to changing conditions. One can summarize the main benefits of using machine learning in biohydrogen generation as follows:[201]

(i) Machine learning can analyse extensive datasets for efficient industrial processes.[35]

(ii) It can uncover patterns and correlations among process variables in bioreactors.

(iii) This information can enhance biohydrogen production yield and efficiency by optimizing process parameters.

(iv) Machine learning can determine the optimal combination of factors to enhance biohydrogen production yield.

(v) Models trained on extensive datasets of microbial genomes and metabolic data can forecast metabolic pathways and energy production capabilities of different microbial strains.

(vi) This information can be used to identify promising microbial strains for biohydrogen production and formulate targeted genetic engineering approaches.

(vii) Predictive models for biohydrogen production can be developed using machine learning algorithms.[37,261]

(viii) The application of machine learning can create real-time tools for production process control and management.

Asrul *et al.*[277] highlight the importance of machine learning in capturing the dynamic interplay in the biohydrogen process—a process that is complex and nonlinear. By utilizing advanced algorithms and predictive models, they can identify optimal methods for producing and storing biohydrogen, enhancing production processes, and managing microorganism conduct. This results in increased manufacturing efficiency, cost savings, and environmental benefits. Machine learning also allows for monitoring biohydrogen production, detecting patterns and forecasting future trends, and enabling operators to make informed decisions about system performance by identifying changes in pH and temperature.

Nasr *et al.*[265] created an ANN model to analyse photos from biohydrogen production systems for the detection and classification of cells and microbial activity. The model utilized 312 data points derived from 25 studies, revealing a robust correlation between the investigational and estimated hydrogen generation. The ANN successfully forecast the hydrogen production profile using the new data, achieving a correlation coefficient of 0.98. These data can be utilized to improve the process and optimize the efficiency of biohydrogen production. The ANN architecture has the potential to optimize biohydrogen production processes and increase efficiency. Aghbashlo *et al.*[278] developed a novel approach to enhance key operational parameters for hydrogen production by photofermentation. They combined a hybrid fuzzy clustering-ranking algorithm with a radial basis function (RBF) neural network. They used the photosynthetic bacterium *Rhodospirillum rubrum* as the carbon source in water-gas shift reactions. The RBF neural network and two outside parameters were used to find the correlation between exergetic outputs. This approach improved rational and process exergy efficiency and decreased normalised exergy destruction.

5.2.1. Production of biohydrogen from organic waste.

A study by Balachandar and Ahmad on the dark fermentation of organic waste, such as food waste and wastewater sludge, showed that biohydrogen production is possible.[279,280] Ahmad's investigation,[280] which integrated dark and photofermentation processes, showcased the economic viability of producing biohydrogen from liquid pineapple waste. The expected net profit from producing 3000 metric tons of biohydrogen in its fluid form was 1.7 times the initial capital investment, yielding a 68% return on investment. This study emphasizes the economic feasibility and attractiveness of biohydrogen production, positioning it as an essential element of a circular economy.

Machine learning models can utilize data from studies on various forms of organic waste. The information may encompass aspects like the composition of organic waste, the temperature and pressure utilized, the length of the process, and the amount of biohydrogen produced. Machine learning models possess the capability to identify the most effective configurations for improving the conversion process from this viewpoint. Models are capable of identifying potential challenges that might arise during the conversion process, including the formation of byproducts or the incomplete transformation of organic waste. Experts and engineers can utilize machine learning algorithms to identify the most effective and cost-efficient methods for producing biohydrogen from organic waste. Fig. 12 demonstrates the methodology for transforming organic waste into biohydrogen through the application of machine learning models.

The investigation evaluated the capacity of ANN and support vector machine (SVM) analysis to predict biohydrogen production from organic waste using experimental data. The findings indicate that SVM demonstrated greater efficacy compared to ANN in generating predictions. The evaluation of the SVM model revealed an R^2 value of 0.98 and a root mean square error of 0.01. Following this, a Genetic Algorithm (GA) was combined with particle swarm optimization to achieve the best

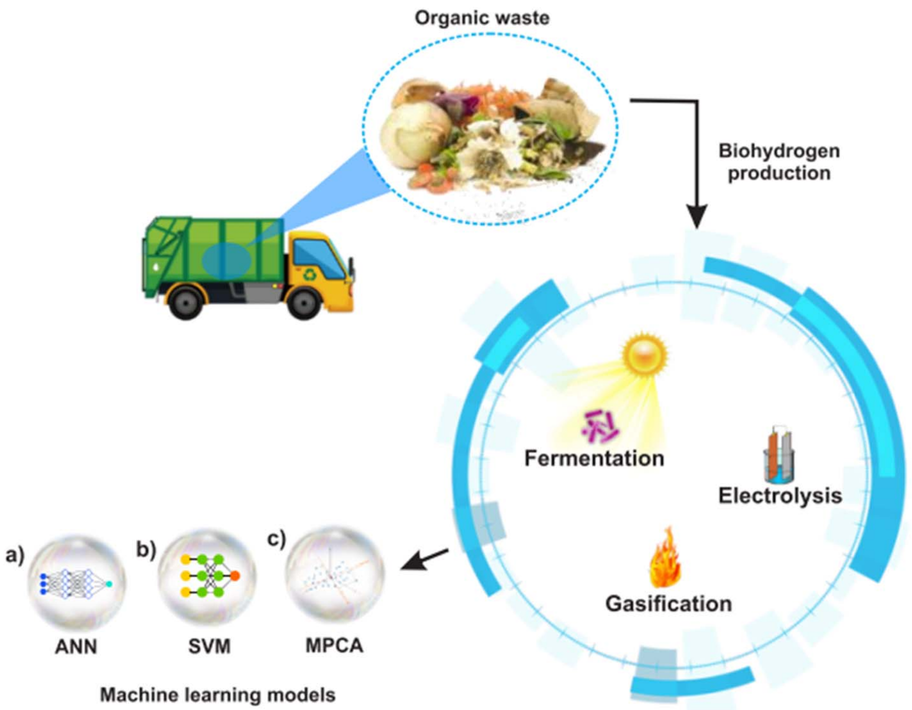

Fig. 12 Employing machine learning algorithms to transform organic waste into biohydrogen. (a) ANN denotes Artificial Neural Network, as noted by Moreno Cárdenas *et al.*[281] and Wang *et al.*[274] (b) Support Vector Machines are referred to as SVM, as noted by Monroy *et al.*[272] (c) MPCA refers to Multi-way Principal Component Analysis.[272]

configurations for the specified processes. Both the GA and Particle Swarm Optimization (PSO) were able to find the best parameter value, but Mahata *et al.*[282] found that the PSO algorithm executed this task significantly more quickly.

5.2.2. Generation of biohydrogen from fatty acids. Fatty acids are regarded as a crucial component of food waste (FW). Fatty acids, particularly those derived from oils and fats, can undergo decomposition into smaller molecules, including volatile fatty acids (VFAs), during the process of anaerobic digestion. Monitoring and forecasting the output, which includes defining biogas and producing volatile fatty acids, is a crucial step in enhancing the biohydrogen production process.[283] A recent study investigated the ability of ANN to forecast the total hydrogen production by analysing the generation of volatile fatty acids.[283] The variables examined in model 1 included time, acetate, and butyrate intensities. Model 2 incorporated lactate, time, propionate, butyrate intensities, and acetate. Model 3 incorporated time along with the cumulative total of all volatile fatty acids. Model 4 incorporated time along with the intensities of butyrate and acetate. All models demonstrated a coefficient of determination (R^2) greater than 0.98, accurately forecasting the total biohydrogen production, its production rate, and the yield. For processes involving pure cultures, utilizing the volatile fatty acid as the input parameter is advisable. However, for methods that involve complex or mixed cultures, it is advisable to utilize an acetate/butyrate model. ANN models, which depend on the variety and amount of volatile fatty acid species, can accurately predict biohydrogen synthesis rates. It is essential to carry out prospective studies to assess the ability of ANN to manage turbulence effectively. The findings from these studies will facilitate the large-scale practical application of ANN. A biohydrogen prediction tool was made using the synthesis and properties of volatile fatty acids as information. This is a promising method, especially when bioprocesses become unstable. It is important to include the metabolic activities of microorganisms and the different types of volatile fatty acids as input variables during the model development phase.[283]

In summary, biohydrogen production utilizes advanced algorithms to improve yield, but challenges arise from limited experimental data. Synthetic data from simulations can provide a more extensive dataset for training algorithms, allowing for more precise outcomes. Advanced algorithms like deep learning can effectively address non-linear relationships between input and output variables.[201] Deng *et al.*[284] and Ganguli and Bhatt[285] have highlighted the potential of machine learning in biohydrogen production. They argue that machine learning can analyse data related to biohydrogen production, identifying patterns that can optimize the process. They suggest that machine learning can identify the most efficient reactors and parameters for maximizing hydrogen yield. Additionally, machine learning can forecast biohydrogen yields based on specific inputs, enabling more informed decision-making. Furthermore, it can identify potential genetic modifications to enhance biohydrogen production efficiency. Overall, the application of machine learning can lead to greater efficiency and cost-effectiveness in biohydrogen production.[201]

6. Applications, obstacles and sustainability of biohydrogen

Rajesh Banu *et al.*[286] and El Barnossi *et al.*[287] have explored the potential of biomass as a valuable resource for biohydrogen production. Biohydrogen is a highly appealing energy source with the highest energy yield per gram, generating no pollutants.[288] Biomass materials can be biologically produced, with only water and energy byproducts. Researchers have applied various methods to produce biohydrogen fuel, and anaerobic fermentation using common food waste like fruit peels.

Kardung and Drabik[289] conducted a study on the development of EU countries' circular bioeconomy (CBE) from 2006 to 2016, analysing factors such as economic importance, agricultural intensification, geographical coverage, and data availability. They also analysed the importance of a bioeconomy within the general German economy from 2002 to 2010, using gross value added and employment as primary indicators. The CBE framework, which combines bioeconomy and circular economy (CE) with a focus on biotechnology, gained interest in the academic literature and policy after their popularization in the 1990s and 2000s. However, Kershaw *et al.*[290] highlighted the limitations of CBE due to narrow problem and solution framing and limited advocates. Ubando *et al.*[34] recently analysed an in-depth review of the various biomass feedstocks and processing technologies used in biohydrogen production. They also talked about how current industries could be integrated into a circular bioeconomic structure.

Below, we outline some primary applications of biohydrogen. These include its use as a clean fuel source for vehicles, as well as its potential in powering fuel cells for generating electricity in both stationary and portable applications. For combined heat and power (CHP), the use of biohydrogen is also critical. It provides a sustainable energy source and contributes to reducing greenhouse gas emissions and enhancing energy efficiency in various applications. We also explore the diverse operational obstacles in the application of biohydrogen that arise during the implementation of sustainable energy solutions. These obstacles can significantly hinder productivity and efficiency within an organization. By identifying and addressing these challenges, we can implement strategies that streamline processes and enhance overall performance. The sustainability assessment for biohydrogen is also explored. This evaluation includes examining the economic viability, environmental impacts, and social acceptance of biohydrogen production.

6.1. Biohydrogen: applications

6.1.1. Energy production and transport industries. The International Renewable Energy Agency (IRENA) anticipates that the transport sector, along with industrial applications in the chemical and steel industries, will utilize a significant portion of the global hydrogen economic potential.[22] Bio-H_2 plays a crucial role in reducing carbon emissions in the transport sector, particularly in heavy-duty transportation. Proton exchange membrane (PEM) fuel cells are receiving significant interest in the application of bio-H_2 within fuel cell technology, with PEM featuring a compact structure with high power density and operating at very low temperatures below 100 °C.[291,292] Through a patented plasma-thermal catalytic conversion process, SGH2-energy is starting the biggest project in the world to make bio-H_2 from waste in Lancaster, California.[293] The facility has the capacity to generate 11 000 kg per day of H_2, translating to 3800 tons annually from 42 000 tons of feedstock. By 2025, the California Energy Commission and the Air Resources Board aim to establish 200 hydrogen refuelling stations, while SGH2 is actively negotiating projects in Europe, Asia, South America, and Australia.[294]

The United States and Japan collaborate on Ways2H to generate bio-H_2 from various sources such as municipal solid waste, biomass, sewage sludge, hazardous medical waste, and plastic waste.[295,296] The system operates through a unique thermochemical process, which includes thermal cracking of organic waste and steam reforming to decompose methane into hydrogen. A mobile demonstration unit, AGM Model 5, is currently operational in Japan, generating 50 kg of H_2 per 1 ton of biomass. The Sunamachi Water Reclamation Centre in Japan has developed a commercial facility that processes 1 ton of sewage sludge daily, converting it into 50 kg of hydrogen daily—sufficient to fuel 10 fuel cell vehicles. An experimental study by Pedro Farrancha[297] showed that food waste DF can generate bio-H_2 in a small-scale system, achieving a peak energy output of 1.6 Wh L^{-1}. The effectiveness of applying bio-H_2 in fuel cells requires further research and trials.

Chung *et al.*[298] conducted an experiment to investigate the impact of cleaning bio-H_2 from palm oil mill effluent by fermenting it on the power output of a proton exchange membrane fuel cell. The study found that the absorption technique outperformed membrane separation in efficiency, with the purified bio-H_2 achieving a purity of 100% H_2. WSW Mobil GmbH initiated the H_2-W project in Wuppertal, Germany, focusing on producing hydrogen-powered buses from municipal solid waste incineration.[299] The technology uses electricity from the waste incinerator to release H_2 through electrolysis. A fuel cell with a capacity of 85 kW is designed to convert hydrogen into electricity for bus propulsion.[300] The Wuppertal facility generates 400 kg of hydrogen per day for the Belgian manufacturer Van Hool, supporting ten fuel cell buses.

6.1.2. Bio-hydrogen in combined heat and power (CHP) applications. The Tokyu Hotel in Kawasaki, Japan, has achieved notable advancements in renewable energy by obtaining 30% of its energy from hydrogen produced through the gasification of waste plastic.[301] Toshiba's H_2Rex fuel cell system harnesses hydrogen to produce electric power and heat, effectively eliminating CO_2 emission. Metacon AB, through its subsidiary Helbio in Greece, developed the "H_2PS-5" system,[302] which incorporates a CHP generation unit. The patented technology encompasses a dual-phase procedure: the processing of fuel followed by the generation of power. The H_2PS-5 produces an electrical output of 5 kW and generates 7 kW of thermal energy, effectively supplying hot water. The anticipated energy production is around 43 MWh of electricity and 60 MWh of heat, corresponding to hot water temperatures between 70 and

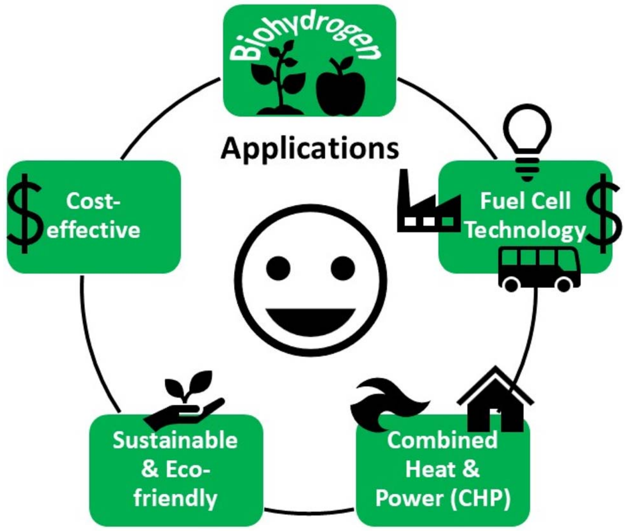

Fig. 13 Schematic illustrating the uses of biohydrogen in fuel cell technology and combined heat and power systems that are sustainable, environmentally benign, and economically viable.

80 °C. The system achieves a peak electrical efficiency of 35%, while its operating costs are significantly reduced, being two times lower than those of conventional diesel generators.[303] H_2PS-5 can be utilized in telecommunication stations, on or off-grid homes, sailing yachts and boats, trucks, and small agricultural operations. Fig. 13 provides a schematic overview of the applications of biohydrogen across various fields, highlighting their sustainability, environmental benefits, and economic viability. This overview points out the advantages of biohydrogen as a clean energy source that can contribute to sustainable development. By showcasing its diverse applications, the figure emphasizes the importance of integrating biohydrogen into various industries for a greener future.

6.2. Biohydrogen: operational obstacles

The utilization of biohydrogen across various sectors encounters several challenges that must be addressed. In the transportation sector, for instance, fuel cell electric vehicles (FCEVs) remain in the early stages of commercialization. Key factors hindering the broader adoption of bio-H_2 in multiple applications include the costs associated with fuel, vehicle materials, and the infrastructure necessary for the hydrogen system. Here are several key operational challenges identified in the applications of biohydrogen. These challenges highlight the complexities involved in implementing biohydrogen technologies effectively. Addressing these issues is crucial for advancing the viability and efficiency of biohydrogen as a sustainable energy source.

6.2.1. Storage. Hydrogen possesses a significant energy density, necessitating the use of large and cryogenic tanks for its storage and transportation.[304,305] The volumetric energy density is relatively low, recorded at 32 MJ L^{-1} under standard room temperature conditions.[304,305] Jets necessitate a blend of liquefied hydrogen and oxygen for propulsion; however, the process of liquefaction involves considerable expenses. The storage of hydrogen in a gaseous state demands high pressures ranging from 700 to 1000 bar, particularly for in-vehicle applications,[306] prompting the investigation of different H_2 storage materials for use in vehicles. The pressurization process also utilizes approximately 10% of the energy content of H_2.[307] H_2 storage uses specialized costly metals or crystalline alumino-silicate materials and alloys, such as zeolites and metal hydrides. Some of the most interesting metal hydrides are MgH_2, $LaNi_5$, $ZrFe_2$, and $NaAlH_4$. They can be used for many things, such as storing heat, controlling neutrons, conducting electricity, and more.[308] Due to their low operating temperature and endothermic behaviour, metal hydrides are considered the safest storage method.[309] Nonetheless, there remains a need for more in-depth investigation into hydrogen storage and transportation.

6.2.2. Purity. Purification is essential for the effective use of produced H_2. Chung *et al.*[298] demonstrate that an efficient power system necessitates high-quality H_2. Purity requirements are crucial in certain applications, as the presence of impurities can lead to significant implications. For instance, fuel cells necessitate the removal of CO_2 from bio-H_2, with a permissible concentration of under 2 mmol mol^{-1}.[310–312] The introduction of impurities in the fuel cell system has the potential to cause irreversible damage to both performance and operational lifespan.[313] Consequently, ISO and SAE published the ISO 14687-3 and SAE J2719-20, 511 standards, which outline the purity characteristics of H_2 utilized in vehicles. The design of these standards ensures adherence to the minimum purity requirements of 99.97 mol% for PEMFCs.[314,315] Researchers have conducted a significant number of studies on H_2 purification systems, and ongoing investigations continue to emerge.[315–317] H_2 purification methods include physical techniques such as adsorption and membrane separation, as well as chemical processes like catalysis and metal hydride separation.[318] Several studies have indicated that adsorption is a more favorable technique because it operates under low temperature and pressure conditions.[25] Nonetheless, the expense associated with the purification process continues to be a challenge that needs to be tackled in order to utilize economical membrane materials, for example. To make sure there is a cheap process that improves the endpoint application tolerance for H_2 purification, researchers are looking into new adsorption materials and metal hydrides that are not poisonous.

6.2.3. Cost. Despite the utilization of H_2 fuel cells in various applications, including transportation and CHP, which provide significant benefits such as high thermal efficiencies, excellent fuel efficiency, minimal engine noise, zero emissions, and fewer moving components, these vehicles remain more costly than their low-carbon counterparts. Natural gas is the primary fuel for CHP applications, which can easily transition to hydrogen-powered (FC-CHPs) with minimal modifications.[22]

6.2.4. Large-scale implementation. Biological methods for producing bio-H_2 present a significant barrier to commercial-scale applications due to low yield. The extended residence time in bioreactors constrains high yield, necessitating larger reactors and additional costs. Solutions include developing novel biocatalysts[25] capable of operating under challenging conditions, such as temperature and pH, and using nanotechnology to enhance substrate conversion rates. Nanoparticles made from gold and iron can transform into metal ions, enhancing microbes and biocatalysts' activities.[319,320] Technical and managerial aspects, such as system design and optimal operating conditions, also restrict widespread implementation. Artificial intelligence (AI) could help by employing optimization algorithms to forecast bio-H_2 production yield.[25,201] Despite these challenges, research continues to improve yields in bio-H_2 production.

6.3. Assessment of biohydrogen sustainability

Assessing sustainability involves critical dimensions such as environmental performance, social considerations, and economic prosperity.[321] These dimensions must be balanced to ensure that development meets present needs without compromising the ability of future generations to meet theirs. By integrating these aspects, organizations can create a holistic approach that fosters long-term viability and resilience. Biohydrogen demonstrates a more advantageous energy ratio and lower greenhouse gas (GHG) emissions when compared to fossil fuel-based methods. This advantage makes it an attractive alternative for sustainable energy production. As research and technology continue to advance, biohydrogen could play a pivotal role in reducing our reliance on fossil fuels and mitigating climate change. Achieving a sustainable replacement for fossil sources requires a focus on maintaining a favourable energy ratio in biohydrogen production pathways.[322] Consequently, it is essential to take biohydrogen into account when strategizing and advancing a hydrogen economy, with attention to both energy and environmental factors.[323] The following subsections offer a brief summary of the sustainability evaluation of biohydrogen.

6.3.1. Economic feasibility of biohydrogen. Recently, Kazmi *et al.*[322] have illustrated the economic feasibility of biohydrogen production from food waste, highlighting its potential to reduce greenhouse gas emissions, optimize resource utilization, and enhance energy sustainability. They developed the proposed model using Aspen Plus®, an esteemed advanced process simulator known for its outstanding simulation capabilities in managing both solids and fluids. Their study primarily examines the use of food waste as feedstock for biogas production, with Aspen Plus® being an essential tool for a thorough analysis of this important phase in the process. The study suggests that implementing this technology can significantly contribute to a circular economy by reducing waste and reusing resources. It also considers feedstock costs, energy input requirements, and potential revenue from byproducts while considering environmental impacts and scalability. The following processes were developed to assess the economic viability of bio-H_2 production from food waste using a comprehensive approach.[322]

6.3.1.1 Fruit waste anaerobic digestion for biogas. This investigation centres on the generation of biogas from food waste *via* the anaerobic digestion process utilizing Aspen Plus. Aspen Plus allows for detailed examination and improvement of key process factors, making it possible to assess different situations and setups while accurately simulating the process. This study employs a thorough methodology aimed at maximizing biogas yield, improving overall efficiency, and enhancing the sustainability of the process.

This anaerobic digestion (AD) model posits that the substrate will comprise proteins, lipids, and carbohydrates. The analysis encompasses the reaction kinetics associated with AD stages and temperature. They employ the non-random two-liquid (NRTL) method for physical properties, which has proven effective for both liquid and vapor phases. It is adept at calculating activity coefficients and managing polar substrates. This model was developed using a previous framework established by Rajendran *et al.*,[324] as it is grounded in AD. They adjusted various parameters, including different substrate compositions, at the initial stage of the simulation to achieve the maximum concentration of methane. This anaerobic digestion model consists of two categories of reaction sets.

(a) Hydrolysis reactions are conducted through the application of reaction rate equations and relevant parameters. The impact of pretreatment, which improves hydrolysis efficiency for various materials, needs to be studied more through a separate set of hydrolysis reactions.

(b) Also, in the acidogenesis and acetogenesis stages, where bacteria that create acids and those that produce acetates work on the broken-down compounds, the model includes the right biochemical reactions and their rates. This detailed representation ensures that the change of soluble compounds into volatile fatty acids (VFAs), alcohols, and acetic acid is accurately recorded during the hydrolysis phase.

They have collaboratively developed this Aspen Plus model from a combination of streams and blocks. The simulation features a stoichiometric reactor (B3) where hydrolysis reactions happen at a high temperature of 55 °C. The output stream S2 serves as the feed for the subsequent stage in the continuous stirred tank reactor (B1), where acidogenic, acetogenic, and methanogenic reactions take place at a temperature of 55 °C and varying hydraulic retention times (HRTs). After the digestion process is completed, the biogas is collected and purified to remove impurities like hydrogen sulphide, moisture, and other contaminants, thereby ensuring the quality and usability of the final product.

6.3.1.2 CO_2 removal from biogas utilizing ionic liquid while integrating the CO_2 liquefaction process. Prior to additional application, biogas, primarily composed of CH_4 and CO_2 derived from the anaerobic digestion process, necessitates purification. The solvent utilized in this process is ionic liquid (IL), facilitating the selective absorption of CO_2 from the biogas mixture.[325] In this case, 1-butyl-3-methylimidazolium tris(perfluoroethyl) trifluorophosphate ([Emim][FAP]) was used as an IL solvent. This perspective involves selecting a suitable IL by evaluating the Aspen Plus model, which takes into account various properties such as solubility, selectivity, and CO_2 absorption capacity.[326,327] The system includes a multistage compressor, a packed absorption column designed for CO_2 absorption, a flash evaporator for the regeneration of the solvent, a centrifugal pump for the recirculation of the solvent, and a pre-absorber solvent cooler. A thorough regression analysis of the experimental data was conducted to elucidate the interaction between IL and biogas components.

6.3.1.3 Conversion of biomethane to biohydrogen. The generation of biohydrogen from biogas using Aspen Plus® can be demonstrated as follows. The process model starts by heating purified biogas, combines it with steam, and proceeds towards the steam methane reforming reactor. Steam reforming is an endothermic reaction that requires a significant amount of heat for it to continue effectively. The reactor maintains temperatures ranging from 900 to 1000 °C. The syngas from the outlet of the reforming reactor is subsequently cooled and directed to the high-temperature water gas shift reactor (HT-WGS). The mixture that comes out of the HT-WGS reaches a temperature of 457 °C and a pressure of 15.75 bar because the water gas shift (WGS) reaction releases heat. Carbon monoxide remains in this mixture in significant quantities. The substance is subsequently cooled to 210 °C at a pressure of 15.70 bar and directed towards the low-temperature water gas shift reactor (LT-WGS). The process referred to as the water-gas shift involves the breakdown of methane into carbon monoxide and hydrogen gas, represented by the following eqn (22).

$$CH_4 + H_2O \rightarrow 3H_2 + CO \tag{22}$$

The LTWGS reactor outlet heats a mixture to 238 °C, then cools to 38 °C at 15.65 bar to separate water. The mixture is directed to the Pressure Swing Adsorption (PSA) unit, which extracts high-purity hydrogen from the gas mixture. The hydrogen is compressed for hydrogen fuel injection into vehicles. The tail gas, containing unreacted CH_4, CO_2, residual CO, and H_2, is mixed with air and preheated before combustion. This procedure increases combustion efficiency and maximizes heat utilization. Flue gas is discharged into the atmosphere at a controlled temperature to mitigate condensation, a process commonly used on an industrial scale.

6.3.1.4 Economic analysis and appraisal. The economic evaluation of hydrogen production centres on analysing the financial feasibility and practicality of the process, including capital and operational expenditure, revenue generation, and the assessment of CO_2 emissions resulting from the anaerobic digestion of food waste. The cost analysis takes into account all components, such as anaerobic digestion, CO_2 scrubbing, and H_2 production. Both total capital costs and operational costs, including plant overhead and administrative expenses, form its foundation. They utilize the Total Annualized Cost (TAC) eqn (23) as follows to facilitate an equitable assessment across all analysed scenarios:[322]

$$\text{TAC} = \left(\frac{\text{TCIP}}{\text{Pay back period}}\right) + \text{TOMC} \tag{23}$$

where TCIP = total capital investment of project and TOMC = total operational and maintenance cost.

The total capital cost (TCC) is closely associated with equipment expenses. They ascertain equipment costs by utilizing parametric relationships and constants obtained from credible literature sources. For compressors and pumps functioning under high pressures, they adopt a methodology influenced by Sinnott,[328] incorporating equipment-specific constants (α, β) and operation-specific dimensions (S). To evaluate the costs associated with processing vessels and equipment, refer to Guthrie,[329] which is based on the dimensions of vessel height and diameter. This approach is particularly useful in situations where comprehensive cost data for comparable equipment is unavailable or when swift cost estimates are necessary. Additionally, the bare modulus method suggested by Turton *et al.*,[330] is used to calculate the purchase cost of intercoolers, taking into account the bare module factor (F_{BM}), pressure factor (W_p), and material factor (W_M). This methodical approach utilizes comprehensive engineering parameters and equipment specifications.

The findings of the economic evaluation regarding H_2 production from biogas are detailed in Table 8. This economic analysis looks at how practical each scenario is by checking the costs involved in making H_2, figuring out which scenario makes the most money and which ones might end up costing more and causing financial problems. The analysis examines the case through three distinct scenarios: anaerobic digestion, CO_2 scrubbing, and H_2 production, while assessing cost savings associated with TCC, TOC, and TAC. The findings indicate that the total carbon cost for anaerobic digestion is 3.15×10^4 \$, where food waste and water are combined to produce raw biogas. The raw biogas is directed to a subsequent stage for CO_2 separation, where CO_2 scrubbing is performed using an ionic liquid, followed by CO_2 liquefaction. The total capital cost (TCC) is calculated at 2.15×10^7 \$, while the total operating cost (TOC) amounts to 4.73×10^8 \$, primarily attributed to electricity consumption in the compressors. The steam reforming process subsequently directs the separated biogas towards hydrogen production, where biomethane reacts with steam to yield bio-H_2. The total capital cost (TCC) is calculated at 1.92×10^6 \$. This cost is due to the use of steam and high temperatures, which require various reactor vessels. Table 8 presents the variation in all costs for each case accordingly.

In conclusion, a thorough economic analysis[322] highlights the significance of every stage. The total capital cost (TCC) for AD is notably lower at 3.15×10^4 USD, indicating that it presents a cost-effective option in the initial stages of generating raw biogas from food waste and water. The phase of CO_2 separation results in elevated costs (TCC of 2.15×10^7 \$), mainly due to the financial implications linked to ionic liquid scrubbing and the liquefaction of CO_2. The total operating cost (TOC) is significantly affected by the electricity consumption in compressors, amounting to 4.73×10^8 USD. The suggested comprehensive method for hydrogen production from biogas highlights the opportunities for financial benefits while aiding in the transition to a more sustainable energy environment.[322] This approach aims to reduce carbon emissions and promotes the utilization of renewable resources, thereby enhancing energy security. By investing in innovative technologies and infrastructure, stakeholders can expect long-term cost savings and improved environmental outcomes.

Table 8 Results of the cost analysis of the three process sections under study[322]

Parameters/case	Anaerobic digestion	Purification of biogas and liquefaction of CO_2	H_2 production
Total capital cost, USD	3.15×10^4	2.15×10^7	1.92×10^6
Total operating cost, USD per year	8.79×10^8	4.73×10^8	4.41×10^8
Total utilities cost, USD per year	8.79×10^8	4.72×10^8	4.40×10^8
Equipment cost, USD	5.31×10^3	3.63×10^6	32.3×10^6
Total installed cost, USD	3.70×10^3	2.53×10^6	22.5×10^6
Total annualized cost, \$ per year	8.79×10^8	4.77×10^8	4.41×10^8

6.3.2. Environmental protection with biohydrogen. Recently, Yang *et al.*[331] evaluated the environmental sustainability of biohydrogen production from municipal wastewater and food waste (FW) using a life cycle assessment (LCA). The study assessed three scenarios: one involving solid enzymes (Scenario 1), another with commercial enzymes (Scenario 2), and a third without enzyme hydrolysis pretreatments (Scenario 3). The investigation performed a comparative analysis of these three scenarios regarding the environmental sustainability of biohydrogen. The primary comparison of significant environmental impact categories from these three biohydrogen production scenarios is as follows:

6.3.2.1 Global warming. The results showed that the greenhouse gas (GHG) emissions from the biohydrogen process in Scenario 1 (528 kg CO_2 eq.) and Scenario 2 (799 kg CO_2 eq.) were much lower than in Scenario 3 (3990 kg CO_2 eq.). This was mainly because using enzymes in the hydrolysis process (in Scenario 1 and Scenario 2) helped break down large organic molecules in the feedstocks more effectively, leading to a higher biohydrogen production. The primary reason for this distinction was that the incorporation of enzymes (Scenario 1 and Scenario 2) in the hydrolysis process could efficiently break down organic macromolecules in feedstocks, resulting in an increased biohydrogen yield.[332–334] Consequently, the reduced environmental impacts of global warming in Scenario 1 and Scenario 2 were identified. The electricity consumption was the primary source of GHG emissions in Scenario 1, amounting to 242.5 kg CO_2 equivalent, and in Scenario 2, reaching 309.4 kg CO_2 equivalent. Scenario 3 primarily produced GHG emissions from the final disposal of biowaste, which amounted to 1392.3 kg of CO_2 equivalent. The increase was largely due to the significant quantity of undigested biowaste residue resulting from the conventional fermentation process in this scenario, which necessitated composting for final disposal and consequently led to the highest levels of GHG emissions.

6.3.2.2 Ecotoxicity on land. Scenario 3 had a bigger negative effect on the environment regarding land pollution, showing 9540 kg of 1,4-DCB (1,4-dichlorobenzene) equivalent, while Scenario 1 showed 1620 kg and Scenario 2 showed 2520 kg. The primary factors influencing this category across all scenarios were the use of chemicals and the transport of FW. Also, the impact of building infrastructure in Scenario 3 (1780.1 kg 1,4-DCB eq.) was much higher than in Scenario 1 (111.7 kg 1,4-DCB eq.) and Scenario 2 (139.1 kg 1,4-DCB eq.) because producing biohydrogen through traditional fermentation in Scenario 3 required a bigger anaerobic digester than in the other two scenarios. Consequently, the consumption of additional resources, including concrete and steel, for infrastructure construction in Scenario 3 resulted in increased environmental impacts.

6.3.2.3 Noncarcinogenic toxicity in humans. The environmental effects related to human noncarcinogenic toxicity in Scenarios 1–3 were found to be 332 kg, 669 kg, and 2150 kg of 1,4-DCB equivalent, respectively. Scenario 3 showed the highest environmental impacts in this area compared to the other scenarios for biohydrogen production. Scenario 3 exhibited the most significant environmental impacts in this category compared to all other scenarios for biohydrogen production. The main cause of human noncarcinogenic toxicity in Scenario 3 was due to the use of chemicals, making up 41.4%, or 890.7 kg 1,4-DCB equivalent. The analysis showed that producing biohydrogen using traditional fermentation methods (Scenario 3), without needing to break down materials first, is expected to have less negative effect on the environment from chemical use, including enzymes. However, Scenario 3 produced the least amount of biohydrogen, which also led to the highest risk of non-cancer-related health issues from chemical use, since all environmental effects were measured based on producing 1 kg of biohydrogen. Consequently, Scenario 3 exhibited the most significant environmental impact due to chemical usage in this category.

6.3.2.4 Scarcity of fossil resources. In this category, Scenario 1 (99.8 kg oil equivalent) and Scenario 2 (152 kg oil equivalent) demonstrated greater environmental sustainability when compared to Scenario 3 (547 kg oil equivalent). The elevated environmental impacts observed across all scenarios in this category stemmed from the operation of electricity and the consumption of chemicals, which ranged from 21.8 to 150 kg oil equivalent. The primary reason for the observed increases was that the majority of operations in the biohydrogen production plant were powered by electricity, including equipment operation and reactor heating, with electricity generation predominantly dependent on non-renewable fossil fuels.[335] On the other hand, making chemicals, like enzymes, used in the biohydrogen production plant required a lot of fossil fuels.[336]

6.3.2.5 Scarcity of mineral resources. This category delineates and contrasts the effects of all biohydrogen generation scenarios using a standardized unit (kg of Cu eq.). Scenario 3 had the most significant environmental consequences in this category (9.46 kg Cu eq.). The effect of infrastructure building in

Scenario 3 exceeded that of Scenario 1 and Scenario 2. Scenario 3 achieved biohydrogen synthesis using standard anaerobic fermentation, resulting in an extended hydrolysis duration compared to Scenario 1 and Scenario 2.[337] Scenario 3, with a consistent processing capacity of 700 m^3 per day for municipal wastewater and 100 t per day for food waste, necessitated a greater volume of fermentation reactors compared to Scenario 1 and Scenario 2. This resulted in increased use of material resources, such as concrete and steel, in infrastructure buildings, yielding the most significant consequences in this category.

6.3.2.6 Utilization of land. The impact category of land use for three biohydrogen production scenarios was examined, with the unit expressed as m^2a equiv. (square meter of land per year). Scenario 1 (47.5 m^2a equiv.) demonstrated the least environmental impact regarding land use for biohydrogen production. Nonetheless, Scenario 3 (75.9 m^2a eq.) demonstrated a superior environmental performance in this category when contrasted with Scenario 2 (137.5 m^2a eq.). The most significant factor influencing land use in Scenario 2 was the use of chemicals, which accounted for 91.8%. This figure was 3.2 and 4.8 times greater than the levels observed in Scenario 1 and Scenario 3, respectively. This situation might be connected to the differences in chemical use in the three biohydrogen production scenarios, especially the kinds of enzymes used, whether they are solid enzymes or commercial enzymes. The solid enzymes, like glucoamylase and protease, used in Scenario 1 can be made continuously by fungi using solid-state fermentation, which means they use less land. In Scenario 2, constantly adding commercial enzymes to the hydrolysis tank with the feedstocks led to higher use of these enzymes and a bigger effect in this area.

Table 9 shows a summary of the life cycle assessment results for three different ways of producing biohydrogen in six important environmental impact areas. These areas include global warming, ecotoxicity on land, noncarcinogenic toxicity in humans, scarcity of fossil resources, scarcity of mineral resources, and land use. The data highlight the advantages and disadvantages of each production method, providing valuable insights for researchers and policymakers aiming to optimize biohydrogen production while minimizing environmental harm. The exploration of biohydrogen production through a comprehensive life cycle assessment reveals a complex interplay between its environmental impacts and production methods.[331] By looking at these six important factors, this analysis highlights the pros and cons of different ways to produce biohydrogen. The insights gleaned from this assessment not only illuminate pathways for enhancing biohydrogen production efficiency but also emphasize the importance of mitigating environmental consequences. As the quest for sustainable energy sources continues, these findings serve as a crucial foundation for developing strategies that optimize biohydrogen output while safeguarding ecological integrity.

In summary,[331] Scenario 1 emerged as the most sustainable option for biohydrogen production, demonstrating the least environmental impact. Furthermore, the utilization of electricity and chemicals significantly influenced the environmental profiles of Scenario 1 and Scenario 2, whereas in Scenario 3, chemical usage and infrastructure development emerged as the primary contributors. Enhancing biohydrogen yield, optimizing chemical usage, conserving electricity, and strategically selecting plant locations can lead to a substantial positive impact on environmental sustainability. The results obtained may serve as compelling evidence for sustainable biohydrogen production when viewed through an environmental lens. This study aimed to contribute to the establishment of a circular economy focused on resource recycling from waste.

6.3.3. Social importance of biohydrogen. Recently, De-León Almaraz *et al.*[338] conducted a comprehensive review of the intricate aspects of social sustainability within the hydrogen economy. They have identified, thoroughly described, ranked, and discussed some primary social aspects. They found problems such as not having a clear definition of the societal value of H_2, not looking deeply into socio-political issues (like geopolitics and well-being), not using social lifecycle assessment (S-LCA) sufficiently, and having hardly any studies focused on social practices and cultural issues. These findings highlight the critical need for more interdisciplinary research that integrates social science perspectives into the development of hydrogen technologies. By addressing these gaps, future studies can better inform policymakers and industry leaders about the societal implications of transitioning to a hydrogen economy. Here we concisely outline the key aspects of social sustainability.

6.3.3.1 Accessibility. The main challenge lies in delivering reliable products at reasonable costs and establishing infrastructure for a sustainable hydrogen supply chain (HSC). To assess hydrogen supply accessibility, targeted metrics must be established, considering both physical and economic

Table 9 Comparative LCA outcomes for three biohydrogen production scenarios across six critical environmental effect areas[331]

Environmental impact categories	Scenario 1	Scenario 2	Scenario 3
Global warming (kg CO_2 eq.)	528	799	3990
Ecotoxicity on land (kg 1,4-DCB equiv.)	1620	2520	9540
Noncarcinogenic toxicity in humans (kg 1,4-DCB equiv.)	332	669	2150
Scarcity of fossil resources (kg oil equiv.)	99.8	152	547
Scarcity of mineral resources (kg of Cu eq.)	1.19	1.77	9.46
Utilization of land (m^2a equiv.)	47.5	137.5	75.9

dimensions. These metrics should reflect the proportion of the population unable to access hydrogen and integrate societal, strategic, and operational performance goals. Sustainability is crucial for HSCs, and new modelling efforts should include sustainable standards in hydrogen infrastructure plans. Communication of sustainability criteria to society is essential for comparisons with alternative energy supply chain options and aligning with frameworks like the Sustainable Development Goals. Conflicts may arise between sustainability criteria and multi-objective optimization initiatives. Polycentric approaches should be considered, integrating various scales and diverse actors. Examining the effects of essential and limited resources on the sustainability, reliability, and resilience of the hydrogen supply chain is crucial. Understanding investors' interest and learning from pilot projects can provide valuable insights into accessibility options, limitations, and potential risks.[339–341] Accessibility intertwines with various social dimensions, requiring further investigation.

6.3.3.2 *Information.* The digital economy presents a significant challenge in providing precise, reliable, and prompt information for the effective implementation of the hydrogen economy. The usability of labelling products developed by H_2 technologies is a significant area for future research. Digitalization and IoT can enhance social awareness,[342] but it is crucial to investigate how public awareness of hydrogen products and technology influences their perception and acceptability. The quantity and nature of information disseminated will impact its acceptability. It is essential to communicate the advantages of transitioning to hydrogen, its limitations, and risks associated with different pathways. The relationship between "information" and "acceptability" is crucial for informed decisions. We anticipate further investigation into public awareness of hydrogen and associated attitudes/acceptability in the coming years.[343] There is ambiguity regarding the specific communication and information tools used, such as collaborative commerce and c-commerce. Initiatives related to training and education, including employee education levels, training programs, and upskilling opportunities, are needed to elucidate the various technologies within the hydrogen economy.

6.3.3.3 *H_2 markets.* The absence of a clear definition regarding the value of H_2 products represents a significant gap in this area. While the advantages related to the environment and flexibility are frequently highlighted, it is essential to establish clear value definitions for various types of hydrogen products to facilitate market deployment. Further investigation into the competitiveness of hydrogen products is essential. The precise definition of hydrogen's value will empower producers to establish pricing while also equipping them to communicate the advantages associated with various hydrogen products, extending beyond mere H_2 colours and emissions. This subject is essential for existing hydrogen users or producers who need to transition from grey to blue or green hydrogen in the coming years.

6.3.3.4 *Acceptability.* The use of questionnaires to assess hydrogen acceptability is growing, but the validity and reliability of these instruments are lacking. Standardization in questionnaire creation is crucial, and further analysis is needed to evaluate stakeholders' acceptability, expectations, and trust.[340,341] Market analyses can also be used to link stakeholder perspectives.[344] Factors influencing acceptability include hydrogen value, safety considerations, conflicts, pandemics, public health effects, and employment opportunities.[345] Insights from demonstration projects[346] and field experiences[347] can provide insights into customer satisfaction. Examining the acceptability of operations and their public perception in relation to energy consumption can also be beneficial. A clear definition of risk in surveys is crucial to avoid ambiguity.[348]

6.3.3.5 *Rules and policies.* The primary obstacle for this category lies in the necessity of having comprehensive policies, standards, and regulations in place. Regulatory and standardization instruments are crucial for accelerating hydrogen utilization.[349] However, once these policies and regulations are established, a pertinent question emerges: what are the impacts of these policies and regulations on the deployment of the hydrogen economy? To answer this question, it is essential to analyse how effective implementation can influence market growth, investment, and technological innovation. Additionally, understanding the balance between regulatory support and industry flexibility will be vital in fostering a thriving hydrogen sector.

6.3.3.6 *Stakeholders.* The primary challenge recognized is "collaboration and leadership" concerning the HSC deployment. While the importance of collaboration is often emphasized in discussions and presentations concerning the hydrogen economy, there exists a notable gap in scientific research regarding the collaboration among stakeholders. The potential for cooperation within a competitive context raises important questions, particularly regarding the levels at which such collaboration might actually occur. For this aspect, it is essential to utilize methods that enhance comprehension of stakeholder dialogue.[350] The analysis of stakeholders presents a complex challenge due to the diversity and varying degrees of influence associated with their roles, which can significantly impact perspectives and interactions within the HSC. A notable gap in the discussion is the cultural dimension, which should be integrated into stakeholder analysis, as ideology and culture significantly shape individuals' perceptions and behaviours.[348]

6.3.3.7 *Political and social aspects.* The hydrogen economy and transition to new energy sources require a comprehensive analysis of social and political factors. We can achieve this by utilizing methodologies such as the Sustainable Development Goals (SDGs)[351] frameworks. The focus should be on energy independence or security, including humanitarian and political aspects of global shifts and geopolitical threats. Social relationships should also consider energy poverty and solidarity.[352,353] We should examine the impact of the introduction of hydrogen products on quality-of-life measures and overall well-being.[354–356] Alternative socio-political aspects include energy geopolitics, the relationship between patriotism and progress, democracy and freedom, the pursuit of a decent life, and principles of equity, fairness, and solidarity. Additionally, the focus should be on diversity and equal opportunities, including gender and indigenous rights.[357] Future analyses should also consider cultural and ethical dimensions.[358]

6.3.3.8 Social and economic aspects. Alongside metrics associated with jobs and employment, several other significant figures pertaining to socioeconomic factors are especially pertinent for hydrogen projects. This information encompasses patterns of energy consumption, effects on the local economy, levels of investment in infrastructure, and environmental advantages like decreases in greenhouse gas emissions. Additionally, data on educational and training opportunities for the workforce can provide insights into the long-term viability and sustainability of hydrogen initiatives. In what ways can the instruments of environmental economics, such as taxes, subsidies, and tradable emission permits—originally designed for addressing externalities—be modified or integrated into the hydrogen economy?[359] The last sentence highlights the need to adapt traditional economic tools to better fit the unique challenges and opportunities presented by the hydrogen sector. By doing so, policymakers can effectively promote sustainable practices while encouraging investment and innovation in this emerging field.

6.3.3.9 Responsibility. The introduction outlines that the concept of "social sustainability" can be examined through various lenses. Different operations may require the use of specific metrics. For instance, the pursuit of gender equality is crucial for the attainment of SDG 5,[360,361] along with the importance of corporate social responsibility,[362–364] among other factors. However, a clear plan for social sustainability is necessary, like the one used in operations management, which includes the four social areas defined by the Global Reporting Initiative (GRI): human rights, labour conditions, society, and product responsibility.[361,362,365] These areas provide a comprehensive framework for organizations to assess their impact and improve their practices. By integrating these metrics into their strategies, companies can enhance their social performance and contribute to broader sustainability goals. We need to work together to agree on how social lifecycle assessment (S-LCA) can be used for HSCs, since it seems to be a useful tool because it is similar in structure and method to environmental LCA. This collaboration will allow us to create standardized approaches that can effectively measure social impacts alongside environmental considerations. By doing so, we can ensure that all aspects of sustainability are addressed, leading to more responsible and ethical business practices in health supply chains.

6.3.3.10 Technological security. Various investigations are currently being conducted regarding the technological safety of hydrogen technology, including the safety risk index,[366] FAST and HAZOP methods,[367] and quantitative risk assessment.[368] These efforts aim to establish comprehensive guidelines and protocols to minimize potential hazards associated with hydrogen production, storage, and utilization. By addressing these safety concerns, researchers hope to foster greater public trust and facilitate the widespread adoption of hydrogen as a sustainable energy source. Every methodology encounters the common challenge of measuring the risk associated with technological maturation. It is essential to establish conditions that promote sustainable growth, encourage responsible business practices, and facilitate lasting employment opportunities in both the medium and long term (European Commission, 2011). Recent studies emphasize the importance of safety risk assessment and HSC reliability, enabling the identification of secure working conditions and the operation of hydrogen technologies. This approach facilitates the implementation of preventive measures that can be effectively communicated to users. Additionally, fostering a culture of continuous improvement and innovation within organizations can further enhance safety protocols and operational efficiency. By prioritizing education and training, businesses can equip their workforce with the necessary skills to adapt to evolving technologies and mitigate potential hazards effectively.

In summary, social dimensions play a crucial role in influencing various aspects of communities, including economic factors, energy consumption, and business operations.[338] These dimensions can significantly impact development at local, regional, and international levels, addressing climate change, and facilitating energy transition. To assess the competitiveness of hydrogen, scenarios, models, and studies should incorporate relevant social dimensions. Existing models focus on singular social indexes, such as job creation or risk index, which are insufficient. Future work should use a framework to support a comprehensive perspective and introduce new contributions. Diverse teams can enhance alignment of efforts and expedite requirements, including public participation, debate, cooperation, product testing, safety, acceptability assessment, policy and regulation, resilience, and reliability. The social context and socio-political and economic dynamics significantly influence strategies related to the hydrogen economy. Engaging the public is essential for an equitable and transparent assessment

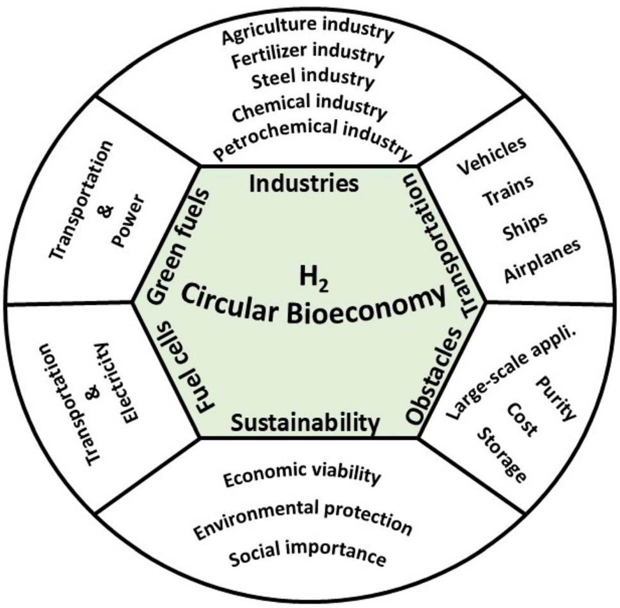

Fig. 14 Circular bioeconomy's connection to fuel cell technology, highlighting its potential in industry and transportation as a green fuel, obstacles in its applications, highlighting its cost-effectiveness and sustainability.

of hydrogen compared to alternative fuels. A consensus within the scientific community on the widespread application of S-LCA and frameworks related to social sustainability is essential. Understanding the integration of hydrogen within social practices, taking into account cultural factors, will facilitate the development of hydrogen markets and smooth project implementation, ensuring hydrogen products are accessible to the society.

Fig. 14 summarizes the applications, obstacles, and sustainability of biohydrogen as described above. Fig. 14 shows how the circular bioeconomy connects with fuel cell technology, highlighting its role as an eco-friendly fuel in industry and transportation, the challenges it encounters, current trends, and biohydrogen sustainability. These advancements could lead to increased efficiency in hydrogen production and improved methods for storage and distribution, ultimately making biohydrogen a more viable alternative to fossil fuels. As research progresses, it is essential to address the economic and infrastructural barriers to fully realize the potential of biohydrogen in achieving a sustainable energy future. The synergy between bioeconomy and fuel cell technology not only promotes a reduction in greenhouse gas emissions but also enhances energy security through the diversification of energy sources. As research progresses, innovations in bio-hydrogen production and storage could further solidify its role as a cornerstone of sustainable energy solutions. Biohydrogen is not only cost-effective and environmentally friendly; it also holds significant social value and is very close to realizing sustainability.

7. Future perspectives and challenges

Achieving the Sustainable Development Goals (SDGs) is crucial in the pursuit of a sustainable future, where carbon neutrality is not just an aspiration but a tangible reality. Biomass emerges as an invaluable feedstock in this journey, harnessing the potential of organic materials to power our energy needs while minimizing environmental impact. By embracing biomass, we unlock a pathway that emphasizes environmental sustainability, ensures resource availability, promotes biological renewability, and encourages recycling practices. This comprehensive approach mitigates climate change and fosters a circular economy that respects and replenishes our natural resources. As we move forward, integrating these principles will be key to creating a resilient and sustainable world for generations to come. In light of these comprehensive approaches, we face certain challenges that will influence our future pathways. We examine several challenges and potential future directions in the following paragraphs.

Thermal plasma-assisted gasification represents a sophisticated method for generating syngas that is abundant in H_2. The separation of H_2 from CO_2 is essential, and at the same time, the generation of value-added compounds from CO_2 can be achieved. This dual approach not only enhances the efficiency of hydrogen production but also contributes to carbon capture and utilization strategies. By converting CO_2 into useful products, the process can help mitigate greenhouse gas emissions while generating economic value. Thermal plasma-assisted gasification can improve hydrogen production by combining carbon capture, utilization, and storage (CCUS). In sorption-enhanced reforming with *in situ* CO_2 capture, a bifunctional material combines a sorbent and a catalyst, resulting in faster CO_2 capture.[118] The catalyst can affect the surface area, grain size, pore volume, and exposure of the sorbent, affecting the kinetics of CO_2 capture. However, the influence of catalytic species in bifunctional materials on sorbent species remains unexplored. Further research is needed to understand the effectiveness of bifunctional materials.

The creation of innovative engineered strains and advancements in combined/hybrid fermentation techniques open up new opportunities for higher production efficiencies of bio-H_2.[22] Another great option to improve the technological and financial aspects of the production of bio-H_2 is the concurrent synthesis of other compounds with value addition. Pre-treatment reduces the lag phase of anaerobic fermentation by removing stiff and inhibitory substrate components that impede the fermentation process. This increases the efficiency of the bioprocess. Pre-treatment procedures are helpful, but they raise production costs, thus their usage must be justified. Also, hybrid systems of bio-H_2 production are considered one of the best solutions to reduce the cost of production and increase the productivity of bio-H_2.

The adaptable approach of MECs in hydrogen production is gaining attention as a viable technology for zero emissions.[246] This method enhances efficiency and reduces reliance on fossil fuels. As researchers continue to refine these processes, the potential for widespread implementation in various industries becomes increasingly promising. However, further research on sustainability is necessary to fully understand the efficiency and viability of this innovative technology in the hydrogen economy. The task includes evaluating the lifecycle impacts of MECs, exploring different feedstocks, and assessing the scalability of the technology in various contexts. By addressing these challenges, we can better position MECs as a cornerstone in the transition to sustainable energy solutions.

Machine learning is a promising tool for improving biohydrogen production, but it faces challenges due to the scarcity of data.[201] The process's intricacies and fluctuations make it difficult to produce adequate data for machine learning algorithms. Existing data often suffer from incompleteness or bias, complicating the training process. Simulated data can address these challenges by producing a more extensive dataset for training algorithms. Integrating simulation with actual experimental data can minimize bias and yield more precise outcomes. Advanced algorithms like deep learning can effectively address non-linear relationships between input and output variables, paving the way for a hopeful future in biohydrogen production.

Metal hydrides offer an attractive way to store a lot of hydrogen at lower temperatures because they quickly release and store hydrogen.[308] Nonetheless, the hydrogen economy necessitates affordable, safe, and environmentally sustainable approaches for the production and separation of hydrogen. We must explore a new method for storing hydrogen at near

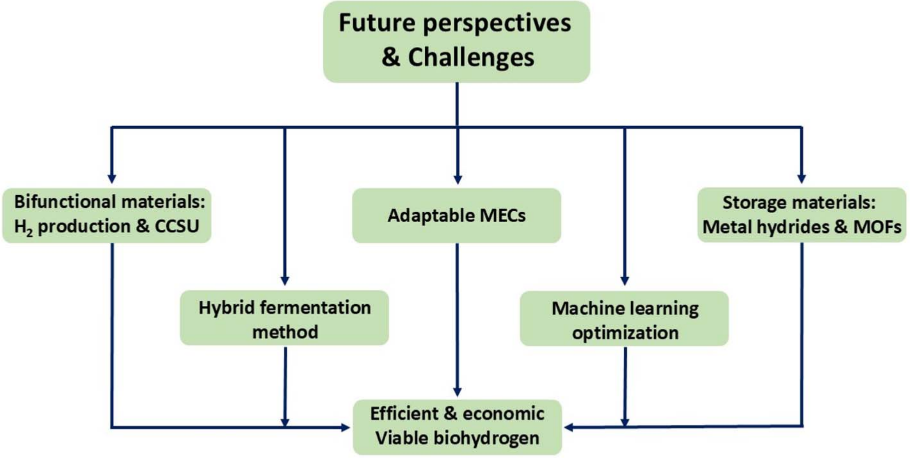

Fig. 15 Future prospects and challenges in the production of efficient and economically viable biohydrogen.

ambient pressure and temperature. A promising approach involves utilizing synthetic adsorbents designed to capture hydrogen within a highly porous and active structure, drawing inspiration from the effectiveness of metal–organic frameworks (MOFs) in CO_2 capture. The potential of these adsorbents to provide a significant capacity for hydrogen under near-ambient conditions is noteworthy. This approach offers the benefit of employing pressure swing desorption to effectively release the adsorbed hydrogen for its subsequent use.

Fig. 15 encapsulates the future perspectives and challenges outlined above. The interplay of these factors can improve the efficiency and cost-effectiveness of biohydrogen production. Moreover, continued research and collaboration among scientists, engineers, and policymakers will be essential to overcome existing barriers and drive innovation in this field. By leveraging advancements in technology and sustainable practices, the potential for biohydrogen to contribute to a cleaner energy landscape becomes increasingly viable.

8. Conclusion

Biohydrogen is rapidly emerging as a promising substitute for conventional fossil fuels, thanks to its impressive energy yield, carbon-neutral characteristics, and sustainable qualities. The proposed biomass-to-sustainable biohydrogen approach presents a promising opportunity for the development of long-term strategic hydrogen gas, and it appears to be nearing realization. The outcomes and findings derived from the current review are as follows. The primary methods for producing H_2 from biomass include thermochemical, biological, and electrochemical processes. The integration of thermochemical processes with advanced technologies, such as plasma assistance, greatly enhances efficiency. It plays a vital role in the gasification of materials, process modelling, sewage sludge treatment, and the improvement of hydrogen production through CO_2 capture and utilization. The scaling of biological and electrochemical methods for hydrogen production presents challenges and results in limited hydrogen yields; nonetheless, there is a growing interest in thermochemical hydrogen generation. Additionally, combining thermochemical methods like pyrolysis and gasification with biological techniques could improve how we treat biomass waste in a way that is eco-friendly and efficient. This integrated approach maximizes hydrogen production and contributes to a circular economy by converting waste into valuable energy resources. As research in this field progresses, further innovations are expected to optimize these techniques, making them more viable for widespread application. Cutting-edge fermentation methods and newly engineered strains offer promising avenues for enhancing the efficiency of bio-H_2 production.

Recent advancements in machine learning offer exciting opportunities for improving large-scale biohydrogen production by analysing extensive datasets and identifying patterns to optimize industrial processes. The utilization of these methods enables the examination of bioreactor datasets, aiding in the discovery of patterns and relationships among process variables. Integrating simulation with actual experimental data can mitigate bias in machine learning and yield more precise outcomes. Outcomes can lead to enhanced efficiency and productivity in biohydrogen production systems. By leveraging these insights, researchers and engineers can design more effective bioprocesses, ultimately contributing to the development of sustainable energy solutions. Recent advancements in biohydrogen production from biomass demonstrate the promise of a circular bioeconomy, linking contemporary industries in a manner that is sustainable for the economy, the environment, and society.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Author contributions

Md. Merajul Islam: conceptualization, validation, visualisation, resource, writing – original draft. Amina Nafees: validation, writing – review & editing.

Conflicts of interest

Authors declare no conflict of interest.

Abbreviation

AD	Anaerobic digestion
AI	Artificial intelligence
ANN	Artificial neural network
APR	Aqueous phase reforming
ATP	Adenosine triphosphate
BECCS	Bioenergy with carbon capture and storage
$BioH_2$	Biohydrogen
BTX	Benzene, toluene, and xylenes
CBE	Circular bioeconomy
CHP	Combined heat and power
CSCWG	Catalytic supercritical water gasification
EAB	Electrochemically active bacterium
FCEVs	Fuel cell electric vehicles
$Fd_{(ox)}$	Oxidized ferredoxin
$Fd_{(red)}$	Reduced ferredoxin
FW	Food waste
GA	Genetic algorithm
GHG	Greenhouse gas
IRENA	International Renewable Energy Agency
LCB	Lignocellulose biomass
LCFs	Lignocellulosic feedstocks
LCOE	Levelized cost of energy
MEC	Microbial electrolytic cell
MFCs	Microbial fuel cells
MHV	Medium heating value
MKLMA	Microbial kinetics Levenberg–Marquardt algorithm
ML	Machin learning
MLPANN	Multilayer perceptron artificial neural network
MPCA	Multi-way principal component analysis
NER	Net energy recovery
PEC	Photoelectrochemical
PEM	Proton exchange membrane
PFL	Pyruvate-formate lyase
PFOR	Pyruvate-ferredoxin oxidoreductase
PHA	Polyhydroxyalkanoate
PNSB	Purple non-sulphur bacteria
PO	Partial oxidation
PQOR	Plastoquinone oxidoreductase
PSA	Pressure swing adsorption
PSI	Photosystem I
PSII	Photosystem II
PSO	Particle swarm optimization
RBF	Radial basis function
RDF	Refuse-derived fuel
ROI	Return on investment
ScWG	Supercritical water gasification
SDGs	Sustainable development goals
S/F	Steam-to-feedstock ratio
SLC	Societal lifetime cost
SOR/F	Sorbent-to-feedstock ratio
SR	Steam reforming
SRC	Short-rotation coppice
SRH	Steam reforming of hydrocarbons
SRM	Steam reforming of methane
SVM	Support vector machine
WGS	Water gas shift

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