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Biomass conversion for sustainable hydrogen generation: A comprehensive review

Sherif Ishola Mustapha [a,c,*], Ifeanyi Michael Smarte Anekwe [a], Stephen Okiemute Akpasi [b], Kabiru Bab Muritala [c], Emmanuel Kweinor Tetteh [b], Atuman Samaila Joel [a], Yusuf Makarfi Isa [a]

[a] School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg 2050, South Africa

[b] Green Engineering Research Group, Department of Chemical Engineering, Faculty of Engineering & the Built Environment, Durban University of Technology, Durban 4000, South Africa

[c] Department of Chemical Engineering, University of Ilorin, P.M.B. 1515, Ilorin, Nigeria

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ABSTRACT

Hydrogen is emerging as a promising and environmentally friendly fuel for the twenty-first century, primarily owing to its eco-friendly nature. The production of hydrogen from renewable biomass sources offers numerous advantages compared to traditional fossil fuel-based methods. Various techniques are currently employed to efficiently and cost-effectively convert biomass into hydrogen. This review provides an up-to-date overview of the advancements in various biomass-to-hydrogen production processes. Additionally, several developmental efforts offer a concise overview of the different technologies utilized in these processes. Furthermore, it conducts a comparative analysis of the existing methods, evaluating their strengths and weaknesses. Moreover, it sheds light on the techno-economic aspects of biomass-to-hydrogen production processes, underlining the practical considerations associated with these technologies. In summary, this work serves as a comprehensive resource, addressing the evolving landscape of hydrogen production from biomass, exploring innovative developments, and providing a thoughtful assessment of the various techniques while considering economic factors.

1. Introduction

Global warming and the increase in greenhouse gas emissions resulting from human activities are driven by the rising consumption of fossil fuels, a trend that has been exacerbated by global population growth. According to the **World Energy Statistical Review 2015**, about 85 % of global energy consumption relies heavily on fossil fuel reserves. This dependence accelerates resource depletion, triggers energy crises, and contributes significantly to environmental degradation, including climate change [1]. As a result of these challenges, one of the most pressing issues of our time is the need to discover sustainable and environmentally friendly methods to meet the growing global energy demand [2,3]. With a focus on environmental protection, researchers actively seek alternative renewable energy sources to replace fossil fuels, aiming to reduce environmental impact and ensure long-term energy security [4,5].

Zhang et al. [6] describe energy carriers, such as hydrogen and renewable energy sources, including biodiesel and bioethanol, as non-toxic, biodegradable, and environmentally friendly, making them ideal for sustainable application and biorefinery [6]. Biodiesel is also technically and financially viable, with easy storage and transport capabilities [7,8]. It is produced through the esterification or transesterification of edible and non-edible fatty acids using low-chain alcohols in the presence of an acid or base catalyst [9]. Its combustion performance is comparable to that of fossil diesel [10]. Bioethanol production has also been widely studied. Various biomasses, including date palm fruit residues, *Delonix regia* pods, and sorghum biomass, have been evaluated for their suitability in bioethanol production through enzymatic hydrolysis followed by yeast fermentation [10–13].

Additionally, considerable research has focused on hydrogen (H_2) production, which is considered one of the most important energy carriers for the future due to its purity and high energy content. Globally, interest in hydrogen is growing, with its energy density of 122 MJ/kg, making it a high-yield energy carrier [14]. Hydrogen can replace 25 kg of traditional fuel with only 9.5 kg and is considered a viable alternative to petrol due to its high octane rating, rapid combustion, high energy density, and low environmental impact [15]. While H_2 offers many advantages over electricity, such as long-distance transport and efficiency

* Corresponding author at: School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg 2050, South Africa.
E-mail addresses: sherif.mustapha@wits.ac.za, mushery2001@yahoo.com (S.I. Mustapha).

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Table 1
The physicochemical characteristics value of different biomass feedstocks for H_2 production.

Biomass Feedstock	High Calorific Power (Kcal/kg)	Elemental Analysis					Humidity (%)	Ash (%)	Ref.
		O (%)	S (%)	N (%)	H (%)	C (%)			
Woods and woody biomass									
Palm empty fruit bunch	4633.6	52.8	0.52	–	4.1	40.8	75.60	1.6	[30]
Sawdust agricultural waste materials	3155.30–4411.48	46.87	0.05	1.68	6.31	44.75	59.38	1.03	[48–50]
Oil palm frond biomass	–	49.8	0.6	–	7.2	41.9	67	4.3	[51,52]
Bamboo	4359–4568	54 ± 3	0.018 ± 0.006	0.6 ± 0.3	6.1 ± 0.2	39 ± 3	44.51	1.4–3.0	[53,54]
Aquatic Biomass									
Synechococcus elongatus	4600.86	25.2	0.069	10.1	6.88	48.8	–	–	[55]
Phaeodactylum tricornutum	4945.03	27	0.207	2.75	6.80	51.1	–	–	[55]
Chlorella vulgaris	5181.64	28.2	0.35	4.81	7.24	52.8	6.8 ± 1.11	5.93 ± 0.81	[55]
Herbaceous biomass									
Corn	7237.03	12.12	S/V	S/V	1.69	85.35	10.01	1.92	[56]
Bagasse	2388.46–2627.3	34.57	0.19	S/V	6.54	58.10	10.21	7.91	[57]
Sunflower husk granules	4394.76	37.2	0.14	0.7	5.8	52.1	5.68	2.8	[58]
Peanut shells	3907.52	34.94	0.13	1.59	5.67	47.52	10.1	11.5	[58]
Olive pits	–	47.93	–	–	6.40	44.81	12	2	[26]
Palm kernel shells	3854.97	30–45	0.05–0.20	–	5.70	45–55	44–55	2–5	[23]
Banana pseudo-stem	3702.11	51.30	–	1.08	5.62	42	91.3 ± 0.5	1.4–3.0	[59–61]
Banana peels	4533.3	45.94 ± 0.17	0.020 ± 0.0955	1.94 ± 0.16	6.19 ± 0.07	35.65 ± 0.21	89.09	13.44	[29,62]
Rice husk and dust	4301.10–4573.50	0.5–0.6	–	37.4 ± 36.6	5.7 ± 6.1	39.8–41.1	9.53	16.21	[63,64]

in energy conversion, it is challenging to store. Being extremely light, hydrogen occupies a large volume at room temperature and pressure, and its flammability adds to storage difficulties [16]. Though numerous storage technologies are under investigation [17], transporting and liquefying H_2 remains costly, requiring expensive equipment [18].

Moreover, biomass conversion methods like pyrolysis and gasification, though effective, require high energy inputs and come with certain limitations [19]. The production of hydrogen (H_2) often relies on natural gas or other fossil fuels, which results in substantial energy consumption and the release of carbon dioxide (CO_2) into the atmosphere [20]. To mitigate these environmental impacts, biomass is emerging as a cleaner alternative for energy production, offering

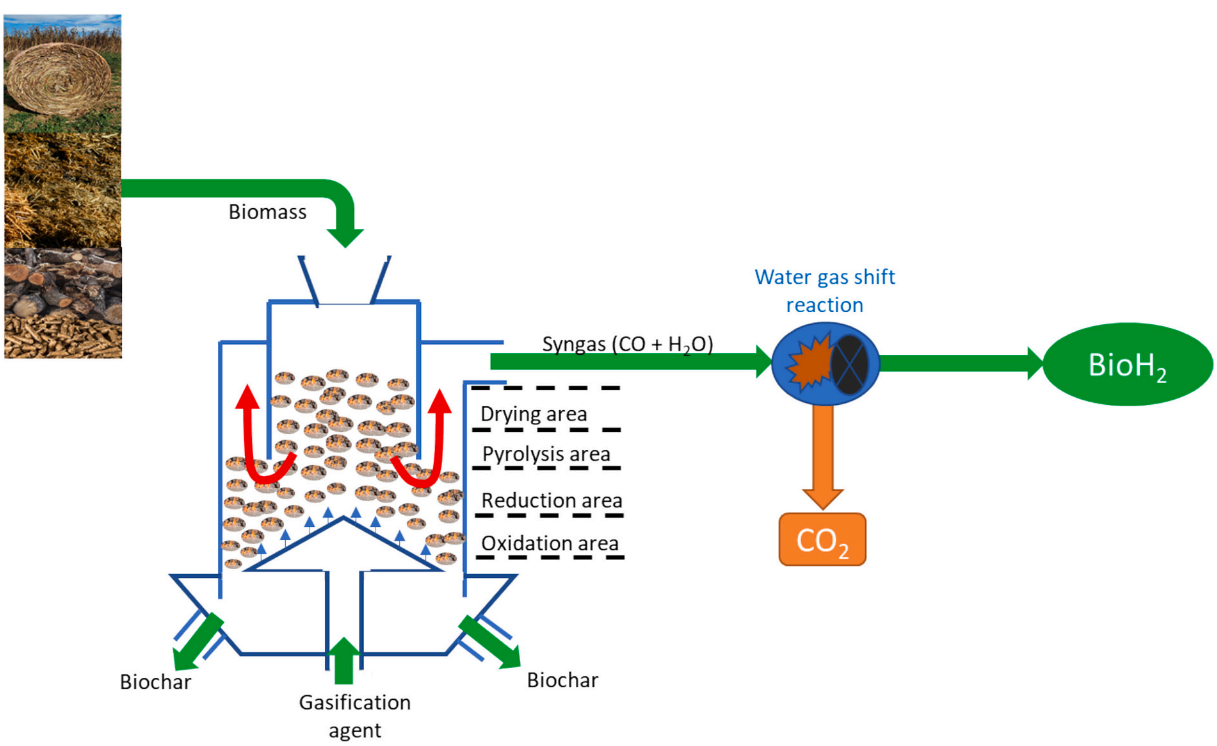

Fig. 1. Catalytic biomass gasification schematic illustration [67].

minimal carbon emissions [21,22]. Unlike solar energy, biomass is a renewable resource with virtually limitless potential. Its high hydrogen and carbon content makes it an ideal feedstock for producing chemical products and fuels [23]. Lignocellulosic biomass, in particular, is a readily available, cost-effective, and non-reactive renewable resource [24]. It ranks as the fourth most significant energy source globally [25], with immense potential for bio-oil production and various chemical raw materials [26].

Several techniques are used to convert biomass into hydrogen, with thermochemical and biochemical methods being the most prominent. Thermochemical conversion processes include liquefaction, pyrolysis, and gasification, with vapour gasification emerging as the most promising for producing hydrogen-rich synthesis gas. This method not only generates hydrogen efficiently but also minimizes environmental impact, avoiding the formation of nitrogen oxides (NOx) and producing very low amounts of CO_2, resulting in "green" hydrogen [27,28]. However, the efficiency of vapour gasification can vary depending on the physical and chemical characteristics of different biomass types [29]. The environmental benefits of biomass as a fuel source are further enhanced by its low sulfur content, which helps reduce acid rain and greenhouse gas emissions compared to fossil fuels [30].

Previous research on biomass conversion for sustainable hydrogen generation has highlighted significant advancements and challenges in this field. Technological advances in thermal conversion processes, such as gasification, pyrolysis, and microwave-assisted pyrolysis, have demonstrated the potential to improve the efficiency and yield of hydrogen production. Studies have explored catalytic gasification and photoelectrocatalysis as promising methods to harness renewable feedstocks for hydrogen generation while reducing environmental impacts [31–38]. Additionally, feedstock utilization has been a key focus, with lignocellulosic materials, agricultural residues, and microalgae identified as abundant and sustainable sources. For instance, optimized conditions for microalgae-based hydrogen production have shown great potential [33,35,37]. Previous works have also addressed the economic and environmental aspects of hydrogen production. The high fermentation and electrochemical conversion costs pose significant barriers to large-scale implementation. However, studies suggest that integrated processes and improved catalysts can reduce costs and enhance sustainability [33,39]. Regional studies, such as those conducted in Kazakhstan and India, have assessed the availability of biomass resources and their conversion potential, demonstrating localized approaches for hydrogen production [34,35]. In South Africa, research emphasizes integrating biomass conversion technologies with renewable energy sources to promote decarbonization [36].

Despite these advancements, several gaps remain. A comprehensive comparative analysis of different biomass-to-hydrogen conversion technologies' efficiency, scalability, and cost-effectiveness is lacking. Furthermore, while some studies address economic considerations, detailed techno-economic feasibility studies are limited. Integrating thermochemical, biochemical, and electrochemical methods into hybrid technologies remains underexplored, and there is a lack of in-depth environmental impact assessments, including life cycle analyses and carbon footprint evaluations [32,40]. This study fills these gaps by providing a holistic and comparative analysis of diverse conversion technologies. It uniquely consolidates thermochemical, biochemical, and emerging hybrid methods advancements, highlighting their strengths, weaknesses, and scalability. The review emphasizes recent developments in innovative approaches, such as catalytic thermal, supercritical, and microbial biomass conversion processes, contributing new insights into sustainable hydrogen production. Moreover, it highlights the practical challenges of these processes while proposing sustainable solutions to reduce costs, improve catalyst efficiency, and facilitate the integration of renewable energy sources. This comprehensive review aims to guide researchers and stakeholders toward optimizing hydrogen production technologies and advancing global efforts to achieve sustainable energy and climate goals.

1.1. Biomass as renewable resources

Biomass consists of organic materials from living organisms, such as plants and animals. The primary feedstocks for bioenergy include forestry and agricultural residues, household and industrial wastes, and specific energy crops [41]. Biomass as a fuel source offers several key advantages, notably its renewability and adaptability. Biomass sources include forestry and agricultural residues, aquatic plants, algae, food processing waste, and wastewater [42]. Dried wastes, such as wood and municipal solid waste, can be combusted directly as fuel, while hydrous biomass (animal waste, sewage sludge) is commonly converted to energy via microbial fermentation. Biomass acts as both a flow and stock energy source. The Earth's forests, covering around 700 billion tonnes, store vast amounts of CO_2, with forests capable of generating about 5 billion tonnes of oil equivalent in energy annually. If used responsibly, these resources could surpass other energy sources in the future. Biomass is typically categorized based on its composition and application, with common categories including wood biomass, herbaceous biomass, aquatic biomass, animal waste, and mixed biomass. The four main biomass sources supporting the energy industry are municipal solid waste, forestry residues, agricultural residues, and cereals [43]. Forest and agricultural waste, with an annual global yield of around 200 billion tonnes, is the most abundant form of biomass. For instance, agricultural residues in China produce up to 900 million tonnes annually, while countries like India, Brazil, and Indonesia also have significant biomass yields. Conversely, nations like Rwanda and Niger produce less than 5 million tonnes annually [44,45].

The calorific value and elemental composition of biomass vary widely, as shown in Table 1. Significant research subjects include Sugarcane bagasse, sawdust, banana tree parts, and bamboo. Crop residues are often left in fields post-harvest and can be utilized for energy production. Specific biomass types, such as *Chlorella vulgaris*, banana pseudostem, and wood sawdust, exhibit the lowest ash content and highest hydrogen content, making them ideal for hydrogen synthesis due to their physicochemical properties. The optimal hydrogen production process depends on the physicochemical properties of the biomass. Like plant residues, high-moisture biomass is more suitable for wet/aqueous conversion processes involving biological reactions. In contrast, dry biomass (e.g., wood chips) is better suited for pyrolysis, gasification, or incineration. Aqueous processing is preferred when the energy required for the end product outweighs the material's moisture content [46]. In addition to moisture, factors such as the cellulose-lignin ratio, metal content, fixed-to-volatile carbon ratio, and ash calorific value are crucial. The first five attributes, particularly moisture, are vital for dry biomass conversion, while moisture and cellulose-lignin content are key for wet biomass conversion [47].

Biomass, derived from organic materials such as plants and animals, serves as a renewable and versatile energy source with diverse feedstocks like forestry residues, agricultural waste, and aquatic plants. Its energy conversion depends on the physicochemical properties of the biomass, with high-moisture types favoring biological processes and dry biomass better suited for pyrolysis and gasification, emphasizing its potential as a sustainable energy alternative.

2. Production processes of hydrogen from biomass – Review of processes

A promising approach to achieving sustainable energy is hydrogen production from biomass. This process utilizes organic materials such as sewage, agro-industrial residues, forestry by-products, and animal waste to generate clean fuel. Several methods facilitate biomass conversion into hydrogen, each employing different mechanisms, catalysts, and operating conditions. This section explores the key processes, including catalytic biomass gasification, biomass pyrolysis, biomass liquefaction, steam reforming, biomass-derived syngas conversion, supercritical conversion, and microbial fermentation.

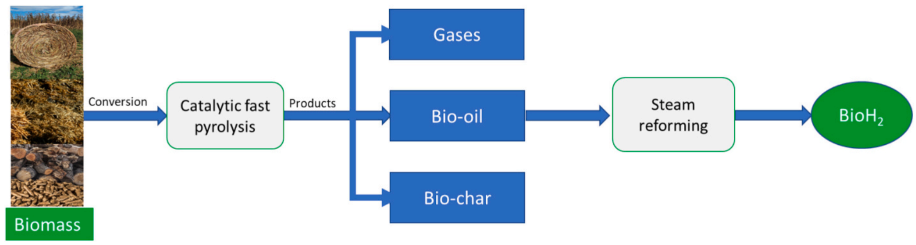

Fig. 2. Schematic Illustration of pyrolysis of biomass [85].

2.1. Catalytic biomass gasification

The catalytic biomass gasification process involves the thermal breakdown of organic material to produce synthesis gas (syngas), primarily consisting of carbon monoxide, hydrogen, and carbon dioxide. This occurs in the presence of a gasifying agent, such as steam, air, or oxygen, along with a catalyst [65,66]. When producing hydrogen through this process, the catalyst is introduced into the gasifier alongside the biomass in carefully calculated ratios, as depicted in Fig. 1. This precise mixing of the catalyst with the biomass ensures optimal interaction during gasification, enhancing hydrogen production efficiency and improving the overall quality of the syngas.

Eq. 1 represents the fundamental equation for biomass steam gasification, providing the core reaction framework for converting biomass into a hydrogen-rich synthesis gas [68]:

$$Biomass + Steam \rightarrow H_2 + CO + CO_2 + CH_4 + LHC + Tar + Char \quad (1)$$

Gasification involves multiple stages, including drying, pyrolysis (thermal decomposition), partial combustion of char, gases, and vapors, followed by gasification of the resulting products [69]. Most reactions occur at high temperatures between 800 °C and 1100 °C [70]. Lower temperatures yield gases with CO, H_2, CO_2, methane, and impurities, while higher temperatures favor syngas production with H_2, CO, CO_2, light hydrocarbons, and fewer contaminants [65]. High-temperature gasification is often preferred for efficient hydrogen production due to faster reactions and enhanced yields [32]. A challenge in gasification is tar formation, which reduces the efficiency and hydrogen yield. Tar forms from the condensation and polymerization of large volatile molecules, contaminating gas products and causing operational issues [71]. Catalysts are employed in the gasification process to mitigate tar formation and improve hydrogen purity [72]. Effective catalysts for biomass gasification should exhibit several key characteristics, such as the ability to break C—C and C—O bonds, water-gas shift (WGS) activity, low coke formation, and resistance to poisoning. They should also maintain thermal and mechanical stability [73]. Common catalysts include natural ores like dolomite and limonite, transition metals like nickel (Ni) and iron (Fe), and alkali and alkaline earth metals like potassium (K) and calcium (Ca), which help convert macromolecular volatiles into smaller molecules like hydrogen [71]. Biochar, produced from biomass pyrolysis, can also act as a catalyst by enhancing the water-gas shift reaction [72]. Using catalysts reduces the activation energy for gasification and decreases process temperatures and time, increases carbon conversion rates [65], and improves hydrogen selectivity in syngas output [67]. Nickel-based catalysts are widely used due to their efficiency in reducing tar and increasing hydrogen yield at relatively low cost [74].

Recent studies have demonstrated the effectiveness of various catalysts. For instance, Çağlı and Ayas [75] found that Ni-loaded kaolin achieved the highest hydrogen yield when used to catalyze the gasification of agricultural wastes. Similarly, experiments using Ni–Ce/CaO catalysts with pine sawdust showed that a Ni/Ce ratio of 2:1 at 600 °C and a steam flow rate of 5 mL/h yielded the highest hydrogen output (12.8 mmol/g) and lowest CO_2 levels [76]. Kang et al. [77] observed that K_2CO_3 and Ni-Ce/Al_2O_3 were highly effective in increasing hydrogen production at temperatures around 650 °C. Another study using calcined dolomite and nickel-based catalysts demonstrated significant tar reduction and improved gas quality, achieving a hydrogen output of 130.28 g H_2/kg of biomass [78]. These findings highlight the critical role of catalysts in optimizing hydrogen production from biomass, enhancing the quality of syngas, and reducing impurities like CO and methane.

Catalytic biomass gasification utilizes high temperatures and catalysts to convert organic materials into hydrogen-rich syngas, with catalysts like nickel and dolomite playing a key role in enhancing hydrogen yield, reducing tar formation, and improving gas quality. Advances in catalyst design, such as Ni-Ce/CaO and K_2CO_3, demonstrate significant improvements in efficiency and hydrogen production, highlighting the process's potential for sustainable energy generation.

2.2. Biomass pyrolysis

Biomass pyrolysis is gaining prominence as a thermochemical process for hydrogen production, with advancements that improve the yield and quality of hydrogen. This technique offers a promising pathway for converting plant-based raw materials into hydrogen-rich syngas, underscoring its potential to meet the growing demand for renewable energy [79]. Pyrolysis operates in an inert environment at temperatures ranging from 250 °C to 900 °C [80], triggering a series of chemical reactions that decompose biomass. This decomposition involves both the direct breakdown of biomass products and the primary degradation of its key components [73]. Biomass pyrolysis involves multiple reaction mechanisms: hemicellulose decomposes between 220 and 315 °C, producing organic acids and sugars; cellulose breaks down between 315 and 400 °C, yielding levoglucosan; and lignin, the most resistant component, degrades over a broader temperature range (200–900 °C) to produce methane, hydrogen, and phenol [81]. The key products of biomass pyrolysis include condensable vapors (biocrude), biochar, and non-condensable gases (such as CO, CO_2, H_2), along with light hydrocarbons like methane (CH_4), ethane (C_2H_6), and ethylene (C_2H_4) [82]. The general reaction for biomass pyrolysis is expressed in Eq. 2:

$$Biomass + Heat \rightarrow H_2 + CO + CO_2 + CH_4 + H_2O + Bio-oil + Char \quad (2)$$

Pyrolysis is categorized into two main types: slow and fast. Slow pyrolysis primarily generates liquid fuels, char, and gas byproducts.

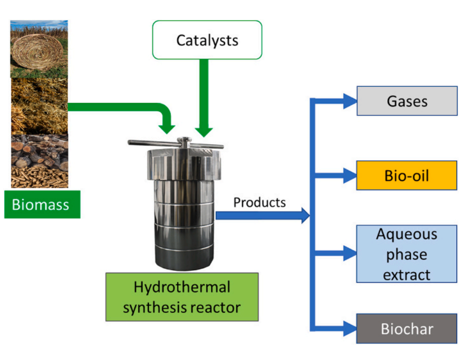

Fig. 3. Schematic illustration of liquefaction of biomass [98].

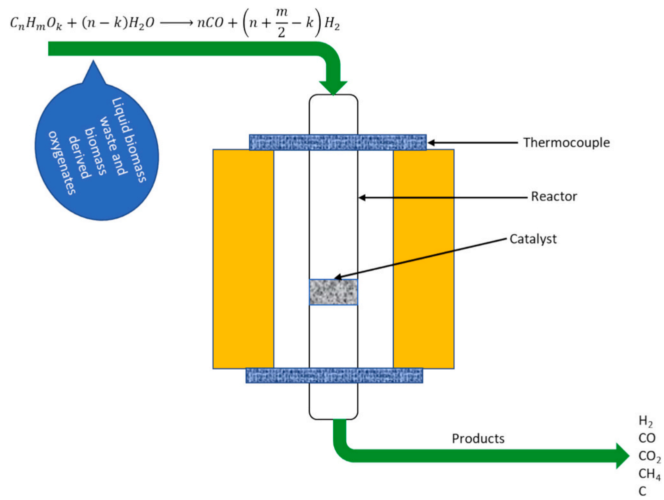

Fig. 4. Mechanisms of biomass steam reforming toward the generation of hydrogen [106].

Although its initial hydrogen yield is relatively low, this can be improved by increasing the temperature and heating rate [83]. In contrast, fast pyrolysis prioritizes hydrogen production, with significantly higher yields at elevated temperatures [84]. Fig. 2 illustrates the mechanism of fast pyrolysis, emphasizing its role in converting biomass into hydrogen gas. These advances in pyrolysis technology enhance its role as a key player in the future of renewable hydrogen production.

In a review by Kalinci et al. [86], it was observed that when plant materials like wood and nutshells are subjected to fast pyrolysis at temperatures between 800 and 900 °C, around 60 % of the biomass is converted into a gas mixture rich in hydrogen and carbon monoxide, with only about 10 % remaining as solid char. This high conversion efficiency positions fast pyrolysis as a strong competitor to conventional gasification techniques. Similarly, Nasir Uddin et al. [82] noted that as the pyrolysis temperature increases, the proportion of gaseous products rises while the production of char and liquid byproducts declines. Research by Demirbas and Arin [87] also demonstrated that temperature increases hydrogen yields significantly. For example, in their study, hydrogen yield grew from 27 to 41 vol% to 41–55 vol% when the temperature was raised from 377 °C to 752 °C.

Catalysts are critical in enhancing hydrogen yields during biomass pyrolysis [73]. Using catalysts, combined with optimized heating rates and extended residence times, can drastically improve hydrogen production [84]. For instance, during the catalytic pyrolysis of waste paper, the gas output increased from 54 % in a non-catalytic process to 75.6 % with the use of a 40 % Co/30 % CeO_2/30 % Al_2O_3 catalyst [88]. In another study, Yang et al. [89] developed a porous Ni—Al nanosheet catalyst to maximize hydrogen production from rice husk in a two-stage reactor system. This catalyst significantly boosted hydrogen production, with molar ratios of H_2/CO nearly ten times higher than non-catalytic processes, emphasizing the impact of catalytic temperature adjustments. The amount of catalyst used also influences gas yield and hydrogen content [84]. For instance, adding 5 % Fe and 1.5 % Ca-based catalyst while increasing nickel loading from 0.2 % to 2.0 %, led to a reduction in tar, increased gas yield (from 21.85 wt% to 33.67 wt%), and promoted the breakdown of large tar molecules, thereby enhancing hydrogen production through more efficient tar cracking, reforming reactions, and the water-gas shift reaction [90].

Advanced pyrolysis techniques such as co-pyrolysis, catalytic pyrolysis, hydropyrolysis, and microwave pyrolysis are also being optimized to improve hydrogen production by enhancing product selectivity, increasing yields, and reducing processing time and temperature [91]. For example, Alvarez et al. [92] found that mixing 20 wt % polypropylene with biomass in the pyrolysis reactor resulted in the highest hydrogen production (36.1 % and 10.98 mmol H_2 g^{-1} sample) and gas output (56.9 %), due to the synergetic effects of co-pyrolysis. Including a Ni/AlO_3 catalyst further increased gas yield and hydrogen production while minimizing byproduct formation. Additionally, reactor design and temperature-time profiles play a significant role in the efficiency of secondary reactions and hydrogen production during pyrolysis, allowing for process optimization based on biomass type and heating method [93].

Biomass pyrolysis is a thermochemical process that converts plant-based materials into hydrogen-rich syngas, with fast pyrolysis and catalytic advancements significantly improving hydrogen yield and process efficiency. Techniques like co-pyrolysis, optimized catalyst use, and innovative reactor designs enhance product selectivity, reduce byproducts, and position pyrolysis as a key contributor to renewable hydrogen production.

2.3. *Biomass liquefaction*

Biomass liquefaction is a thermochemical process that converts solid biomass into liquid fuels, primarily biocrude oil, using heat and pressure in the presence of a solvent. One of the most used methods for hydrogen production through liquefaction is hydrothermal liquefaction (HTL). HTL stands out because it efficiently processes high-moisture biomass without drying, making it an ideal choice for converting wet biomass into energy-rich products, such as biocrude, hydrogen, and hydrochar. This approach is increasingly favored for both sustainable energy generation and waste management [94]. The process occurs in a closed, oxygen-free reactor at moderate temperatures and high pressures, where the biomass is broken down into incondensable gases (CO_2, CO, CH_4, H_2), biocrude, and solid hydrochar (see Fig. 3). Unlike other methods, HTL produces products with a higher energy content and greater heat recovery efficiency [95,96]. Beyond the initial hydrogen generated from biomass, additional hydrogen can be obtained by upgrading or reforming the biocrude produced in this process [97]. Moreover, like other thermochemical processes, adding a catalyst during liquefaction significantly enhances hydrogen production.

Shende et al. [99] demonstrated that hydrothermal liquefaction (HTL) of cotton biomass at 250 °C using a $NiSO_4$ catalyst produced a gas mixture containing 3.12 vol% hydrogen, alongside biocrude (61.2 wt%) and char (28.8 wt%). Notably, combining HTL with solar photocatalytic reforming (PR) using a Pt/TiO_2 catalyst led to a significant increase in hydrogen yield. The integrated process achieved a total hydrogen yield of 20.94 vol%, with 48.7 vol% of the hydrogen stored in C1-C3 acids in the biocrude. Additionally, the photocatalytic reforming step contributed another 17.82 wt% hydrogen. In a separate study, Tungal and Shende [100], investigated the HTL of pinewood at temperatures ranging from 200 to 275 °C using various nitrate salt catalysts ($Ni(NO_3)_2$, $Ca(NO_3)_2$, $Co(NO_3)_2$, and $Fe(NO_3)_3$). Among the catalysts tested, $Ni(NO_3)_2$ exhibited the highest selectivity, producing 12.26 mol% hydrogen at 275 °C, and yielding 55 wt% biocrude at 250 °C. These findings highlight the role of catalysts in enhancing hydrogen production and optimizing biocrude yields in biomass liquefaction processes.

Biomass liquefaction, particularly hydrothermal liquefaction (HTL), converts wet biomass into energy-rich products like biocrude, hydrogen, and hydrochar under moderate temperatures and high pressures without drying. The use of catalysts and process integrations, such as solar photocatalytic reforming, significantly enhances hydrogen yields and optimizes the efficiency of this sustainable energy and waste management approach.

2.4. *Steam reforming process*

Steam reforming (SR) is a widely used method for producing hydrogen from biomass by reacting carbon-rich feedstocks, such as bio-oil, alcohols, and syngas, with steam at high temperatures (typically above 700 °C). This process results in a hydrogen-rich gas and carbon

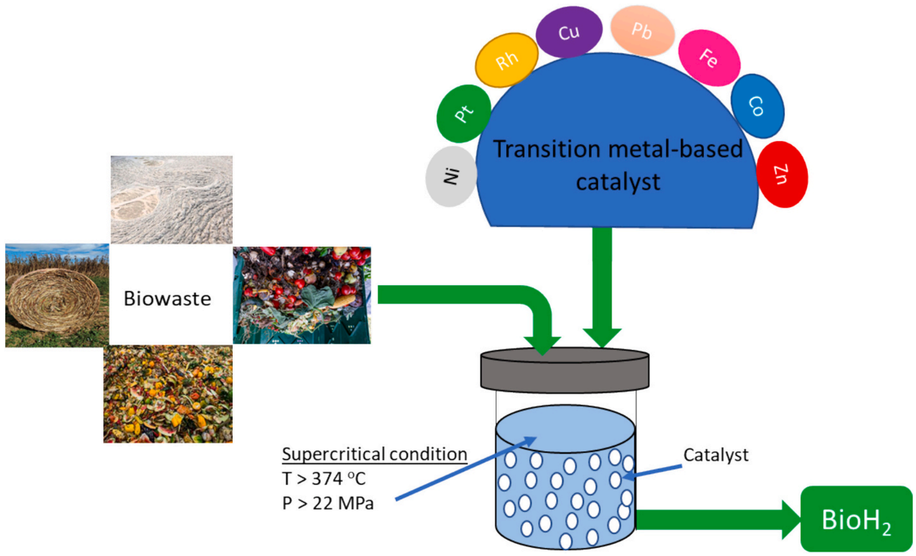

Fig. 5. Illustration of Supercritical conversion of biomass into hydrogen [116].

dioxide as a byproduct [101]. Among various thermochemical techniques for hydrogen production, SR stands out for its efficiency in converting liquid hydrocarbons and gasified biomass tar into hydrogen [102]. In fact, SR is considered the most established and efficient method for hydrogen production, accounting for approximately half of the global hydrogen supply [103]. Biomass-derived feedstocks, including bio-oil, syngas, and tar, are commonly reformed into hydrogen through SR, leveraging their carbon and hydrogen content. As shown in Fig. 4, these feedstocks undergo reforming to produce a renewable hydrogen source. Various SR techniques have been developed to optimize hydrogen production. For example, Kaiwen et al. [104]] describe a process where biomass is first dried and pyrolyzed to generate bio-oil, gas, and char. The pyrolysis products are then fed into a gasifier to produce syngas, which is cooled and compressed before reacting with high-temperature steam in a reformer to generate hydrogen. The steam reforming reaction for any organic molecule containing oxygen is represented by the following equation, as reported by Kumar et al. [105]:

$$C_xH_yO_z + (2x - z)H_2O \rightarrow xCO_2 + (2x + (y/2) - z)H_2 \tag{3}$$

Where 2 + (y/2×) - (z/x) moles of hydrogen can be generated for every mole of carbon in the feedstock.

For effective SR technology, the ideal feedstocks should be rich in organic molecules with low levels of heavy metals to minimize impurities [106]. The efficiency of hydrogen production largely depends on the choice of catalyst. High-quality catalysts should have key attributes such as high catalytic activity, excellent H_2 selectivity, strong metal support interaction, a mesoporous structure, and stability under reaction conditions. Additionally, they should meet criteria such as ease of regeneration, recyclability, and cost-effectiveness for large-scale applications [102]. This combination of optimal feedstocks and catalysts is crucial for ensuring hydrogen production's high yield and sustainability via steam reforming.

Recent studies have focused on optimizing the steam reforming (SR) process to improve hydrogen yield and reduce costs. A significant part of this research has explored innovative catalysts that enhance the efficiency and selectivity of reforming reactions, such as nickel-based catalysts supported on various substrates [85,107]. These advancements aim to increase the reaction efficiency and reduce unwanted byproducts. One promising approach is the combination of biomass pyrolysis with steam reforming, which takes advantage of the volatile compounds generated during pyrolysis. For instance, Yu et al. [108] studied this method using cobalt recovered from $LiCoO_2$ battery cathodes as a catalyst. They found that using coconut shell carbon (CC) at a reduction

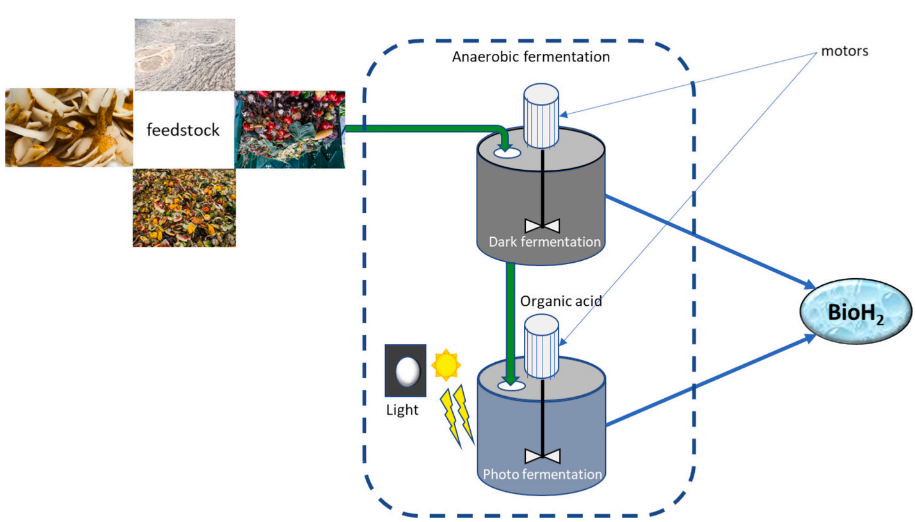

Fig. 6. Graphical Representation of Dark and Photo Fermentation-Based Biohydrogen Production [125].

temperature of 800 °C produced 24.9 mmol/g of hydrogen, demonstrating the effectiveness of integrating pyrolysis with SR for hydrogen production.

Additionally, Brito et al. [107] focused on optimizing the steam reforming of syngas derived from gasifying various biomass types, such as lignin, miscanthus, and eucalyptus. Using thermodynamic equilibrium simulations in Aspen plus V12, the study examined the impact of temperature (200–1100 °C), steam-to-carbon (S/C) ratios (0−10), and pressure (1–20 bar) on hydrogen yield. They found that gasification of unconditioned lignin produced the highest hydrogen output (61.8 %) and purity (51.2 %), significantly improving from an initial yield of 19 %. Moreover, the study demonstrated that higher S/C ratios and temperatures above 700 °C prevented coke formation and improved overall hydrogen production efficiency. Further advancements in catalytic steam reforming have been made using nickel-based commercial catalysts in fluidized bed reactors. These setups require a high steam-to-carbon ratio (9:1) to limit char and coke formation, which can result from the breakdown of complex carbohydrate compounds. In one study, when the process temperature reached 850 °C, hydrogen output reached 90 % of the theoretical maximum during eight hours of operation. A secondary water-gas shift reactor further improved the hydrogen yield by 5–7 % [109]. These findings underscore the importance of catalyst selection, temperature control, and process integration for optimizing hydrogen production in SR processes.

Steam reforming (SR) is an efficient thermochemical process for producing hydrogen from biomass-derived feedstocks like bio-oil and syngas by reacting them with steam at high temperatures, often exceeding 700 °C. The process relies on optimized catalysts, temperature control, and feedstock quality to maximize hydrogen yield, minimize impurities, and enhance the sustainability of renewable hydrogen production.

2.5. Supercritical conversion of biomass

Supercritical transformation of biomass into hydrogen is an innovative and efficient technique that utilizes the unique properties of water in supercritical conditions to convert biomass into hydrogen-rich gas. When water exceeds its critical point (>22 MPa and > 374 °C), it becomes supercritical, gaining both liquid- and gas-like characteristics. This transformation reduces mass transfer resistance, increases gas solubility, enhances reactant diffusivity, and accelerates reaction rates, making supercritical water (SCW) a powerful medium for biomass conversion into hydrogen [110–112]. One of the key advantages of SCW is its much lower dielectric constant compared to subcritical water, making it an excellent solvent for organic materials, polymers, and gases [113]. In supercritical water gasification (SCWG) (as shown in Fig. 5), SCW acts as both the solvent and reaction medium, facilitating the breakdown of biomass into syngas (CO, CO_2, H_2, and CH_4) while minimizing the formation of char [114]. This is because SCW can dissolve organic intermediates from biomass degradation, reducing their reassembly into tars and chars, common byproducts in traditional gasification methods [99]. Additionally, as SCW behaves as a weak electrolyte, it favors free radical reactions over ionic ones, further promoting hydrogen gas release during gasification [115]. However, to maximize hydrogen production, downstream upgrading is necessary to convert bound hydrogen into molecular hydrogen, thus enhancing the purity of the hydrogen gas [112].

Supercritical water gasification also offers environmental benefits by preventing the formation of pollutants like sulfides, suspended particles, and nitrogen compounds, which are common in conventional gasification and combustion processes [117]. The concentrations of syngas generated during SCWG are influenced by several process variables, including pressure, temperature, residence time, feed concentration, particle size, and catalyst presence [110]. Research has shown that appropriate catalysts significantly enhance gasification efficiency and hydrogen production, even at lower temperatures, by reducing activation energy requirements [66,77,115]. Catalysts in SCWG are crucial for lowering operational conditions such as pressure, residence time, and temperature, improving gasification rates, increasing H_2 selectivity, and enhancing overall carbon conversion, making the process more efficient and sustainable.

Gong et al. [118] explored the use of *Enteromorpha prolifera* in supercritical water gasification (SCWG) to produce hydrogen-rich syngas, examining the effects of different catalysts (KOH, Ni, K_2CO_3, and $AlCl_3$) and reaction parameters. The study found that the highest hydrogen yield of 19.5 mol/kg was achieved under optimal conditions: 400 °C, 30 min of reaction time, 95 % moisture content, and 10 wt% $AlCl_3$, representing a yield 145 times greater than non-catalyzed reactions. Similarly, Sathish et al. [119] demonstrated the potential of SCWG in hydrogen production from expired bread waste, with longer reaction times (60 min) significantly increasing the total gas output, gasification efficiency, and hydrogen selectivity. Additionally, the co-gasification of biomass and plastic has shown superior performance in supercritical water gasification. Babatabar et al. [120] reported successful hydrogen production from sugar beet pulp (SBP) and high-density polyethylene (HDPE) using SCWG. The optimal conditions for SBP gasification were 460 °C, 30 min, and 1.04 wt% feedstock concentration, which maximized hydrogen yield. Blending SBP with 40 wt% HDPE further enhanced hydrogen production, peaking at 8.95 mmol/g, and adding a cost-effective Ni–Cu/AC-CaO catalyst boosted hydrogen yield by 3.8 times and total gas yield by 2.4 times.

Moderate temperatures (400–500 °C) combined with heterogeneous catalysts have also increased gas yield and improved hydrogen selectivity [121]. Nanda et al. [122] studied the gasification of waste tires using subcritical and supercritical water, achieving maximum hydrogen production of 14.4 mmol/g at 625 °C, 60 min of reaction time, and 5 wt % feed concentration. Using catalysts such as Ni/SiO_2-Al_2O_3 and Ru/Al_2O_3 improved hydrogen yield to 19.7 mmol/g. Similarly, Babaei et al. [123] used SCWG to convert poultry manure into hydrogen, optimizing hydrogen selectivity to 36.42 % with a nickel catalyst under 450 °C, 15 min, and 2.5 wt% feedstock concentration. Moreover, predictive modeling has been employed to optimize hydrogen yield in supercritical biomass conversion. Liu et al. [117] developed a Gibbs free energy minimization model for SCWG of rice straw, predicting that higher temperatures, lower biomass concentrations, and lower pressures significantly enhance hydrogen production, with a maximum yield of 47.17 mol/kg at 650 °C, 25 MPa, and 5 wt% rice straw.

Supercritical water gasification (SCWG) leverages the unique properties of water in its supercritical state (above 374 °C and 22 MPa) to efficiently convert biomass into hydrogen-rich syngas while minimizing char and pollutant formation. Catalysts play a critical role in enhancing hydrogen yield, improving gasification rates, and reducing operational conditions, making SCWG a promising and sustainable approach for hydrogen production.

2.6. Microbial conversion of biomass – Fermentation process

Microbial conversion of biomass leverages the metabolic capabilities of specific microorganisms to transform organic matter into hydrogen gas. This eco-friendly method uses diverse biomass sources such as agricultural residues, food waste, and energy crops. The main route for this conversion is fermentation, where microbial activity drives chemical reactions that break down complex organic compounds into simpler molecules, producing hydrogen as a valuable byproduct. Among biomass types, carbohydrates hold significant promise for efficient hydrogen production through fermentation processes [110]. Fermentation for hydrogen generation is broadly categorized into dark and photo fermentation (Fig. 6). These pathways rely on different bacterial strains and substrates to optimize hydrogen production. In dark fermentation, anaerobic bacteria such as *Clostridium* and *Enterobacter* break down carbohydrates without light, releasing hydrogen and organic acids as byproducts. On the other hand, pHoto fermentation uses photosynthetic bacteria that convert organic acids into hydrogen under light conditions. Both pathways are critical to enhancing sustainable hydrogen production from organic waste [124]. This process provides an alternative renewable energy source and a viable solution for managing waste, aligning with global efforts toward a circular economy.

Dark fermentation (DF) is considered the most promising and well-understood biotechnological method for biohydrogen production from biomass [126]. It is gaining traction among biological hydrogen production processes due to its simplicity, independence from light, and ability to convert a variety of carbohydrate-rich organic substrates into hydrogen [127]. In this process, anaerobic bacteria produce hydrogen through enzyme-driven reactions, primarily catalyzed by Fe-only and Fe—Fe hydrogenases. Glucose-to-acetate conversion is often used as a reference for estimating theoretical hydrogen yields [128]. Many organic substrates can be used for dark fermentation, including municipal solid waste, lignocellulosic biomass, industrial wastewater, and sugar-rich lignocellulosic materials [129]. Mesophilic cultures inoculate the feedstock, and a stirred reactor is typically employed to replicate the dark fermentation process under continuous stoichiometric reactions [130]. The most researched and efficient hydrogen-producing bacteria in DF are species like *Clostridium*, *Acinetobacter*, *Enterobacter*, *Escherichia*, and *Bacillus* [66]. Recent studies have also shown that mixed microbial cultures from diverse sources offer advantages such as lower operational costs, simplified processes, and the ability to utilize various raw materials [131,132]. During dark fermentation by facultative anaerobes, substrates undergo glycolysis to form pyruvate, which is then split into acetyl-CoA and formate. Formate is further broken down into CO_2 and H_2 by formate hydrogen lyase [129]. Additionally, as described by Dikshit, Poddar Dikshit et al. [31], two key hydrogen-producing enzymes, nitrogenase and hydrogenase, are involved in the butyrate and acetate pathways during dark fermentation. The acetate pathway theoretically yields four moles of hydrogen per mole of glucose, while the butyrate pathway yields two. This theoretical difference highlights the efficiency of various fermentation pathways in hydrogen production [133].

The efficiency of dark fermentation for hydrogen production depends on several factors, including biomass pretreatment, sugar content, microbial strains, and critical process parameters like partial pressure, temperature, hydraulic retention time (HRT), and pH. Optimizing reactor design, enriching the microbial inoculum, and pretreating the substrate are essential strategies for improving hydrogen yields and production rates [131,134]. Various studies have explored how these parameters affect hydrogen production through dark fermentation. For instance, Soares et al. [131] evaluated the use of brewer's spent grain (BSG) hydrolysate under different conditions, such as temperature, pH levels, and inoculum ratios. The study achieved a maximum hydrogen yield of 4160 mL/L. Namdarimonfared et al. [135] investigated continuous hydrogen production using an anaerobic packed bed biofilm reactor with paper mill effluent as the substrate without pretreatment. By adjusting the HRT between 24 and 1.2 h, they observed the highest hydrogen concentration (41.5 %) at a 4-h HRT. Similarly, other research focused on a two-stage process combining dark fermentation and anaerobic digestion to produce both biomethane and biohydrogen from paper mill effluent, reporting a hydrogen yield of 35.1 mL H_2 g^{-1} COD at 55 °C and an initial pH of 5 [136].

Meanwhile, photo fermentation (PF) utilizes light energy to generate hydrogen and carbon dioxide from organic substrates through the action of photosynthetic bacteria. Various green, purple sulfur and purple non-sulfur bacteria (PNSB) play key roles in this process [137]. PNSB, in particular, are effective photo-fermenters, capable of growing in photoautotrophic and chemoheterotrophic conditions, utilizing diverse organic and inorganic carbon sources for hydrogen production without generating oxygen [138,139]. Photo-fermentation typically involves using a photoreactor in a lighted incubator to stimulate hydrogen production [140], as illustrated in Fig. 6. Light energy activates nitrogenase enzymes in the bacteria, leading to the reduction of protons and the creation of biohydrogen through ATP hydrolysis. Without nitrogen, the reducing agents and ATP are fully redirected toward biohydrogen production, as shown in the simplified chemical Eq. [124].

$$16ATP + 16H_2O + N_2 + 10H^+ + 8e^- \xrightarrow{|hv|} 16ADP + 16pi + 2NH_4^+ + H_2 \quad (4)$$

Ammonia, hydrogen, adenosine diphosphate (ADP), and inorganic phosphates (pi) are the key products generated during photo-fermentation, catalyzed by the nitrogenase enzyme. This process involves protons and electrons reacting with nitrogen and ATP, enabling hydrogen production through the bacterial photosystem [134,141]. In this system, light energy and biomass provide two electrons and four ATP molecules to drive the nitrogenase enzyme, generating hydrogen [134]. The versatility of microorganisms in photo-fermentation, capable of utilizing a wide range of substrates under mild pressure and temperature conditions, makes this process highly promising for hydrogen production [138]. One of the key advantages of photo-fermentation is its ability to process large amounts of substrates with an abundant supply of raw materials [110]. Several studies have optimized processing factors to maximize hydrogen production. For example, Mishra et al. [142] explored using immobilized inoculum for photo-fermenting dark-fermented palm oil mill effluent (DPOME). By employing response surface methodology (RSM) and a central composite design (CCD), they optimized factors such as light intensity, starting pH, and inoculum-substrate percentage (ISP), achieving the highest hydrogen yield of

Table 2
Comparison of Hydrogen Production Methods from Biomass Conversion Processes.

Process	Reaction Mechanism	Energy Requirements	Feedstock Flexibility	H_2 Yield		Ref
				mmol/g	Vol%	
Catalytic Biomass Gasification	Drying followed by pyrolysis, oxidation, gasification, and addition of catalyst	High Temperature(800–1100 °C), High Pressure upto 33 bar	Suitable for a wide range of dry biomass and polymeric waste	3–200	25–90	[1–5]
Biomass Pyrolysis	Thermal cracking to bio-oil, gas, and char	Moderate (200–800 °C)	Limited to dry biomass; sensitive to feedstock	9–109	10–60	[2,6,7]
Biomass Liquefaction	Hydrothermal reactions in subcritical water	medium temperature (280–370 °C), high pressure (10–25 MPa)	Handles wet and dry biomass effectively	3.2–75	_	[2,8,9]
Steam Reforming	Reforming bio-oil or oxygenates with steam	High temperatures (700–1100 °C), pressures (3.0–25 bars)	Works well with bio-oil, bioethanol, or gaseous intermediates	_	25–98	[10–13]
Supercritical Conversion of Biomass	Hydrothermal reactions in superheated water	High temperature and pressure (≥374 °C, ≥22 MPa)	Suitable for wet biomass and complex substrates	1.0–60	_	[14–16]
Microbial Conversion (Fermentation)	Biological breakdown of organic wastes by heterotrophic anaerobic bacteria	Low (ambient to 60 °C), pH(≤7.0)	Requires pretreated, fermentable biomass	0.1-958[a]		[17,18]

* a - (mL/g).

147 mL H_2 per gram of COD removed under optimal conditions. Similarly, Lu et al. [143] examined the influence of iron ions on biohydrogen production from corn stalks. They enhanced the growth and metabolic pathways of HAU-M1 bacteria by adding various concentrations of Fe^{2+} and Fe^{3+} to the fermentation medium. Their findings revealed that the optimal concentration of 2500 μmol/L Fe resulted in a maximum hydrogen yield of 70.25 mL/g.

Nanocatalysts have also shown promise in boosting hydrogen production. Liu et al. [144] explored the effects of nickel ferrite ($NiFe_2O_4$) photo nanocatalysts on hydrogen production using various light sources, including an incandescent lamp, a Xenon lamp, and a 532 nm laser. Under optimal conditions with a 150 mg/L concentration of $NiFe_2O_4$ and incandescent lamp excitation, the maximum hydrogen generation rate was 9.17 mL/h, with a cumulative hydrogen volume of 568.8 mL. A combined two- or three-stage process incorporating both dark and photo-fermentation outperforms either method individually for greater efficiency. This integrated approach enhances biohydrogen yield by converting more substrates into hydrogen, utilizing a broader light spectrum, and recycling organic acids that would otherwise go unused [124]. An example of two-stage fermentation has the following reaction combining both dark and photo-fermentation.

Stage 1: Anaerobic bacterial dark fermentation process

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \quad (5)$$

Stage 2: Photo-fermentation process by photoheterotrophic bacteria

$$CH_3COOH + 2H_2O \rightarrow 2CO_2 + 4H_2 \quad (6)$$

In a study by Zhang et al. [145], the hydrogen production potential of corn stover was evaluated using three fermentation methods: dark fermentation (DF), dark-photo co-fermentation (DPCF), and photo-fermentation (PF). Among these methods, photo-fermentation (PF) showed the highest total hydrogen yield, producing 141.42 mL(g TS)$^{-1}$. In contrast, dark fermentation (DF) generated a lower yield of 36.08 mL (g TS)$^{-1}$, but it demonstrated the shortest lag time for hydrogen production, making it more efficient in terms of start-up speed. Additionally, dark-photo co-fermentation (DPCF) achieved the highest initial hydrogen generation rate of 1.88 mL(g TS)$^{-1}$ h^{-1}, with an initial hydrogen content of 44.40 %, highlighting its effectiveness at the early stages of production. The study also compared the energy conversion efficiencies of the three methods: PF reached 10.12 %, DF was lower at 2.58 %, and DPCF had an intermediate value of 6.45 %. This indicates that while PF is more effective at producing hydrogen over time, DPCF offers an appealing balance between rapid initial hydrogen generation and total yield, making it a viable option for optimizing biohydrogen production.

Microbial conversion of biomass through fermentation utilizes microorganisms to break down organic matter into hydrogen gas, with dark fermentation and photo fermentation as the primary pathways. These eco-friendly processes, enhanced by optimizing microbial strains, substrates, and process conditions, offer sustainable hydrogen production and waste management solutions, aligning with global circular economy goals.

2.7. Merits and demerits of different hydrogen production processes

Various technologies have been developed for biomass conversion into hydrogen, each with distinct advantages and challenges. Table 2 presents a comparison of hydrogen production methods from biomass conversion. Understanding these trade-offs is crucial to optimizing performance, improving productivity, and minimizing costs. Factors such as feedstock type, target products, operational scale, and economic feasibility significantly influence the choice of biomass conversion method. Some established processes, such as steam reforming and catalytic gasification, are well-known for efficiently generating large

Table 3
Summary of Merits and Demerits of Hydrogen Production Processes from Biomass.

Process	Merits	Demerits	Ref.
Catalytic Biomass Gasification	- High hydrogen-rich syngas - Utilizes diverse biomass feedstocks - Lower production costs compared to electrolysis -Tar reduction compared to non-catalytic gasification -It can be implemented at various scales -It has a low net carbon emission	-Catalyst deactivation issues - Requires high temperatures - Biomass pretreatment like drying and size reduction improves conversion but raises costs. -Post-treatment of exit gases and residuals is requested.	[65,76,146,147]
Biomass Pyrolysis	- Flexible feedstock options - Low-pressure operation - Lower energy input than gasification - No oxygen is needed.	- Lower hydrogen yield compared to gasification - Challenges with hydrogen purification and separation from complicated gas mixtures -Formation of TAR that must be treated and it is not easy to manage	[81,147–149]
Biomass Liquefaction	- Efficient conversion of wet biomass - Produces high-energy-density bio-oil - Lower emissions	- High capital costs - Complexity in processing and purification of bio-oil - Expensive reactors	[149–151]
Steam Reforming of Biomass	- High hydrogen yield and low environmental problems - Established technology - Can utilize existing natural gas infrastructure	- Typically requires high temperatures - Requires pre-treatment of biomass - Sensitive to feedstock composition - Carbon capture needed	[102,106,152]
Biomass-Derived Syngas Conversion	- Versatile product applications (fuels, chemicals) - Can integrate with existing processes	- Requires efficient syngas cleaning - Hydrogen yield can vary based on feedstock - Selecting the appropriate reactor might be challenging	[153–155]
Supercritical Conversion of Biomass	- Operate at a reduced temperature than alternative methods of gasification. - Can process wet biomass without drying - Acting as both a medium and a catalyst - Produces high-quality hydrogen than other gasification technologies - Providing an extra source of H_2 and free radicals - Hydrogen-rich gases formed under SCWG are likewise easier to separate, at least to some extent	- High energy requirements to reach supercritical conditions - Complexity of reactor design - High cost of reactor	[121,156,157]
Microbial Conversion (Fermentation)	- Low energy input - Utilizes diverse organic waste - Environmentally friendly	- Lower yield of hydrogen than with previous techniques - Slow reaction kinetics. - Sensitive to pH and temperature fluctuations - Limited understanding of microbial communities	[158–160]

Table 4
Comparative Techno-Economic Analysis of Biohydrogen Production Technologies.

Biohydrogen Production Technology	Capital Cost ($ Million)	Operational Cost ($ Million)	Energy Efficiency (%)	Feedstock Type	Hydrogen Yield Sale (U.S.$/kg)	Environmental Impact	Potential for Scale-Up	Ref
Catalytic supercritical water	6.25 M	3.59 M	_	Soybean straw	1.94	Low	Medium. Still at the developmental stage	[161]
Gasification	118.56 M	92	_	Wood chips and wood pellets	$2.84/kg	Low	High	[162]
Dark fermentation	0.9 M	0.2 M	61	Waste bread	$14.9/kg	Low	Medium	[163]
Steam Reforming	0.05 M	1.2 % of Capital cost 0.0063 M (excluding the cost of feedstock)	_	Bio-oil	$2.42/kg	Medium	Medium	[164]
Catalytic pyrolysis	346 million	$145.8 million/year	16.8	Microalgae remnant	$1.80/l	Low	Medium	[165]
Biomass fast pyrolysis	$287 M	$109	_	Corn stover	$0.82/l	Medium	Medium	[166]
Dark fermentation	2 M	1.2 M	_	Agriculture waste	$2.7/kg	Low	Medium	[167]
Steam Reforming	1.9	441 M	___	Food waste	_	Medium	High	[168]

quantities of hydrogen. However, these methods often have higher costs and more complex infrastructure requirements. On the other hand, techniques like microbial fermentation provide more environmentally friendly solutions but tend to produce hydrogen at lower rates and yields. For instance, steam reforming of bio-oil is a well-established process, offering high hydrogen yields but at the expense of increased energy requirements and carbon emissions. Supercritical water gasification (SCWG) provides cleaner hydrogen with fewer pollutants, yet it demands higher pressure and temperature conditions, increasing operational costs. Biological processes, such as dark fermentation and photo-fermentation, are more sustainable but typically have lower efficiency and require more optimization of operational parameters like temperature, pH, and reactor design to improve yields. Each technology involves cost, operational complexity, efficiency, and environmental impact trade-offs. Microbial fermentation methods, for example, are simpler and more eco-friendly but generally suffer from lower hydrogen production rates than thermochemical methods. On the other hand, gasification technologies offer higher efficiency but may involve higher capital investment and greater technical complexity. Table 3 details the advantages and disadvantages of various biomass-to-hydrogen conversion methods, helping to clarify each process's efficiency, economic viability, and environmental footprint. Understanding these factors is essential for designing sustainable hydrogen generation systems that align with the growing demand for clean energy solutions. (See Table 4.)

3. Techno-economic evaluations of biohydrogen production

The development and optimization of biomass-based hydrogen generation systems rely heavily on Techno-Economic Evaluation (TEE). TEE is essential for effectively allocating resources, reducing production costs, and promoting economically viable hydrogen fuel [169]. Key factors that TEE considers include market demand for hydrogen, the availability and cost of biomass or wastewater, technology maturity, and capital and operating expenses. These elements directly influence the viability of various biomass-to-hydrogen manufacturing techniques economically [170]. By assessing hydrogen production technologies from economic, technological, and sustainability perspectives, TEE provides valuable insights into their feasibility and profitability [171]. It helps identify critical challenges that must be overcome for production to be cost-effective [172]. One of the major hurdles in hydrogen synthesis is the high cost involved in both the production and purification processes [173]. In industrial hydrogen production, two main expenses govern the evaluation: capital investment (CAPEX) and operational costs (OPEX) [174]. From a techno-economic approach, the primary goal is to maximize hydrogen output while reducing CAPEX and OPEX, thereby improving the commercial viability of large-scale hydrogen production from biomass [170].

Biohydrogen production methods, such as gasification, pyrolysis, fermentation, and supercritical conversion, demand substantial investments in infrastructure. This includes the setup of reactors, catalysts, feedstock preprocessing equipment, and support systems like gas cleanup or purification units. The capital expenditures (CAPEX) for these technologies are greatly influenced by the operational scale and complexity of the technology involved [175]. Additionally, operational costs (OPEX) encompass expenses related to feedstock acquisition, labor, maintenance, and energy consumption. The variability in biomass quality and pricing makes feedstock costs a critical factor in OPEX [176]. Furthermore, supercritical conversion and steam reforming are energy-intensive, with energy costs representing a significant portion of operational expenses. Catalyst costs are part of operational expenses due to the need for frequent renewal or replacement, particularly in catalytic gasification and, to a lesser extent, reforming processes, as catalysts degrade over time [65]. The levelized cost of energy (LCOE) and hydrogen (LCOH) targets were previously set by the U.S. Department of Energy (DOE) without subsidies. However, challenges like inefficient production technologies, high energy costs, and significant capital and operational expenditures (CAPEX & OPEX) have hindered achieving competitive LCOH compared to conventional fossil fuels [177].

Several studies have examined capital and operational costs for biohydrogen production via both thermochemical and biological methods. For instance, Kazmi et al. [178] investigated biomass gasification for hydrogen production using sunflower husk pellets and waste glycerol in an Aspen Plus® simulation, estimating a total capital cost of $2.93 million and annual operating costs of $14.58 million. Similarly, Sara et al. [179] evaluated a biomass gasification plant that operates between 850 and 950 °C with lignocellulosic biomass at a 20 kg/h feed rate. This plant's gasifier and portable purification unit (PPU) were estimated to have annual hardware costs of €35 and €25.54, respectively. The cost of producing hydrogen was calculated at €12.75/kg, with a projected annual revenue of €3.7 million. In another study, Salkuyeh et al. [180] compared biomass gasification using fluidized bed (FB) and entrained flow (EF) reactors, finding the FB process to be more cost-efficient with a minimum selling price (MSP) of 2.8 EUR/kg H_2, while the EF process incurred higher costs (3.1 EUR/kg H_2) due to greater capital expenditures. The cost of producing hydrogen was further raised by 3 % for FB gasification and 11 % for EF gasification with the addition of carbon capture and liquefaction technologies.

For biomass pyrolysis, CAPEX includes direct costs like instrumentation, electrical control systems, and installation, alongside indirect engineering and construction costs [181]. OPEX encompasses variable costs such as feedstock transportation, raw materials, chemicals, electricity, and fixed expenses, including labor and maintenance [182]. According to Qureshi et al. [173], the cost of producing hydrogen through catalytic pyrolysis is influenced by several factors, including feedstock price, catalyst usage, reactor size, and operating conditions, with a production cost of $2.57 per kg of H_2 and $0.92 per kg of biomass. Damian et al. [79] assessed biomass pyrolysis in India, finding up to 80 % efficiencies, with capital expenditures ranging from 300 to 1200 million INR. The economic viability of this process is supported by increasing hydrogen market demand, projected to exceed 8–10 million metric tons annually. However, government support, incentives, and renewable energy laws are necessary for the broad acceptance of biomass pyrolysis.

Furthermore, a study by Wee et al. [183] analyzed the techno-economic viability of employing steam reforming to produce hydrogen from palm oil mill effluent (POME) in Malaysia. Their analysis estimated a capital investment of RM 142.49 million, with annual operational costs at RM 58.67 million. The process was capable of producing 963.31 t of high-purity hydrogen per year. With an 8.5-year payback period and an 18.48 % return on investment (ROI) over 20 years, the study highlighted the potential economic viability of this hydrogen production method. Similarly, Kazmi et al. [168] evaluated the steam reforming of food waste for biohydrogen production, revealing significant capital costs. The study reported that hydrogen generation alone required an investment of approximately $1.92 million. The CO_2 separation stage, however, was notably more expensive, with costs amounting to $21.5 million due to the inclusion of ionic liquid washing and CO_2 liquefaction systems. Additionally, operational costs were substantial, driven largely by high electricity consumption for compressors, which contributed to a total operating cost of around $473 million.

Various research studies have explored the techno-economic evaluation of biological processes for biohydrogen production. Among these, dark fermentation (DF) stands out as the most thoroughly studied method in techno-economic analyses (TEA) due to its maturity, cost-effectiveness, ease of industrial integration, and compatibility with existing infrastructure. These advantages make DF more favorable compared to other methods like photo-fermentation (PF) and photolysis [176]. For instance, Nikolaidis and Poullikkas [184] reported that DF, with a cost of 2.57 USD per kg of hydrogen, is more economical than PF, which has a higher cost of 2.83 USD per kg. Additionally, a techno-economic analysis was carried out by Han et al. [185] on a hydrogen production process that combined dark fermentation and solid-state fermentation. It was discovered through their evaluation that the economic viability of this combined approach achieved a hydrogen production cost of USD 2.29 per cubic meter, a payback period of five years, and an IRR of 20.2 %.

As highlighted in Table 4:, while some biohydrogen production technologies are technically and economically viable, others, such as gasification and catalytic supercritical water conversion, demand substantial investment and optimization to compete in the hydrogen market. It is essential to select the appropriate technology based on several factors to ensure sustainable and cost-effective hydrogen generation from biomass. These include feedstock availability and cost, capital and operating expenses structure, hydrogen yield, environmental considerations, and scalability potential. A careful balance of these variables is key to achieving long-term commercial success in biohydrogen production.

Techno-Economic Evaluation (TEE) is crucial for assessing the feasibility and profitability of biohydrogen production methods, balancing costs such as CAPEX and OPEX against hydrogen yield and market demand. By optimizing factors like feedstock availability, technology maturity, and operational efficiency, TEE guides the development of cost-effective and scalable biomass-to-hydrogen technologies for sustainable energy solutions.

4. Challenges and solutions in biohydrogen production processes

This section highlights the challenges associated with biohydrogen production processes and the potential strategies to address them. Presently, around 80 % of the world's energy comes from fossil fuels, which are extensively used in residential, industrial, and commercial settings [186]. Unfortunately, this reliance on fossil fuels is a major contributor to global warming and climate change [187]. Although projections show that fossil fuel consumption will drop below the current 80 % by 2050, the urgency to shift toward alternative, low-carbon energy sources remains critical [188,189]. Renewable energy, particularly biofuels, represents a sustainable solution to the environmental and economic issues posed by fossil fuels. Among the various types of biofuels, biohydrogen stands out due to its pollution-free by-products (mainly water vapour) and higher energy conversion efficiency [190]. With an energy density of 120 kJ/g, biohydrogen surpasses fossil fuels such as coal (35 kJ/g), gasoline (41.2 kJ/g), and diesel (42.9 kJ/g), making it an exceptionally efficient energy carrier [191]. Biohydrogen can be produced from diverse biomass sources, including agricultural residues, industrial and municipal wastes, and microbial pathways. Several production routes are commonly explored: biophotolysis, photofermentation, dark fermentation, gasification, and microbial electrolysis cells (MECs). Each of these pathways, while promising, presents unique challenges. For instance, the efficiency of microbial routes is often hindered by the complexity of biomass feedstock, operational conditions, and microbial strains, all of which require optimization. Furthermore, each biohydrogen production method faces scalability, cost, and conversion efficiency challenges. These challenges, including the high energy input for some processes (like gasification), the limited light conversion efficiency in photobiological methods, and substrate pretreatment requirements in fermentation, must be addressed to enhance biohydrogen production on an industrial scale. This section will delve into the specific challenges linked to each production route, examining both the technical and economic obstacles that must be overcome for biohydrogen to become a competitive renewable energy solution.

4.1. Challenges of biohydrogen production processes

4.1.1. Challenges of biohydrogen through dark and photo fermentation processes

Dark fermentation, which utilizes microorganisms primarily sourced from wastewater streams and agricultural residues, is considered one of the more developed technologies for biohydrogen production [190]. However, this process faces significant challenges, particularly around pretreatment. Pretreatment is crucial for breaking down the complex, recalcitrant structures of biomass, such as lignocellulose, into simpler sugars like glucose, cellobiose, and xylose. This step increases the availability of monomeric sugars required for hydrogen production but can be energy-intensive and costly [192]. Moreover, lignocellulosic materials also produce inhibitors such as 5-hydroxymethylfurfural (5-HMF) and furfural during pretreatment, which can hinder microbial activity and reduce hydrogen yields [134,193,194].

Another issue with dark fermentation is the formation of by-products like acetic, propionic, and butyric acids. These by-products compete for the energy needed by the microorganisms to produce hydrogen, ultimately lowering overall hydrogen yields [195]. Additionally, glucose, the primary substrate, is rapidly metabolized, often dropping to zero concentration, which limits sustained hydrogen production. Light intensity and wavelength also impact dark fermentation, particularly for systems that rely on light-sensitive microorganisms, limiting scalability and making location-specific considerations important [196]. Other factors influencing hydrogen production in dark fermentation include inoculum selection, temperature, hydraulic retention time, hydrogen partial pressure, and the composition of the fermentation end products

[197,198]. Anaerobic microorganisms in these processes are highly sensitive to oxygen, and even minimal oxygen exposure can severely inhibit hydrogen production. Facultative anaerobes can uptake oxygen more efficiently than strict anaerobes, making the former less cost-effective due to their oxygen-related challenges [199–201]. Maintaining optimal temperature and pH levels is also essential, as fluctuations can negatively affect fermentation efficiency [202–204].

Sourcing sustainable biomass for fermentation is another major challenge. The costs associated with collecting, transporting, and processing feedstock can be prohibitively high, particularly if large-scale hydrogen production is targeted [205]. Additionally, substrate contamination by other microorganisms can inhibit or outcompete hydrogen-producing bacteria, further complicating the process [206]. Reactor design and scalability also pose challenges for both dark and photofermentation. The size and design of the reactor can limit the volume of the fermentation broth, reducing the overall hydrogen yield. Moreover, factors like land availability, seasonal variations, and regulatory frameworks can influence the viability of biohydrogen production. Public acceptance and supportive policies will be crucial for advancing the adoption of these technologies [207]. By addressing these issues through improved pretreatment techniques, better microbial strain selection, and more efficient reactor designs, biohydrogen production can become more viable and economically competitive.

4.1.2. Challenges of biohydrogen production through photolysis

Photolysis, a process utilizing light energy to split cyanobacteria or microalgae via photosynthesis for biohydrogen production [208], faces several key challenges. One of the primary obstacles is the high production cost, which is tied to the low efficiency of light absorption. The effectiveness of the photocatalytic process hinges on how well the photocatalyst can absorb sunlight and convert it into chemical energy [209–211]. Many photocatalysts have a limited absorption range, typically restricted to the ultraviolet portion of sunlight, making light energy harvesting inefficient and consequently lowering overall hydrogen production efficiency [212–214]. Another issue is the electron-hole recombination during photolysis. While hydrogen is produced through reduction and oxidation as electrons and holes are generated, the recombination of these carriers disrupts the reactions necessary for hydrogen generation, reducing efficiency [215]. Additionally, photolysis produces hydrogen and oxygen simultaneously, necessitating the use of separation techniques that increase costs and create safety concerns, as the mixture of hydrogen and oxygen is highly explosive [216]. Economic and scalability issues further challenge photolysis. The photocatalysts used in the process can be expensive or rare, hindering large-scale hydrogen production. Transitioning from laboratory-scale operations to industrial-scale production introduces difficulties in ensuring uniform light distribution, maintaining the stability of photocatalysts over long periods, and effectively collecting the hydrogen produced [217]. Furthermore, the storage and transportation of hydrogen add complexity. As a low-density gas, hydrogen requires high-pressure tanks and extremely low temperatures for safe storage and transport, further escalating costs [218–220]. Addressing these technical and economic hurdles is critical to making photolysis a more viable method for sustainable hydrogen production.

4.1.3. Challenges of biohydrogen production through gasification process

The gasification process for biohydrogen production involves converting biomass into a hydrogen-rich synthetic gas (syngas) consisting of hydrogen, carbon monoxide, and other gases through high-temperature treatment with limited oxygen or steam [221]. However, several challenges hinder the efficiency and scalability of this method. One of the primary issues is the variability in biomass feedstock [222]. Biomass can vary in composition, moisture content, and energy density, affecting gasification performance and hydrogen yields [223–225]. Selecting feedstock with consistent quality is challenging, and pretreatment steps like drying or size reduction are often required, adding complexity and cost to the process. Another major challenge is tar formation. During gasification, complex hydrocarbons (tar) are produced, which can clog equipment, contaminate syngas, and ultimately reduce hydrogen yields [226]. Removing tar is difficult and necessitates additional processing steps such as thermal cracking, scrubbing, or catalytic cracking, further increasing costs [227]. Moreover, gasification requires extensive gas cleaning and conditioning due to impurities like sulfur compounds, nitrogen oxides, and particulate matter, which must be removed to prevent catalyst poisoning and ensure high-purity hydrogen [228]. This purification process is energy-intensive and technologically demanding, often involving advanced techniques such as pressure swing adsorption or membrane separation, which are costly [229].

Gasification also poses environmental concerns, particularly the emission of greenhouse gases (GHGs) [197]. If not properly optimized, carbon utilization can lead to emissions of air pollutants such as nitrogen oxides (NOx) and sulfur oxides (SOx), necessitating mitigation measures that add to the cost of hydrogen production. The technical complexity of controlling the gasification process further complicates its use. Accurate temperature, pressure control, and gas composition analysis are crucial for optimizing hydrogen production. System integration, such as incorporating combined heat and power (CHP) systems, introduces additional operational challenges and costs [196]. Finally, the sustainability and availability of biomass feedstock raise concerns. Biomass used for hydrogen production can compete with other vital uses such as food and animal feed, creating resource competition. Additionally, gasification processes often require large land areas, potentially leading to deforestation or soil degradation, posing a risk to the environment [205].

4.1.4. Challenges of biohydrogen production through microbial electrolysis cells (MECs)

Microbial Electrolysis Cells (MECs) are a promising technology for biohydrogen production, utilizing microorganisms to convert organic matter into hydrogen gas by applying an external electric current [230]. However, several challenges limit their widespread adoption. One of the key challenges is the high external voltage required to drive the electrochemical reactions. Achieving a positive energy balance, where the energy produced by the hydrogen exceeds the input energy, remains difficult. This limits the overall efficiency and economic viability of MECs. Microbial performance and selection are also crucial factors. Hydrogen production efficiency depends on the activity of electrogenic bacteria in the anode chamber [197]. Maintaining high microbial activity over time is challenging, as is ensuring the formation of biofilms on the electrodes, which are essential for facilitating electron transfer. However, managing biofilm thickness and activity over extended periods is complex, as is understanding microbial interactions and stability in the system [231]. Electrode design is another significant hurdle. MEC electrodes must have a high surface area, good conductivity, and biocompatibility. Finding materials that meet these requirements is difficult and costly. Additionally, electrodes are prone to fouling due to organic and inorganic matter, reducing their lifespan and necessitating costly cleaning or replacement [207]. High-performance materials like platinum are often used, but their high cost limits large-scale application.

Environmental factors, such as temperature fluctuations, also impact MEC performance. Low temperatures can reduce microbial activity and hydrogen production, making MECs less efficient during colder seasons. Maintaining optimal pH levels in both the anode and cathode chambers is critical for microbial activity and hydrogen production, presenting further challenges in large-scale applications. Lastly, regulatory and market barriers hinder the implementation of MECs [232]. Strict regulatory frameworks related to waste management, energy production, and environmental concerns may increase the costs and complexity of MEC adoption. Additionally, uncertainties about the long-term performance of MECs, coupled with competition from more established hydrogen production technologies, limit their broader application

[233].

4.1.5. Challenges of hydrogen production through pyrolysis

Pyrolysis has emerged as a promising low-carbon technology for hydrogen production [234]. However, several inherent challenges must be addressed for its broader implementation. Solid carbon is one of the primary by-products of pyrolysis, which can be valuable in specific industries like carbon black for tires and batteries. However, if the demand for carbon in these industries is insufficient, managing the large volume of solid carbon becomes a significant logistical challenge. This includes the safe storage, handling, and transportation of the material. Additionally, pyrolysis requires extremely high temperatures, typically exceeding 800 °C, to break down methane into hydrogen and solid carbon [235]. Maintaining these temperatures over long periods is energy-intensive, and if the energy source comes from fossil fuels, it negates the carbon-reduction benefits of the process. Improving the energy efficiency of pyrolysis is crucial to making the process both economically and environmentally viable.

To enhance efficiency, catalysts are often used in pyrolysis. However, developing highly active catalysts, stable at high temperatures, and resistant to deactivation is expensive [236]. Catalysts can degrade or become poisoned by impurities in the biomass feedstock, reducing their effectiveness and requiring frequent replacement, which further drives up costs. From a cost perspective, hydrogen produced via pyrolysis must compete with other methods, such as steam methane reforming (SMR), carbon capture and storage (CCS), and water electrolysis. The high energy input and the complexities of managing solid carbon make pyrolysis less economically attractive than these established methods. Scaling up pyrolysis from the laboratory or pilot stage to commercial production also presents technical and economic challenges [237]. Building and operating large-scale pyrolysis plants involves significant capital investments. Since pyrolysis technology is still in its early stages of development and optimization, investing in it can be considered high-risk. In terms of market development, additional infrastructure is required for both hydrogen distribution and storage and for managing the carbon by-products. These logistical challenges and potential regulatory and policy barriers could hinder the market entry of pyrolysis-based hydrogen production. Supportive government policies, including favorable pricing mechanisms, are crucial to ensure that pyrolysis can compete with more established hydrogen production technologies. Without such support, pyrolysis might struggle to gain traction in a market dominated by other well-established methods [238].

4.1.6. Challenges of hydrogen production through steam reforming

Steam methane reforming (SMR) is currently the most widely used method for hydrogen production, primarily relying on natural gas as the feedstock [239]. Despite its dominance in the industry, several key challenges hinder its long-term sustainability and environmental viability. One of the most significant challenges associated with SMR is its high carbon dioxide (CO_2) emissions. The process generates approximately 9–12 units of CO_2 for every unit of hydrogen produced, making SMR a major contributor to greenhouse gas emissions [240]. While carbon capture and storage (CCS) technologies can help mitigate this, they introduce additional complexity and considerable costs, making widespread implementation less attractive. Another critical challenge is the energy-intensive nature of SMR. The process requires large amounts of heat to drive the endothermic reactions, and this heat is typically generated by burning natural gas, further exacerbating CO_2 emissions [241]. This energy demand not only reduces the overall efficiency of SMR but also makes the process highly reliant on natural gas availability and price [242]. Any fluctuations in natural gas prices can significantly impact the cost-effectiveness of hydrogen production via SMR [243]. Additionally, the infrastructure required for SMR, including reformers, heat exchangers, and pressure swing adsorption units, is capital-intensive. The high upfront costs for setting up these facilities present a barrier to entry for many companies, particularly when compared to alternative hydrogen production methods.

Another limitation of SMR is its lack of flexibility in adjusting production rates [244]. Compared to more modern or renewable hydrogen production methods, SMR is less adaptable to fluctuating demand, which can hinder its competitiveness in dynamic energy markets. Environmental regulations pose further challenges to the SMR process. Stricter government policies and international agreements to reduce carbon emissions could delay the adoption and implementation of SMR technologies. Public perception and acceptance of SMR are also critical, as investors and stakeholders may be reluctant to invest in a process associated with significant CO_2 emissions, especially in the global shift toward more sustainable energy solutions. These challenges collectively highlight the limitations of SMR in a world increasingly focused on reducing carbon footprints and embracing renewable energy alternatives.

4.1.7. Challenges of hydrogen production through liquefaction process

Liquefaction is crucial for hydrogen production, enabling large-scale storage and long-distance transportation [245]. However, this process has several challenges, primarily due to its high energy requirements. Hydrogen liquefaction requires cryogenic temperatures, typically below −253 °C, which consume a significant amount of energy, about 25–35 % of the hydrogen's energy content [246]. This substantial energy demand lowers the overall efficiency of hydrogen as a fuel, making the process both costly and environmentally less sustainable. In addition to the energy intensity, the capital costs associated with hydrogen liquefaction are high. Constructing and operating liquefaction plants requires specialized equipment, such as cryogenic compressors and storage tanks, which further increases the expenses. Even with advanced insulation, hydrogen boil-off is a persistent issue, where some liquid hydrogen evaporates due to heat ingress, leading to energy losses during storage and transportation over time [247]. Material selection presents another challenge for hydrogen liquefaction. Equipment and storage tanks must be made from materials that maintain their structural integrity and performance at extremely low temperatures [248]. These specialized materials are expensive and further drive-up hydrogen production costs. Safety is a critical concern due to hydrogen's highly flammable and explosive nature. At cryogenic temperatures, any breach in containment could lead to rapid vaporization and potential explosions, increasing the risks associated with hydrogen liquefaction [249]. While hydrogen liquefaction is vital for large-scale storage and transport, its challenges, ranging from energy consumption and material costs to safety risks, present significant barriers to wider adoption.

4.2. Addressing some of the challenges in the biohydrogen production process

4.2.1. Overcoming low yields in biohydrogen production

To address the low-yield challenges in biohydrogen production, enhancing the metabolic pathway of microorganisms is crucial. This can be achieved through several strategies, including genetic engineering, process modifications, efficient bioreactor design, and carefully selecting bacterial strains. Notably, maximizing hydrogen production often correlates with the formation of butyrate, whereas lower yields are linked to the production of less desirable by-products such as propionate, alcohol, and lactic acid [14]. To optimize hydrogen yield, it is essential to shift microbial metabolic processes from producing alcohol and lactate toward generating acetate and butyrate. One effective method involves metabolic engineering, where the microorganism's biochemical pathways are restructured to channel resources more efficiently toward hydrogen production. Genetic and metabolic modifications are another promising approach [14]. These techniques enhance hydrogen production by altering the natural metabolic pathways in hydrogen-producing microbial strains. Importantly, genetic modifications in this context are not focused on introducing new functions to the microorganisms but rather on disrupting or modifying existing genes.

This optimization of the microorganism's inherent genetic makeup boosts the efficiency of the hydrogen production process without drastically changing the organism's nature. By fine-tuning these strategies, the overall hydrogen yield can be significantly increased, paving the way for more sustainable and efficient biohydrogen production systems.

4.2.2. Addressing the high cost of biohydrogen production

Hydrogen production through biomass gasification faces two primary challenges: the high capital cost of equipment and the fluctuating costs of biomass feedstock. To address the issue of capital expenses, ongoing research has focused on improving gasification technology, notably by replacing the traditional cryogenic method for oxygen extraction with advanced membrane technology. This innovation not only reduces costs but also enhances the extraction and purification of hydrogen from the gas stream, as seen in coal gasification. Developing and implementing advanced membranes are pivotal to improving hydrogen yield during the process. Optimizing the sequence of events in gasification is another essential strategy for improving efficiency [250,251]. Advanced modeling tools like FACTSAGE, MATLAB, and Design Expert are increasingly used to fine-tune gasification conditions and predict outcomes. These tools help identify the optimal parameters, such as temperature and pressure, to maximize hydrogen production while minimizing energy input and waste generation [252]. On the feedstock side, achieving cost-effective and consistent pricing remains a critical challenge. This can be mitigated through improvements in cropping systems and the development of feedstocks specifically bred for gasification, ensuring both the input materials' reliability and cost-effectiveness. The success of biomass gasification as a hydrogen production method will depend largely on this strategic approach to feedstock management, combined with the insights gained from commercial deployment of the technology.

Due to the energy-intensive nature of gasification, a thorough economic evaluation is vital for assessing the cost and efficiency of different gasification processes [253,254]. Such assessment can provide a foundation for determining the most cost-effective scale and technology combinations. However, a comprehensive techno-economic analysis is necessary to compare the viability of hydrogen produced via biomass gasification with conventional fossil fuels [167,255]. This analysis will offer insights into how biohydrogen can be positioned competitively within the energy market, considering both the cost and environmental impacts. Addressing the variability of hydrogen production during biomass gasification is also important, especially in mitigating inconsistencies that can arise during fermentation and other bioprocesses. A multifaceted approach combining technological optimization, feedstock management, and thorough economic analysis is crucial for overcoming the challenges in biomass gasification for hydrogen production.

4.2.3. Further development of hydrogen technologies

Hydrogen, recognized as an eco-friendly energy carrier with no direct environmental footprint, is crucial for advancing global energy systems. So far, the focus has been on reducing overall costs and diversifying applications [256]. To enhance hydrogen production and expand its applications, several key issues must be addressed:

i. **Electricity Costs**: One significant challenge in power-to-hydrogen applications is the high cost of electricity, driven primarily by taxes. To mitigate this, policymakers should consider exemptions from taxes and levies on electricity used for hydrogen production. Additionally, implementing regulations that encourage avoiding electricity consumption during peak demand times could further reduce costs.

ii. **Hydrogen Transport**: Establishing dedicated gas pipeline systems for hydrogen transport is critical for its large-scale use. Although research suggests that hydrogen can be transported through existing natural gas pipelines, national licensing restrictions remain a hurdle. Revisiting and revising these legal frameworks could expand power-to-gas applications and facilitate smoother integration of hydrogen into existing energy infrastructure.

iii. **Renewable Energy Integration**: In countries like those in North America and Europe, there has been a decline in electricity production from renewable sources. To combat this, prioritizing connecting renewable energy sources to the grid is essential. Regulations prioritizing renewable energy feed-ins while ensuring compensation when renewables are curtailed due to grid congestion will help maintain a stable energy supply and foster growth in hydrogen production from renewable sources.

Addressing these issues, which include electricity costs, infrastructure for hydrogen transport, and renewable energy prioritization, will be key to unlocking the full potential of hydrogen in the global energy transition.

5. Prospects and future work consideration in biohydrogen production

5.1. Global perspective and prospects for hydrogen production

Globally, governments are tasked with balancing several priorities, including job creation, economic resilience, natural resource development, and environmental protection. While the potential of a hydrogen economy is politically attractive, it may still be too early to fully embrace it as a sustainable solution, as it may not yet align with broader societal interests. Europe has taken the lead in developing hydrogen-powered energy systems, with more than 300 companies across the

Table 5
Some of the global hydrogen production projects.

Project Name	Country	Year	Technology/ Energy source	IEA H_2 capacity	Refs
Nikola	United States	2020	ALK	463.00	[257]
Lake Charles Methanol	United States	2022	Fossil	251,354.60 nm^3 H_2/h	
North West Sturgeon refinery	Canada	2019	Fossil	169,307.01 nm^3 H_2/h	
Yumen Oilfield 160 MW Renewables Hydrogen Production Demonstration Project	China	2023	Solar	7000 tpa	[258]
Zhangjiakou Green Hydrogen Energy Integration Demonstration Base Project	China	2022	Wind	2800 tpa	
Fortescue-Egypt-gH2 project	Egypt	2022	Electrolyser	300,000 tpa	[259]
Amun project	Morocco	2019–2025	Solar and wind	900000tpa	[260]
Herning Electrolyser Plant	Denmark	2023–2025	Electrolyser Plant	500 MW/yr to expand to 5GW	[261,262]
Belfort Alkaline Electrolyser Gigafactory	France	2023–2023	Wind/solar	100 MW/yr	[262]

ALK - Alkaline electrolysis; tpa – tonnes per year, nm^3 H_2/h – normal cubic metre per hour.

European Union active in the hydrogen and fuel cell industries, including their respective supply chains [256]. The region's market potential for hydrogen-based solutions is significant. North America is similarly positioned for a transformation in the hydrogen industry due to its established oil and gas infrastructure, diverse energy resources, and broad demand across various sectors. Unlike regions solely focusing on green hydrogen, North America has demonstrated enthusiasm for blue and green hydrogen solutions, recognizing the economic and environmental benefits [257]. This positions it to be a key player in the global hydrogen market. Techno-economic analyses consistently underscore the viability of hydrogen systems, particularly in facilitating renewable energy integration and reducing greenhouse gas emissions [256].

However, significant investment is required to build the necessary infrastructure to establish a global hydrogen economy, especially in developing a reliable hydrogen distribution network comparable to fossil fuels. A major financial challenge lies in determining whether the energy needed to produce hydrogen and subsequently convert it back into electricity justifies the investment. While technological advancements have reduced some barriers, there is consensus that future improvements and cost reductions will likely be incremental. Nevertheless, forecasts suggest a significant decrease in hydrogen production costs, particularly in sectors like energy and transportation, where hydrogen could help achieve lower carbon emissions than fossil fuels. The growing political support for hydrogen reflects this potential, and the industry is witnessing increased commercial viability [14]. Nonetheless, further efforts are needed to create a global, safe, and accessible hydrogen distribution network. Data from the International Energy Agency (IEA), shown in Table 5, highlights progress in global hydrogen production projects from 2019 onward, indicating positive steps toward a sustainable hydrogen economy.

5.2. Future work considerations

Investments and advancements in hydrogen technology can potentially drive the development of new industries globally, creating skilled jobs and fostering economic growth. To successfully transition to a hydrogen economy, hydrogen production technologies must be improved with a strategic and interdisciplinary mindset. Key areas for focus include:

5.2.1. Improvement in the research and development (R&D) sector

Theoretical research is crucial for advancing hydrogen production technologies. At the microscopic level, interfacial and atomic engineering methods can provide new insights into the steam reforming of hydrocarbons, potentially leading to significant breakthroughs in efficiency and performance [263]. Additionally, computational modeling and simulation techniques are invaluable for predicting, evaluating, and optimizing various hydrogen production methods [264]. These tools guide experimental research and help fine-tune process conditions, increasing overall efficiency while driving down production costs [265]. Furthermore, research and development play a key role in improving the performance and affordability of hydrogen-based technologies such as fuel cells and hydrogen fuels. Advancements in these areas are essential to making hydrogen a more viable and competitive energy option. By combining theoretical research with practical development, the future of hydrogen production can be shaped by innovation and cost-efficiency.

5.2.2. Development of raw materials

The next crucial step is to fully harness the potential of raw materials for hydrogen production. Leveraging diverse sources such as waste, biomass, and renewable resources can significantly lower production costs while delivering social and environmental benefits. By diversifying feedstocks, the hydrogen industry can enhance sustainability and reduce reliance on traditional, non-renewable resources. This will boost economic efficiency and contribute to a circular economy where waste and by-products are minimized. Several innovative approaches have already been explored, such as converting plastic waste into hydrogen [266], utilizing seawater for electrolysis [267], and employing genetically engineered microbes (GEM) and residual waste for biohydrogen production [268]. These initiatives inspire further research into alternative feedstocks and pave the way for new advancements in hydrogen production. By learning from these studies, researchers and industries can continue innovating, developing, and scaling technologies that capitalize on more sustainable and cost-effective raw materials.

5.2.3. Process coupling and sustainable energy utilization

A process-coupling strategy is recommended to tackle the complexity and high energy consumption of current hydrogen production technologies. This approach combines multiple processes to enhance overall efficiency. One promising hybrid is the pyro-gasification or combination of pyrolysis with steam reforming, gaining prominence as an efficient and environmentally friendly way to produce energy and valuable chemicals from renewable resources and waste. Another notable example is the development of hybrid systems that integrate hydrogen production with electrolysis, thereby optimizing the conversion of resources and reducing energy losses [269]. By merging these key processes, operational synergies can be achieved, boosting performance and cost-effectiveness. Additionally, incorporating sustainable energy sources such as solar, geothermal, nuclear, and wind power is critical to improving the efficiency of hydrogen production technologies [270]. These renewable energy sources not only reduce reliance on fossil fuels but also increase operational flexibility and convenience. The integration of renewables into hydrogen production strengthens the future market potential of hydrogen as a clean energy solution while improving competitiveness. By coupling processes and using sustainable energy, the hydrogen sector can significantly enhance production efficiency, decrease costs, and improve environmental sustainability, thereby strengthening the market's long-term prospects.

6. Conclusion

Biohydrogen has emerged as a promising alternative to fossil fuels, offering a viable pathway toward a zero-carbon economy due to its potential for carbon-neutral emissions. This review has demonstrated the adaptability of biomass as a renewable feedstock for hydrogen production through various thermochemical and biological processes, including steam reforming, liquefaction, pyrolysis, and catalytic gasification. These methods have shown notable advantages in hydrogen yield, energy efficiency, and environmental sustainability. The analysis underscores the significance of emerging technologies, such as microbial and supercritical biomass conversion, in enhancing the commercial feasibility of biohydrogen production. However, several persistent challenges hinder large-scale implementation, including high production costs, catalyst efficiency optimization, and feedstock variability. Addressing these barriers requires a multi-faceted approach integrating innovative catalytic materials, process intensification strategies, and advanced separation technologies to improve efficiency and scalability.

From a broader perspective, the findings of this review align with global efforts to transition toward cleaner energy sources. Techno-economic analysis confirms that biohydrogen production offers significant economic and environmental benefits, provided key challenges such as supply chain logistics, financial viability, and policy support are effectively addressed. Future research should prioritize optimizing process designs, utilizing diverse biomass feedstocks, and integrating carbon capture technologies to enhance sustainability. Interdisciplinary collaboration among industry, policymakers, and researchers will be essential for accelerating commercialization and establishing a resilient hydrogen economy. Overcoming current challenges and leveraging advancements in green hydrogen production will position biohydrogen as a cornerstone of sustainable energy systems, contributing to long-term energy security and climate change mitigation.

These efforts will enhance energy security, reduce carbon emissions, and accelerate the transition to a renewable hydrogen economy. Ultimately, this work lays the foundation for technological innovation, policy development, and large-scale adoption, paving the way for a carbon-neutral future.

CRediT authorship contribution statement

Sherif Ishola Mustapha: Writing – original draft, Project administration, Methodology, Conceptualization. **Ifeanyi Michael Smarte Anekwe:** Writing – original draft, Methodology, Conceptualization. **Stephen Okiemute Akpasi:** Writing – original draft, Methodology. **Kabiru Bab Muritala:** Writing – original draft, Methodology. **Emmanuel Kweinor Tetteh:** Writing – review & editing, Writing – original draft, Methodology. **Atuman Samaila Joel:** Writing – review & editing, Writing – original draft, Methodology. **Yusuf Makarfi Isa:** Writing – review & editing, Supervision, Resources.

Declaration of competing interest

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

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Data availability

No data was used for the research described in the article.

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