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Biomass-to-Hydrogen Conversion: Fundamentals, Technologies and Performance Trade-offs

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Abstract: Hydrogen is attracting increasing attention as a low-carbon energy carrier, but its environmental benefits depend strongly on the production pathway. Biomass provides a renewable feedstock for hydrogen production while enabling the utilization of agricultural residues, forestry wastes, algae, and organic wastes. Major biomass-to-hydrogen routes include gasification, pyrolysis–reforming, hydrothermal gasification, dark fermentation, photo-fermentation, photobiological conversion, and microbial electrolysis. These technologies differ substantially in reaction mechanisms, feedstock requirements, hydrogen productivity, energy demand, and technological maturity. This review examines the fundamental mechanisms of biomass-to-hydrogen conversion and summarizes recent advances in major thermochemical, biological, and bioelectrochemical routes. Particular emphasis is placed on the trade-offs among hydrogen yield, productivity, energy efficiency, environmental impact, and economic feasibility. The analysis indicates that technology selection should be tailored to feedstock characteristics, with thermochemical routes generally favored for dry biomass and hydrothermal or biological pathways offering advantages for wet and organic-rich feedstocks. Future development will depend on integrated biomass utilization and carbon management.

1. Introduction

Hydrogen has long been used in petroleum refining and chemical manufacturing, but its potential role in a low-carbon energy system extends beyond these established applications. It is being considered for direct reduced iron, synthetic fuels, long-distance transport, and energy storage, while conventional industrial uses continue to account for most global hydrogen demand. According to the International Energy Agency, global hydrogen demand exceeded 100 Mt in 2025, while demand for low-emissions hydrogen approached 1 Mt. The scale of the existing market, together with the very small contribution of low-emissions production, highlights the difficulty of decarbonizing the current hydrogen supply[1].

The current hydrogen supply remains dominated by fossil resources. Natural gas and coal account for the overwhelming majority of hydrogen production, and their environmental performance is closely related to the amount of carbon released during conversion. The IEA

estimates that unabated natural-gas-based hydrogen is associated with approximately 10–12 kg CO_2-equivalent per kilogram of H_2, whereas unabated coal-based production produces approximately 22–26 kg CO_2-equivalent per kilogram of H_2. Renewable-electricity-driven electrolysis offers a lower-emission alternative when electricity has a low carbon intensity, but its competitiveness remains sensitive to electricity costs, electrolyzer utilization, and the availability of renewable power[1,2].

Biomass presents a different opportunity. It contains chemically stored energy and can be obtained from agricultural residues, forestry wastes, food-processing by-products, algae, sewage sludge, and other organic resources. The use of residues and wastes is particularly attractive because hydrogen production can be linked to waste treatment and resource recovery. Recent reviews have consequently considered biomass-derived hydrogen within a broader framework of biomass valorization, where hydrogen is one of several possible products rather than the only objective[3,4].

A range of conversion routes is available. Gasification produces synthesis gas at elevated temperatures and can be followed by reforming and water-gas shift reactions to enrich hydrogen. Pyrolysis generates bio-oil, gases, and char and can be coupled with catalytic reforming when hydrogen is the desired major product. Hydrothermal gasification is particularly relevant to wet biomass because the feedstock can be processed without conventional drying. Biological approaches follow a different reaction framework. Dark fermentation relies on microbial metabolism, photo-fermentation can further utilize fermentation products, and microbial electrolysis combines biological oxidation with electrochemical hydrogen generation[5–8].

The major difficulty in comparing these approaches is that the highest reported hydrogen yield does not necessarily correspond to the best overall process. Feedstock composition, moisture content, pretreatment, reaction temperature, reactor configuration, catalyst stability, microbial activity, gas purification, and energy demand can all alter the final outcome. A route that works well for dry and relatively homogeneous lignocellulosic residues may be much less attractive when applied to a wet and heterogeneous waste stream. A recent assessment of agricultural residues in Vietnam, for example, showed that the relative suitability of gasification, pyrolysis, and fermentation changes when technical, economic, and environmental indicators are considered together[9].

This review focuses on the relationship between biomass characteristics, hydrogen-forming mechanisms, conversion technologies, and overall process performance. The first part discusses the influence of biomass composition and the major mechanisms responsible for hydrogen formation. The major thermochemical, biological, and bioelectrochemical technologies are then considered together with recent developments in catalysts, reactor design, and process integration. The different pathways are subsequently compared in terms of hydrogen yield, productivity, energy efficiency, environmental impact, economic feasibility, and feedstock compatibility. The final section discusses the main barriers and possible directions for integrated biomass-to-hydrogen systems.

2. Fundamentals of Biomass-to-Hydrogen Conversion

2.1. Biomass characteristics and hydrogen-production potential

Biomass is inherently heterogeneous rather than a standardized chemical feedstock. Its composition varies with plant species, geographical origin, cultivation conditions, processing history, and storage. Relevant feedstocks for hydrogen production include lignocellulosic residues, carbohydrate-rich wastes, algae, sewage sludge, and other organic waste streams. The properties that most directly influence conversion include moisture, structural carbohydrate content, lignin fraction, ash, elemental composition, volatile matter, and inorganic constituents[3–6].

Lignocellulosic biomass is dominated by cellulose, hemicellulose, and lignin. Cellulose is a relatively ordered polysaccharide composed mainly of glucose units, while hemicellulose contains a more heterogeneous mixture of sugars and is generally more readily hydrolyzed. Lignin is an aromatic, highly cross-linked polymer and is considerably more resistant to biological degradation. Standard biomass characterization therefore treats structural carbohydrates and lignin as distinct fractions when evaluating biomass conversion behavior[10]. These differences also affect hydrogen production. Cellulose and hemicellulose provide relatively accessible carbohydrate structures for fermentation after suitable pretreatment, whereas lignin tends to produce aromatic compounds, phenolics, and char during thermochemical conversion[3,4].

Moisture content can be equally important. Drying wet biomass before conventional pyrolysis or gasification consumes energy and may become a major contributor to the overall process burden. Hydrothermal processing takes a different approach because water remains in the reaction environment. This makes wet resources such as algae, sludge, and some food wastes particularly attractive candidates for hydrothermal conversion. A review of hydrothermal biomass processing emphasized that avoiding conventional drying is one of the principal advantages of this route[6]. Experimental work with pellets made from agricultural residues also demonstrated that hydrothermal gasification performance is sensitive to temperature, reaction time, and feed-to-water ratio[11].

Mineral constituents add another level of complexity. Alkali and alkaline-earth elements can influence gasification chemistry and sometimes act as natural catalysts, but ash deposition and mineral accumulation may also interfere with reactor operation and catalyst stability. These effects are particularly relevant when heterogeneous agricultural and waste biomass are processed. Recent reviews of catalytic biomass gasification consequently place substantial emphasis on feedstock ash and mineral composition[5,12].

The hydrogen content of a biomass should not be interpreted as a direct measure of its hydrogen-production potential. During gasification and reforming, water participates in hydrogen-forming reactions, while the carbon originally present in the biomass is distributed among CO, CO_2, CH_4, char, and other products. The final amount of recoverable H_2 therefore depends on reaction pathways and carbon conversion as well as on the initial elemental composition. This distinction is particularly important when comparing technologies that handle carbon differently.

Feedstock characteristics also influence the choice of process. Carbohydrate-rich materials may be favorable substrates for fermentation, while highly lignified materials can require substantial pretreatment before biological conversion. Thermochemical processes are generally more tolerant of structural recalcitrance, although moisture and ash can become important limitations. The suitability of a technology should therefore be assessed in relation to the physical and chemical properties of the feedstock rather than independently of them.

2.2. Fundamental mechanisms of hydrogen formation

Thermochemical hydrogen production involves a network of primary and secondary reactions. Biomass first undergoes thermal decomposition, generating volatile compounds, condensable products, and char. These products subsequently participate in gasification, cracking, reforming, water-gas shift, methanation, and carbon-deposition reactions[5,13].

$$C + H_2O \rightarrow CO + H_2$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

$$C_nH_m + nH_2O \rightarrow nCO + (n + m/2)H_2$$

These reactions provide the fundamental chemical basis for H2 formation during biomass

gasification. Their relative importance depends on temperature, steam availability, the gasifying medium, residence time, and catalyst properties. A 2024 meta-analysis of biomass gasification found that biomass properties strongly affect syngas production in air gasification, while the steam-to-biomass ratio is an important determinant under steam gasification[13].

Tar formation illustrates the importance of secondary chemistry. Heavy organic compounds produced during biomass decomposition may condense downstream or undergo further reactions to form carbon deposits. Catalysts can promote tar cracking and reforming, but the same high-temperature conditions can also accelerate sintering and coking. The development of catalysts that retain activity during prolonged operation is therefore as important as maximizing initial catalytic activity[5,12].

Pyrolysis follows a related but distinct pathway. Instead of directing most carbon immediately into a gas phase, biomass is divided among bio-oil, non-condensable gas, and char. When hydrogen is the principal target, the volatile and liquid products generally require subsequent reforming. The resulting hydrogen performance therefore reflects both the initial pyrolysis step and the efficiency of the catalytic conversion that follows.

Mbeugang et al. investigated a catalysis/sorption-enhanced pyrolysis–gasification process using Ni-based catalysts and calcined dolomite. Catalyst support had a marked influence on H_2 production, and simultaneous catalytic reforming and CO_2 capture performed better than sequential operation under the conditions investigated. The Ni–Cu/γ-Al_2O_3 catalyst combined with calcined dolomite reached an H_2 concentration of 87.06 vol% in the reported system[16]. This value should be regarded as a condition-specific result rather than a universal performance benchmark.

Hydrothermal gasification follows similar carbon–water chemistry under high-pressure aqueous conditions. Hydrolysis, depolymerization, and decomposition can precede the main gasification and reforming reactions. Its primary advantage is therefore related to feedstock handling and reaction environment rather than to a fundamentally different source of hydrogen[6,17].

Biological hydrogen formation is governed by microbial metabolism. During dark fermentation, carbohydrates are hydrolyzed and metabolized, with reducing equivalents distributed among H_2, CO_2, volatile fatty acids, alcohols, and biomass[18]. Under an acetate-type pathway, the theoretical maximum can be expressed as:

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

which yields a theoretical stoichiometric value of 4 mol H_2 per mole of glucose. This represents a theoretical pathway rather than a practical universal yield. Competing metabolic reactions and microbial growth consume part of the available reducing equivalents, and accumulated hydrogen can further alter the metabolic balance[7,18].

The behavior of mixed microbial communities is especially relevant to real waste streams. Mohanakrishna and Pengadeth emphasized that mixed cultures are attractive for scale-up because they can respond more robustly to changes in substrate composition and environmental conditions than highly specialized pure cultures[18]. Dursun demonstrated hydrogen production from quinoa residues using dark fermentation and also characterized the microbial community involved in the process[19].

Photo-fermentation can further utilize organic acids that remain after dark fermentation. Recent reviews have consequently investigated dark and photo-fermentation as sequential rather than isolated processes[20]. Photobiological hydrogen production relies on photosynthetic microorganisms and hydrogen-evolving enzymes, but oxygen sensitivity remains a major obstacle because oxygenic photosynthesis and H2 evolution are difficult to sustain simultaneously[21].

Microbial electrolysis cells use a different mechanism. Organic matter is oxidized biologically at the anode, releasing electrons and protons, while hydrogen is produced at the cathode. The

possibility of using organic wastewater as both a treatment target and an electron donor makes MECs particularly interesting for waste-derived hydrogen production[8,22].

2.3. Pretreatment and key factors governing hydrogen production

Pretreatment is particularly important when lignocellulosic substrates are subjected to biological conversion. Mechanical milling can increase surface area, while alkaline, acidic, hydrothermal, oxidative, and biological treatments can alter the lignin–carbohydrate matrix. The objective is to improve substrate accessibility without creating an energy, chemical, or inhibitor burden that offsets the benefit of pretreatment.

Zhao et al. identified pretreatment as an important determinant of biomass dark fermentation and emphasized that it must be considered together with downstream microbial conversion[7]. Recent work has also examined sequential processes in which fermentation products themselves contribute to biomass pretreatment. One study of municipal solid waste used starch-derived volatile fatty acids generated during an initial fermentation stage to assist lignocellulose pretreatment and subsequent hydrogen production[23].

For thermochemical conversion, temperature is one of the principal process variables. Increasing temperature generally accelerates decomposition, reforming, and gasification, while excessive temperature increases energy demand. Meta-analysis of biomass gasification has shown that biomass properties, gasifying agent, temperature, and reactor configuration all influence syngas production[13]. Data-driven analysis has also been applied to identify the relative importance of catalyst and operating variables for selective H2 formation from biomass gasification[24].

Biological conversion is more sensitive to microbial physiology pH, substrate concentration, temperature, inoculum composition, and hydrogen partial pressure influence both microbial growth and product distribution. A recent study demonstrated that a self-adaptable acetate buffer system substantially increased hydrogen production from cellulose by limiting excessive acidification of the fermentation broth[25]. Such results illustrate the sensitivity of biohydrogen processes to apparently small changes in the chemical environment. As summarized in Table 1, feedstock characteristics and process conditions exert different levels of influence on thermochemical and biological hydrogen production, which partly explains the distinct performance characteristics of these pathways.

Table 1. Key factors governing biomass-to-hydrogen conversion

Technology	Main feedstocks	Conversion mechanism	Operating conditions	Main advantages	Major limitations	Technology maturity
Gasification	Dry lignocellulosic biomass, agricultural residues	Thermal decomposition, gasification and WGS	High temperature	High productivity, broad feedstock tolerance	Tar, catalyst deactivation, gas purification	High
Pyrolysis–reforming	Lignocellulosic biomass	Pyrolysis followed by catalytic reforming	High temperature	Hydrogen-rich gas and co-products	Coke deposition, complex bio-oil	Moderate–high
Hydrothermal gasification	Wet biomass, algae, sludge	Hydrothermal decomposition and reforming	High T/P	Suitable for wet feedstocks, avoids drying	High pressure, corrosion	Moderate
Dark fermentation	Carbohydrate-rich wastes	Microbial fermentation	Mild	Low temperature	Low productivity, incomplete	Moderate

				, waste utilization	conversion	
Photo-fermentation	Organic acids, fermentation effluents	Photosynthetic bacterial metabolism	Mild + light	Additional H_2 recovery	Light limitation	Low–moderate
Photobiological production	Algae, cyanobacteria	Photosynthetic H_2 evolution	Mild + light	Direct solar-energy utilization	Oxygen sensitivity, low productivity	Low
Microbial electrolysis	Wastewater, organic-rich streams	Microbial oxidation + electrochemical H_2 evolution	Mild + external voltage	H_2 + wastewater treatment	Electrode/membrane cost, stability	Low–moderate

3. Biomass-to-Hydrogen Conversion Technologies and Recent Advances

3.1. Thermochemical conversion

Thermochemical conversion has been widely investigated for biomass hydrogen production because it can handle a broad range of solid feedstocks and does not rely on the biological accessibility of structural carbohydrates. Gasification, pyrolysis followed by reforming, and hydrothermal gasification are the main routes considered in this area, although their operating requirements and suitable feedstocks are quite different [5,6].

Gasification has the longest development history among these approaches. Biomass is converted into a mixture of H_2, CO, CO_2, CH_4, light hydrocarbons, and tar under an oxidizing or steam-containing atmosphere. The choice of gasifying agent affects both the composition of the raw gas and the subsequent purification requirements. Air is attractive because of its low cost, but the nitrogen introduced into the system dilutes the product gas. Oxygen avoids this problem but requires an additional oxygen supply. Steam is often preferred in hydrogen-oriented systems because it participates directly in gasification, reforming, and the water-gas shift reaction [5,13].

Considerable effort has been devoted to catalyst development, particularly for tar conversion and hydrogen enrichment. Nickel-based catalysts remain common because they provide good reforming activity without the cost associated with many noble metals. Their performance, however, is strongly affected by coking, sintering, and poisoning. Promoters and alternative supports have therefore been explored to improve activity and stability [5,12].

The influence of catalyst composition can be seen in several recent experimental studies. Acevedo-Páez et al. investigated Ni-, Ca-, and K-containing mordenite catalysts during palm-kernel-shell gasification at 900 °C. Under their optimized conditions, the H_2 concentration reached 72.9 mol% with the Ni/Ca/K catalyst [14]. Yeşilova et al. examined Al–Ni catalysts in fixed-bed gasifiers and reported a maximum H_2 concentration of 65 vol% at 900 °C in the updraft configuration [15]. These results are useful as representative examples of catalyst-assisted gasification, although the reported values depend on the individual feedstock, reactor, and operating conditions and should not be treated as general benchmarks.

Pyrolysis–reforming follows a somewhat different route. Biomass is first separated into bio-oil, non-condensable gases, and char, after which the volatile and liquid fractions can be further converted to H_2-rich gas. The additional reforming step increases the fraction of biomass carbon entering the gas phase, but the composition of bio-oil is considerably more complicated than that of a single model compound. Aromatic and oxygenated species can undergo secondary reactions and promote coke formation, making catalyst lifetime a persistent concern.

Mbeugang et al. investigated a combined catalytic and sorption-enhanced pyrolysis–gasification process using Ni-based catalysts and calcined dolomite. The composition of the catalytic system had a clear influence on the resulting gas. Under the reported conditions, Ni–Cu/γ-Al_2O_3 together with calcined dolomite produced an H_2 concentration of 87.06 vol% [16]. The study is particularly relevant to process intensification because catalytic reforming and CO_2 removal were addressed within the same system. The reported H_2 concentration, however, reflects a specific experimental configuration rather than the general performance of pyrolysis–reforming.

Hydrothermal gasification is better suited to feedstocks for which water is an intrinsic part of the resource. Conventional thermal conversion of wet biomass can require considerable energy simply to remove moisture, whereas hydrothermal treatment retains water in the reaction environment [6,17]. This makes the route interesting for algae, sludge, food wastes, and other wet materials. The main difficulties shift toward reactor engineering: high pressure, corrosion, salt deposition, and materials stability all need to be managed before the process can be considered broadly scalable.

More recent work is also moving toward multifunctional systems. Lithium manganate has been investigated as a bifunctional material for biomass gasification, while Ni/Ca-based materials have been used to combine catalytic conversion with in situ CO_2 capture [26,31]. The idea is to reduce the number of separate downstream operations and, where possible, shift the reaction equilibrium toward hydrogen formation. Biomass gasification has also been coupled with other industrial gas streams. Pel áez et al., for example, examined the use of residual steelmaking gases together with biomass-derived gas, with additional steam reforming and water-gas shift steps used to upgrade the combined stream [27].

Chemical-looping configurations represent another emerging direction. Instead of supplying oxygen directly to the biomass reactor, oxygen transfer is mediated by a solid carrier. Wu et al. reported negative net global warming potential for one biomass-gasification/chemical-looping configuration under the system boundaries used in their assessment [28]. Such results are encouraging from a carbon-management perspective, although the process remains less mature than conventional gasification and still requires further work on cost, material durability, and reactor integration.

3.2. Biological and bioelectrochemical conversion

Biological hydrogen production operates under very different conditions from thermochemical conversion. Dark fermentation is the most established route among the biological approaches considered here, while photo-fermentation, photobiological hydrogen production, and microbial electrolysis provide alternative ways of recovering hydrogen from organic matter [7,8,20,21].

Dark fermentation is particularly attractive when the feedstock contains readily biodegradable carbohydrates. Mixed microbial cultures are often favored for waste-derived substrates because they can tolerate changes in composition and operating conditions [7,18]. The limitation is that only part of the reducing power of the substrate is recovered as H_2. Acetate, butyrate, ethanol, and other metabolites retain a substantial fraction of the original carbon and reducing equivalents. Improving hydrogen production therefore requires more than increasing substrate concentration; microbial community structure and metabolic pathways have to be considered as well.

The transition from model substrates to real wastes has generated a range of different results. Mart ńez-Fraile et al. investigated lactate-driven dark fermentation using organic wastes from solid-waste treatment plants and found that hydrogen production varied with waste composition and loading [29]. Dursun obtained hydrogen from quinoa residues and also examined the microbial communities present during fermentation [19]. Rashidi et al. explored co-fermentation of sugarcane vinasse and bagasse, taking advantage of the complementary characteristics of the two residues [30].

Together, these studies illustrate the flexibility of dark fermentation, but they also show why results obtained with purified glucose or other model substrates cannot be transferred directly to heterogeneous wastes.

Photo-fermentation provides a possible second stage for fermentation systems. Organic acids remaining after dark fermentation can be further metabolized by photosynthetic bacteria, allowing part of the residual substrate to be recovered as additional hydrogen [20]. The main practical difficulty is illumination. Increasing cell density improves substrate utilization but reduces light penetration, so the reactor cannot simply be scaled by increasing its volume.

Photobiological hydrogen production faces a related problem. Photosynthetic microorganisms can generate reducing equivalents for hydrogen evolution, but hydrogenases are generally sensitive to oxygen. Maintaining photosynthetic activity while creating an intracellular environment favorable for H_2 evolution is therefore difficult. Chen et al. reviewed recent work on microalgal systems and highlighted oxygen control and hydrogenase activity as central research issues [21]. The technology remains scientifically attractive, but low volumetric productivity and photobioreactor requirements continue to limit its practical maturity.

Microbial electrolysis follows another route. Organic substrates are oxidized by microorganisms at the anode, while the released electrons and protons are used to generate H_2 at the cathode. This makes MECs especially interesting for wastewater treatment, since the same organic matter can serve as the treatment target and electron source [8,22]. Much of the recent work has concentrated on electrode materials, cathode catalysts, membrane configuration, and microbial communities. Even so, electrode cost, membrane resistance, biofouling, and long-term stability remain difficult issues.

3.3. Integrated and emerging conversion strategies

The recent literature is increasingly concerned with what happens to the material that remains after the first hydrogen-producing step. This has encouraged the development of sequential and coupled systems rather than single-stage processes.

A straightforward example is the combination of dark fermentation with photo-fermentation. The first stage consumes readily available organic substrates, while the second stage is intended to make use of residual organic acids [20]. MECs can be used for a similar purpose, particularly when the fermentation effluent contains enough biodegradable organic matter to support anodic oxidation [22]. Pretreatment and hydrogen production can also be connected more closely. One recent study used volatile fatty acids generated from municipal solid waste fermentation to assist lignocellulose pretreatment before subsequent hydrogen production [23].

Thermochemical processes have followed a similar path. Pyrolysis can be coupled directly with catalytic reforming, while CO_2 capture can be incorporated into gasification. Quan et al. reported enhanced hydrogen production using Ni/Ca-based catalysts for in situ CO_2 capture during biomass gasification [31]. Such systems are attractive because gas conversion and purification are no longer treated as completely separate operations.

The integration of biomass conversion with existing industrial processes is another area of interest. Pel áez et al. considered residual steelmaking gases as part of a biomass-based hydrogen process, using additional reforming and water-gas shift reactions to improve the use of the combined gas stream [27]. The potential benefit in such cases comes from using heat and gaseous intermediates that already exist within an industrial system.

Carbon utilization also changes the way biomass hydrogen systems are evaluated. Part of the biomass carbon can be released as CO_2, while another fraction may be retained in biochar or incorporated into other products. Li et al. evaluated oriented biomass pyrolysis for hydrogen-rich

gas and biochar production using life-cycle and economic assessments, illustrating that hydrogen and carbon products can have to be considered together [32]. Chemical looping and CCS provide additional options for managing biomass-derived carbon [28,33].

Taken together, these developments point toward a broader biomass-refinery concept. Different fractions of the same feedstock do not necessarily need to follow the same conversion route. Cellulose and hemicellulose may be directed toward biological conversion, lignin-rich fractions toward thermochemical processing, and residual carbon toward stable carbon products. The major characteristics and current limitations of the principal biomass-to-hydrogen technologies are summarized in Table 2.

Table 2. Comparison of major biomass-to-hydrogen conversion technologies.

Factor	Thermochemical conversion	Biological conversion	Influence on H_2 production
Feedstock composition	Strong	Strong	Determines intermediates and conversion pathway
Moisture	Strong	Moderate	Influences drying requirement and energy demand
Temperature	Strong	Strong	Controls reaction rate or microbial activity
Pretreatment	Moderate	Strong	Improves substrate accessibility
Steam-to-biomass ratio	Strong	Not applicable	Affects gasification and reforming reactions
Catalyst	Strong	Not applicable	Promotes reforming and tar conversion
pH	Limited	Strong	Regulates microbial metabolism
Microbial community	Not applicable	Strong	Determines metabolic pathways
H_2 partial pressure	Moderate	Strong	Can inhibit H_2-forming reactions
Residence time	Strong	Strong	Determines conversion extent

4. Comparative Evaluation and Performance Trade-offs of Biomass-to-Hydrogen Technologies

Biomass-to-hydrogen studies do not usually report their results on a common basis. Hydrogen yield may be given per gram of biomass, per gram of volatile solids, per mole of substrate, or per unit reactor volume, while some gasification studies report only the H_2 concentration in the product gas. Feedstock composition and reactor conditions also vary considerably. These differences make direct ranking of reported maximum values unreliable.

4.1. Hydrogen yield and productivity

Hydrogen yield is important, but it does not answer how quickly the process can deliver hydrogen. Thermochemical conversion generally benefits from rapid thermal decomposition and gas-phase reactions, and continuous gasification is therefore attractive when high throughput is required [5,13]. Catalyst-assisted systems can further improve hydrogen concentration by promoting reforming and water-gas shift reactions [14–16].

The situation is different for biological processes. The rate of hydrogen formation depends on microbial growth, substrate uptake, metabolic pathway, and hydrogen inhibition. Changes in the substrate can produce substantial differences in productivity. Continuous dark-fermentation experiments, for example, have shown that different sugars can support markedly different hydrogen-production rates under comparable operating conditions [18,24]. A relatively high substrate-specific yield is consequently not sufficient to judge whether a biological route can compete at reactor scale.

For practical comparison, yield and productivity should therefore be treated as complementary

indicators. Thermochemical systems generally have the advantage in throughput, whereas biological systems can become attractive when the feedstock is dilute, wet, or already part of a waste-treatment process.

4.2. Energy demand and process efficiency

The energy balance is strongly influenced by the physical state of the biomass. Drying is a relatively minor issue for dry agricultural or forestry residues, but it can become a major penalty when conventional gasification or pyrolysis is applied to wet materials. Hydrothermal gasification avoids this particular step by accepting wet feedstocks directly [6,17]. The associated high pressure means that the energy advantage cannot be assumed in every case, but it can become important for high-moisture resources.

Biological routes operate at much lower temperatures, yet this does not automatically make them the lowest-energy options. Longer retention times can require larger reactors, and pretreatment, pumping, mixing, illumination, gas recovery, and effluent treatment all contribute to the system energy demand [7,20]. A meaningful comparison should therefore be based on energy consumed per unit of recovered H_2 rather than simply on reaction temperature.

4.3. Environmental and economic considerations

Biomass residues and wastes can offer an environmental advantage because their conversion may provide both energy recovery and waste-management benefits. The picture becomes less favorable when long transport distances, intensive pretreatment, or external process heat are required. Life-cycle studies have also shown that the treatment of co-products can significantly affect the final environmental profile [3,32].

Carbon management is particularly relevant to biomass hydrogen. Chemical looping and CCS can lower net greenhouse-gas emissions, but both require additional equipment and energy. Wu et al. reported a negative net global warming potential for a chemical-looping biomass hydrogen system under their selected system boundary [28]. In contrast, techno-economic analysis has shown that incorporating CCS raises the levelized cost of hydrogen compared with corresponding non-CCS configurations [33]. The two findings are not contradictory; they illustrate the usual environmental–economic trade-off associated with carbon capture.

Hydrogen cost is also affected by factors that are sometimes overlooked in reactor-level studies. Feedstock collection and transport, drying, pretreatment, catalyst replacement, gas cleanup, hydrogen separation, and compression can all become important. An assessment of agricultural residues in Vietnam found that gasification, pyrolysis, and fermentation did not occupy the same position when technical, economic, and environmental criteria were evaluated together [9]. Similar conclusions have been reported in broader techno-economic assessments of biomass-derived hydrogen [34].

4.4. Technology maturity and feedstock matching

Technological maturity provides another useful basis for comparison. Conventional gasification benefits from a well-developed engineering base and extensive experience with syngas production and treatment. Pyrolysis–reforming is supported by mature thermal and catalytic technologies but still faces difficulties associated with complex bio-oils and catalyst lifetime. Hydrothermal gasification is attractive for wet biomass but requires high-pressure equipment and suitable materials [5,6].

Dark fermentation has a substantial research base but remains sensitive to substrate composition

and microbial stability. Photo-fermentation and photobiological routes face additional limitations from light utilization and biological control. MECs are less mature than conventional gasification, but their ability to combine wastewater treatment with hydrogen recovery gives them a distinct application niche [7,8,20–22].

The most appropriate technology therefore depends strongly on the feedstock. Dry lignocellulosic residues are often suitable for gasification or pyrolysis–reforming because little energy is needed for drying. Wet biomass such as algae and sludge may instead favor hydrothermal processing [6,17]. Carbohydrate-rich waste streams are promising substrates for dark fermentation, while VFAs produced during fermentation can provide additional feed for photo-fermentation or MECs [20,22]. Organic-rich wastewater is particularly well matched to MECs when hydrogen recovery and wastewater treatment are considered together. These relationships are summarized in Table 3.

The comparison suggests that there is no single biomass-to-hydrogen pathway that performs best across all conditions. Thermochemical routes tend to offer higher throughput and wider tolerance of solid feedstocks, while biological and bioelectrochemical systems can be more attractive for wet, dilute, or already-liquid organic resources. The most defensible basis for technology selection is therefore the match between feedstock characteristics and process requirements, with hydrogen yield considered together with productivity, energy demand, environmental performance, and cost.

Table 3. Feedstock-oriented selection of biomass-to-hydrogen conversion technologies.

Biomass/feedstock	Main characteristics	Suitable technologies	Main consideration
Dry lignocellulosic residues	Low moisture, high structural carbon	Gasification, pyrolysis–reforming	High productivity and thermal conversion
Wet biomass	High moisture	Hydrothermal gasification	Avoiding drying penalty
Carbohydrate-rich wastes	High biodegradable organic content	Dark fermentation	Substrate conversion and productivity
Fermentation effluents	Rich in VFAs	Photo-fermentation, MEC	Further recovery of residual organics
Organic-rich wastewater	Dilute organics, high water content	MEC	Combined treatment and H_2 recovery
Algal biomass	High moisture, photosynthetic origin	Hydrothermal, photobiological	Moisture and light utilization

The most meaningful question is consequently not which technology produces the largest hydrogen yield under optimized laboratory conditions. It is which route provides an acceptable balance of hydrogen recovery, production rate, energy consumption, carbon utilization, environmental performance, and cost for a specific biomass resource. This system-level perspective is particularly important when the feedstock itself has a waste-treatment value.

5. Challenges, Future Perspectives and Conclusions

Several barriers still separate laboratory-scale biomass-to-hydrogen research from large-scale implementation. Biomass composition varies considerably between sources, which complicates process control and limits direct transfer of results obtained with model substrates. Pretreatment, transportation, drying, catalyst replacement, and hydrogen purification can further increase the energy and economic burden. Thermochemical systems still need better control of tar and catalyst deactivation, while biological and bioelectrochemical processes face productivity, stability, and scale-up constraints[3–8].

Future research should therefore place greater emphasis on integrated biomass utilization. Cascade fermentation, pyrolysis–reforming, chemical looping, in situ CO_2 capture, and thermochemical–biological coupling offer ways of distributing biomass carbon among hydrogen

and other useful products[3,16,27,28,31–33]. Such approaches are unlikely to be universally superior, but they may provide better system-level performance when the conversion pathway is selected according to the feedstock.

Overall, biomass is best regarded as a complement to other low-emissions hydrogen routes rather than as a universal substitute for electrolysis. Its particular value lies in the possibility of combining hydrogen production with the utilization of agricultural residues, organic wastes, and other difficult-to-use resources. The long-term development of biomass-derived hydrogen will depend on matching feedstock characteristics with appropriate conversion technologies and evaluating energy use, environmental impact, economics, and carbon management from the outset. More consistent reporting of hydrogen yield, productivity, energy efficiency, carbon conversion, gas purity, and process stability will also be necessary for meaningful comparison across the field.

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