Review

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Renewable Hydrogen from Biomass: Technological Pathways and Economic Perspectives

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Abstract: Hydrogen is undoubtedly one of the most promising alternatives for generating energy with low environmental impact. However, most hydrogen produced today is derived from fossil fuels, which negatively impacts the environment. In this context, biomass conversion technologies emerge as a sustainable and environmentally friendly alternative to conventional fossil-based processes for hydrogen production. The main objective of this study is to underscore the potential of biomass-derived hydrogen, as one of the key sustainable energy solutions. This work reviews diverse biological and thermochemical pathways for biomass-derived hydrogen production, noting challenges in technology and feedstock diversity. Biomass offers local availability and economic benefits, potentially yielding negative emissions. Biological methods like bio-photolysis and fermentation promise low-energy, waste-recycling solutions despite operational constraints. Thermochemical processes, influenced by biomass type and energy content, favor economies of scale and conventional gasification for economic viability. Hydrothermal gasification shows promise for high-moisture feedstocks. Overall, while thermochemical processes suit centralized large-scale hydrogen production, biological pathways offer decentralized options, necessitating continued innovation for integration into future energy strategies.

Keywords: Renewable hydrogen; biomass; chemical methods; biological methods; membrane separation systems

1. Introduction

Growing global concern about issues related to energy security, energy availability, greenhouse gas (GHG) emissions, and climate change is leading governments around the world to establish programs that enable a transition to a low-carbon economy. In this sense, new strategies are being established and implemented to reduce the energy sector's carbon intensity on a global scale and achieve a robust industry with low or zero carbon emissions. However, despite these policies, fossil fuels are likely to remain an important part of the world's energy supply for decades to come, especially in emerging economies where access to cheap and reliable energy is essential to keep up with their technological and social progress [1]. The cheapest form of energy production is based on burning fossil fuels, which generates significant CO_2 emissions. Hydrogen (H_2) is an alternative to fossil fuels that has the potential to assist in the achievement of carbon neutrality. Hydrogen only emits water when burned, but depending on how it is produced, it may or may not be considered carbon neutral [2]. In this context, hydrogen has gained projection on the European and international agenda as a key factor in facilitating the European Union's (EU) transition towards climate neutrality by 2050 and reducing its dependence on fossil fuels. Many consider hydrogen to be a transformative factor revolutionizing the energy system[3].

The hydrogen economy is defined as a new industry that depends on hydrogen as a commercial fuel [4]. Large-scale hydrogen production using available sustainable energy sources can replace the current fossil fuel-based energy economy. This transition involves the simultaneous development of hydrogen production, storage, transportation, and distribution, needing strategic political support. In the long term, hydrogen can reduce energy consumption and emissions while stimulating economic growth and creating new employment opportunities. This vision can become a reality if hydrogen can be produced economically and environmentally from renewable energy sources [3].

There are several types of hydrogen, classified based on the energy source and production process. A color code system is currently used to categorize H_2 according to its production method (Figure 1) [5,6].

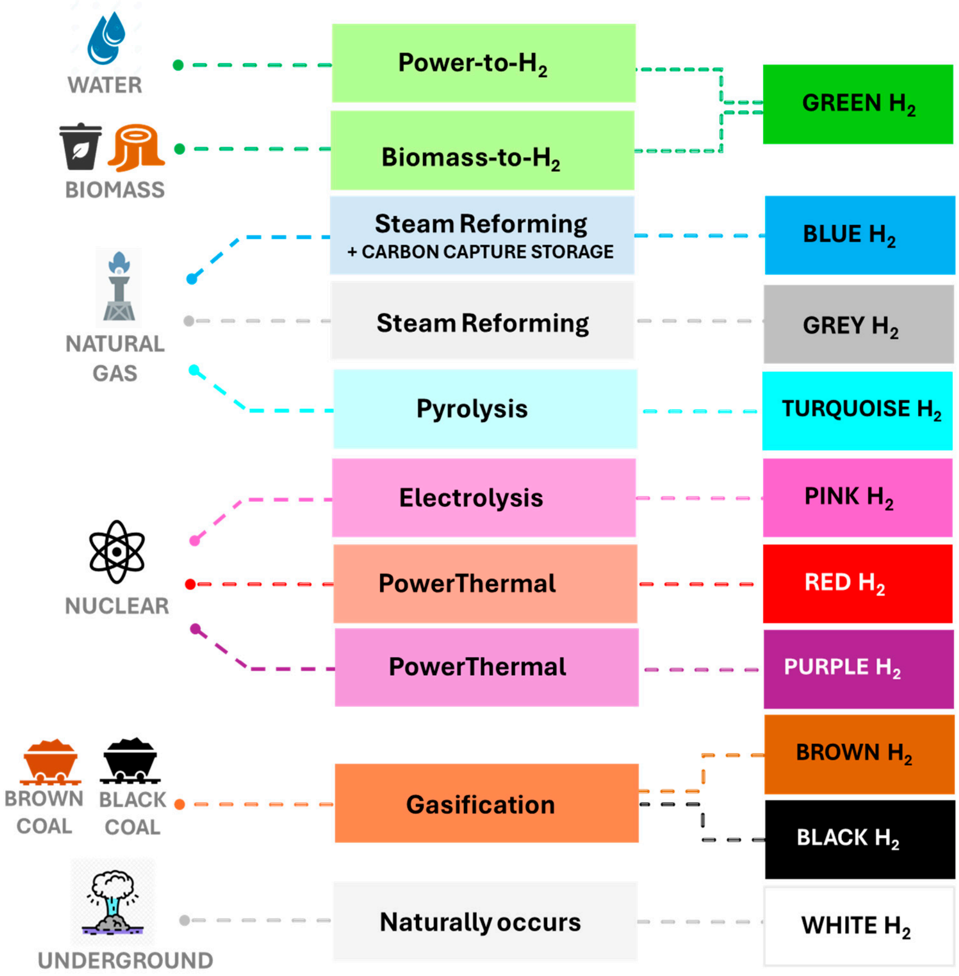

Figure 1. The main color codes of hydrogen, considering the type of energy and technology operated for its production process.

Gray hydrogen is produced by steam reforming, partial oxidation, or gasification of fossil fuels such as natural gas, oil, and coal. This is the most widely used method to produce hydrogen, accounting for 95 % of world production in 2020 [7]. Blue hydrogen is produced in the same way as gray hydrogen, but carbon capture technology is used to prevent the release of carbon dioxide into the atmosphere. The captured carbon dioxide represents between 85 % and 95 % of the total produced and is stored underground using industrial carbon capture and storage techniques, but some of the generated carbon dioxide cannot be captured. Although this form of hydrogen production reduces the environmental impact of carbon dioxide capture, the long-term impacts of storage are uncertain, and leakage can still negatively affect the environment and climate in the future [5]. As its name suggests, renewable hydrogen (renewable-H_2) is the cleanest form of hydrogen with zero carbon emissions, produced from renewable sources such as water, biomass, and others, using energy from renewable sources such as wind, solar, and hydro [8]. White hydrogen, also known as geological or natural hydrogen, refers to molecular hydrogen that forms and accumulates naturally on Earth. This hydrogen is generated primarily through a geochemical process known as serpentinization. Recent studies have confirmed the presence of vast geological formations where hydrogen has accumulated over time. For this reason, white hydrogen is being considered another promising source of hydrogen, with a key role in the planet's energy transition [9].

Clean hydrogen is essential for a sustainable industrial policy, as outlined in the European Green Deal. It is considered a fundamental factor in accelerating the elimination of fossil fuels and ensuring economic and social well-being. The Hydrogen Strategy for a Climate Neutral Europe, adopted in 2020 by the European Commission, encompasses the entire hydrogen supply chain with the aim of creating favorable conditions to increase supply and demand, improve industrial competitiveness, and ensure the energy security in the European Union (EU) [10]. This was also emphasized in the REPowerEU plan, which set ambitious targets to increase hydrogen production from renewable sources to 10 million tons of annual domestic production and an additional 10 million tons of annual imports by 2030 [11].

Currently, the most widely used method to produce renewable-H_2 is water electrolysis using electricity from renewable sources. Nevertheless, there are several other possible pathways for renewable-H_2 production, including biological methods (e.g., bio-photolysis, photo-fermentation, dark fermentation, and a hybrid strategy that combines dark fermentation and photosynthetic activities) and thermochemical methods (e.g., gasification, pyrolysis, and hydrothermal processes) [8,12].

Several reviews have been published in the scientific literature over time, which have allowed the global community to follow the advances in renewable-H_2 production. For instance, Akhlaghi and Najafpour-Darzi [12] discussed the production of hydrogen through biological processes, including the used microorganisms, the type of substrates and their concentrations, the role of chemical addition, and operating conditions (temperature, pH, and agitation). Previously, the biological methods of renewable-H_2 production were also studied by Mudhoo et al. [13] and Singh et al.[14]. These studies represented important scientific contributions to our understanding of the biological processes involved in hydrogen production. Renewable-H_2 production processes by thermochemical methods have also been reviewed. Chong et al. [15] discussed the steam reforming of liquid biomass residues and biomass-derived oxygenates. Other studies analyzed the production of renewable-H_2 from biomass by pyrolysis [16–20], gasification [21–25] and supercritical water gasification [26–29]. Moreover, production methods of renewable-H_2 using biomass and its derivatives as raw material were also studied. Pal et al. [8] presented an extensive study on the technologies available to produce hydrogen derived from biomass. In the same framework, Shahbaz et al.[30] discussed biomass processing and conversion technologies to produce hydrogen and analyzed membrane hydrogen separation systems.

Despite the significant number of available scientific literature, there is still a need to address the operating principles of renewable-H_2, as well as the technical-economic viability of each production method. This review aims to give a contribution by providing an analysis of hydrogen production from biomass by biological and thermochemical methods, the main production pathways from both methods, process parameters and their influence on hydrogen yield, advantages and challenges for each method, and an overview on techno-economic and life cycle aspects in each hydrogen production methodology.

2. Type of Biomass Used in Renewable-H_2 Production

According to the United Nations Framework Convention on Climate Change (UNFCCC) [31], the term "biomass" refers to non-fossilized and biodegradable organic materials derived from plants, animals, and microorganisms. This includes by-products, residues, and waste from agriculture, forestry, and related industries, as well as non-fossilized and biodegradable organic fractions of industrial and municipal waste. Biomass also encompasses gases and liquids obtained from the decomposition of non-fossilized and biodegradable organic matter. Nowadays, biomass is an increasingly important renewable feedstock for hydrogen production. There are significant amounts of biomass available that can be utilized for this purpose, and biomass can be classified into six types based on its origin, according to Figure 2.

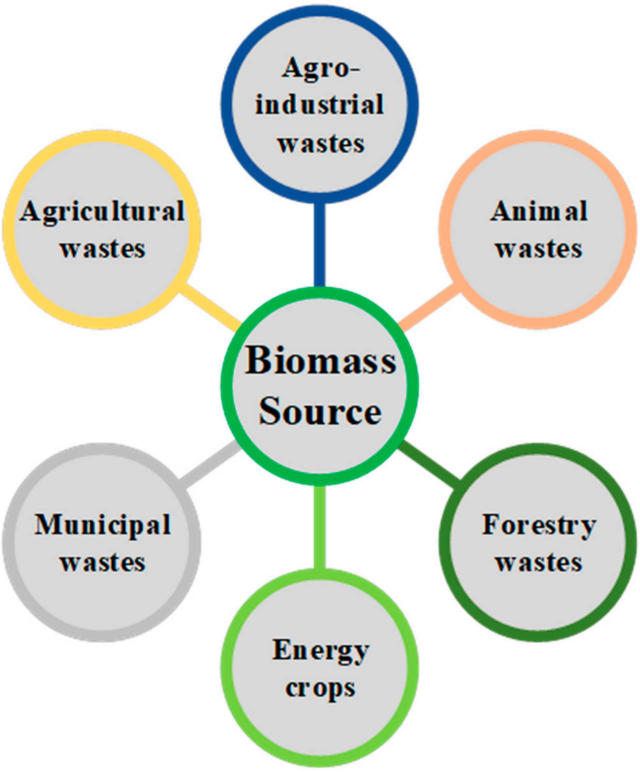

Figure 2. Types of biomass with potential to be used in renewable-H_2 production.

Agricultural waste encompasses straw, husk, stems, leaves, seeds, and other by-products derived from various crops such as corn, rice, wheat, and others. Typically, these wastes persist in the fields post-harvest. Agro-industrial waste primarily results from the industrial processing of various agricultural crops, including wheat, corn, rice, soybeans, barley, rapeseed, sugar cane, sugar beet, olive, among others. Annually, approximately 3.3 Gt/year of agricultural waste is generated, with China, the United States, Brazil, and India being its main producers. Some of this waste is utilized as animal feed, and others are employed in energy generation, albeit with low efficiency. The considerable abundance and availability of agricultural waste hold significant potential to update energy markets and gradually replace fossil fuels [32,33].

Forest wastes consist of branches, leaves, bark, and other wood fragments. Lignocellulosic biomass generally comprises 35-55 % cellulose, 25-40 % hemicellulose, 15-25 % lignin, 2-16 % ash, and a lower proportion of extracts and proteins. Most woody biomass, without foreign matter such as "dirt" (leaves and needles), has an ash content of less than 2 %, while agricultural and agro-industrial waste can contain up to 20 %. In terms of elemental composition, forest wastes tend to exhibit slightly higher amounts of carbon and hydrogen compared to agricultural and agro-industrial wastes. The heating value of these wastes can vary between 8-20 MJ/kg, depending on the ash and moisture contents [32,34].

Animal waste comprises excrement, urine, hair, feathers, blood, fur, etc. These wastes pose a source of pollution, unpleasant odors, and a threat to health. Thus, relevant regulations order the adoption of appropriate management methods. An effective technique is anaerobic digestion, which yields biogas as a potential source for green hydrogen production or electricity production in power plants or internal combustion engines (ICE) [35].

Energy crops are cultivated specifically to provide biomass and fall into two categories: herbaceous and woody. Herbaceous energy crops, such as switchgrass, miscanthus, bamboo, sweet sorghum, and others, are perennial grasses that are harvested annually after two to three years establishment period to achieve full productivity. On the other hand, short-rotation woody crops, including hybrid poplar, eucalyptus, hybrid willow, silver maple, and others, are fast-growing hardwood trees that can be harvested five to eight years after planting. The cultivation of these species can lead to improvements in water and soil quality, enhancement of wildlife habitats, diversification of income sources, and overall increase in agricultural productivity compared to annual crops [35,36].

Municipal solid waste (MSW) constitutes a heterogeneous mixture, encompassing household waste, in addition to tree prunings, garden waste, and other miscellaneous residues. Usually, MSW consists of 61.3 % organic material, 16.3 % plastic, 11.4 % refuse-derived fuel (RDF), and 3.7 % recyclable materials. Its organic fraction presents an average composition that includes carbohydrates (41-62 %), proteins (15-25 %), and lipids (13-30 %), which can be effectively converted into eco-friendly biofuels and value-added products [37]. According to a study by Khan et al.[38], the annual generation of MSW is estimated to be approximately 2,010 million tons, with 33 % of this volume remaining unmanaged. This proportion is anticipated to increase in the coming years, particularly in developing countries, posing a significant challenge to environmental sustainability. Consequently, there is an urgent requirement for the implementation of effective strategies to address the escalating growth of MSW on a global scale [39]. Table 1 shows the lignocellulosic and elemental composition of examples of biomass wastes from each of the above-mentioned types.

Table 1. Lignocellulosic composition and elemental analysis of various biomass wastes fitting into the types of biomass with potential to be used in renewable-H_2 production.

Feedstock	**Lignocellulosic composition and elemental analysis (wt.% dry basis)**								**Ref.**
	CE	**HCE**	**LIG**	**A**	**C**	**H**	**N**	**S**	
	Agricultural and agro-industrial wastes								
Cornstalk	45.1	29.7	5.7	4.0	41.6	5.5	1.1	---	[40]
Barley straw	46.0	23.0	15.0	4.3	44.7	6.3	0.5	0.6	
Cypress	43.2	26.3	28.2	2.3	48.9	6.0	0.3	---	
Corn straw	30.8	25.5	16.8	7.0	44.6	5.5	0.9	0.1	
Peanut straw	36.6	20.3	18.4	13.1	41.4	5.5	1.3	0.2	
Sugarcane bagasse	46.5	36.4	19.0	1.2	44.8	6.1	2.6	0.7	[41]
Blackcurrant pomace	17.4	8.9	30.9	4.5	50.3	6.8	1.9	0.2	
Bagasse	41.3	23.7	25.6	6.2	43.2	5.5	0.5	---	
Salad dressing	---	---	---	4.9	65.6	10.0	1.0	---	
Vegetable	---	---	---	2.4	44.6	6.4	2.2	---	
Soybean straw	42.4	22.1	18.9	4.4	46.0	6.1	1.4	0.1	
Rice straw	46.3	31.1	10.2	15.1	41.3	5.3	1.1	0.1	[42]
Paulownia	42.4	25.2	23.4	---	45.5	6.3	---	---	
Litsea cubeba seeds	---	---	---	6.4	59.6	9.3	1.7	---	[43]
Forestry wastes									
Furniture Sawdust	32.6	37.2	22.2	0.8	47.4	5.7	0.2	---	[42]
RFB from eucalyptus	---	---	---	1.2	49.7	6.5	0.07	---	
Pine sawdust	---	---	---	0.8	50.4	5.8	0.2	0.03	
Pistachio shell	---	---	---	0.3	50.0	5.9	0.4	0.10	
RFB from pine	---	---	---	1.2	51.4	6.6	0.2	0.01	[44]
Rubber woodchip	---	---	---	1.1	46.4	5.7	0.2	---	
Sawdust	---	---	---	1.8	51.3	6.1	0.1	0.02	
Softwood pellets	---	---	---	0.6	54.6	5.8		0.03	
Animal wastes									

Swine manure	15.1	19.9	0.9	22.3	33.5	6.2	2.8	---	
Cattle manure	---	---	---	7.2	35.4	4.7	2.4	---	
Broiler manure	21.3	19.5	1.4	34.7	29.9	3.8	2.7	---	[41]
Beef	---	---	---	2.3	61.3	9.3	6.2	---	
Chicken	---	---	---	4.7	45.9	6.9	12.6	---	
Swine manure	12.2	34.0	5.4	17.1	49.7	6.8	4.7	---	
Dairy manure	17.1	18.1	5.2	38.5	50.6	6.7	2.5	---	
Beef manure	30.1	26.7	10.8	43.0	54.5	6.6	3.4	---	[45]
Laying hen manure	31.1	34.3	2.4	38.0	52.9	6.7	4.1	---	
Sheep manure	20.9	19.2	3.8	28.9	51.7	6.5	3.6	---	
MSW and industrial wastes									
Sewage sludge	---	---	---	39.2	43.4	5.9	3.2	---	[41]
Dewatered sewage sludge	0.3	4.1	18.0	41.8	25.6	4.4	4.6	0.15	
Pulp/paper sludge	---	---	---	15.0	45.6	5.2	7.2	1.70	
Activated sludge	---	---	---	23.6	38.0	5.2	7.2	0.75	
Municipal sludge	---	---	---	22.9	36.9	5.3	3.7	---	[46]
Refinery oily sludge	---	---	---	27.8	42.7	5.4	4.1	1.23	[47]
Portugal MSW	---	---	---	14.9	48.0	6.3	1.4	0.7	[48]
Brazil MSW	---	---	---	14.3	49.7	7.2	0.8	0.7	

Abbreviations: Cellulose (CE), Hemicellulose (HCE), Lignin (LIG), Carbon (C), Hydrogen (H), Sulfur (S), Nitrogen (N), Volatile matter (VM), Fixed carbon (FC), moisture (M), and ash (A) contents. Residual Forestry Biomass (RFB).

3. Methods for Renewable- H_2 Production from Biomass

Despite hydrogen being the most abundant element in the universe and being widely distributed on our planet, it is not directly available in its pure form. Instead, it is typically bound to other chemical elements, and separating it requires energy-intensive conversion processes that generally cannot be accomplished in a single step. This is especially true for feedstocks derived from biomass, where the hydrogen must be separated from the other constituent elements. Essentially, two methods are used to separate the hydrogen from biomass, biological and thermochemical, as depicted in Figure 2. In this work, “renewable-H_2” encompasses biohydrogen from microorganisms as well as hydrogen produced via thermochemical conversion of biomass, so all biomass-derived hydrogen production technologies.

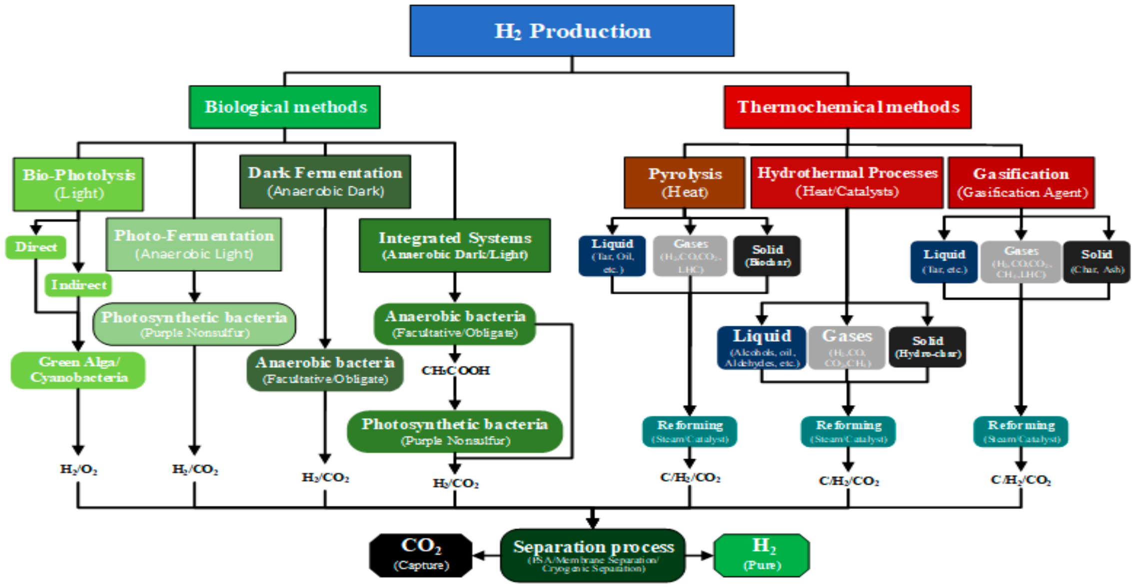

Figure 2. Schematic diagram of the technological routes for the conversion of biomass into hydrogen.

3.1. Biological Methods

Hydrogen production by biological methods entails using microorganisms to produce hydrogen through metabolic processes such as fermentation or photosynthesis and is generally classified as a light-dependent or light-independent process [49]. Light-dependent methods include photo-fermentation and bio-photolysis (direct or indirect) using algae or microalgae, while dark fermentation takes place in a light-independent process using bacteria [48]. Hydrogen production from algae, microalgae, and bacteria has the advantage of producing high yields at low temperatures (usually between 20 and 45 °C) and low cost compared to other production methods [50]. However, some secondary reactions that normally accompany the production of hydrogen, such as oxygen generated in photosynthesis and organic acids from the decomposition of organic compounds, inhibit hydrogen production and consequently lower yields [51,52]. Integrated systems, such as co-fermentation and photo-fermentation, provide possible solutions to these problems and constitute alternative methods for sustainable hydrogen production, increasing efficiency, as well as the production rate and hydrogen yield [52]. Bio-photolysis (direct or indirect), photo-fermentation, dark fermentation, and integrated systems will be described in the following sections.

3.1.1. Bio-Photolysis

The hydrogen production via bio-photolysis is primarily based on photosynthetic oxygenic microorganisms, including green microalgae (*e.g., Chlamydomonas reinhardtii, Chlorella vulgaris, Scenedesmus obliquus, and Chlorococcum minutum*) and cyanobacteria (*e.g.,Nostoc* sp., *Cyanothece* sp.) [53–58]. These microorganisms use solar energy to drive water-splitting photosynthesis and transfer high-energy electrons to generate hydrogen, utilizing the enzyme hydrogenase as a catalyst [59].

Bio-photolysis directs the reductants produced by splitting water for the evolution of hydrogen without entering the Calvin cycle or pentose phosphate pathway, which involves photochemical oxidation in the thylakoid membrane of algae and cyanobacteria. In these organisms, light-absorbing pigments are organized into two functional assemblies: photosystems (PS) I and II. Under anaerobic conditions or when the system absorbs a lot of energy, certain microorganisms direct excess electrons to hydrogenase, converting proton (H+) ions into renewable-H_2. The electrons and protons generated in the process can be recombined to form 98 % pure renewable-H_2 using the chloroplast enzyme dehydrogenase. Bio-photolysis is classified into direct bio-photolysis (DbP) and indirect bio-photolysis (i-DbP) [60].

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In the context of DbP, photoautotrophic organisms employ the catalytic activity of the enzyme hydrogenase to convert water molecules into molecular hydrogen and oxygen under anaerobic conditions, utilizing light absorbed by PSII. These organisms harness light energy to extract electrons and protons from water molecules. Subsequently, these extracted electrons and protons are used to reduce ferredoxin (Fd) and nicotinamide adenine dinucleotide phosphate (NADP) [61]. The general reactions characterizing DbP are outlined below in equations 1 and 2.

$$H_2O\ Light \rightarrow\ 2H^+ + 2e^- + \frac{1}{2}O_2\ \ (1)$$

$$2H^+ + 2e^-\ \ \ Hydrogenase\ \ \ \leftrightarrow\ \ 2H_2\ \ (2)$$

i-DbP is a two-step process in which cyanobacteria and microalgae produce hydrogen and oxygen in separate reactions. In the first step, carbohydrates are synthesized using light energy, carbon dioxide is fixed, and oxygen is produced. In the second step, hydrogen is produced from the synthesized carbohydrates using cell metabolism under anaerobic conditions [62]. Cyanobacteria are preferred for i-DbP because of their ability to use the enzymes nitrogenase and hydrogenase for hydrogen evolution, while microalgae rely solely on hydrogenase. Nitrogenase has the advantage of acting unidirectionally, while hydrogenase acts bidirectionally. The general reaction for the formation of hydrogen by cyanobacteria can be represented by the following equations [12]:

$$6CO_2 + 6H_2O\ Light \rightarrow\ C_6H_{12}O_6 + 6O_2\ \ (3)$$

$$C_6H_{12}O_6 + 6H_2O\ Light \rightarrow\ 12H_2 + 6O_2\ \ (4)$$

The i-DbP begins when cyanobacteria fix carbon dioxide and use sunlight to produce cell substances and oxygen [63]. NADPH generated during metabolism is transferred to the plastoquinone pool (PQ) and PSII. The electrons produced by PSII are transported by ferredoxin through PSII and PSI to hydrogenase. Hydrogenase then catalyzes the reaction where H+ is converted into renewable-H_2 [62]. Nitrogen (N_2) fixation is performed by the hydrogenase uptake composed of small (hupS) and large (hupL) subunits. The hydrogen produced by nitrogenase can be reabsorbed by H_2-capturing hydrogenase, while simultaneously, oxygen is removed by nitrogenase. This process protects O_2-sensitive enzymes and indirectly improves hydrogen production. Some filamentous cyanobacteria, such as *Anabaena*, *Calothrix*, and *Nostoc*, have developed heterocysts, which are micro-anaerobic environments that aid in nitrogen fixation and can enhance hydrogen production [64]. Table 2 summarizes some works using bio-photolysis to H_2 production.

Table 2. Summary of relevant works using bio-photolysis for hydrogen production.

Microorganism	Substrate	Operating conditions	Hydrogen yield	Ref.
Chlorella sp.	30 mM glucose	Temp.: 25-42 °C; Light intensity: 120 µmol/m²/s; Incubation time: 70 h; pH: 8.6; Medium: MA; Reactor type: serum bottle reactor.	140-160 (mL/L)	[65]
C. vulgaris	Crude glycerol	Temp.: 30 °C; Light intensity: 48 µmol/m²/s, Incubation time: 72 h; pH: 6.8; Medium: Modified TAP; Reactor type: 1 L bioreactor	11.65 (mL/L)	[66]
C. reinhardtii	-	Temp.: 25 °C; Light intensity: 200 µmol/m²/s; Incubation time: 140 h; pH: 7.2; Medium: TAP; Reactor type: 250 mL Erlenmeyer flasks	225 (mL/L)	[67]
C. vulgaris	Corn stalk	Temp.: 30 °C; Light intensity: 108 µmol/m²/s; Incubation time: 144 h; pH: 7.0; Medium:	220 (mL/L)	[68]

		Modified BG-11; Reactor type: 500 mL bioreactor		
C. *sorokiniana*	Acetate	Temp.: 30 °C; Light intensity: 120 μmol/m²/s; Incubation time: 222 h; pH: 7.2; Medium: BG-11; Reactor type: 500 mL Erlenmeyer flasks	147 (mL/L)	[69]
C. reinhardtii	Starch	Temp.: 28 °C; Light intensity: 50 μmol/m²/s; Incubation time: 144 h; pH: 7.5; Medium: TAP-C; Reactor type: 500 mL Erlenmeyer flasks	118 (mL/L)	[70]
P. boryanum	DCMU	Temp.: 22 °C; Light intensity: 50 μmol/m²/s; Incubation time: 188 h; pH: 7.5; Medium: 0.5 mM N; Reactor type: Roux bottle	115 (mL/L)	[71]
C. reinhardtii	-	Temp.: 24 °C; Light intensity: 60 μmol/m²/s; Incubation time: 204 h; pH: 7.2, Medium: TAP-S; Reactor type: 500 mL Duran glass bottles.	61.7 (mL/L)	[72]
Anabaena sp.	Glucose	Temp.: 24 °C; Light intensity: 4400 lux; Incubation time: 156 h; pH: 9.2; Medium: BG-11, Reactor type: 500 mL Duran glass bottles.	13.15 (mmol H_2/mg Chla)	[73]
Arthrospira sp.	0.10 % glucose	Temp.: 30 °C; Light intensity: 40 μmol/m²/s; Incubation time: 156 h; pH: 9.0; Medium: ZN_0.	3.61 (μmol H_2/mg Chla/h)	[74]
Chlamydomonas sp.	-	Temp.: 24 °C; Light intensity: 60 μmol/m²/s; Incubation time: 372 h; pH: 7.2; Medium: TAP-S; Reactor type: 500 mL Duran glass bottles.	9.23 (μmol H_2/mg Chla/ h)	[75]

Abbreviations: Tris-Acetate-Phosphate (TAP), Blue-Green (BG), 3-(3,4-dichlorophenyl)-1,1-dimethylurea (DCMU).

The optimization of operational conditions is essential for increasing hydrogen production through bio-photolysis using microalgae or cyanobacteria. Table 3 summarizes the main factors that affect hydrogen yield from bio-photolysis.

Table 3. Summary of the main parameters affecting hydrogen yield in bio-photolysis.

Parameters	Effect on renewable-H_2 yield
Temperature	• The optimum temperature for hydrogen production varies markedly among the species. • Highest hydrogen yields for cyanobacteria occur between 30-40 °C but some strains demonstrate highest production at a lower temperature range (20-25 °C) [76,77].

pH	• Hydrogen production by cyanobacteria showed the highest yield at pH 8.0, with acidic pH (4.5) reducing hydrogen production by 83 %. The optimal pH range for maximum hydrogen production across most species is between 6.0 and 8.0 [76]. • Hydrogen production was considerably reduced at an initial acidic pH (5.0) and increased progressively in alkaline conditions, reaching maximum yield at pH 9.0 [76].
Oxygen content	• Oxygen in the medium inhibits renewable-H_2 production by the enzyme hydrogenase, with production ceasing when oxygen concentration fully inactivates the catalytic process [78]. • Simultaneous oxygen and hydrogen production requires the removal of oxygen from the medium to ensure process efficiency [78].
Light intensity	• Hydrogen production by *C. reinhardtii* showed that the yield increased progressively from 60 to 200 μE m^{-2} s^{-1}, reaching the highest production. Increasing the light intensity to 300 μE m^{-2} s^{-1} demonstrated a light saturation with decrease in hydrogen production [67].
Nitrogen and sulfur limitation	• The continuous hydrogen production from cyanobacteria was reported to reach the highest yield in nitrogen and sulfur deprivation [74]. Sulfur privation leads to an anaerobic environment enhancing the ability of microalgae to produce hydrogen [79].
Organic carbon	• Organic carbon sources improve the growth of the mixotrophic cyanobacteria and help to produce hydrogen by promoting an anaerobic environment adequate to reach higher process efficiency [73].
Cell density and culture age	• High cell density in the photobioreactor limit the light supply per cell, decreasing photosynthesis and increasing respiration. Even younger cultures having less biomass, show higher hydrogen production due to the exponential phase cells that are more metabolically active compared to the older ones [73].

3.1.2. Fermentation

In photo-fermentation, hydrogen is generated during the degradation of organic compounds by photosynthetic bacteria, primarily purple non-sulfur bacteria (e.g., *Rhodobacter sphaeroides, Rhodobacter capsulatus, Rhodobacter sulfidophilus, Rhodopseudomonas palustris*, and *Rhodospirillum rubrum*), which are known as PNS bacteria. This process is catalyzed by nitrogenase with the help of light energy [80]. The organic substrates are metabolized through the tricarboxylic acid (TCA) cycle (also known as the citric acid cycle), which provides the necessary reducing power and carbon intermediates for hydrogen production [81]. Hydrogen production by PNS bacteria via the TCA cycle follows a series of biochemical steps: Initially, the carbon substrate undergoes oxidation to produce carbon dioxide, H^+ ions, and electrons. These electrons are then transferred to nitrogenase, facilitated by the oxidation/reduction of electron carriers such as NAD(P)H and ferredoxin (Fd). Simultaneously, ATP required for nitrogenase activity is generated by PSI in the photosynthetic membrane, utilizing light energy, and through ATP synthase. Subsequently, nitrogenase reduces protons (H^+) to produce molecular hydrogen (H_2). Additionally, uptake hydrogenase enzymes play a role in the metabolism by catalyzing the conversion of hydrogen back into electrons and protons under certain conditions [12]. Notably, one molecule of hydrogen is produced per molecule of nitrogen fixed during ammonia production [82], as seen in equation 5.

$$N_2 + 8e^- + 8H^+ + 16ATP \rightarrow 2NH_3 + H_2 + 16ADP + 16P_i \quad (5)$$

In the absence of nitrogen, nitrogenase loses its ability to fix nitrogen and instead catalyzes an alternative reaction that produces hydrogen, as shown in equation 6.

$$N_2 + 8e^- + 8H^+ + 16ATP \rightarrow 4H_2 + 16ADP + 16P_i \quad (6)$$

Under these conditions, PNS bacteria typically utilize organic acids such as acetic acid ($C_2H_4O_2$), butyric acid ($C_4H_8O_2$), or lactic acid ($C_3H_6O_3$) to generate hydrogen [83]. They can also utilize monosaccharides such as glucose and polysaccharides such as starch for hydrogen production [63]. However, this reaction requires a significant expenditure of intracellular energy in the form of ATP molecules. While this process is energetically demanding, it is highly efficient for hydrogen production since all available protons can be converted to renewable-H_2 [82].

The efficiency of photo-fermentation in the production of hydrogen is influenced by various factors, including anaerobic conditions, light intensity, temperature, pH, wavelength, substrate concentration, and type. Nitrogenase is highly sensitive to oxygen and is irreversibly inactivated by it [82]. Thus, maintaining anaerobic conditions by excluding oxygen from the reaction environment enhances hydrogen production [12]. To achieve efficient hydrogen production, it is necessary to maintain the temperature between 31-36 °C, light intensity between 6-10 klux, optimal pH between 6.8-7.5, and a wavelength range between 400-1000 nm. Another critical factor is the concentration and type of substrate [84]. Studies indicate that PNS bacteria exhibit higher hydrogen production rates with fatty acid substrates, such as short-chain fatty acids and volatile fatty acids (e.g., acetate, butyrate, lactate, malate, etc.), while hydrogen production is low for sugar substrates [55,56].

Dark fermentation primarily uses anaerobic microorganisms (e.g., Enterobacter cloacae, Escherichia coli, Klebsiella pneumoniae, Bacillus subtillis – facultative anaerobes; and Clostridium butyricum, Clostridium acetobutylicum, Clostridium thermocellum and Thermoanaerobacterium thermosaccharolyticum – strict anaerobes) in the absence of light, typically at mesophilic temperatures (between 25-45 °C) or thermophilic temperatures (45-80 °C), and sometimes at extreme thermophilic temperatures (> 80 °C) . In addition to hydrogen, other gases such as carbon dioxide, carbon monoxide, and hydrogen sulfide can be released under these conditions. A primary source of hydrogen is the glucose molecules present in carbohydrates and other feedstocks [85].

The hydrogen yield and effluent composition from dark fermentation are highly dependent on the metabolic pathways used by microorganisms. The first pathway, used by facultative anaerobes, involves pyruvate formate lyase (PFL). The second pathway, used primarily by strict anaerobes, involves pyruvate ferredoxin oxidoreductase (PFOR) [86]. During hydrogen production via glucose, complex compounds are first hydrolyzed into simpler molecules like glucose. This glucose is then anaerobically degraded to produce NADH, pyruvate, and ATP [87]. In the PFL pathway, pyruvate is converted to formate and acetyl-CoA with the help of coenzyme A (CoA-H). Formate is then oxidized to carbon dioxide and hydrogen either via the formate-H_2 lyase (NiFe-hydrogenase) pathway or a formate-dependent [FeFe] hydrogenase pathway. In the PFOR pathway, pyruvate is broken down to produce reduced ferredoxin and acetyl-CoA, facilitated by ferredoxin oxidase and CoA-H. Reduced ferrodoxin is then oxidized while producing hydrogen through a ferredoxin-dependent hydrogenase (Fd-[FeFe]) [88]. Additionally, hydrogen can be produced using NADH through the reduction of ferredoxin, the reduction of a hydrogenase (NADH-[FeFe]), or the oxidation of NADH by Fd-NADH-[FeFe]. Acetyl-CoA can be further converted into acetic acid, butyric acid, or ethanol using NADH, resulting in various dark fermentation liquid effluents. Other liquid effluents, such as propionate, butanol, and lactate, can also be produced [87].

Theoretical yield of renewable-H_2 produced through dark fermentation is 4 mol H_2/mol $_{glucose}$, with acetic acid as the final product. However, this yield is reduced to 2 mol H_2/mol $_{glucose}$ when butyric acid is the final product, as indicated by the reactions shown in equations 7 and 8 [62,63].

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2C_2H_4O_2 + 4H_2 + 2CO_2 \quad (7)$$

$$C_6H_{12}O_6 \rightarrow C_4H_8O_2 + 2H_2 + 2CO_2 \quad (8)$$

Under anaerobic conditions, the thermodynamics of acid formation favors the production of both acetic and butyric acids, resulting in their presence among the metabolites of the final dark fermentation product. Therefore, the hydrogen yield is always less than 4 mol H_2/mol $_{glucose}$ [87].

Table 4 summarizes works on hydrogen production using both photo- and dark fermentation, highlighting used inocula, substrates, main operating conditions and maximum hydrogen yields.

Table 4. Summary of relevant works using photo- and dark fermentation for hydrogen production.

		Photo-fermentation		
Inoculum	**Substrate**	**Operating conditions**	**Max. cumulative hydrogen yield**	**Ref.**
C. butyricum and *R. palustris*	Rice straw	Temp.:30 °C; pH 7.0; Light intensity: 6000 lux	463 (mL H_2/g $_{VS}$)	[89]
R. pseudopalustris DSM 123	Tequila vinasses	Temp: 30 °C; pH 7.0; Light intensity: LED lamp (13.5 W/m^2); Inoculum: 3.3 g/L cell suspension	260 (mL H_2/L)	[90]
HAU-M1 (*R. sphaeroides* (9 %), *R. palustris* (28 %), *R. rubrum* (27 %), *R. capsulata* (25 %) and *R. capsulatus* (11 %)	Corn stover	pH 7.0; Light intensity: 3000 lux; Inoculum:30 % 150 mg/g $_{TS}$; TiO_2/Activated carbon fiber addition of 100 mg/ L	74.0 (mL H_2/g $_{TS}$)	[91]
		Temp.= 30 °C; pH 7.0; Light intensity: 3000 lux; Substrate concentration: 25 g_{DM}/L,	68.4 (mL H_2/g $_{DM}$)	[92]
R. sphaeroides NCIMB8253	Combination of palm oil (25%, v/v), pulp and paper (75%, v/v) mill effluents	Temp.: 30 °C; Light intensity: 7000 lux; Combined substrate (25 vol.% POME and 75 vol.% PPME)	14.4 (mL H_2/mL $_{medium}$)	[93]
		Dark fermentation		
Inoculum	**Substrate**	**Operating conditions**	**Max. cumulative hydrogen yield**	**Ref.**
Sludge from an anaerobic digester of a wastewater treatment plant	Food waste	Temp.: 35 °C; pH 5.3; HRT: 36 h	0.900 (mol H_2/mol $_{substrate}$)	[94]
Escherichia coli XL1-Blue/*Enterobacter cloacae* DSM 16657	Beverage wastewater	Temp.: 37 °C; pH 6.5	0.259 (mol H_2/mol $_{substrate}$)	[95]
Fermentative consortium MC 1 (mostly Firmicutes and Bacteroidota phyla)	Food waste + Fe-modified biochar	Temp.: 55 °C; pH 7.0; Inoculation ratio: 10 vol.%	74.9 (mL H_2/g $_{VS}$)	[96]
Inoculum sourced from activated	Corn stover + thermally	Temp.: 35 °C	82.4 (mL H_2/g $_{TS}$)	[97]

sludge from a wastewater treatment facility	modified maifanite			
Anaerobic granules collected from an anaerobic digester of a wastewater treatment plant	Cassava processing wastes (cassava pulp and cassava processing wastewater)	Temp.: 35 °C; pH 6.0; HRT: 132 h	225.2 (mL H_2/g VS)	[98]
Anaerobically digested sludge, collected from a primary anaerobic digester	Pruning wastes + food-rich MSW	Temp.:37 °C; pH 5.0 and 7.0; HRT: 72 h	84.0 (mL H_2/g VS)	[99]
Granular sludge from an upflow anaerobic sludge blanket treating papermaking wastewater	Corn straw + excess sludge	Temp.= 35 °C; pH 7.0; HRT: 17 days	101.8 (mL H_2/g VS)	[100]
Anaerobic sludge obtained from an anaerobic digester	Swine manure + food waste	Temp.= 35 °C; pH from 5.5 to 6; HRT: 4 days	275.6 (mL H_2/g VS)	[101]

Abbreviations: Volatile Solids (VS), Dry Matter (DM), Total Solids (TS), Palm Oil Mill Effluent (POME), Pulp and Paper Mill Effluent (PPME), Hydraulic Retention Time (HRT).

The maximum production of hydrogen through photo- and dark fermentation depends on several factors, which together lead to higher yields and greater efficiency of fermentative bacteria. Table 5 summarizes the main factors that affect hydrogen yield from photo- and dark fermentation.

Table 5. Summary of the main parameters affecting hydrogen yield in photo- and dark fermentation.

Parameters	Effect on renewable-H_2 yield
Inoculum	• In photo-fermentation, using purple non-sulfur bacteria like *Rhodobacter* sp. and high light intensity can enhance hydrogen production, with mixed strains further improving yield [80]. • In dark fermentation, hydrogen yield depends on using strict (e.g., Clostridium sp.) or facultative anaerobic bacteria, and can be enhanced by techniques such as immobilization and adding metal ions or oxide nanoparticles [80].
Temperature	• The fermentative bacterial community produces hydrogen over a wide temperature range, with mesophilic (35-40 °C) and thermophilic (50-60 °C) conditions being most commonly used due to their influence on pH and VFA production [102].

pH	• In photo-fermentation an acidophilic pH favors hydrogen production whereas in dark fermentation a near-neutral pH is more efficient for hydrogen production. In an appropriate range, increasing pH could increase the ability of hydrogen-producing bacteria, but pH at much higher levels could decrease hydrogen production [103,104].
Type of substrate	• Substrate choice depends on cost, availability, carbohydrate content, and fermentability. While glucose is common, solid waste and industrial wastewater are promising for economic and sustainability reasons, with minimal pre-treatment influencing the optimal substrate selection for hydrogen production [105].
Substrate concentration	• Maximum hydrogen production correlates positively with substrate concentration, providing sufficient nutrition for photosynthetic bacteria to maintain hydrogen production [92]. • In photo-fermentation, a very high substrate concentration may significantly increase the butyric acid concentration, lowering the pH and ceasing hydrogen production [106].

3.1.3. Integrated Systems

The combination of photo-fermentation and dark fermentation processes in an integrated system presents a promising technological option for hydrogen production. This approach allows for the optimal utilization of the intrinsic advantages of each process, leading to increased efficiency and sustainability. The integration of photo-fermentation and dark fermentation can occur as a single-step process, using the co-cultivation of H_2-producing bacteria in dark fermentation and photosynthetic bacteria in the photo-fermentation process, or as a two-stage process, where the effluent from dark fermentation is used as a substrate for the photo-fermentation process, thereby enhancing renewable-H_2 production. Due to the relatively low yields of the single-stage process, the two-stage process presents itself as more relevant. In this system, during stage I, dark fermentation bacteria break down glucose and produce hydrogen and intermediate products, mainly acetic acid (equation 7), which are then converted to hydrogen by photo-fermentative bacteria in stage II (equation 9) [78].

$$2C_2H_4O_2 + 4H_2O \rightarrow 8H_2 + 4CO_2 \quad (9)$$

Based on the results of the integrated process equations, it is theoretically possible to achieve a maximum hydrogen yield of 12 mol H_2/ mol $_{\text{substrate}}$, assuming glucose as the sole substrate in dark fermentation, where acetic acid is the predominant metabolite [87]. However, to optimize production efficiency, several parameters of the effluent from the dark fermentation process, such as concentration, composition, and pH, must be adjusted through pretreatments, as well as the type of photo-fermentative bacteria used.

3.1.4. Advantages and Challenges of the Different Biological Methods for Renewable-H_2 Production

The comparison of biological methods for hydrogen production focuses on major advantages, and challenges. Each method—direct bio-photolysis (DbP), indirect bio-photolysis (i-DbP), photo-fermentation, dark fermentation, and integrated systems—offers distinct benefits and faces specific limitations (as seen in Figure 3).

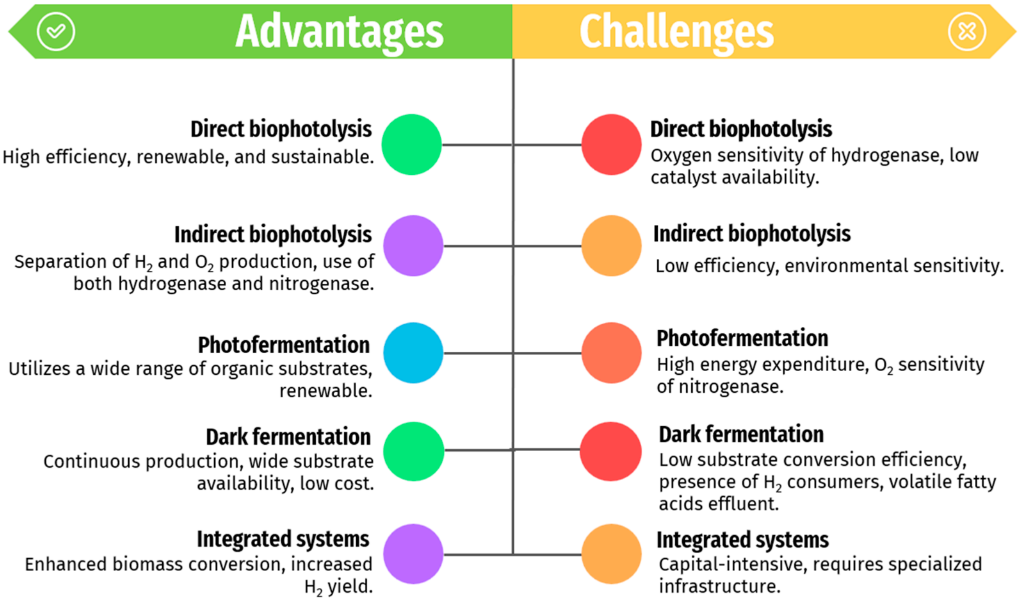

Figure 3. Advantages and challenges related with the biological methods for renewable-H_2 production mentioned in this work.

DbP demonstrates high energy efficiency, reaching up to 12.2 % in green algae [107]. Comparatively, DbP generally outperforms i-DbP (max efficiency 4.1 %), photo-fermentation (max efficiency 8.5 %), and dark fermentation (max efficiency 12.0 %) [88,107]. Despite its efficiency, DbP is hindered by oxygen produced during PSII, which strongly inhibits hydrogenases, thereby reducing hydrogen production [108]. Mitigation strategies such as inert gas purging, oxygen production blockers (e.g., copper), and sulfur deprivation have been explored [109,110].

i-DbP offers advantages such as renewability, sustainability, scalability, and integration potential with existing infrastructure. However, it suffers from low efficiency, limited catalyst availability, environmental sensitivity, and technological challenges, necessitating further research and development for improved performance and cost-effectiveness [14,59,61].

Dark fermentation is a well-established method for renewable-H_2 production, leveraging a wide range of substrate sources and operating continuously in the absence of light. It ensures stable and reliable hydrogen production at a lower cost [111]. Nevertheless, its efficiency in converting substrates into hydrogen is limited by competition from hydrogen-consuming microorganisms within the mixed microflora. These include homo-acetogens, hydrogenotrophic methanogens, sulfate-reducing bacteria, nitrate-reducing bacteria, and propionate producers, which decrease net hydrogen production. Moreover, dark fermentation generates effluents rich in volatile fatty acids (VFAs), necessitating costly treatment before discharge [87]. Integration with other biological methods like photo-fermentation offers potential solutions for enhancing overall hydrogen yield and mitigating effluent challenges. In that sense, integrated systems, which combine dark and photo-fermentation, show potential for maximizing hydrogen yield through synergistic effects [12]. However, further research and technological advancements are crucial to enhance their efficiency and scalability, since implementing integrated systems can be capital-intensive and requires specialized infrastructure as a primary drawback [63].

3.2. Thermochemical Methods

The thermochemical methods used for converting biomass to renewable-H_2 are processes that involve the application of heat and the chemical transformation of biomass to obtain hydrogen. These methods can produce hydrogen directly from biomass or from intermediate products (e.g., methanol, ethanol, etc.) obtained from the depolymerization of biomass. In general, thermochemical methods include gasification, pyrolysis and hydrothermal processes.

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3.2.1. Gasification

Gasification is a thermochemical process wherein a carbonaceous substrate, such as biomass, undergoes transformation into a combustible gas at high temperatures (700 to 1200 °C). This process occurs in the presence of a gasification agent of limited concentration, including air, oxygen, steam, carbon dioxide, or their mixtures [112]. The primary product of gasification is syngas, a gaseous fuel composed predominantly of hydrogen, carbon monoxide, carbon dioxide, nitrogen, tars, char (a solid carbonaceous product), ash, and particles. Equation 10 illustrates the general equation for biomass steam gasification:

$$Biomass + Steam \rightarrow H_2 + CO + CO_2 + CH_4 + LHC + Tar + Char \quad (10)$$

The composition and lower heating value (LHV) of syngas depend on the type of biomass and the gasification agent employed. Syngas produced using air as the gasification agent typically has an LHV ranging from 4-8 MJ/Nm^3, while steam, oxygen, or their mixtures yield syngas with an LHV between 8-20 MJ/Nm^3 [112].

Gasification processes are classified based on the gasifier type and the heat source. Direct and autothermal gasification involves the use of air or oxygen, with partial combustion of biomass providing process heat, while indirect and allothermal gasification uses steam with external heat sources. Indirect and allothermal gasification, is preferred for hydrogen production due to its promotion of the steam reforming (SR) reaction within the syngas. This reaction enhances hydrogen yield compared to air gasification, which primarily promotes combustion and results in a high proportion of nitrogen in the syngas [113]. The SR reaction in gasification reduces the carbon-to-hydrogen (C/H) mass ratio in the syngas, improving its composition by decreasing the volume of light hydrocarbons and tar. This optimization not only increases hydrogen production but also mitigates issues such as pipe blockage and corrosion caused by polymerization and condensation of tars [114]. Figure 4 depicts the mechanisms and stages of hydrogen production during biomass steam gasification.

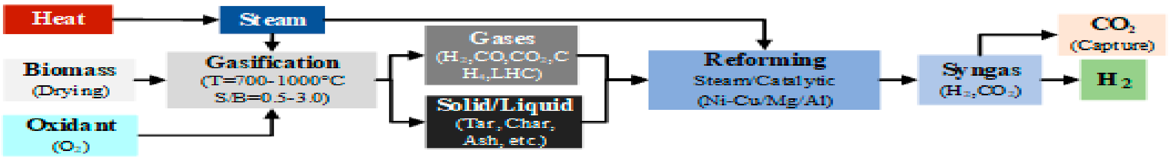


Figure 4. Renewable-H$_2$ production process from biomass gasification.

During steam gasification, several additional reactions occur. After the drying step, the biomass undergoes a pyrolysis reaction, which converts it into a gas rich in carbon monoxide, carbon dioxide, methane, light hydrocarbons (e.g., ethylene), char, and tar [115] , as shown in equation 11.

$$Biomass \rightarrow CO + CO_2 + CH_4 + LHC + H_2O + Char + Tar \quad (11)$$

Tar is a complex, condensed mixture of polycyclic aromatic hydrocarbons (PAHs) and oxygenated molecules, including alcohols, phenols, and furans. Under steam gasification temperature conditions (700-1000 °C), homogeneous reactions such as cracking and steam reforming alter the structure of these oxygenated molecules. During reforming reactions, tar breaks down into carbon monoxide, hydrogen, char, and polycyclic aromatic hydrocarbons (PAH), as shown in equation 12 [116]. PAH can further be converted to carbon monoxide and hydrogen by thermal cracking at extremely high temperatures (~1250 °C), as a part of heterogeneous reactions.

$$Tar + H_2O \rightarrow CO + CO_2 + H_2 + Char \quad (12)$$

The reforming reactions occur in the presence of steam and carbon dioxide, converting light hydrocarbons like methane and ethylene into carbon monoxide and hydrogen, as illustrated in equations 13 to 17:

$$2CH_4 + O_2 \rightarrow 2CO + 2H_2 \quad (13)$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad (14)$$

$$C_2H_4 + 2CO_2 \rightarrow 4CO + 2H_2 \quad (15)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (16)$$

$$C_2H_4 + 2H_2O \rightarrow 2CO + 4H_2 \quad (17)$$

During tar cracking, the light hydrocarbons and carbon oxides are generated, along with hydrogen. These compounds are stable under cracking/reforming operating conditions. Additionally, the water-gas shift (WGS) reaction converts carbon monoxide in the presence of water to a mixture of carbon dioxide and hydrogen, as shown in equation 18:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (18)$$

The addition of steam to the gasification process enhances this reversible reaction by shifting it towards the production of hydrogen [21]. The WGS reaction is exothermic, and increasing the temperature shifts the equilibrium towards the reactants, resulting in the formation of carbon monoxide and water, according to Le Chatelier's principle. Finally, heterogeneous reactions also occur, as described by equations 19 to 22, including the oxidation of carbon and the Boudouard reaction, where carbon formed during pyrolysis is converted to carbon monoxide and carbon dioxide [114].

$$C + O_2 \rightarrow CO_2 \quad (19)$$

$$2C + O_2 \rightarrow 2CO \quad (20)$$

$$C + CO_2 \rightarrow 2CO \quad (21)$$

$$C + H_2O \rightarrow CO + H_2 \quad (22)$$

To enhance hydrogen production yield via steam gasification, various parameters must be optimized, including biomass characteristics, operating temperature, steam-biomass ratio (S/B), and catalysts [21]. Table 6 provides a summary of the impacts of these parameters.

Table 6. Summary of the main parameters affecting hydrogen yield in biomass steam gasification.

Parameters	Effect on renewable-H$_2$ yield
Temperature	• Raising the temperature promotes endothermic reactions such as hydrocarbon reforming (equation 12), methane reforming (equation 16), and carbon gasification (equation 22), which increase gas production and the volumetric fraction of hydrogen in syngas [117,118]. • Increasing the temperature also decreases the tar content in syngas [118]. • However, temperatures above 950°C can suppress the WGS reaction (equation 18), which is an exothermic reaction, leading to a decrease in the hydrogen fraction in syngas [119,120].
Steam to biomass ratio (S/B)	• The S/B ratio significantly influences syngas composition and energy input during biomass gasification. • A low S/B ratio leads to solid carbon and methane formation. • Increasing steam supply promotes reforming reactions of carbon and methane into carbon monoxide and hydrogen. • Beyond a S/B ratio of 1.3, excess steam reduces solid carbon and methane, increasing hydrogen and carbon dioxide formation. • Steam facilitates carbon monoxide reduction via the WGS (equation 18) and hydrocarbon reforming reactions (equations 12, 16, 17). • Optimal S/B ratios up to 1.3 enhance hydrogen formation, while ratios exceeding 1.3 reduce temperature and increase tar formation [114,121,122].

Biomass characteristics	• Type of biomass: Composition rich in cellulose and lignin enhances gaseous product yield and hydrogen fraction in syngas [122,123]. • Particle size: Smaller particles increase surface area, improving heat transfer, gasification rate, and hydrogen content, while reducing tar. Particles <1 mm may increase energy consumption [21,122]. • Moisture percentage: Optimal 10-15% by weight; >40% leads to low temperatures, high energy use, and reduced gasification efficiency and hydrogen concentration [121,124]. • Ash content: High ash increases coke and particulate production in syngas, needing effective gas-cleaning processes [123,124].
Catalysts	• Enhance hydrogen and carbon monoxide production by improving heat and mass transfer efficiency during gasification (equations 18-22) [125]. Catalysts also aid in tar removal, boosting hydrogen output and overall gasification performance, thus increasing renewable-H_2 production [114]. Common catalysts include Ni-based, alkali metals (e.g., K_2CO_3, Na_2CO_3), alumina, alumina silicate, $ZnCl_2$, and dolomite [21].

3.2.2. Pyrolysis

Pyrolysis is a thermochemical process that involves the decomposition of biomass into solid, liquid, and gaseous fractions through the application of heat in an inert atmosphere [126]. During the pyrolysis process, the large hydrocarbon molecules present in biomass are broken down into smaller molecules through several reaction mechanisms. Hemicellulose is the first component of biomass to undergo decomposition, occurring within the temperature range of 220-315 °C, resulting in the production of acetic acid, other organic acids, sugars, and furans. Cellulose degradation occurs subsequently, within the temperature range of 315-400 °C and leads to the formation of levoglucosan and other anhydrocelluloses [127]. Lignin, which contains multiple aromatic rings, is particularly challenging to degrade and its decomposition occurs over a broad temperature range (200-900 °C), producing various compounds including oligomers, monomers of polysubstituted phenols, hydrogen and methane as the primary products [128].

Pyrolysis can be carried out within the temperature range of 400-800 °C, and depending on the operating temperature, heating rate and residence time, it can be classified into three types: slow pyrolysis, fast pyrolysis, and flash (ultra-fast) pyrolysis. Figure 5 shows the mechanisms and stages of hydrogen production by biomass pyrolysis, and equation 23 presents the general pyrolysis reaction [114].

$$Biomass + Heat \rightarrow H_2 + CO + CO_2 + CH_4 + H_2O + \text{Bio-oil} + Char \quad (23)$$

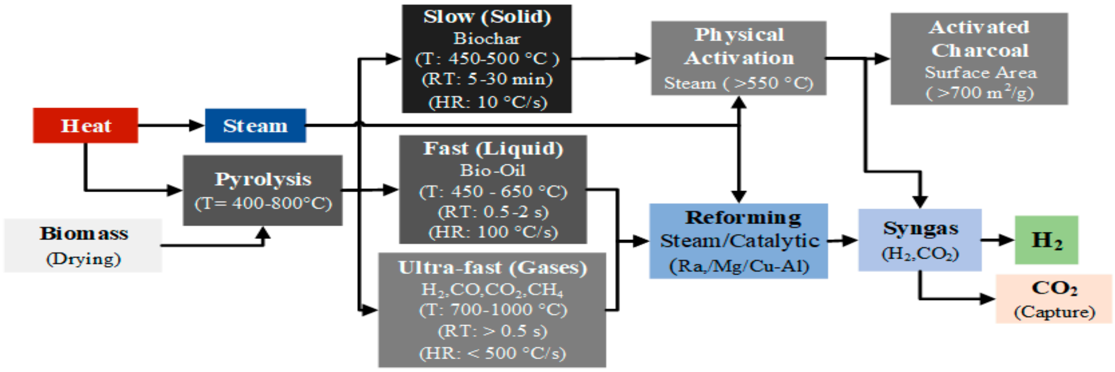


Figure 5. Renewable-H_2 and activated charcoal production process from biomass pyrolysis.

Optimizing various parameters is essential for improving hydrogen production yield through pyrolysis. These parameters include biomass characteristics, temperature, heating rate, residence time, and catalyst usage [21]. Table 7 presents the main parameters that affect hydrogen yield in the biomass pyrolysis process.

Table 7. Summary of the main parameters affecting hydrogen yield in biomass pyrolysis.

Parameters	Effect on renewable-H_2 yield
Temperature	• Below 450 °C, mainly biochar is produced [129]. • 450-600 °C promotes bio-oil formation [129]. • 600-900 °C favors gaseous products, including hydrogen [130].
Heating rate	• Conventional pyrolysis (< 50 °C/min, < 450 °C) favors biochar formation [131]. • Fast pyrolysis (> 10-200 °C/s, 450-600 °C) promotes bio-oil production (> 75 wt.%) [130]. • Flash pyrolysis (> 1000 °C/s, 600-900 °C) favors gaseous products, including hydrogen [128].
Biomass characteristics	• Herbaceous biomass (high hemicellulose, moderate lignin/cellulose) yields more gas [132]. • Woody biomass (high lignin/cellulose) yields more biochar and bio-oil [132]. • Particle size affects performance: small particles (< 0.1 mm for flash pyrolysis, < 1 mm for fast pyrolysis) enhance gas production [129].
Residence time	• Slow pyrolysis (> 5 min) at low temperatures promotes biochar formation [132]. • Rapid pyrolysis (0.5-10 s) at high temperatures favors bio-oil production [133]. • Flash pyrolysis (< 2 s) at very high temperatures promotes gasification and hydrogen formation [134].
Catalysts	• Catalysts enhance bio-oil production by increasing H/C ratio and reducing oxygen content [135]. • Acid catalysts (e.g., metal oxides, zeolites) and basic catalysts (e.g., alkali metal oxides, metal chlorides) are used [136]. • Catalysts reduce reaction temperature and activation energy, improving efficiency [135].

3.2.3. Hydrothermal Processes

Hydrothermal processes are thermochemical methods that operate at high temperatures and pressures, exceeding the saturation pressure of water. This environment facilitates various reactions that modify the physicochemical and magnetic properties of water, including its density, dielectric constant, and ionic product. These reactions contribute to the production of energy-dense fuels and high-value chemicals. Researchers categorize hydrothermal processes into three main types based on temperature range and target products: Hydrothermal Carbonization (HTC), Hydrothermal Liquefaction (HTL), and Hydrothermal Gasification (HTG) [137] (Figure 6).

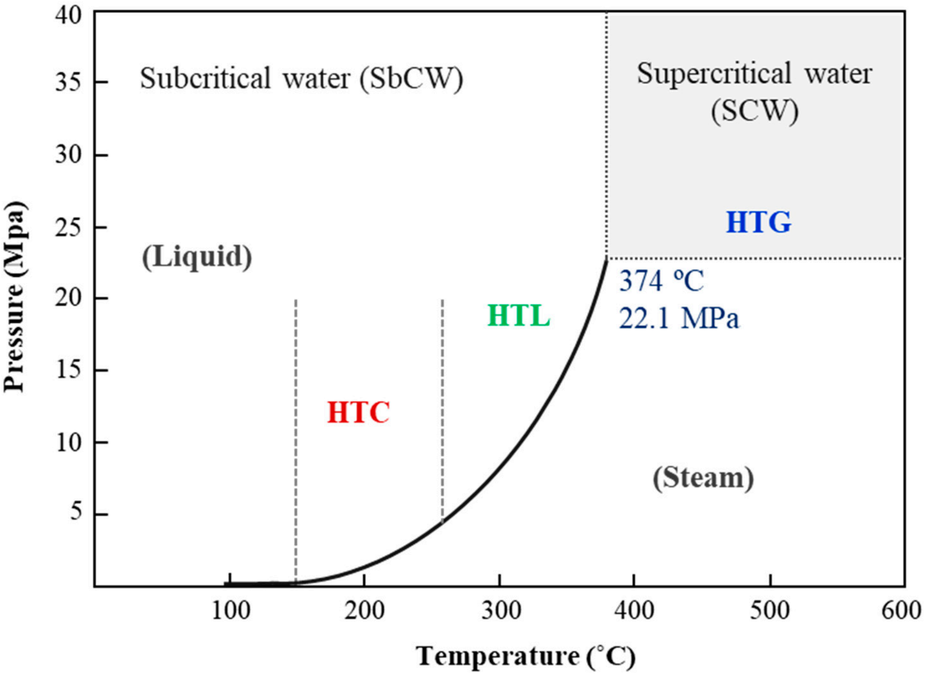


Figure 6. Phase diagram of water illustrating the regions where hydrothermal processes occur, delineating the conditions under which Hydrothermal Carbonization (HTC), Hydrothermal Liquefaction (HTL), and Hydrothermal Gasification (HTG) take place.

Biomass HTC represents an efficient and ecologically favorable method for producing hydrochar, a carbon-rich solid fuel with high energy density. This process converts various biomass feedstocks into smokeless solid fuels, operating at pressures between 2 and 10 MPa and temperatures from 180 to 250 °C [138]. Hydrochar can be further processed to produce activated carbon by employing physical activation with steam at high temperatures (500-900 °C), achieving surface areas exceeding 700 m^2/g [139].

On the other hand, HTL chemically transforms biomass mostly into biocrude, a type of crude oil like pyrolysis bio-oil, under conditions of high temperature (280–370 °C) and high pressure (10–25 MPa). This process also yields by-products in solid, aqueous, and gaseous phases characterized by their high energy content and enhanced heat recovery capabilities compared to other methods [140]. Further processing of biocrude through reforming techniques can convert it into biomethane and hydrogen [141].

Finally, HTG, also known as Supercritical-Water Gasification (SWG), leverages the unique properties of water in its supercritical state to function both as a solvent and a reactant. This process efficiently converts biomass into hydrogen and carbon dioxide through catalytic cracking and steam ($T \geq 374$ °C, $P \geq 22$ MPa) [142]. Under these conditions, water serves as an oxidant and engages in a steam reforming reaction with biomass, as depicted in equation 24, producing hydrogen, methane, carbon monoxide, and carbon dioxide.

$$Biomass + H_2O \rightarrow H_2 + CO + CO_2 + CH_4 \quad (24)$$

This initial reaction is followed by homogeneous gas-gas reactions, leading to the formation of hydrogen and carbon dioxide, as detailed in equations 25, 26, and 27 [142].

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad (25)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (26)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (27)$$

Figure 7 depicts the specific operating parameters essential for optimizing the conversion of biomass into these valuable gases and activated charcoal through hydrothermal processes. This figure highlights the critical temperature and pressure settings required to maximize efficiency and product yield in the biomass conversion process.

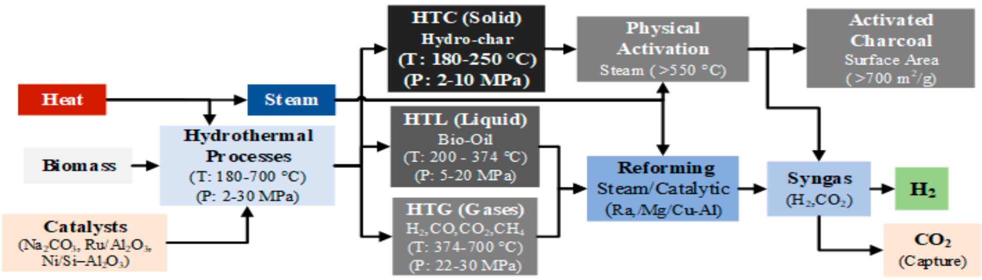


Figure 7. Renewable-H_2 production process from biomass hydrothermal processes.

As HTG (and the other hydrothermal processes) involves the use of water as both the reaction and reagent medium, it eliminates the need to dry the feedstock before the process. This results in significant reduction in energy consumption [143]. Consequently, this technique holds great promise for the gasification of biomass with high moisture content. Furthermore, it can achieve high biomass conversion rates (up to 100 %), high volumetric hydrogen content in final gaseous products (≥ 50 %) and produce no tar or other by-products [144]. Achieving these high yields requires the optimization of several parameters, including the operating temperature, operating pressure, reagent concentration, and reaction time. Table 6 provides a summary of the effects of these key parameters.

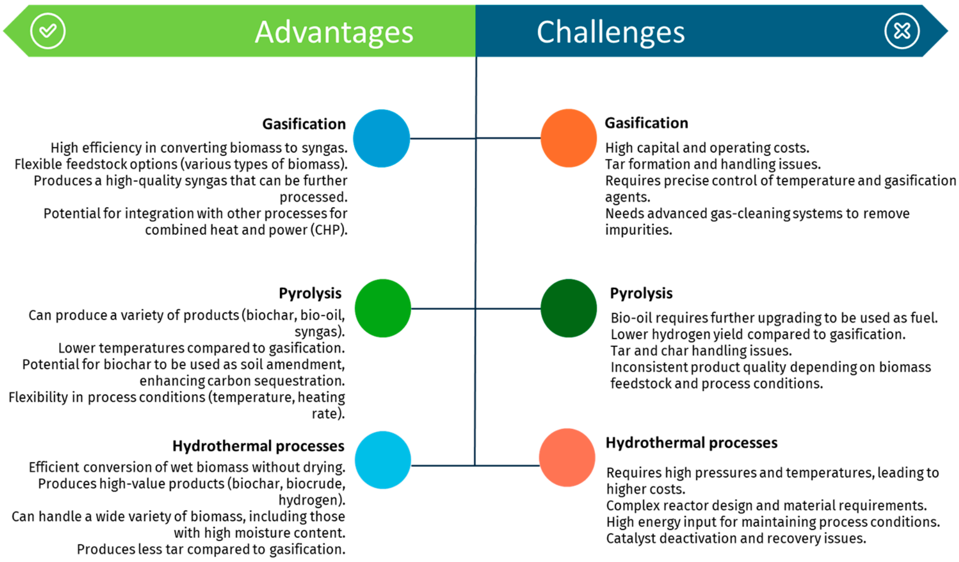
Table 6. Summary of the main parameters affecting hydrogen yield in biomass HTG.

Parameters	Effect on renewable-H_2 yield
Temperature	• Lower temperatures result in low hydrogen yields, gasification rate, and carbon gasification rate [143]. • Increasing temperature enhances gasification rate and H_2 production due to reduced dielectric constant of supercritical water [145]. • Excessively high temperatures escalate operating costs and energy consumption, necessitating an optimal reaction temperature balance [122].
Pressure	• Supercritical conditions require a reaction pressure exceeding 22 MPa [21]. • Higher pressure increases the dielectric constant of supercritical water, hindering organic dissolution and promoting undesirable ionic reactions [145]. • Optimal pressure range for highest H_2 yields is between 22 and 30 MPa [143].
Reagent concentration	• Excessive reagent concentration reduces contact area, decreasing H_2 and CO production during HTG [146]. • Low biomass to water ratio enhances conversion efficiency to gas, particularly under high temperature conditions [145]. • High-concentration HTG improves technology competitiveness but requires further research for high hydrogen yields [122].

Catalysts	• Homogeneous catalysts like alkaline catalysts (e.g., K_2CO_3, NaOH) accelerate C-C bond cleavage and WGS reaction [147]. • Advantages include economical cost, high conversion rates, and suitability for batch and continuous processes [122,145]. • Challenges include reactor fouling and corrosion [122,145]. • Heterogeneous catalysts, e.g., Ni, Pt, Rh, supported on various materials, offer recovery and reuse benefits, reducing overall costs [122]. • Preferred for selectivity and inertness but face challenges like deactivation and poisoning from heteroatom-containing compounds [145].

3.2.4. Advantages and Challenges of the Different Thermochemical Methods for Renewable-H_2 Production

Thermochemical methods offer a versatile approach to converting biomass into renewable hydrogen, each with its unique advantages and challenges. Figure 8 summarizes the key benefits and obstacles associated with gasification, pyrolysis, and hydrothermal processes, highlighting their potential and limitations in sustainable hydrogen production



Gasification
High efficiency in converting biomass to syngas.
Flexible feedstock options (various types of biomass).
Produces a high-quality syngas that can be further processed.
Potential for integration with other processes for combined heat and power (CHP).

Gasification
High capital and operating costs.
Tar formation and handling issues.
Requires precise control of temperature and gasification agents.
Needs advanced gas-cleaning systems to remove impurities.

Pyrolysis
Can produce a variety of products (biochar, bio-oil, syngas).
Lower temperatures compared to gasification.
Potential for biochar to be used as soil amendment, enhancing carbon sequestration.
Flexibility in process conditions (temperature, heating rate).

Pyrolysis
Bio-oil requires further upgrading to be used as fuel.
Lower hydrogen yield compared to gasification.
Tar and char handling issues.
Inconsistent product quality depending on biomass feedstock and process conditions.

Hydrothermal processes
Efficient conversion of wet biomass without drying.
Produces high-value products (biochar, biocrude, hydrogen).
Can handle a wide variety of biomass, including those with high moisture content.
Produces less tar compared to gasification.

Hydrothermal processes
Requires high pressures and temperatures, leading to higher costs.
Complex reactor design and material requirements.
High energy input for maintaining process conditions.
Catalyst deactivation and recovery issues.

Figure 8. Advantages and challenges related with the thermochemical methods for renewable-H_2 production mentioned in this work.

Steam gasification represents an effective pathway to produce hydrogen from biomass with minimal environmental impact, capitalizing on the widespread abundance of biomass resources. This technology holds promise for sustainable hydrogen production. Nonetheless, its primary drawbacks encompass a substantial initial investment, limited energy efficiency, and significant tar formation within the syngas.

Similarly, pyrolysis, a well-established thermochemical process, has gained considerable attention for producing hydrogen through the thermal conversion of biomass. This process is highly promising for decarbonizing the economy by leveraging renewable and sustainable raw materials, offering high energy efficiency and scalability [126,148]. However, pyrolysis poses significant challenges, including issues related to hydrogen separation and purification from complex gas mixtures, minimizing GHG emissions, and managing the high costs and complexity associated with large-scale hydrogen production [149].

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HTG has also emerged as a highly promising technology for hydrogen production, particularly due to its ability to directly gasify biomass with high moisture content. This method exhibits high reaction efficiency and yields substantial hydrogen production [150]. However, HTG has some drawbacks, such as high energy consumption rates and technological requirements for the equipment used, resulting in significant investment and maintenance costs [122]. Consequently, scalability is limited, and no large-scale commercial system of this technology is currently known. Each of these technologies offers unique advantages and faces specific challenges, underscoring the need for continued research and development to optimize their viability for large-scale hydrogen production.

4. Techno-Economic Overview of Renewable-H_2 Production Technologies

Table 7 presents a comparison between capital costs, hydrogen costs, production efficiencies, and Technology Readiness Levels (TRLs) for various hydrogen production technologies with varying feedstocks.

Table 7. Comparison of different hydrogen production technologies.

Process	Feedstock	Capital Costs (M€)	H_2 cost (€/kg)	Efficiency (%)	TRL	Ref.
SRM with CCS	Natural gas + Water	764	1.0-1.1	76	8-9	[151,152]
SRM without CCS	Natural gas + Water	1068-1419	1.3-1.5	72-84	8-9	
CC with CCS	Coal + Water	545.6	1.63	60	8-9	[153]
CG without CCS	Coal + Water	435.9	1.34	---	---	
ATR with CCS	Natural gas + Oxygen	1090	1.23	75	7-8	[152,154]
ATR without CCS	Natural gas + Oxygen	1536	1.66	60	6-7	
NGD with CCS	Natural gas + Heat	1143	2.55	70	7-8	[154,155]
NGD without CCS	Natural gas + Heat	1363	2.65	60	6-7	
Biomass pyrolysis	Biomass + Heat + Steam	53.4–3.1	1.3-2.2	17-33	4-5	[156]
Biomass gasification	Biomass + Water	149.3–6.4	1.8-2.1	35–50	7-8	[157]
Hydrothermal gasification	Biomass + Heat + Steam	---	1.5-3.2	70	2-3	[154]
DbP	Sun + Water + Algae	50 $/m2	2.13	12.2	2-3	[158]
i-DbP	Water + Algae	135 $/m2	1.42	4.1	2-3	
Dark fermentation	Biomass + Anaerobic bacteria	---	2.57	12	4-5	
Photo-fermentation	Sunlight + Biomass	---	2.83	8.5	4-5	
Solar PV electrolysis	Power-Water	12–54.5	5.8-23.3	20	4-5	
Solar thermal electrolysis	Heat + Water	421–22.1	5.1-10.5	30-36	3-4	
Wind electrolysis	Power +Water	504.8–499.6	5.9-6.0	80-90	6-7	[159]
Nuclear electrolysis	Power + Water	---	4.2-7.0	50-60	3-4	[160]

Nuclear thermolysis	Heat + Water	39.6-2107.6	2.2-2.6	40-50	2-3	
Solar thermolysis	Sunlight + Water	5.7-16	8.0-8.4	17	4-5	[161]
Photo-electrolysis	Sunlight + Water	---	10.36	8-14	2-3	[158]

Abbreviations: Steam Reforming of Methane (SRM), Carbon Capture and Storage (CCS), Autothermal Reforming (ATR), Natural Gas Decomposition (NGD), Photovoltaics (PV).

Renewable-H_2 production cost is still higher compared to grey hydrogen, which can put at risk the net zero emissions target by 2050. It is important to get an overview of the techno-economics associated with the production of this renewable gas to know the best current scenarios, and how less favorable cases can be improved in the right direction.

As seen in Table 7, renewable-H_2 cost is associated with the production technology. In 2021, the levelized cost of hydrogen (LCOH) obtained from natural gas steam reforming ranged from 0.92 to 2.8 €/kg H_2 [162]. According to the recent International Energy Agency's hydrogen report (IEA), this route is still the cheapest option to generate hydrogen in most regions of the world, compared for instance, with the use of fossil fuels with carbon capture technologies (LCOH 1.4-3.3 €/kg H_2) and low-carbon electricity (LCOH 3.1-11 €/kg H_2). Although hydrogen from water electrolysis is beyond of the scope of this study, techno-economic analysis (TEA) of electrolysis will also be presented below for comparative purposes since this is the state-of-the-art technology for renewable-H_2 generation.

The LCOH from water electrolysis depends on the cost of renewable electricity, which, in turn, is related to the plant location. The White Paper [163] produced by the International Council on Clean Transportation (ICCT) reported the cost of onsite hydrogen generation from electrolysis in the EU using mid-level and optimistic scenarios. According to this work, LCOH varies significantly across the EU, mostly due to different trends in the price of renewable electricity and tax fees. In 2050, green hydrogen could be produced at a cost around 2.5-3.5 €/kg H_2 in most of the EU countries (20 out of 26). However, for the same period, LCOH is expected to be higher in some EU member states, ranging from 4.2 €/kg H_2 in Denmark to 5.2 €/kg H_2 in Germany. Overall, countries with lower levelized electricity costs, such as Sweden, Finland, Portugal, and Spain, will enable lower hydrogen production prices.

Green hydrogen production costs are also related with the renewable energy source. Solar and wind hydrogen exhibit similar LCOH, always considering the best-case scenarios, and, for the latter, onshore wind hydrogen production appears to be more cost-effective than offshore wind, because of the lower capital expenditures (CAPEX) of onshore technologies [164]. For example, in 2020, the EU LCOH for solar hydrogen production ranged from 3.5 €/kg in Portugal to almost 15 €/kg in Norway. The LCOH for onshore wind based-hydrogen was 3–4 €/kg while that coming from offshore wind ranged between 3.2 and 8.0 €/kg. The recent report by Hydrogen Europe [165] states average renewable hydrogen production costs in the EU in 2022 of 5.2 €/kg using solar PV (in Portugal) and 5.7 €/kg with wind power (in Austria). This document provides a good overview about the hydrogen production costs from various technologies in the EU, declaring that the production of renewable hydrogen in some European countries is already a cost-competitive alternative to traditional routes based on fossil fuels. For instance, renewable hydrogen could potentially be obtained from onshore wind at costs as low as 3.1 €↨/kg with onshore wind in Norway and Ireland and 4.4 €/kg from solar PV in Spain and Portugal. LCOH by methane steam reforming in the Euro-zone is estimated at 5.7 €/kg H_2, in 2022.

The type of electrolysis technology, alkaline water electrolysis (AWE), proton exchange membrane (PEM) water electrolysis and solid oxide electrolysis cells (SOEC), has also an impact on the LCOH. Jang et al. [166] analysed the cost of generating hydrogen from the three water electrolysis systems and they calculated unit hydrogen production cost of 7.9, 7.0, and 6.6 €/kg H_2 for PEM, AWE, and SOEC combined with waste heat, respectively.

4.1. Biological Methods

Han et al. [167] carried out a techno-economic analysis of a hydrogen production process combining solid state fermentation and dark fermentation. This study demonstrated the economic feasibility of the proposed process with a hydrogen production cost of 2.1 €/m^3 H_2 for a payback period of 5 years and an internal rate of return (IRR) of 20.2 %. Hosseinzadeh et al. [168], estimated the average value of hydrogen production from a dark fermentation pilot plant with a processing capacity of 8–45 g H_2/kg biomass at 2.1 €/kg H_2. Recently, Alam and Nayan [169] proposed a simulation model for renewable-H_2 production by dark fermentation of wastewater sludge. Their study showed that hydrogen can be produced from dark fermentation at 10.5 €/ kg H_2 for a biomass processing capacity of 23 t/day, which could be considerably lowered to 5.4 €/ kg H_2 by scaling up to a 500 t/day capacity.

Although anaerobic digestion (AD) is mostly used to produce biogas/biomethane it can be also used to generate renewable-H_2 through the reforming of the obtained biogas/biomethane. Szima et al. [170] estimated a LCOH of 0.15 €/Nm^3 for a flexible hydrogen and power co-generation plant based on dry reforming of biomethane with low CO_2 emissions. A similar technological path for the combined production hydrogen and power was investigated by Cormos et al. [171], showing LCOH costs of 58 €/MWh. The authors concluded that capital costs have the highest influence on LCOH followed by biogas costs and plant availability factor, while operating costs have minor impacts.

Hydrogen production from cow manure through the integration of psychrophilic AD and dry methane reforming was studied in by Hajizadeh et al. [172]. The process was optimized to reach the highest methane conversion and the lowest energy consumption. The economic analysis conducted by the authors indicated that hydrogen production cost depends on hydrogen production rate, with higher production rates resulting in lower production costs. The best case-scenario was found for a plant capacity of 45.5 kg/h H_2, yielding hydrogen production costs of 1.28 €/kg H_2.

Byun and Han [173] evaluated the economic viability of using anaerobic digestion of food waste followed by biomethane steam reforming to generate renewable-H_2. The capital cost of the biodigester is the major cost driver. This integrated process allowed for a hydrogen minimum selling price (MSP) of 24.2 €/kg H_2, which was affected by the plant's capacity. For the most favorable case of 2000 t H_2/d processing capacity, hydrogen could be generated at an MSP of 5.5 €/kg H_2, which is comparable with fossil-based hydrogen processes.

4.2. Thermochemical Methods

The economics of various biomass-to-biofuel scenarios were examined by Anex et al. [174], and the authors assessed that hydrogen produced via biomass pyrolysis has the lowest production cost, due to its low capital operating cost, at 0.53 €/kg H_2. In an early study by Tan et al. [175], hydrogen MSP from biomass pyrolysis was found to be 1.64 €/ kg H_2. The research conducted by Lepage et al. [114] compares the economic feasibility of several biomass-based technologies for hydrogen production. According to these authors, traditional natural gas steam reforming appeared to be the cheapest option with hydrogen production costs below 0.92 €/kg H_2, but biomass pyrolysis could yield renewable-H_2 production costs going from 1.17 to 2.37 €/kg H_2. Brown et al. [176] modeled the techno-economics of corn stover fast pyrolysis for hydrogen generation and reported higher hydrogen production costs (1.9–2.8 €/kg H_2) when compared to the previously described works. A recent work by Li et al. [177] analyzed the production of hydrogen and biochar from corn straw pyrolysis. The authors reported that the costs related with biomass feedstock were the highest (68 %), followed by catalyst costs (12 %). Personnel wages and benefits accounted for 8 % of the total costs, while electricity represented 4 % of the total costs. Assuming an annual processing of 40,000 tons of corn straw, a maximum return of 805 million euros, and an IRR of 22 % in 7.3 years were estimated.

Salkuyeh et al. [178] investigated the economic aspects associated to the production of hydrogen from biomass gasification in two reactor configurations, fluidized bed (FB), and entrained flow (EF). The authors also explored the effect of implementing carbon capture and liquefaction units in the hydrogen production costs. The FB gasification technology allowed for a more cost-effective hydrogen production process with a hydrogen MSP at 2.8 €/kg H_2. The higher hydrogen price for the

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EF process (3.1 €/kg H_2) was mostly due to the higher CAPEX of this type of gasifier. The integration of carbon capture and liquefaction systems led to increased hydrogen production costs, by 3 % and 11 % for the FB and EF processes, respectively.

Shaikh et al. [179] used an Aspen Plus simulation to assess the TEA of a combined cycle, biomass calcium looping gasification for the co-generation of hydrogen and electricity. The cost of hydrogen production was estimated to be 2.2 €/kg H_2 with an IRR of 17.43 % and a payback period of 7.35 years. The combined hydrogen-electricity process appeared to be more economically feasible than the production of electricity.

Other works also analyze the techno-economic feasibility of hydrogen from biomass gasification. For instance, Lepage et al. [114] reported hydrogen production costs at 1.1-3.2 €/kg H_2, while Wang et al. [180] found lower production cost values (0.9 €/kg H_2). Al-Qahtani et al. [181] compared the economics of hydrogen production from biomass gasification with and without carbon capture and storage (CCS) technology. The authors found that adding CCS resulted in an increased LCOH from 2.2 to 3.4 €/kg H_2.

As for hydrothermal processes, the economic evaluation of hydrogen produced from the HTG of soybean straw identified a MSP of 1.79 €/kg H_2 [182]. The work by Cook and Hagen [183] assessed the economics of three case studies (facilities) for hydrogen production via biomass gasification in the United States. Biomass supply costs and hydrogen transportation distance were pointed out as the most significant factors affecting the overall production costs. The best-case scenario showed the lowest transportation cost of hydrogen at 3.19 €/kg H_2, which could increase up to 3.78 €/kg H_2 in the less favorable scenario.

5. Environmental Impact Assessment Overview of Renewable-H_2 Production Technologies

Life Cycle Assessment (LCA) is a vital tool for determining the environmental impact of a product over its entire life cycle, enabling the comparison of different production technologies. The environmental effects of renewable hydrogen production haven bee presented by a ICCT White Paper [184] where a LCA methodology is applied to calculate the GHG intensity of eight hydrogen production technologies. These include biological pathways from various feedstocks, as well as thermochemical and electrochemical routes. The study highlights that hydrogen produced from forestry biomass gasification and water electrolysis powered by renewable electricity results in lower GHG emissions. Conversely, hydrogen derived from biomethane reforming, sourced from wastewater sludge or manure anaerobic digestion, can significantly reduce GHG emissions, depending on methane leakage during biomethane production. As expected, hydrogen produced from fossil fuels shows the highest GHG intensities among the analyzed technological routes, with values exceeding those of the fossil comparator.

Camacho et al. [185] carried out a detailed LCA of a combined dark fermentation/anaerobic digestion wastewater process for hydrogen generation. The authors studied different feedstocks, including wine molasses mixed with wastewater treatment plant (WWTP) sludge, cheese whey and sugar beet molasses. For the determination of the system boundaries, cradle-to-gate and gate-to-gate approaches were applied and the following impact categories were analyzed: CC - Climate change, FE - Freshwater eutrophication, FRS - Fossil resource scarcity, LU - Land use, ME - Marine eutrophication, TA - Terrestrial acidification, TE - Terrestrial ecotoxicity, and WC - Water consumption. The authors demonstrated that the environmental impact depends on the feedstock used to obtain hydrogen. For the cradle-to-gate approach and the Midpoint analysis, sugar beet molasses exhibited the best environmental profile among the feedstocks considered, with lower impact in four of the eight studied categories. In contrast, cheese whey showed the worst relative environmental profile. It was found that hydrogen obtained from wine molasses and WWTP sludge (9.13 kg CO_2/Nm^3 H_2) and sugar beet molasses (3.56 kg CO_2/Nm^3 H_2) led to a lower carbon footprint than fossil fuel hydrogen (12.08 kg CO_2/Nm^3 H_2).

Barghash et al. [186] pointed out the beneficial effect of using solar energy in the reduction of the environmental footprint of the production of hydrogen from dark fermentation. The GHG emissions for the process carried out with and without solar energy were -1.12×10^4 kg CO_2-eq and

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3.13×10^4 kg CO_2-eq, respectively. Zheng et al. [187] used LCA to analyze the environmental impacts of hydrogen production through the fermentation of food waste. The results indicated that electricity, hydrogen compression and food waste transport were the main environmental contributors. The studied hydrogen production route showed lower GHG emissions (10.1 kg CO_2-eq) when compared to conventional methane steam reforming (10. 6 kg CO_2-eq) and water electrolysis (28.4 kg CO_2-eq). However, it presented a higher carbon footprint than the gasification of poplar wastes (1.5 kg CO_2-eq). Nevertheless, it should be noted that biomass gasification LCA does not consider the emissions associated with hydrogen compression. Ma et al. [188] proved the positive effect of incorporating CCS technologies in the hydrogen production from corn straw gasification, which can lead to negative GHG emissions. Chen et al. [189] applied LCA to estimate the environmental performance of a solar-assisted hydrothermal gasification of biomass, in a pilot plant for hydrogen production. The authors detailed that system operation was the major environmental contributor, with the solar concentrator construction representing 78 % of the total Global Warming Potential (GWP). The use of solar energy for heating instead of electricity allowed to reduce the environmental impact by 90 %. Moreover, the environmental profile of biomass gasification combined with chemical looping for hydrogen generation has been recently evaluated by Wu et al. [190]. This integrated process appears to be a promising option to lower GHG emissions related to the production of renewable-H_2, as evidenced by their negative GPW of -15.13 and -17.00 kg CO_2-eq using air and oxygen as gasifying agents, respectively.

Overall, these studies underscore the importance of feedstock selection, energy sources, and technological integration in reducing the environmental impacts of hydrogen production from biomass. Biological methods, like dark fermentation, vary significantly based on feedstock, with some showing lower impacts. Thermochemical methods, such as biomass gasification, benefit greatly from technologies like carbon capture and solar assistance, which can reduce or even negate GHG emissions. Optimizing these factors is crucial for minimizing the environmental footprint of renewable hydrogen production.

6. Conclusions

The significance of hydrogen as a future fuel is increasingly acknowledged. Hydrogen derived from biomass, represents a compelling alternative for sustainable and eco-friendly energy generation. This study reviews the predominant biological and thermochemical pathways employed for hydrogen production from biomass. Comparing different biomass-based hydrogen production is quite difficult, mostly due to the high diversity in technologies, feedstocks, operating conditions, scale, and level of maturity,

A key strength of biomass as renewable energy for hydrogen generation is its versatility. It can be obtained and delivered locally, contributing to the development of regional economies and decreasing the carbon footprint of the process, leading even to negative emissions for some types of feedstocks such as manure. Moreover, there is a wide variety of biomass with the potential for hydrogen production through different technologies, including sewage, forestry and agro-industrial residues, and animal wastes, which lessens the negative effects related to the seasonal availability of some kinds of biomass.

The most utilized biological methods encompass direct and indirect bio-photolysis, photo-fermentation, and dark fermentation. These methods offer a promising alternative to obtaining renewable hydrogen with low energy consumption since they occur at ambient pressure and temperature, also helping with organic waste recycling. Biological hydrogen production technologies are not so affected by plant size as thermochemical processes but face other limitations. Low hydrogen production rates and strict operating requirements of these processes, such as light intensity, temperature, water, pH, absence of oxygen, substrate concentration, and type are the main drawbacks of biological routes. Adding metal-based nanoparticles, microbes' immobilization, genetic modification of microorganisms, and improved bioreactor design are some of the considered approaches to circumvent these limitations and enhance the hydrogen productivity of biological processes. Despite the intensive research in this field, the scale-up of biological technologies for hydrogen production depends largely on developing innovative solutions to improve the efficiency and productivity of these processes.

One of the major factors influencing a thermochemical plant's profitability is the type of biomass used, since its composition, namely its energy content, directly impacts the amount of hydrogen produced. Clearly, the higher the energy content, the higher the hydrogen production and the lower the break-even point of the facility. Biomass purchase prices, which vary with the type and location of biomass or biomass mix, also affect the hydrogen production cost and consequently, the project's financial performance. Strategies to reduce costs and improve profitability and sustainability include using residual biomass and wastes locally sourced and highly available and identifying synergies with other sectors (e.g., agro-industrial, forestry, waste management).

Thermochemical biomass-to-hydrogen projects must also cope with economic constraints directly related to plant processing capacity. Depending on the technology, there will be a size plant ceiling, below which the project will not be economically viable. As a thumb rule, economies of scale apply, turning more cost-effective larger biomass thermochemical processing plants. However, these processes are context-sensitive, thus case studies are always recommended to get a more realistic perspective on the techno-economic feasibility of the project.

Considering merely the economic factors, technological maturity level, and hydrogen production, conventional gasification is the most suitable way to obtain renewable hydrogen from biomass to date. Hydrothermal gasification is likely the best technology to produce hydrogen from biomass (particularly high moisture feedstocks) in the coming years, as it offers the benefits of high and cost-competitive hydrogen production combined with high efficiency.

Overall, thermochemical processes represent effective solutions for centralized hydrogen generation at a large scale, while biological pathways are more convenient for local production at a small scale.

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