

Review

Microalgal Hydrogen Production in Relation to Other Biomass-Based Technologies—A Review

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Abstract: Hydrogen is an environmentally friendly biofuel which, if widely used, could reduce atmospheric carbon dioxide emissions. The main barrier to the widespread use of hydrogen for power generation is the lack of technologically feasible and—more importantly—cost-effective methods of production and storage. So far, hydrogen has been produced using thermochemical methods (such as gasification, pyrolysis or water electrolysis) and biological methods (most of which involve anaerobic digestion and photofermentation), with conventional fuels, waste or dedicated crop biomass used as a feedstock. Microalgae possess very high photosynthetic efficiency, can rapidly build biomass, and possess other beneficial properties, which is why they are considered to be one of the strongest contenders among biohydrogen production technologies. This review gives an account of present knowledge on microalgal hydrogen production and compares it with the other available biofuel production technologies.

Keywords: hydrogen; biofuels; microalgae; fermentation; thermochemical methods



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1. Introduction

The negative environmental impact of the economy drives the need for low-emission production technologies, including the deployment of clean and efficient energy generation solutions. Hydrogen meets the criteria of a low-impact energy carrier [1]. The calorific value of hydrogen ranges from 10.8 MJ/m_N³ to 12.75 MJ/m_N³, making it suitable for wide use in heating, power generation, and car/air transportation [2]. However, hydrogen is currently used on a limited and marginal basis as an energy source, mostly in the refining industry, space technology, and fuel cells [3,4]. The main barrier to more widespread use is the lack of viable methods of hydrogen production and storage—or at least ones which would be both technologically feasible and cost-effective [5]. Conventional hydrogen production technologies are mainly thermo-chemical (including combustion, gasification, thermochemical liquefaction, and pyrolysis) or based on water pyrolysis [6]. However, not only are such solutions burdened by high investment costs, they are also energy-intensive and pollution-generating [7]. It is estimated that almost 96% of industrial hydrogen is produced by converting fossil fuels [8,9].

Biomass-based technologies, as well as methods that harness biological processes of microorganisms, are becoming more and more viable as means of hydrogen production [10,11]. They consist mostly of organic-feedstock fermentation (carried out by specialised groups of bacteria) and intracellular biochemical processes conducted by certain microalgae species [12,13]. Microalgae possess very high photosynthetic efficiency, can rapidly build biomass, are resistant to various contaminants, are amenable to genetic manipulation and can be sited on land that is unsuitable for other purposes. Given these considerations, microalgae seem to represent the most promising route of biohydrogen production [14,15].

High hydrogen production rates by microalgae are predicated, in part, on efficient biomass growth. The most promising technologies for microalgal cultivation and growth are the ones that use seawater, thanks to its wide availability and low acquisition cost [16,17]. Algae can be cultured using a variety of methods, from strictly monitored methods in technologically advanced designs, to less predictable methods in open systems [18]. The open systems include traditional ponds (ground or concrete), circular ponds with mechanical mixing, race track-type ponds with a paddle wheel, and cascade ponds [19]. Closed systems consist of various types of photobioreactors. Unlike open systems, closed cultures enable constant monitoring of illumination intensity/time and culture temperature, while also providing protection against predators, parasites and competitive species of algae [20,21]. The most commonly used are sack systems of “large bags”, tubular photobioreactors (horizontal, vertical, or inclined at any angle), Biocoil-type reactors, and plate photobioreactors [22]. Systems that produce microalgal biomass for hydrogen are usually closed in order to prevent contamination of the culture and control process parameters [23].

H₂ production set-ups usually use single-celled algal species, specifically the ones that possess the particular metabolic and enzymatic qualities required for hydrogen production [24]. These include green-algae and blue-green algae taxa, especially *Chlamydomonas reinhardtii*, *Platymonas subcordiformis*, and the genus *Chlorella* sp. [25]. The aim of the present work is to give an account of present knowledge on microalgal hydrogen production and compare it with the other available biofuel production technologies.

2. Thermochemical Methods of Producing Hydrogen from Conventional Fuels

One of the methods of hydrogen production is steam reforming, i.e., the steam-assisted conversion of hydrocarbons, mainly methane, over a metallic (e.g., Ni-based) catalyst. The mechanism of this process lies in the reaction of steam with methane in the presence of a metallic catalyst, resulting in a synthesis gas (syngas) composed of carbon monoxide, hydrogen, and carbon dioxide [26,27]. Conventional energy carriers are used in the processes, leading to release of CO₂ into the atmosphere [28]. Substrates (including natural gas, hard coal, brown coal, and petroleum) are subjected to thermochemical conversion at temperatures ranging from 700 to 1100 °C [29].

Goicoechea et al. examined the effect of temperature, pressure, and steam input on steam reforming of acetic acid. Hydrogen productivity was found to be the highest at 700–1000 °C and a H₂O/CH₃COOH ratio of 2:1. Pressure had the least impact on hydrogen production efficiency during acetic acid reforming [30]. It has been shown that biofuels, including methanol, ethanol, biodiesel, and methane-containing biogas, can also be used for hydrogen production through steam reforming [31,32]. Methane is a crucial resource, especially for the chemical and petrochemical industries. Steam reforming of methane is a well-explored process with high efficiency (53–99%) [33,34].

Nahar et al. investigated steam reforming of biodiesel using two Ni-supported Ca-Al and Ce-Zr catalysts. The process was run at 650 °C H₂. Production efficiency varied between 91% and 94%, depending on the catalyst [35]. The H₂O/C ratio increased from 2 to 3, which is advantageous for H₂ production. Hammoud et al. converted methanol into H₂ at almost 52% efficiency against the stoichiometric potential, using Cu-based catalysts for steam reforming. The best performance was achieved with a 10% Cu catalyst. This particular process was operated in a fixed-bed reactor at a temperature range of 200–250 °C [36]. Charisiou [37] and Remón [38] point to steam reforming as a viable method of producing hydrogen from glycerin—a by-product of biodiesel production from vegetable oil and bioethanol.

Steam reforming is performed in sorption reactors, continuous reactors, and membrane biological reactors. This method requires a low ratio of water vapour to carbon in order to maximize thermal efficiency and hydrogen yields. Also important is the separation of the gas constituents, particularly CO₂, with increasing focus being put on combining the two processes to increase the fuel-to-hydrogen conversion efficiency [39].

Another thermochemical H₂ production technology described in the literature is the partial oxidation of organic compounds at 1127–1427 °C and 3–10 MPa [40]. This process is based on converting hydrocarbons to syngas with a suitable H₂/CO ratio [41]. The procedure is carried out in the presence of pure oxygen, using Ni-based catalysts with platinum, rhodium, palladium or ruthenium compounds [42]. Partial oxidation systems can take most gaseous and liquid hydrocarbons as a feedstock. It is a time-efficient, exothermic process with short thermochemical reaction times [43]. Effective, economically-viable and technologically-feasible systems have been sought for partial oxidization of feedstocks like bioethanol, methane or butanol, where oxidization is achieved by airborne oxygen, thus reducing costs and operational difficulties associated with pure oxygen feeds [44]. Huang et al. used Ni-based catalysts to improve the hydrogen production efficiency in partial oxidation of n-butanol. During the process, butanol was converted and oxidized to H₂, CO, and CO₂, with the conversion efficiency range calculated at 93% to 100%, and a CO separation efficiency of 70% [45]. According to the literature, partial oxidation can also be used to convert methane into hydrogen [8].

The conversion of conventional energy carriers to hydrogen by partial oxidation has a 20%+ efficiency, with the exact ratio determined by the catalysts used. Some authors, such as Chen et al. observed 95% methane-to-hydrogen conversion when using glycine-based catalysts with 99% CO separation efficiency [46]. Zhang et al. obtained a methane conversion rate of 72–93% over Ni-based catalysts at 650–700 °C. H₂ selectivity ranged from 83–98%; while CO separation did not exceed 90% [47]. Shan et al. converted methane to hydrogen through partial oxidation at rates no higher than 70%. This process was operated between 500 and 900 °C [48]. Researchers have demonstrated that conversion efficiency is mainly determined by the catalyst, process temperature, and hydraulic retention time [47,49].

Partial oxidation of organic compounds is mainly performed in fixed-bed reactors, with ongoing research efforts aiming to increase the efficiency of the process and the selectivity of the produced gases [50].

Autothermal reforming is a hybrid method combining the two previous processes [51]. It does not require any external heat to be supplied, relying instead on to the energy released from oxidizing organic feedstock, which increases the temperature and activates the thermochemical conversion cascade [52,53]. The most commonly cited limitations of this method include coke formation, decreasing catalyst efficiency, and catalyst deactivation, which can be caused by sulphur compounds in the fuels. For the process to be efficient and optimal, a suitable catalyst must be used. As with the previous methods, the most common choices are Ni-based catalysts and precious metals, such as platinum, rhodium, and ruthenium [54,55]. Likewise in other thermochemical methods, catalysts for autothermal reforming should be low-cost, highly reactive and durable [56]. The primary feedstocks used in autothermal reforming processes are petrol and diesel oil, though ethanol or methane are often used as well [57].

Palma et al. examined the viability of extracting hydrogen from natural gas in an autothermal reforming process. The authors used catalysts containing ZrO₂ and Al₂O₃, achieving 95% and 88% methane-to-hydrogen conversion respectively [58]. In a study by Czernik and French, the authors reported yields corresponding to 70–83% of the stoichiometric potential, converting pyrolysis-derived bio-oil to hydrogen. The process was run in a reformer at 800–850 °C with platinum-based catalysts, yielding 9–11 g H₂/100 g bio-oil [59]. Gallucci et al. carried out an autothermal ethanol reforming process in a fluidised-bed membrane reactor, achieving 100% conversion of the tested organic feedstock into synthetic gas. The study also noted a 97% rate of pure hydrogen recovery from the gas mixture [60]. Steam reforming is usually done in multi-section membrane reactors and fluidised-bed membrane reactors. The main function of membrane reactors is to integrate the production and separation of hydrogen in a single unit [60,61].

Gasification of coal or coke is a high-temperature process very similar to steam reforming [62]. The feedstocks used in this technology are highly important for hydrogen

production due to their widespread use, availability and low market price [63]. The technology is based on incomplete combustion in limited oxygen [64]. S installations usually provide for controlling the input of steam/air into the syngas-producing system, with the resulting gas composed primarily of H₂ and CO [65]. Water vapour, oxygen, hydrogen, air, and carbon dioxide can all act as gasifying agents [66]. The gas produced by gasification can be used in a multitude of applications, including for power generation and home heating, for fuel in gas turbines, as well as for manufacturing chemicals, methanol, hydrogen, and liquid fuels [67].

Gasification is a highly efficient and cost-effective process of producing energy and is in fact one of the principal technologies for converting coal to hydrogen [68]. The barriers to further development of this method mainly lie in its high investment costs, technological problems, and significant CO₂ emissions into the atmosphere [69]. Numerous researchers have noted a correlation between the efficiency of the process and optimal O₂/C ratios. Studies confirm that coal to syngas conversion increases proportionally to the O₂/C ratio [70]. The efficiency of the process and the composition of the resulting gas are closely linked with temperature and the steam-to-carbon ratio, among other parameters. As these values increase, so does the process efficiency and H₂/CO ratio in the produced gas [71].

Gasification of coal or petcoke is currently done in three types of reactors and their modifications: moving-bed, fluidized-bed, and entrained-bed [72]. Temperature and pressure parameters are kept in the ranges of 1200–1600 °C and 5–8 MPa, depending on the reactor design and type, which also determines the dosing method and fuel flow in the reaction zone. Using conventional substrates leads to a near 100% gasification efficiency, whereas biomass-based systems produce 45 to 70% of the stoichiometric values [73].

Deniz et al. achieved a hydrogen production efficiency of 62.5% using *Posidonia oceanica* seaweed as the gasification substrate. The process was operated at a temperature of 600 °C [74]. Calzavara et al. reached their peak efficiency (76%) through gasification of maize at 745 °C and 2.8 MPa [75]. Other researchers have attained 70% efficiency by gasifying chicken manure [76]. Ge et al. achieved 100% gasification of coal in a microreactor at 700 °C and 25 MPa over a K₂CO₃ catalyst. Hydrogen accounted for 60% of the resultant gas [77].

Hydrogen can also be produced using plasma technology. In this process, hydrocarbons are separated into hydrogen and solid carbon at 1600–2000 °C in the presence of air or pure nitrogen [78]. The efficiency of plasma technology is highly determined by how the plasma flame and the fuel are made to interact. Gasification efficiency can be improved by supplying feedstock to the centre of the plasma flame and increasing its residence time in the flame, resulting in an increased H₂ fraction and calorific value of the gas [79]. Syngas composition was found to vary significantly depending on the oxygen/feedstock ratio [80]. High concentrations of H₂ and CO have been noted for low O₂ /substrate ratios, ranging from 0.0 to 0.3. Syngases have been found to contain high quantities of CO₂ if this value exceeded 0.8. [81].

Microwave plasma technologies, where the gasifying agents are steam and air, are becoming increasingly popular due to their hydrogen productivity [82]. Yoon et al. (2013) explored gasification of glycerin—a by-product of biodiesel production—using plasma technology. The researchers used microwaves to generate the plasma. The process produced a gas comprising of: H₂—57%, CO—35%, CO₂—65% and CH₄—1%. H₂ and CO₂ levels increased with steam input, while CO decreased. The gas composition did not change significantly between steam-to-fuel ratios of 1.6 to 2.4 [81]. In another study, Yoon and Lee examined the use of microwave plasma for coal gasification. They showed that it was possible to produce syngas with a hydrogen content of 60% with no oxygen present, though at lower feedstock conversion efficiencies and gas yields [79]. In turn, Hong et al. exposed coal to a microwave plasma torch, resulting in a biogas composed of: H₂—48%, CO—23%, CO₂—25% and CH₄—4%, and maximum performance achieved with a carbon/steam ratio of 1.36 [83].

Water electrolysis is an electrochemical process in which the electrical energy supplied to the system is used to separate the water molecule into atomic oxygen and hydrogen gas [84]. The cathodes are usually mild steel or nickel-based electrodes, the anodes are usually made of or coated with nickel [85]. This process has an efficiency of 65–80% and produces highly pure hydrogen (99.999%) without traces of other gases [86]. The technologies for hydrogen production can be divided into three categories based on the electrolyte used: liquid-electrolyte alkaline electrolysis, membrane electrolysis, and high-temperature (steam) electrolysis [87]. The most important factors in the practical applicability of this hydrogen production technology are the cost and the availability of energy [88]. Fiegenbaum et al. achieved electrolysis efficiencies between 93 and 99% using a combination of tetrafluoroborate acid and triethylammonium propanesulfonic acid as an electrolyte, and a platinum electrode. The process was run at 25–80 °C [89]. Perez–Herranz et al. managed to increase energy efficiency from 57.8% to 70% by increasing the operating temperature of the electrolyser from 33 °C to 45 °C. A 30% NaOH solution was used as the electrolyte [86]. Hug et al. also achieved an electrolysis efficiency of over 70% in a 10 kW alkaline electrolytic cell [90]. Ando and Tanaka reached 90% efficiency of electrolysis using a system that produced hydrogen and hydrogen peroxide simultaneously. Hydrogen electrodes with platinum and hydrogen peroxide electrodes with carbon material operated in a NaOH solution electrolyte [91].

3. Thermochemical Methods of Producing Hydrogen from Biomass

Biomass gasification is a process that converts the feedstock into a gas mixture of H₂, CO, CO₂, and CH₄ at temperatures above 1000 K and in the presence of a gasification agent, such as steam, oxygen or air [92]. The literature data confirms that 60% hydrogen content in the gas mixture can be achieved given optimal operating conditions, i.e., temperatures between 900 and 1400 °C, and biomass moisture content of 10–20% [93]. Feedstocks used for gasification usually contain less than 35% water [94]. The main practical limitations of biomass gasification lie in the formation of tar and significant amounts of ash and volatile impurities, including carbon particles, alkali metals, nitrogen/sulphur oxides, and chlorides [95]. Another significant hurdle is the difficulty in maintaining a constant process efficiency and syngas composition [96]. Analyses to date have detected significant discrepancies in the final composition of the syngas, even when the operational conditions and the compositional/physical parameters of the supplied biomass were the same [97].

Biomass used for gasification includes agri-food industry waste, forestry waste, and agricultural waste [98,99]. There have also been reports indicating successful use of aquatic plant biomass for gasification [100]. Research is underway to test the gasification of coal-biomass and coke-biomass blends [101]. This technology reduces the proportion of fossil fuels needed to produce syngas, CO₂ emissions, the amount of tar in the final gas, and provides a more stable process [102]. Improving the operation of reactors is crucial for the development of biomass gasification technology. Industrial-scale experiments and systems usually operate on fixed-bed, fluidised-bed, and entrained-bed designs [103].

Literature reports confirm that processes based on algal biomass gasification are feasible [74]. For instance, Werle conducted a comparative study to investigate thermochemical conversion of algal (*Phaeophyta*) biomass and granulated sewage sludge. The process was run in a fixed-bed system. An analysis of the gas composition showed that fuel from gasification of algae had two times the methane and much lower CO compared to the gas produced by sludge incineration, while having a similar hydrogen content (around 5% by volume) [103]. In turn, Song et al. gasified biomass in a fluidised bed and analysed the efficiency of the process in relation to the temperature. The biomass was gasified at 720–920 °C. As the temperature increased, the H₂ fraction in the final gas decreased from 71.5 to 52.7%, with CO proportion increasing instead. The highest carbon-to-hydrogen conversion rate and the most favorable composition of the final gas (approx. 60% H₂) was achieved at 820 °C [104].

Biomass pyrolysis is a process conducted at 650–1000 K and 0.1–0.5 MPa in the absence of oxygen [105]. The technology can be used to convert organic substrates into liquids (a mixture of hydrocarbons), solids (coal), and a mixture of gases (H_2 , CH_4 , CO , and C_2H_6 , C_2H_2) [106]. The liquid fraction can then be steam reformed to boost hydrogen production [107]. In fact, most gaseous compounds can be converted to hydrogen given suitable conditions. If sufficiently high temperature (above 900 °C), rapid heating, and extended volatile phase residence times are ensured during biomass pyrolysis, the resultant hydrogen yields are higher [105]. Zhao et al. subjected rice husks to pyrolysis and secondary steam reforming. The pyrolysis was done at 923 K with 18 min of residence time. The resultant oil and gas fractions were further processed via steam reforming at 1123 K and steam-to-carbon ratio of 2. The process produced a hydrogen yield of 65 g H_2 /kg biomass and over 60% H_2 content in the gas [107]. Alvarez et al. used a combined process (pyrolysis + steam reforming) to boost hydrogen yield. The wood sawdust feedstock was amended with polypropene at different weight ratios. A 80:20 biomass-to-polypropene was found to produce the best results, with a hydrogen concentration of 36.1%. When a Ni/Al_2O_3 was introduced to the steam reforming process, the H_2 fraction increased to 52.1% [108].

Literature reports point to the possibility of using the biomass of aquatic plants, including algae, as a feedstock for pyrolysis [109]. Table 1 shows the productivity of different alga species used in this process in different studies.

Lin et al. examined hydrogen yields in a plasma reactor at different microwave power levels (800–1000 W range). *Spirulina* algae were chosen as the feedstock for pyrolysis. A near 45% gas-volume fraction of hydrogen was achieved at peak yields (31 mg H_2 /g dry mass algae) in the group treated with 1000 W microwaves [110]. A study by Maddi et al. compared the efficiency of pyrolysis between lignocellulosic biomass, *Lyngbya* sp. and *Cladophora* sp. algae sampled from eutrophic water bodies. The process temperature was 600 °C. The best performance was achieved with *Lyngbya* sp., resulting in a 48.7% hydrogen fraction in the pyrolytic gas, compared to the 44.5% in the gas derived from pyrolysis of corncob [111].

Hydrogen production via supercritical substrate conversion involves subjecting water to a pressure of 22 MPa and temperatures in the range of 400 to 650 °C. Under these conditions, water exhibits both liquid-like and gas-like properties. The supercritical water is used to depolymerise the biomass (feedstock for hydrogen production) [112]. The heating rate is a key determinant of efficiency and final gas composition. Temperatures over 500 °C with higher heating rates lead to higher yields and inhibit the formation of harmful chemicals, such as tars, phenols, and furfurals [113]. The advantage of supercritical biogas conditioning is that it avoids feedstock drying, eliminating several processing steps required by other thermochemical hydrogen production methods [114]. This makes it a very promising technology for harnessing algal biomass as a substrate for supercritical conversion [115]. Alvarez et al. produced hydrogen via supercritical conversion of the substrate (sawdust). Hydrogen yields were maximised (80 mol/kg biomass) at 25 MPa and 600 °C. Moisture content in the feedstock is also a significant factor—the best results were achieved with biomass containing 95% water [108]. Similarly, Lu et al. have found that the highest hydrogen yields (90 mol/kg biomass) were generated from feedstock with 95% water content at 25 MPa and 900 °C. Less water in the substrate led to sharp losses in hydrogen yields [116]. Lu et al. (2008) gasified corncob amended with sodium salt in the presence of carboxy methyl cellulose in a fluidised-bed reactor, reaching a hydrogen yield of 12 mol/kg substrate. The maximum performance was achieved when the feedstock contained 3% corncob and 2% salt, with 60 s of reaction time. Hydrogen fractions in the resultant gas ranged from 32 to 36%. The operating conditions were as follows: 25 MPa; 650 °C [117].

Table 1. Comparison of pyrolysis products from different taxonomic groups of algae.

Microalgal Strains/ Biomass	Process	Alga Type	Reactor Type	Temp. [K]	Products [%]			Energy Yield [MJ/kg]	Ref.
					Oil Fraction	Gas Fraction	Solid Fraction		
<i>Nannochloris</i> sp.	Direct pyrolysis catalytic pyrolysis	<i>Nannochloris</i> sp.	Fixed-bed reactor	573–773	20.0–31.1	18.9–33.5	24.2–45.3	24.6	[109]
<i>Nannochloropsis</i> sp.		<i>Nannochloropsis</i> sp.			10.0–19.0	11.0–34.0	56.0–19.0	32.7	
<i>Chlorella protothecoides</i>	Rapid pyrolysis	<i>Chlorella protothecoides</i>	Fluidised-bed reactor	773	17	28	55	29.0	[118]
<i>Microcystis Aeruginosa</i>	Catalytic pyrolysis	<i>Microcystis Aeruginosa</i>	Fluidised-bed reactor		23	56	21	30.0	
<i>Chlorella protothecoides</i>	Rapid pyrolysis	<i>Chlorella protothecoides</i>	Fluidised-bed reactor	773	58	30.0	12.0	41.0	[119]
<i>Tetraselmis chunii</i>		<i>Tetraselmis chunii</i>			43	20	37	3.4	
<i>Chlorella vulgaris</i>	Slow pyrolysis	<i>Chlorella vulgaris</i>	Conventional tubular oven	773	41	25	34	1.8	[120]
<i>Chlorella like</i>		<i>Chlorella like</i>			41	22	37	4.8	
<i>Chaetoceros muelleri</i>		<i>Chaetoceros muelleri</i>			33	14	53	1.2	
<i>Dunaliella tertiolecta</i>		<i>Dunaliella tertiolecta</i>			24	13	63	2.4	
<i>Synechococcus BGAB</i>		<i>Synechococcus BGAB</i>			38	18	44	1.4	
blue-green algae (>90% <i>Microcystis</i>)	Pyrolysis	blue-green algae (>90% <i>Microcystis</i>)	Fixed-bed reactor	773	26.66–54.97	16.25–41.33	57.09–20.39	31.9	[121]

4. Biological Methods of Producing Hydrogen from Biomass

4.1. Fermentation

Many authors contend that bacterial fermentation is the most efficient method of converting biomass to hydrogen [122,123]. The literature includes accounts of hydrogen-production processes that utilize organic feedstock with various parameters, including organic waste from agricultural, food, meat, and paper industries, as well as livestock manure, slurry, and effluent [124,125]. The types of fermentation most crucial to hydrogen production are butyrate/butanol fermentation, typical of the genus *Clostridium* sp., and mixed-acid fermentation, mostly used by the family *Enterobacteriaceae* (*Escherichia coli*, *Enterobacter aerogenes*, *Klebsiella pneumoniae*, *Vibrio cholerae*, *Shigella dysenteriae*) and *Bacillus* sp. [126].

The mechanism of biohydrogen formation in anaerobic processes involves the reduction of protons by hydrogenase, using electrons donated by ferredoxin. The electrons are released by the degradation of glucose to pyruvate, which is then oxidised to acetyl-CoA and CO₂. A diagram of an example biohydrogen production by *Clostridium* sp. bacteria is presented in Figure 1.

Kumar and Das [127,128] provide a detailed outline of hydrogen production mechanisms via fermentation by *Enterobacter cloacae* IIT—BT 08, using different sources of organic matter. Using sucrose and cellobiose as feedstock led to the highest hydrogen yields at 6.0 H₂ mol/mol substrate and 5.4 H₂ mol/mol substrate, respectively, with a production rate of 35.6 mmol H₂/dm³·h. The authors surpassed this production rate in a different study, reaching 75.6 mmol H₂/dm³·h. In this case, the reactor used to grow anaerobic bacteria was packed with lignocellulosic materials, including rice straw, bagasse, and coconut coir. The reactor packed with coir performed the best. The authors attribute this

finding to the higher cell density in the coir matrix, perhaps due to the largest active surface area available to cells. A study by Wu et al. investigated fermentation of swine manure supplemented with glucose. Hydrogen production was $2.25 \text{ dm}^3/\text{dm}^3 \cdot \text{d}$, whereas the hydrogen content of biogas peaked at 36.9%. The authors also looked at optimum pH for fermentation and noted the best performance at pH 5.0, which ensured stable hydrogen production and concentration throughout the experiment (22 d). The experiment used an ASBR system, with a glucose degradation efficiency ranging from 98.5 to 99.6% [129]. Fang and Liu tested a dark hydrogen fermentation process in a 3 L reactor at a pH range of 4.0–7.0. A synthetic medium with $7.0 \text{ g}/\text{dm}^3$ glucose was fed into a digester. The process turned stable after 14 days and degraded 90% of the glucose. The hydrogen yields at optimal pH (5.5) reached $2.1 \text{ mol H}_2/\text{mol glucose}$ with 64% hydrogen content in the biogas [130]. Kim et al. achieved a hydrogen production of $128 \text{ cm}^3/\text{g COD}_{\text{removed}}$. The hydrogen yield was close to $110 \text{ cm}^3/\text{dm}^3 \cdot \text{h}$. Food waste was fermented using *Clostridium beijerinckii* KCTC 1785. The process was run at pH 5.5 and $40 \text{ }^\circ\text{C}$ [131]. Song et al. used cow dung compost for dark fermentation and obtained a hydrogen yield of $290.8 \text{ cm}^3/\text{dm}^3$ culture. The feedstock input into the system had a concentration of $10 \text{ g}/\text{dm}^3$. Initial pH was around 7.0. The dominant hydrogen producers were *Clostridium* sp. and *Enterobacter* sp. [132].

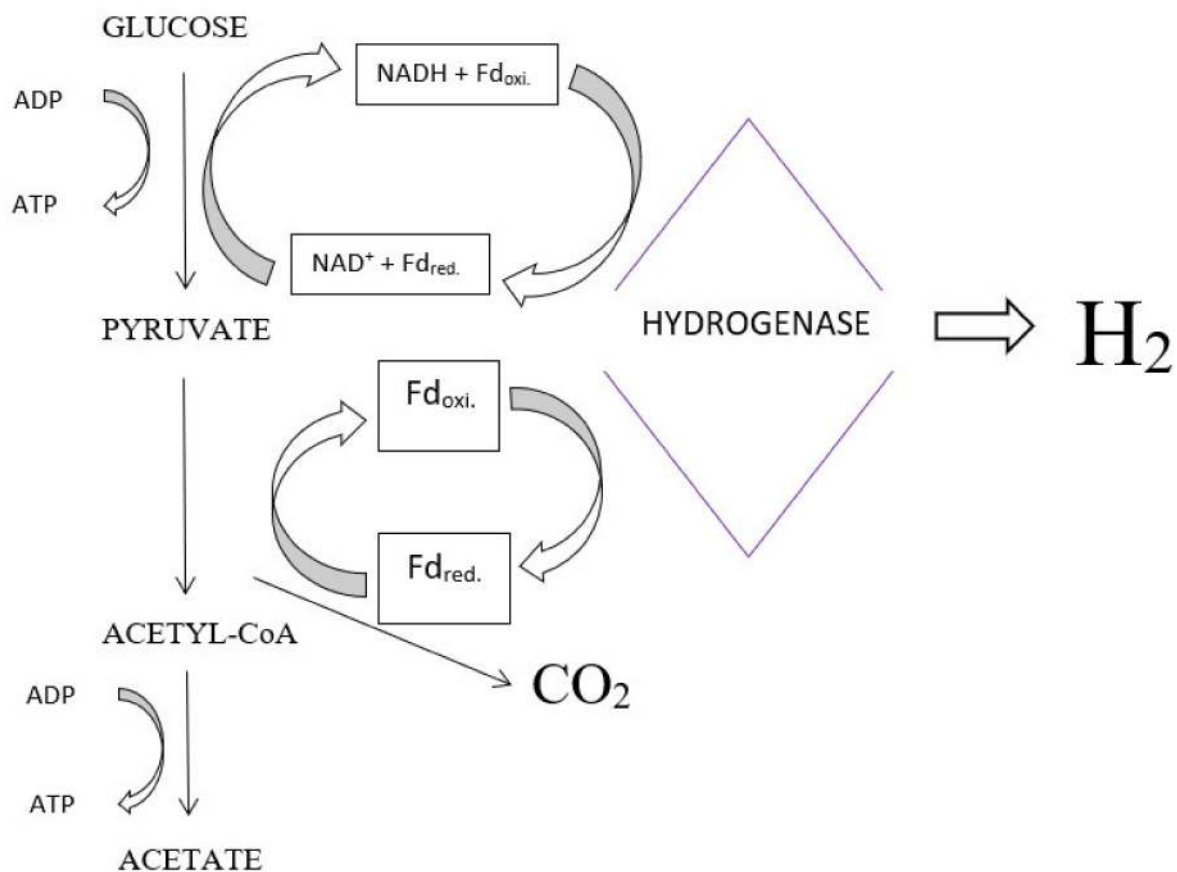


Figure 1. Diagram of hydrogen production by *Clostridium* sp.

Fermentative hydrogen production is influenced by many factors and system parameters, including substrate type, substrate concentration, hydraulic retention time (HRT), type of digester, pH, temperature and microbial strain [133]. Even trace amounts of oxygen in the system inhibit hydrogenase activity in obligate anaerobes, which is why it is usually the safer choice to use facultative anaerobes, with *Clostridium* sp. and *Enterobacter* sp. being the most common. This is due to the fact that these bacteria better tolerate oxygen in bioreactors [134]. Optimal pH for efficient hydrogen production ranges from

5.0 to 6.0. Lower values have a direct effect in switching microbial metabolism towards biochemical processes that lead to different make-up of the resultant gas and decreased hydrogen production. Furthermore, pH under 4.0 can inhibit microbial growth [129]. Conversely, increased pH induces methanogenic bacteria to grow, consuming hydrogen to produce methane [135]. One simple technological procedure, commonly used to eliminate methanogenic bacteria from the communities in anaerobic sludge, is to perform heat treatment at 80–104 °C [136]. Heat conditioning of anaerobic microflora ensures the survival of hydrogenous spore-forming microbes, including *Clostridium* sp. and *Bacillus* sp. [137]. Short hydraulic retention times (12 h or less) can also be used to limit the growth of bacteria that compete with hydrogen-producing microbes [138]. The efficiency of hydrogen fermentation can be hampered by undissociated volatile fatty acids generated in the reactor [135]. Partial pressure of gaseous hydrogen has also been identified as an important factor. Excessive hydrogen levels in the system lead to accumulation of propionic acid and butyric acid, reducing hydrogen production. Reducing the pressure—and thus, the hydrogen concentration—can significantly improve performance [139]. Other parameters are also important, including substrate profile, nitrogen levels (used as a nutrient by microorganisms) or iron levels (involved in hydrogenase activity). According to literature data, iron levels should be kept between 10 and 100 mg/dm³ [126].

4.2. Photofermentation

Photofermentation is done by anaerobic bacteria capable of converting organic acids to hydrogen and CO₂ [140]. Most common photosynthesizers include green/purple sulphur and non-sulphur bacteria. The species most widely covered in the literature are: *Rhodobacter spheroides*, *Rhodobacter capsulatus*, *Rhodobacter sulidophilu*, *Rhodopseudomonas palustris*, *Rhodopseudomonas sphaeroides*, and *Halobacterium haobium* [141]. Nitrogenase is the primary photofermentative enzyme, capable of catalyzing its reaction in either direction [142]. In the presence of inhibitory nitrogen, electrons are transferred by ferredoxin and used by microorganisms to reduce molecular nitrogen into ammonia. In a nitrogen-deprived environment, electrons carried by nitrogenase reduce protons into molecular hydrogen. Nitrogenase activity can be inhibited by oxygen, ammonia or excessive C/N [143]. The biochemistry of photofermentative hydrogen production involves the transfer of electrons released during the decomposition of organic substrate by ferredoxin, which are taken up by nitrogenase and used to reduce protons to molecular hydrogen. The energy necessary for protein-mediated electron transfer is derived from the light source. A diagram of the photofermentation process is presented in Figure 2.

Achieving suitable conditions for photofermentation requires a source of bright 400–1000 nm light (6–10 klux), a temperature between 30 °C and 36 °C, and near-neutral pH (6.8–7.5) [144]. Optimal illumination intensity boosts hydrogen production rates and yields. However, due to the high running costs of such a solution, alternating light-dark cycles are usually used instead. The cycles tend to be equal in length, 12/12 h being the most common regime [145]. Hydrogen yields produced through photofermentation are also largely and directly determined by the type and design of the bioreactor [146]. Tubular, column and flat-plate reactors are the most common [147]. These units are typically closed and hermetically sealed, preventing contamination, oxygen penetration and growth of competing microbial species. Bioreactors currently used for photofermentation are similar in design to those used for cultivating and growing microalgae [148].

Yetis et al. studied photofermentative hydrogen production by *Rhodobacter spheroides* O.U.001 using sugar refinery wastewater as feedstock. The hydrogen yield was 3.8 cm³/dm³·h. When malic acid was added to the feedstock, production rate increased to 5.0 cm³/dm³·h [149]. Eroglu et al. demonstrated that colored and organic-rich wastewater needs to be diluted. Dilution of olive mill wastewater led to hydrogen production of 13.9 dm³ H₂/dm³ by *Rhodobacter sphaeroides* O.U.001 [141]. Oh et al. used *Rhodopseudomonas palustris* P4 for photofermentation, producing 2.4–2.8 mol H₂/mol acetic acid [150]. Argun and Kargi investigated the effect of different light sources and intensities on photofer-

mentative hydrogen production by *Rhodobacter sphaeroides*-RV. Fatty acids derived from ground wheat starch served as the feedstock. Tests with halogen lamps led to the highest hydrogen production of 252 cm³ and production efficiency of 781 cm³ H₂/g fatty acids. A light intensity of 5 klux provided the best performance in terms of hydrogen production at 1037 cm³/g fatty acids [151]. Laocharoen and Reungsang ran a photofermentative process using *Rhodobacter sphaeroides* KKU-PS5. The operational parameters of the fermentation were as follows: temperature—30 °C; light intensity—6 klux; initial pH—7.0. Malic acid at a concentration of 30 mmol/dm³ served as the primary feedstock for the microorganisms. Hydrogen production yields and rates were 1330 cm³ H₂/dm³, 3.80 mol/mol malate, and 11.08 cm³ H₂/dm³·h respectively [152]. The efficiencies of photofermentative biohydrogen production, according to literature data, are presented in Table 2.

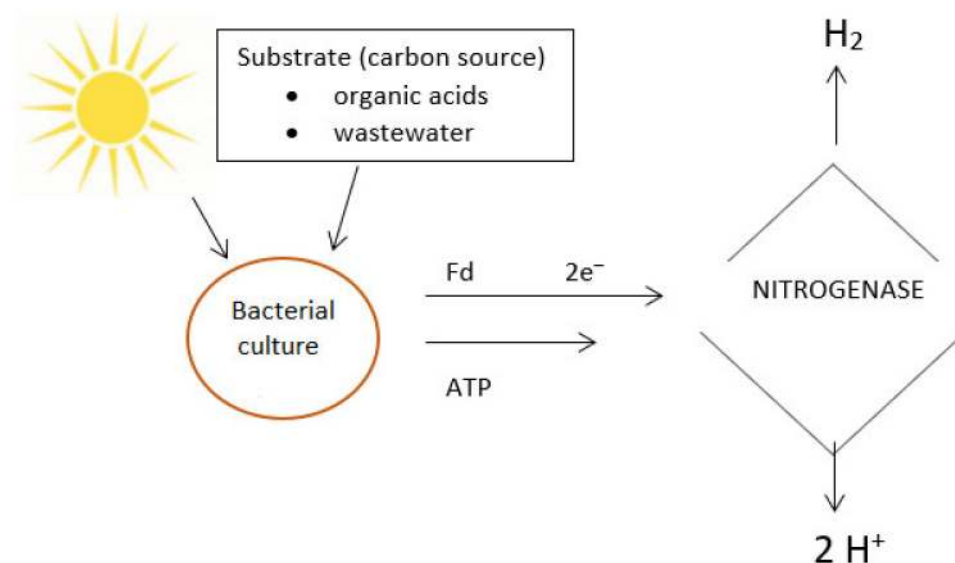


Figure 2. Diagram of photofermentative hydrogen production by microbes.

Literature data indicate that a combination of dark and photofermentation is a valid method of enhancing hydrogen production [153]. Dark fermentation produces organic acids and alcohols as by-products, which serve as a carbon source for the bacteria involved in photofermentative hydrogen production [154]. Integrated biological processes significantly improve the ratio of energy stored in the hydrogen to the energy needed to maintain the culture. This ratio was 3.0 in studies by Manish and Banerjee [155].

Nath et al. applied glucose for hydrogen production by *Enterobacter cloacae* strain DM11, with dark fermentation as the first stage of the process. The gas yield amounted to 1.86 mol H₂/mol glucose. The spent medium from the fermentation, which mainly contained acetic acid, was then used as a source of carbon for photofermentation by *Rhodobacter sphaeroides* O.U.001, which resulted in an additional 1.5 to 1.72 mol H₂/mol of acetic acid [156]. Yokoi et al. increased the gas production twofold by using *Clostridium butyricum* and *Rhodobacter* sp. M-19, with a total yield of 6.6 mol H₂/mol glucose [157].

Khanal et al. produced 7.2 mol H₂/mol glucose by using starch production waste as the basic feedstock for fermentation, and photofermented the residue (which contained lactic, butyric and acetic acids) [164]. Yokoi et al. have produced similar results using *Clostridium butyricum*, *Enterobacter aerogenes*, and *Rhodobacter* sp. M-19 grown on potato-processing waste [165]. Cheng et al. conducted a two-stage hydrogen production process using *Arthrospira platensis* pre-treated with microwaves and H₂SO₄. Dark fermentation of the feedstock (containing 10 g/dm³ glucose) resulted in a hydrogen yield of 96.6 cm³/g dry matter. The spent solution had a high NH₄⁺ content of 31.6–96.6 mM. This residue was then treated by ion exchange to prevent interference with subsequent biochemical processes, removing 91.8–95.8% ammonium ions. The treated residue could then be further

photofermented, resulting in hydrogen production of 240.4 cm³/g dry matter. The entire system produced a total of 337 cm³ H₂ per gram of dry matter feedstock [166].

Table 2. Comparison of literature data on photofermentative hydrogen productivity.

Organism	Substrate	Light Intensity [W/m ²]	Temp. [°C]	H ₂ Production	Ref.
<i>Rhodobacter sphaeroides</i> O.U.001	olive mill wastewater	150	30	35 dm ³ H ₂ /dm ³ _{substrate}	[141]
<i>Rhodobacter capsulatus</i> JP91	glucose	175	30	5.5 mol H ₂ /mol _{glucose}	[158]
<i>Rhodobacter capsulatus</i>	sucrose (sugar industry molasses)	200	30	10.5 mol H ₂ /mol _{sucrose}	[159]
<i>Rhodobacter capsulatus</i>	sucrose	200	30	14 mol H ₂ /mol _{sucrose}	[159]
<i>Rhodobacter capsulatus</i> JY91	glucose	200	30	3.3 mol H ₂ /mol _{glucose}	[160]
<i>Rhodobacter sphaeroides</i> O.U. 001	milk industry wastewater	116	28	3.2 dm ³ H ₂ /dm ³ _{substrate}	[161]
<i>Rhodobium marinum</i>	soy sauce production wastewater	240	30	2.14 molH ₂ /mol _{glucose}	[162]
<i>Rhodobium marinum</i>	sugar cane bagasse	240	30	41 cm ³ H ₂	[162]
<i>Rhodobacter capsulatus</i>	malonate	200	30	3.7 mol H ₂ /mol _{substrate}	[163]
<i>Rhodobacter capsulatus</i>	acetate	200	30	2.5 mol H ₂ /mol _{substrate}	[163]

The performance of hybrid systems was also examined by Su et al., who set up an integrated dark and photo fermentation process with cassava starch as the substrate (10–25 g/dm³ concentration). The dark fermentation stage produced 240.0 cm³ hydrogen per gram of starch at a concentration of 10 g/dm³, with the maximum production rate being 84.4 cm³ H₂/dm³·h at a concentration of 25 g/dm³. The by-products of this stage—acetate and butyrate—were then used as substrates for fermentation in the presence of *Rhodopseudomonas palustris*. The yield at this stage amounted to 131.9 cm³ H₂/g starch at a rate of 16.4 cm³ H₂/dm³·h. Acetate and butyrate conversion capacities were respectively 89.3% and 98.5%. The total hydrogen yield of the two-stage process was 402.3 cm³/g starch [167]. In another study, Su et al. presented a method for improving hydrogen yields in a two-stage process. Hydrogen production during the dark fermentation stage reached 1.72 mol/mol glucose at a rate of 100 cm³ H₂/dm³·h. In the photofermentation stage, the yield was 4.16 mol/mol glucose. Metabolites from the dark cycle were converted in this stage with an efficiency of 92.3% (acetate) and 99.8% (butyrate). The two-step process yielded 5.48 mol H₂/mol glucose [168].

There has been an increasingly prevalent opinion that hybrid systems are capable of producing 12 mol H₂/mol glucose at their peak, which had once been considered a purely theoretical threshold [169].

5. Hydrogen Production Using Algae

The production of hydrogen through biological processes carried out by algae involves direct biophotolysis with photosynthetic production of hydrogen from water, using photo energy to break down the water molecule into hydrogen and oxygen [170]. This is mainly mediated by hydrogenase activity, which catalyses reversible H₂ oxidation and generates gaseous hydrogen by reducing protons [171]. Hydrogen production through microalgal photolysis is facilitated by two transmembrane peptide complexes: photosystem I (PSI) and photosystem II (PSII). The exposure of both complexes to solar radiation results in the breakdown of the water molecule. PSII produces O₂, while PSI uses the electrons generated in the process to reduce CO₂ and construct cellular material (under aerobic conditions); alternatively, the electrons are transferred by ferredoxin to hydrogenase and used for hydrogen production. Anaerobic conditions are required to induce hydrogen production and hydrogenase activity. Sulphur deprivation causes reversible inactivation of

PSII, leading to the inhibition of oxygen evolution by photosynthesis. Oxygen levels drop below those used up by respiratory metabolism. However, photosystem I (PSI) remains active, transferring the electrons to hydrogenase through ferredoxin, and thus activating hydrogen production [93]. A diagram of the biochemical hydrogen production process via direct biophotolysis of water by specialized microalgae is shown in Figure 3.

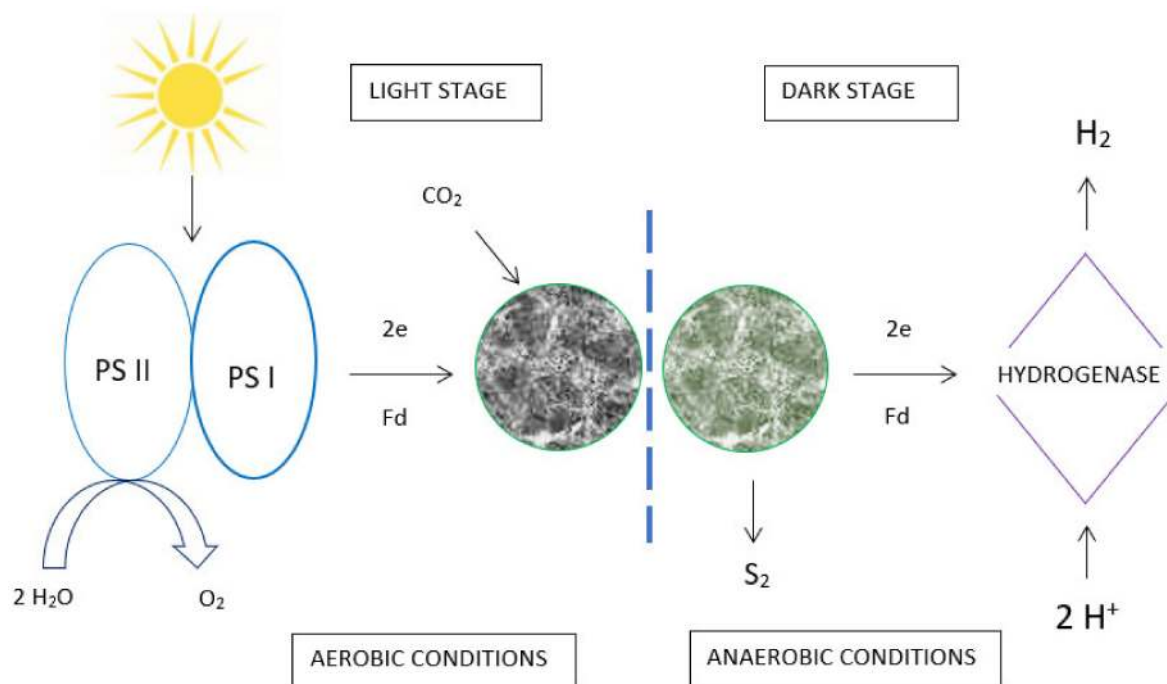


Figure 3. Diagram of direct water photolysis.

In the presence of organic substrates, the hydrogen-producing microalgal species can grow mixotrophically during light periods via growth and heterotrophically in the dark [172]. When the light supply to the culture system is limited, the algae metabolise the available simple organic compounds and use them for maintaining cellular processes and synthesising biomass [173].

It has been demonstrated that environments with oxygen levels kept below 0.1% provide the best conditions for cell systems to produce hydrogen [174]. The most common strategy for removing sulphur from the growth medium is to centrifuge the algal culture, and then suspend the concentrated and dewatered biomass in the medium, which has its sulphur replaced with chlorine compounds [175]. This centrifugation-based process has been shown to be costly and time-consuming, while also destroying some of the cellular material. Alternatively, the culture medium can be diluted to reduce sulphur in the system. However, this procedure requires more time for depleting the sulphur and reaching anaerobic conditions [174].

It is also difficult to pinpoint the right cultivation time and moment of initiating hydrogen production. Some authors have stated biomass production should be terminated in the middle of the exponential growth phase [176], whereas others have argued that higher algal cell densities directly improve efficiency and increase hydrogen production time [24]. Ji et al. have produced, at a cell density of 0.5 g/dm^3 , a hydrogen yield of $16 \text{ cm}^3/\text{g biomass}$, whereas higher cell densities (3.2 g/dm^3) ultimately led to a production of $49 \text{ cm}^3 \text{ H}_2/\text{g biomass}$. The conversion of light to hydrogen energy was 0.3%. Higher substrate density led to a near-tenfold increase in the gas production rate [24].

Most of the scientific publications on the subject have reported that single-cell algae are capable of producing H_2 with high efficiency. The species most commonly used by researchers is *Chlamydomonas reinhardtii*, commonly found in soil and saltwater [174]. Studies using this species report H_2 yields of $90\text{--}110 \text{ cm}^3/\text{dm}^3$ [177], with even higher

levels of 80–140 cm³/dm³ reached in some cases [178]. Faraloni et al. achieved a hydrogen production of 150 cm³/dm³ in a *Chlamydomonas reinhardtii* culture grown in olive mill wastewater [179]. A study by Skjanes et al. examined the hydrogen production capacity of 21 green algae species in an isolated anaerobic environment. The most productive strains were: *Chlamydomonas reinhardtii*, *Chlamydomonas euryale*, *Chlamydomonas noctigama*, *Chlamydomonas vectensis*, *Chlorella pyrenoidosa*, *Oocystis*, *Desmodesmus subspicatus*, and *Pseudokirchneriella subcapitata*. The top producer (at almost 140 cm³/dm³) was *Chlamydomonas reinhardtii*, followed by *Chlamydomonas noctigama* at 80 cm³/dm³ and *Chlamydomonas euryale* at 22 cm³/dm³ [178].

The algae of the genus *Chlorella* sp. have significant potential for producing hydrogen [180]. The species is attractive due to its eurybiontic nature, its great adaptability to changing environmental conditions, its resistance to pollution, and fast growth rate [181]. Scientific studies confirm that *Chlorella* sp. algal biomass can be used for efficient hydrogen production, comparable to other algal species more commonly used with this technology [25]. Zhang et al. investigated how nutrient-deprived media affected hydrogen production by *Chlorella protothecoides* algae. The hydrogen yield from the nitrogen-deprived medium was 110.8 cm³/dm³ culture. Simultaneous nitrogen and sulphur deprivation increased the yield to 140.4 cm³/dm³ culture [180]. Chader et al. compared hydrogen productivity and tolerance to oxygen across three algae species: *Chlorella sorokiniana*, *Chlorella salina*, and *Chlorella* sp. Ultimately, *C. sorokiniana* proved to be the best hydrogen producer with an output of 147 cm³ during the 220-h experiment. However, this strain had low tolerance to environmental oxygen at 2%. The other two microorganisms produced lower hydrogen yields, but were able to tolerate oxygen levels between 11% and 15.4% [182]. In turn, Song et al. achieved hydrogen yields ranging from 260 to 480 cm³/dm³ with *Chlorella* sp. The system performed best at 37–40 °C, with yields of 183 to 238 cm³/dm³·h at 30 mM initial glucose [25]. Genetic modifications of *Chlorella* sp. have been shown to enable hydrogen production without alternating between anaerobic and aerobic conditions and limiting sulphur in the culture [183]. Amutha and Murugesan investigated hydrogen production by *Chlorella vulgaris* MSU 01 algae, growing the biomass and producing hydrogen on different carbon substrates, including corn stalks. The algal biomass grew fastest on corn stalks at a concentration of 4 g DM/dm³. The biomass was used to produce hydrogen in a 0.5 dm³ bioreactor, yielding 220 cm³/dm³ culture after 6 days of the experiment. The average hydrogen production rate was 26 cm³/dm³·d [184].

Other works have examined the use of *Platymonas subcordiformis* for biohydrogen production in alternating light and dark conditions, with external carbon sources such as acetate, glucose, sucrose or other simple carbohydrates. Average hydrogen production efficiency ranges from 78 cm³/dm³ to a high as 158 cm³/dm³ culture [185]. Ji et al. explored the production of hydrogen by *Tetraselmis subcordiformis* in media deprived of different nutrients, such as nitrogen, sulphur, and phosphorus. The nitrogen-depleted experimental variants performed the best, yielding 55.8 cm³/dm³ culture [186]. This species is of interest for the production of organic substrates and biological hydrogen, as it is fast and easy to grow in reactors. There is a growing body of research on harnessing this species of microalgae as an immediate product in energy-carrier production technologies [185,186]. Biohydrogen yields from microalgae, as reported in literature data, are presented in Table 3. Biohydrogen production using algal biomass is comparative to that of cellulose-based biomass (Table 4).

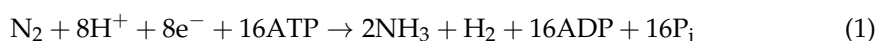
Table 3. Comparison of literature data on microalgal hydrogen productivity.

Microalgal Strains/Biomass	Condition	Performance H ₂ Production [cm ³ /dm ³]	Ref.
<i>Platymonas Subcordiformis</i>	torus photobioreactor two-phase incubation 0–1000 μmol photon/m ² ·s	157.7	[24]
<i>Chlamydomonas reinhardtii</i>	CST-PBR (continuously stirred type photobioreactor) 140 μE/m ² ·s, 100 rpm	321.0	[175]
<i>Chlamydomonas reinhardtii</i>	cylindrical flasks, 100 μE/m ² ·s, 28 °C	180.0	[177]
<i>Chlamydomonas reinhardtii</i>	glass photobioreactors, 300 μE/m ² ·s, 30 ± 1.5 °C, 400–500 rpm	120.0	[178]
<i>Chlorella vulgaris</i> MSU 01	illumination of 8 klux (2 nos.)—halogen lamps	220	[184]
<i>Tetraselmis Subcordiformis</i>	two-phase incubation, 160 μE/m ² ·s, 25 °C, 150 rpm	55.8	[186]
<i>Chlamydomonas reinhardtii</i>	flat PBRs, two-phase incubation, 70 × 2 μE/m ² ·s	210.9	[187]
<i>Platymonas Subcordiformis</i>	-	50.0	[188]

Table 4. Comparison of literature data on algal and cellulose-based biomass for biohydrogen production.

Feedstock	Condition	Performance H ₂ Production [cm ³ /gTS]	Ref.
<i>Arthrospira platensis</i>	batch, 35 °C	96.6	[166]
<i>Chlamydomonas reinhardtii</i>	batch, 37 °C	40.0	[189]
<i>Chlorella</i> sp.	batch, 35 °C, pH = 6.5	6.1	[190]
<i>Chlorella Pyrenoidosa</i> sp.	batch, 35 °C, pH = 6.0	8.8	[191]
<i>Chlorella vulgaris</i>	batch, 35 °C	41.2	[192]
<i>Chlorella vulgaris</i> ESP6	batch, 35 °C	81.0	[193]
<i>Nannochloropsis Oceanica</i> sp.	batch, 35 °C, pH = 6.0	0–2.0	[194]
<i>Scenedesmus obliquus</i>	batch, 37 °C	90.3	[195]
Corn cob	batch, 60 °C, pH = 7	3.23–3.27	[196]
Corn stalk	batch, 60 °C, pH = 7	3.28–3.47	[196]
Corn stalk	batch, 36 °C, pH = 7.5	79.8	[197]
Corn Straw	batch, 35 °C, pH = 6.0	69.6–93.4	[198]
Delignified wood	batch, pH = 7	2.5–7.8	[199]
Grass	batch, 35 °C, pH = 7	72.2	[200]
Grass silage	batch, 37 °C, pH = 7	37.8	[201]
Poplar leaves	batch, 35 °C, pH = 7	33.45	[202]
Rice Straw	batch, 55 °C, pH = 6.5	24.8	[203]

Another biochemical hydrogen production process mediated by algae is indirect biophotolysis. It has been demonstrated in cyanobacteria, which (via photosynthesis) accumulate carbohydrates from CO₂ reduction, which in turn are decomposed by fermentation. The process is mediated by photosystem I. The PSI proteins transfer electrons to ferredoxin using light energy [204]. Carbon dioxide and enzymes play an important role in the indirect biophotolysis process. CO₂ is a carrier of electrons and protons formed during the water molecule degradation, whereas enzymes, including nitrogenase and two NiFe hydrogenases, catalyse the reduction of atmospheric nitrogen to ammonia with simultaneous proton reduction and hydrogen release, as in Equation (1) [205]:



nitrogenase can also reduce protons into molecular hydrogen, as in Equation (2):



Blue-green algae are a particularly promising taxonomic group for hydrogen production. Their value lies in the fact that they are susceptible to genetic modification, have low environmental requirements, and do not need any specific nutrients to be fed into the system [205,206].

An experiment performed by Troshina et al. is one of the examples of using blue-green algae biomass to produce hydrogen [207]. A population of *Gloeocapsa alpicola* Calu 743 was grown in limited nitrate to boost hydrogen production. This resulted in high H_2 production at 25 $\mu\text{L}/\text{h}$ per mg dry matter. It was found that the hydrogen was produced by means of biodegrading the glycogen accumulated in the cells during photoautotrophic growth [207]. A similar study was conducted by Aoyama et al. using the filamentous blue-green algae strain *Spirulina platensis* NIES-46. Hydrogen was produced at an efficiency of around 2 $\mu\text{mol}/\text{mg}$ dry matter [208]. The process also produced ethanol and low-molecular-weight organic acids (primarily acetic acid). Khetkorn et al. investigated the viability of hydrogen production by cyanobacteria (*Anabaena siamensis* TISTR 8012). An exogenous carbon source in the form of 0.5% fructose was fed into the system to boost biochemical conversion processes. The process was run under continuous illumination of 200 $\mu\text{E}/\text{m}^2 \cdot \text{s}$. The hydrogen yield amounted to 32 $\mu\text{mol}/\text{mg}$ Chl $\alpha \cdot \text{h}$ [209]. The same authors later conducted another experiment with this species, reaching a production rate of 29.7 $\mu\text{mol}/\text{mg}$ Chl $\alpha \cdot \text{h}$ [210].

Due to the hazards associated with conventional methods of producing hydrogen, biological processes are becoming an increasingly attractive alternative. Among the presented methods of obtaining hydrogen fuel, intracellular direct biophotolysis by microalgae seems to be the most environmentally sustainable. This technology also supports a wide range of species and process conditions. The experiments are conducted in variable environmental conditions to produce high concentrations of algal biomass and hydrogen. As such, the potential shown by biological and biochemical processes in microbial cells warrants more attention.

The literature reports show that *Platymonas subcordiformis* can be a source of value-added substances such as sugars, proteins or fats, given optimal culture conditions [211,212]. The great potential of *Platymonas subcordiformis* algae lies in their fast biomass growth, resistance to various types of pollution, high adaptability, and compatibility with different culture media of various physico-chemical parameters, including industrial and municipal wastewater [213,214]. There is also a fast-growing body of research on harnessing *Platymonas subcordiformis* planktonic algae by switching their metabolism towards hydrogen production [215].

Most publications focus on producing *Platymonas subcordiformis* biomass on media prepared from distilled water and chemical reagents that provide optimal conditions for microalgal growth [175,185]. Xie et al. has reported a *Platymonas subcordiformis* biomass of 3680 $\text{mg}_{\text{DOM}}/\text{dm}^3$ grown on the same type of medium [216], while Ji et al. achieved a biomass production of 3200 $\text{mg}_{\text{DOM}}/\text{dm}^3$ in similar conditions [24].

Ran et al. cultivated *Platymonas subcordiformis* in a medium prepared with water from the southern part of Bohai Bay (China). This led to the conclusion that a satisfactory rate of algal growth can only be achieved if the bay waters were supplemented with micronutrients. The final biomass measured by the density of microalgal cells in the culture medium ranged from 1.85 to $2.0 \cdot 10^6$ cells/ cm^3 [217].

There are also literature reports confirming that *Platymonas* sp. algae can be grown in a blend of municipal sewage and industrial (textile) sewage [218]. The assayed chlorophyll levels were 2.8 $\mu\text{g}/\text{cm}^3$ for *Platymonas suecica* and 7.3 $\mu\text{g}/\text{cm}^3$ for *Platymonas chunii*. In another study, a population of *Platymonas subcordiformis* was found to exhibit high rates of nutrient take-up from aquaculture wastewater. Nitrogen and phosphorus removal were in the ranges of 87.0–95.0% and 98.0–99.0% respectively [214].

Most studies use closed culture systems due to the need to monitor and culture multiple process parameters that directly affect microalgal growth in hydrogen production systems [219,220]. Most literature reports focus on photobioreactors with an active volume range of 250–5000 mL. Low-volume bioreactors can be placed in incubators to stabilise culture conditions [185,221]. Dasgupta et al. [219] and Oncel and Kose [222] present a wide variety of reactor types used to cultivate algal and produce hydrogen. Flat-panel reactors, tubular reactors (horizontal or vertical), and various digesters are all cited as viable options. A *Platymonas subcordiformis* biomass grown by Guo et al. in a column reactor reached levels that correspond to a phytoplankton concentration of $4.0 \cdot 10^6$ cells/cm³, which translates to algal dry matter of 2500 mg_{DM}/dm³ [188]. Ji et al. obtained a *Platymonas subcordiformis* biomass concentration of 1800 mg_{DM}/dm³ in a study conducted in an air-lift tubular reactor with a working volume of 500 cm³ [186]. Due to the strictly controlled nature of microalgal biomass production, the equipment enabled multiparametric monitoring of the culture. Units of this type are often fitted with additional valves for transporting gas out or air/CO₂ into the reactor [223]. One example of this design is the photobioreactor used by Ji et al. to cultivate *Platymonas subcordiformis*. The set-up was used both to grow biomass and produce hydrogen. The authors obtained a microalgal biomass concentration of 3200 mg_{DM}/dm³ [24].

Xie et al. used an analogous type of photobioreactor to produce similar levels of *Platymonas subcordiformis* biomass at 3680 mg_{DM}/dm³. The culture was grown in mixotrophic conditions with glucose as an exogenous source of carbon. Initial glucose levels in the medium were 24 g/dm³ [200], confirming that hydrogen-producing *Chlamydomonas reinhardtii* algae can produce high yields using process parameters similar to those presented in our paper. Experiments Oncel and Vardar-Sukan [175] and Oncel and Sabankay [207] indicate that culture conditions—such as temperature, pH, light intensity, and the regime of dark/light cycles—should be precisely controlled.

Xie et al. found a decrease in chlorophyll content in *Platymonas subcordiformis* cultures stimulated by added glucose. The chlorophyll content in the photoautotrophic culture (without external carbon source) was, on average, twice as high than in the mixotrophic culture, where glucose was added to the culture medium [216]. A similar trend was observed by Faraloni et al. in a *Chlamydomonas reinhardtii* culture grown in a medium made from wastewater rich in organic acids and carbohydrates. The chlorophyll content was 25 mg/dm³, being significantly lower than in the control microalgae grown in a mineral medium, which were found to contain 50 mg/dm³ chlorophyll (a). The culture was grown mixotrophically at 28 °C, and exposed to a light intensity 70 μmol E/m²·s. In the control, the chlorophyll concentration grew throughout the experiment (70 h) and only stabilised at the last stage of growth. In contrast, the same parameter stabilised as soon as after 20 h of the incubation of the culture supplemented with industrial wastewater and remained so throughout [179].

Fluctuations in the level of photosynthetic pigments can occur in response to changes in microbial metabolism in photoautotrophic and mixotrophic conditions. In the autotrophic culture, microalgal growth is fuelled directly by photosynthesis (driven by light energy). In mixotrophic environments, an additional source of energy is provided in the form of an exogenous carbon substrate (easily degradable organic compounds). Photosynthesis, which stimulates the formation of pigments in microalgae such as *Platymonas subcordiformis*, is inhibited by such input [224].

The addition of glucose can cause a successive reduction in pH during the culture process. The significant decrease in pH can be caused by the biological conversion of glucose to soluble carbon dioxide. This process has been shown to cause photosynthesis inhibition, which leads directly to reduced growth of algal populations [179].

The same was observed by Guo et al. after feeding large quantities of CO₂ into the system. By the end of the experiment, the pH in purely air-mixed photobioreactors grew to 9–1. In contrast, the variants where cultures were saturated with CO₂-supplemented air (at 15% CO₂), the pH gradually fell to 5–6 [188]. In another study, Guo et al. suggested that

reduced microalgal growth may also be caused by excessive biomass concentrations which limit the passage of light. This was further evidenced by an analysis of nutrient removal in the growth medium, which showed that the take-up of biogenic compound slowed down after a few days of culture [214].

The growth of *Platymonas subcordiformis* algae is highly determined by the salinity of the medium [225]. Khatoon et al. showed that 30 ppt salinity maximised the growth of *Platymonas subcordiformis* biomass cultivated under controlled conditions. Higher (40 ppt) or lower (20 ppt) values led to significantly reduced final biomass, while also adversely affecting intracellular protein, lipid, and carbohydrate levels. The authors also sought to identify the best pH levels for fast biomass growth and found that pH levels below 7.5 and above 8.5 limited the growth rate of *Platymonas subcordiformis* populations and the content of value-added substances in the cells [211]. These findings are corroborated by Yao et al., who noted that algal production was maximised at 27.0 g/dm³ NaCl, which corresponds to 30–33 ppt salinity. The biomass concentration was 4.6 g_{DM}/dm³ growing at a rate of 0.68 g_{DM}/dm³·d [212]. Another study examining the starch accumulation capacity of *Platymonas subcordiformis* showed that the microalgae in the reactor grew to 5.7 g_{DM}/dm³ and contained 40 do 60% dry matter starch. Culture conditions were determined by the initial KNO₃ in the medium. The system performed best at 37–40 °C at 11 mM KNO₃ [226]. These levels of pH and salinity in the medium have also been found to be optimal by Guan et al. [185] and Ji et al. [24]. In a study by Guan et al., *Platymonas subcordiformis* algae were grown in a medium with 30–33 ppt salinity at 25 °C and a pH of 8.2 [185]. Ji et al. (2010) used similar cultivation conditions, with identical salinity ranges and temperatures, but lower pH (7.5) [24].

Ji et al. [186] and Guo et al. [188] and Ran et al. [217] for producing *Platymonas subcordiformis* biomass used an alternating illumination regime with a 14 h light cycle and 10 h dark cycle. In these cases, the microalgae were grown in tubular photobioreactors. Other researchers explored different light periods—12 h or 8 h [218,227]. In a study by Oncel and Vardar-Sukan, extending the dark period led to decreasing hydrogen yields and biomass content. The author reported inferior performance compared to cultures grown autotrophically, regardless of the light/dark regime used [187].

Due to the specific metabolic processes in *Platymonas subcordiformis* cells, this microalgal species is considered to be a strong contender among potential biohydrogen sources. Hydrogen production is induced by removing sulphur from the medium and maintaining anaerobic conditions to activate hydrogenase [60]. The literature includes two methods of inducing hydrogen production in *Platymonas subcordiformis* biomass. One commonly used method calls for concentrating and dehydrating the microalgal biomass via centrifugation, after which the biomass is fed into the culture medium (which has had its sulphur replaced with chlorine compounds). However, research to date has demonstrated that centrifugation is a costly and time-consuming procedure that is difficult to automate [174]. It does, however, boast the clear benefit of effectively removing the sulphur-rich culture medium [175,221]. One alternative presented in the literature is the dilution of sulphur-rich media, which directly reduces the sulphur fraction in the system. However, despite its effectiveness, this procedure requires much more time for reaching anaerobic conditions, inducing hydrogenase activity and initiating hydrogen production [215]. Research to date has clearly shown that efficiency of microalgal biohydrogen production is directly affected by the method used to limit sulphur in the culture medium [228].

Laurinavichene et al. tested a hydrogen production process using *Chlamydomonas reinhardtii* cultures. In the course of the experiment, two sulphur-deprivation procedures were compared, i.e., centrifugation and dilution. Centrifugation was found to provide better performance in terms of eliminating sulphur from the medium, establishing anaerobic conditions and producing hydrogen. Total hydrogen production post-centrifugation amounted to 180 mL/dm³ whereas dilution led to a 22% lower yield [177].

Dębowski et al. examined a novel and heretofore untested method of separating microalgal biomass based on membrane microfiltration. It was hypothesised that this

alternative method of separating and dewatering microalgae biomass would lower the cost of the process and improve performance [229]. Literature reports also prove that centrifugation often destroys algal cells and intracellular structures, which reduces the population of active organisms and thus the amount of gaseous metabolic products [177,228].

A study by Tamburic et al. compared how three sulphur-deprivation procedures—dilution, centrifugation, and sulphur control in the biomass—affected hydrogen productivity. The experiment used *Chlamydomonas reinhardtii* microalgae grown in plate photobioreactors. Diluted cultures produced a hydrogen yield of $23.6 \text{ cm}^3/\text{dm}^3$ at a rate of $0.18 \text{ cm}^3/\text{dm}^3 \cdot \text{h}$. Centrifugation resulted in much higher hydrogen production efficiency, yielding $102.7 \text{ cm}^3/\text{dm}^3$ at a rate of $1.11 \text{ cm}^3/\text{dm}^3 \cdot \text{h}$. Finally, by controlling nutrient levels during microbial cultivation, including sulphur and acetate, the authors achieved a hydrogen production efficiency of $130 \text{ cm}^3/\text{dm}^3$ at a rate of $1.30 \text{ cm}^3/\text{dm}^3 \cdot \text{h}$, thus exceeding the performance of the centrifugation-based system by 9.7% [228].

Ji et al. presented a different strategy of activating hydrogenase. The authors tested hydrogen production efficiencies in relation to the nutrient-depletion procedure. *Platymonas subcordiformis* were chosen as the biological specimen for testing, grown until reaching the exponential growth phase. The biomass was then suspended in one of the three media, which were deprived of either nitrogen, phosphorus or sulphur, depending on the variant. Hydrogen yields were maximised in the N-depleted system, reaching $55.8 \text{ cm}^3/\text{dm}^3$. The S- and P-depleted variants provided only a third and a sixth of this amount, respectively [186].

A study by Faraloni et al. confirms that mixotrophic culture conditions enhance hydrogen production by microalgal cells. A medium prepared with olive mill wastewater as the base directly promoted accumulation of carbohydrate compounds in algal cells, which boosted hydrogen productivity. The exact biohydrogen yield in this case was $150.8 \text{ cm}^3 \text{ H}_2/\text{dm}^3$. By comparison, a biomass grown on typical synthetic medium yielded $100.2 \pm 9.5 \text{ cm}^3 \text{ H}_2/\text{dm}^3$ [179].

This positive effect of mixotrophic cultures on hydrogen production by *Platymonas subcordiformis* has been corroborated by Ran et al. This group explored hydrogen production enhancement by using media amended with exogenous carbon sources and phosphorus. The addition of glucose to the medium resulted in a hydrogen yield of $146.35 \pm 11.01 \text{ cm}^3$ —offering a 10–19% improvement over purely autotrophic systems [217]. Algal cultures grown on carbon-enriched media accumulate larger intracellular reservoirs of nutrient stores. These deposits help microalgae survive in the adverse environments maintained at the hydrogen production stage [230].

Laboratory-scale research is underway to develop an efficient hydrogen production method using *Platymonas subcordiformis* algae and focuses primarily on identifying optimal technological parameters for best performance. There have been divergent reports on how much biohydrogen can be extracted. The highest production by volume has been reported by Ji et al., who achieved $157.7 \text{ cm}^3/\text{dm}^3$ hydrogen at $3.2 \text{ g}/\text{dm}^3$ algal density [24]. By comparison, the hydrogen yields achieved by Guo et al. did not exceed $50 \text{ cm}^3/\text{dm}^3$ with *Platymonas subcordiformis* growth in the system being around $3.8 \times 10^6 \text{ cells}/\text{cm}^3$ [188]. Ji et al. reported similar performance, obtaining $55.8 \text{ cm}^3/\text{dm}^3$ hydrogen by maintaining a biomass concentration of $6 \times 10^6 \text{ cells}/\text{cm}^3$ [186].

6. Conclusions

One of the priorities for researchers, designers, and operators of energy systems is the development and effective deployment of clean energy technologies on an industrial scale. This is due to the need to reduce carbon dioxide emissions, thus directly mitigating the fast-progressing climate change and related phenomena. Even now, there are studies available that substantiate the viability of efficient, cost-effective production and use of biofuels, which will stabilise the prices of conventional energy carriers. Biofuels will enable countries without access to fossil fuel deposits to achieve partial energy independence, create jobs in the fuel and energy sector, and make a push towards a low-carbon economy. There are high hopes that hydrogen will be one such fuel.

Attempts to deploy biofuel production systems have shown that such installations are technologically complex, difficult to maintain, and require high investment costs, which directly hampers their commercial viability. Therefore, new, alternative, and competitive solutions need to be sought, ones which would balance cost-effectiveness with environmental benefits.

Use of microalgae is a highly promising method of producing hydrogen via biological processes. There is sufficient data from laboratory-scale studies to start experiments in pilot systems on a semi-industrial scale. However, validation tests must be carried out to verify whether natural water or wastewater can be used as nutrient sources. Other technological issues to be addressed are ways to enrich, refine, store and use biohydrogen.

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References

1. Yu, M.; Wang, K.; Vredenburg, V. Insights into low-carbon hydrogen production methods: Green, blue and aqua hydrogen. *Int. J. Hydrogen Energy* **2021**, *46*, 21261–21273. [\[CrossRef\]](#)
2. Meier, K.; Kurtz, C.; Weckerle, C.; Hubner, M.; Bürger, I. Air-conditioning system for vehicles with on-board hydrogen. *Appl. Therm. Eng.* **2018**, *129*, 1150–1159. [\[CrossRef\]](#)
3. Bizon, N.; Raceanu, M.; Koudoumas, E.; Marinoiu, A.; Karapidakis, E.; Carcadea, E. Renewable/Fuel Cell Hybrid Power System Operation Using Two Search Controllers of the Optimal Power Needed on the DC Bus. *Energies* **2020**, *13*, 6111. [\[CrossRef\]](#)
4. Chen, S.; Kumar, A.; Wong, W.C.; Chiu, M.-S.; Wang, X. Hydrogen value chain and fuel cells within hybrid renewable energy systems: Advanced operation and control strategies. *Appl. Energy* **2019**, *233*, 321–337. [\[CrossRef\]](#)
5. Hu, G.; Chen, C.; Lu, H.T.; Wu, Y.; Liu, C.; Tao, L.; Men, Y.; He, G.; Li, K.G. A Review of Technical Advances, Barriers, and Solutions in the Power to Hydrogen (P2H) Roadmap. *Engineering* **2020**, *6*, 1364–1380. [\[CrossRef\]](#)
6. Cao, L.; Yu, I.K.M.; Xiong, X.; Tsang, D.C.W.; Zhang, S.; Clark, J.H.; Hu, C.; Ng, Y.H.; Shang, J.; Ok, Y.S. Biorenewable hydrogen production through biomass gasification: A review and future prospects. *Environ. Res.* **2020**, *186*, 109547. [\[CrossRef\]](#) [\[PubMed\]](#)
7. Chen, J.; Fan, Y.; Jiaqiang, E.; Cao, W.; Zhang, F.; Gong, J.; Liu, G.; Xu, W. Effects analysis on the gasification kinetic characteristics of food waste in supercritical water. *Fuel* **2019**, *241*, 94–104. [\[CrossRef\]](#)
8. Fakeeha, A.; Ibrahim, A.A.; Aljuraywi, H.; Alqahtani, Y.; Alkhodair, A.; Alswaidan, S.; Abasaheed, A.E.; Kasim, S.O.; Mahmud, S.; Al-Fatesh, A.S. Hydrogen production by partial oxidation reforming of methane over Ni catalysts supported on high and low surface area alumina and zirconia. *Processes* **2020**, *8*, 499. [\[CrossRef\]](#)
9. Parkinson, B.; Balcombe, P.; Speirs, J.F.; Hawkes, A.D.; Hellgardt, K. Levelized cost of CO₂ mitigation from hydrogen production routes. *Energy Environ. Sci.* **2019**, *12*, 19–40. [\[CrossRef\]](#)
10. Rajabi Hamedani, S.; Villarini, M.; Colantoni, A.; Moretti, M.; Bocci, E. Life Cycle Performance of Hydrogen Production via Agro-Industrial Residue Gasification—A Small Scale Power Plant Study. *Energies* **2018**, *11*, 675. [\[CrossRef\]](#)
11. Shahbaz, M.; Al-Ansari, T.; Aslam, M.; Khan, Z.; Inayat, A.; Athar, M.; Naqvi, S.R.; Ahmed, M.A.; McKay, G. A state of the art review on biomass processing and conversion technologies to produce hydrogen and its recovery via membrane separation. *Int. J. Hydrogen Energy* **2020**, *45*, 15166–15195. [\[CrossRef\]](#)

12. Mahata, C.; Dhar, S.; Ray, S.; Das, D. Effect of thermal pretreated organic wastes on the dark fermentative hydrogen production using mixed microbial consortia. *Fuel* **2021**, *284*, 119062. [[CrossRef](#)]
13. Tsegaye, B.; Jaiswal, S.; Jaiswal, A.K. Food Waste Biorefinery: Pathway towards Circular Bioeconomy. *Foods* **2021**, *10*, 1174. [[CrossRef](#)]
14. Nagarajan, D.; Chang, J.-S.; Lee, D.-J. Pretreatment of microalgal biomass for efficient biohydrogen production—Recent insights and future perspectives. *Bioresour. Technol.* **2020**, *302*, 122871–122885. [[CrossRef](#)]
15. Shobana, S.; Kumar, G.; Bakonyi, P.; Saratale, G.D.; Al-Muhtaseb, A.a.H.; Nemestóthy, N.; Bélafi-Bakó, K.; Xia, A.; Chang, J.-S. A review on the biomass pretreatment and inhibitor removal methods as key-steps towards efficient macroalgae-based biohydrogen production. *Bioresour. Technol.* **2017**, *244*, 1341–1348. [[CrossRef](#)]
16. Cordier, C.; Guyomard, K.; Stavrakakis, C.; Sauvade, P.; Coelho, F.; Moulin, P. Culture of Microalgae with Ultrafiltered Seawater: A Feasibility Study. *Sci. Med. J.* **2020**, *2*, 56–62. [[CrossRef](#)]
17. Dębowski, M.; Zieliński, M.; Kazimierowicz, J.; Kujawska, N.; Talbierz, S. Microalgae Cultivation Technologies as an Opportunity for Bioenergetic System Development—Advantages and Limitations. *Sustainability* **2020**, *12*, 9980. [[CrossRef](#)]
18. Barbosa, R.C.; Soares, J.; Martins, M.A. Low-cost and versatile sensor based on multi-wavelengths for real-time estimation of microalgal biomass concentration in open and closed cultivation systems. *Comput. Electron. Agric.* **2020**, *176*, 105641. [[CrossRef](#)]
19. Dębowski, M.; Zieliński, M.; Krzemieniewski, M.; Dudek, M.; Grala, A. Microalgae—Cultivation methods. *Pol. J. Nat. Sci.* **2012**, *27*, 151–164.
20. Dębowski, M.; Zieliński, M.; Grala, A.; Dudek, M. Algae biomass as an alternative substrate in biogas production technologies—Review. *Renew. Sustain. Energy Rev.* **2013**, *27*, 596–604. [[CrossRef](#)]
21. Xiaogang, H.; Jalalah, M.; Jingyuan, W.; Zheng, Y.; Li, X.; Salama, E.-S. Microalgal growth coupled with wastewater treatment in open and closed systems for advanced biofuel generation. *Biomass Convers. Biorefin.* **2020**, *17*, 1–20. [[CrossRef](#)]
22. Yen, H.-W.; Hu, I.-C.; Chen, C.-Y.; Nagarajan, D. Design of photobioreactors for algal cultivation. *Biofuels Algae* **2019**, 225–256. [[CrossRef](#)]
23. Mohan, S.V.; Rohit, M.V.; Subhash, G.V.; Chandra, R.; Devi, M.P.; Butti, S.K.; Rajesh, K. Biofuels from algae. In *Algal Oils as Biodiesel*; Pandey, A., Chang, J.-S., Soccol, C.R., Lee, D.-J., Chisti, Y., Eds.; Elsevier: Amsterdam, The Netherlands, 2019; pp. 287–323. [[CrossRef](#)]
24. Ji, C.F.; Legrand, J.; Pruvost, J.; Chen, Z.A.; Zhang, W. Characterization of hydrogen production by *Platymonas Subcordiformis* in torus photobioreactor. *Int. J. Hydrogen Energy* **2010**, *35*, 7200–7205. [[CrossRef](#)]
25. Song, W.; Rashid, N.; Choi, W.; Lee, K. Biohydrogen production by immobilized *Chlorella* sp. using cycles of oxygenic photo-synthesis and anaerobiosis. *Bioresour. Technol.* **2011**, *102*, 8676–8681. [[CrossRef](#)]
26. Franchi, G.; Capocelli, M.; De Falco, M.; Piemonte, V.; Barba, D. Hydrogen Production via Steam Reforming: A Critical Analysis of MR and RMM Technologies. *Membranes* **2020**, *10*, 10. [[CrossRef](#)]
27. Park, H.-G.; Han, S.-Y.; Jun, K.-W.; Woo, Y.; Park, M.-J.; Kim, S.K. Bench-Scale Steam Reforming of Methane for Hydrogen Production. *Catalysts* **2019**, *9*, 615. [[CrossRef](#)]
28. Chen, L.; Qi, Z.; Zhang, S.; Su, J.; Somorjai, G.A. Catalytic Hydrogen Production from Methane: A Review on Recent Progress and Prospect. *Catalysts* **2020**, *10*, 858. [[CrossRef](#)]
29. LeValley, T.L.; Richard, A.R.; Fan, M. The progress in water gas shift and steam reforming hydrogen production technologies—A review. *Int. J. Hydrogen Energy* **2014**, *39*, 16983–17000. [[CrossRef](#)]
30. Goicoechea, S.; Ehrich, H.; Arias, P.L.; Kockmann, N. Thermodynamic analysis of acetic acid steam reforming for hydrogen production. *J. Power Sources* **2015**, *279*, 312–322. [[CrossRef](#)]
31. Pashchenko, D. Thermochemical waste-heat recuperation by steam methane reforming with flue gas addition. *Int. J. Energy Res.* **2019**, *43*, 2216–2226. [[CrossRef](#)]
32. Wang, G.; Wang, F.; Chen, B. Performance Study on Methanol Steam Reforming Rib Micro-Reactor with Waste Heat Recovery. *Energies* **2020**, *13*, 1564. [[CrossRef](#)]
33. Mosinska, M.; Szyrkowska, M.I.; Mierczynski, P. Oxy-Steam Reforming of Natural Gas on Ni Catalysts—A Minireview. *Catalysts* **2020**, *10*, 896. [[CrossRef](#)]
34. Sadooghi, P.; Rauch, R. Experimental and modeling study of catalytic steam reforming of methane mixture with propylene in a packed bed reactor. *Int. J. Heat Mass Transf.* **2014**, *78*, 515–521. [[CrossRef](#)]
35. Nahar, G.; Dupont, V.; Twigg, M.V.; Dvininov, E. Feasibility of hydrogen production from steam reforming of biodiesel (FAME) feedstock on Ni-supported catalysts. *Appl. Catal. B Environ.* **2015**, *168–169*, 228–242. [[CrossRef](#)]
36. Hammoud, D.; Gennequin, C.; Aboukais, A.; Abi Aad, E. Steam reforming of methanol over x % Cu/Zn–Al 400 500 based catalysts for production of hydrogen: Preparation by adopting memory effect of hydrotalcite and behavior evaluation. *Int. J. Hydrogen Energy* **2015**, *40*, 1283–1297. [[CrossRef](#)]
37. Charisiou, N.D.; Siakavelas, G.I.; Papageridis, K.N.; Motta, D.; Dimitratos, N.; Sebastian, V.; Polychronopoulou, K.; Goula, M.A. The Effect of Noble Metal (M: Ir, Pt, Pd) on M/Ce₂O₃- γ -Al₂O₃ Catalysts for Hydrogen Production via the Steam Reforming of Glycerol. *Catalysts* **2020**, *10*, 790. [[CrossRef](#)]
38. Remón, J.; Jarauta-Córdoba, C.; García, L.; Arauzo, J. Analysis and optimisation of H₂ production from crude glycerol by steam reforming using a novel two step process. *Fuel Process. Technol.* **2016**, *145*, 130–147. [[CrossRef](#)]

39. Palo, E.; Salladini, A.; Morico, B.; Palma, V.; Ricca, A.; Iaquaniello, G. Application of Pd-Based Membrane Reactors: An Industrial Perspective. *Membranes* **2018**, *8*, 101. [[CrossRef](#)]
40. Moharana, M.K.; Peela, N.R.; Khandekar, S.; Kunzru, D. Distributed hydrogen production from ethanol in a microfuel pro-cessor: Issues and challenges. *Renew. Sustain. Energy Rev.* **2011**, *15*, 524–533. [[CrossRef](#)]
41. Yerga, R.M.N. Catalysts for Production and Conversion of Syngas. *Catalysts* **2021**, *11*, 752. [[CrossRef](#)]
42. Lopez-Urionabarrenechea, A.; Acha, E.; Adrados, A.; Solar, J.; Caballero, B.M.; De Marco, I. Use of a Reforming Catalyst for Hydrogen Production in the Carbonization Process of Torrefied Biomass. *Catalysts* **2020**, *10*, 1300. [[CrossRef](#)]
43. Molino, A.; Larocca, V.; Chianese, S.; Musmarra, D. Biofuels Production by Biomass Gasification: A Review. *Energies* **2018**, *11*, 811. [[CrossRef](#)]
44. Safarian, S.; Unnthorsson, R.; Richter, C. Simulation and Performance Analysis of Integrated Gasification–Syngas Fermentation Plant for Lignocellulosic Ethanol Production. *Fermentation* **2020**, *6*, 68. [[CrossRef](#)]
45. Huang, L.; Zhou, J.; Hsu, A.T.; Chen, R. Catalytic partial oxidation of n-butanol for hydrogen production over LDH-derived Ni-based catalysts. *Int. J. Hydrogen Energy* **2013**, *38*, 14550–14558. [[CrossRef](#)]
46. Chen, Y.; Zhou, W.; Shao, Z.; Xu, N. Nickel catalyst prepared via glycine nitrate process for partial oxidation of methane to syngas. *Catal. Commun.* **2008**, *9*, 1418–1425. [[CrossRef](#)]
47. Zhang, Y.; Li, Z.; Wen, X.; Liu, Y. Partial oxidation of methane over Ni/Ce-Ti-O catalysts. *Chem. Eng. J.* **2006**, *121*, 115–123.
48. Shan, W.; Fleys, M.; Lapique, F.; Swierczynski, D.; Kiennemann, A.; Simon, Y.; Marquaire, P. Syngas production from partial oxidation of methane over Ce₁–XNi₁O₁ catalysts prepared by complexation–combustion method. *Appl. Catal. A Gen.* **2006**, *311*, 24–33. [[CrossRef](#)]
49. Pelletier, L.; Liu, D.D.S. Stable nickel catalysts with alumina-aluminum phosphate supports for partial oxidation and carbon dioxide reforming of methane. *Appl. Catal. A Gen.* **2007**, *317*, 293–298. [[CrossRef](#)]
50. Dashliborun, A.M.; Fatemi, S.; Najafabadi, A.T. Hydrogen production through partial oxidation of methane in a new reactor configuration. *Int. J. Hydrogen Energy* **2013**, *38*, 1901–1909. [[CrossRef](#)]
51. Martínez-Rodríguez, A.; Abánades, A. Comparative Analysis of Energy and Exergy Performance of Hydrogen Production Methods. *Entropy* **2020**, *22*, 1286. [[CrossRef](#)] [[PubMed](#)]
52. Jimmy, U.; Mohamedali, M.; Ibrahim, H. Thermodynamic Analysis of Autothermal Reforming of Synthetic Crude Glycerol (SCG) for Hydrogen Production. *Chem. Eng.* **2017**, *1*, 4. [[CrossRef](#)]
53. Xiang, D.; Li, P.; Yuan, X. Process Modeling, Optimization, and Heat Integration of Ethanol Reforming Process for Syngas Production with High H₂/CO Ratio. *Processes* **2019**, *7*, 960. [[CrossRef](#)]
54. Goula, M.A.; Polychronopoulou, K. Editorial—Special Issue “Catalysis for Energy Production”. *Catalysts* **2021**, *11*, 785. [[CrossRef](#)]
55. Meloni, E.; Martino, M.; Palma, V. A Short Review on Ni Based Catalysts and Related Engineering Issues for Methane Steam Reforming. *Catalysts* **2020**, *10*, 352. [[CrossRef](#)]
56. Ghaffari Saeidabad, N.G.; Noh, Y.S.; Alizadeh Eslami, A.; Song, H.T.; Kim, H.D.; Fazeli, A.; Moon, D.J. A Review on Catalysts Development for Steam Reforming of Biodiesel Derived Glycerol; Promoters and Supports. *Catalysts* **2020**, *10*, 910. [[CrossRef](#)]
57. Yan, Y.; Zhan, J.; Zhang, L. Properties of thermodynamic equilibrium-based methane autothermal reforming to generate hydrogen. *Int. J. Hydrogen Energy* **2013**, *38*, 15744–15750. [[CrossRef](#)]
58. Palma, V.; Ricca, A.; Ciambelli, P. Structured catalysts for methane auto-thermal reforming in a compact thermal integrated reaction system. *Appl. Therm. Eng.* **2013**, *61*, 128–133. [[CrossRef](#)]
59. Czernik, S.; French, R. Distributed production of hydrogen by auto-thermal reforming of fast pyrolysis bio-oil. *Int. J. Hydrogen Energy* **2014**, *39*, 744–750. [[CrossRef](#)]
60. Gallucci, F.; Annaland, M.V.S.; Kuipers, J.A.M. Pure hydrogen production via autothermal reforming of ethanol in a fluidized bed membrane reactor: A simulation study. *Int. J. Hydrogen Energy* **2010**, *35*, 1659–1668. [[CrossRef](#)]
61. Ju, D.G.; Jo, S.B.; Ha, D.S.; Kim, T.Y.; Jung, S.Y.; Chae, H.J.; Lee, S.C.; Kim, J.C. Enhanced Ni-Al-Based Catalysts and Influence of Aromatic Hydrocarbon for Autothermal Reforming of Diesel Surrogate Fuel. *Catalysts* **2019**, *9*, 573. [[CrossRef](#)]
62. Abejón, R.; Fernández-Ríos, A.; Domínguez-Ramos, A.; Laso, J.; Ruiz-Salmón, I.; Yáñez, M.; Ortiz, A.; Gorri, D.; Donzel, N.; Jones, D.; et al. Hydrogen Recovery from Waste Gas Streams to Feed (High-Temperature PEM) Fuel Cells: Environmental Performance under a Life-Cycle Thinking Approach. *Appl. Sci.* **2020**, *10*, 7461. [[CrossRef](#)]
63. Li, W.; He, S.; Li, S. Experimental Study and Thermodynamic Analysis of Hydrogen Production through a Two-Step Chemical Regenerative Coal Gasification. *Appl. Sci.* **2019**, *9*, 3035. [[CrossRef](#)]
64. Porada, S.; Czerski, G.; Dziok, T.; Grzywacz, P.; Makowska, D. Kinetics of steam gasification of bituminous coals in terms of their use for underground coal gasification. *Fuel Process. Technol.* **2015**, *130*, 282–291. [[CrossRef](#)]
65. Seyednejadian, S.; Rauch, R.; Bensaid, S.; Hofbauer, H.; Weber, G.; Saracco, G. Power to Fuels: Dynamic Modeling of a Slurry Bubble Column Reactor in Lab-Scale for Fischer Tropsch Synthesis under Variable Load of Synthesis Gas. *Appl. Sci.* **2018**, *8*, 514. [[CrossRef](#)]
66. Barisano, D.; Canneto, G.; Nanna, F.; Villone, A.; Fanelli, E.; Freda, C.; Grieco, M.; Cornacchia, G.; Braccio, G.; Marcantonio, V.; et al. Investigation of an Intensified Thermo-Chemical Experimental Set-Up for Hydrogen Production from Biomass: Gasification Process Performance—Part I. *Processes* **2021**, *9*, 1104. [[CrossRef](#)]
67. Martino, M.; Ruocco, C.; Meloni, E.; Pullumbi, P.; Palma, V. Main Hydrogen Production Processes: An Over-view. *Catalysts* **2021**, *11*, 547. [[CrossRef](#)]

68. Mehmeti, A.; Angelis-Dimakis, A.; Arampatzis, G.; McPhail, S.J.; Ulgiati, S. Life Cycle Assessment and Water Footprint of Hydrogen Production Methods: From Conventional to Emerging Technologies. *Environments* **2018**, *5*, 24. [[CrossRef](#)]
69. Zaccara, A.; Petrucciani, A.; Matino, I.; Branca, T.A.; Dettori, S.; Iannino, V.; Colla, V.; Bampaou, M.; Panopoulos, K. Renewable Hydrogen Production Processes for the Off-Gas Valorization in Integrated Steelworks through Hydrogen Intensified Methane and Methanol Syntheses. *Metals* **2020**, *10*, 1535. [[CrossRef](#)]
70. Zhang, H.X.; Zhang, Y.K.; Zhu, Z.P.; Lu, Q.G. Circulating fluidized bed gasification of low rank coal: Influence of O₂/C molar ratio on gasification performance and sulphur transformation. *J. Therm. Sci.* **2016**, *25*, 363–371. [[CrossRef](#)]
71. Poudel, J.; Choi, J.H.; Oh, S.C. Process Design Characteristics of Syngas (CO/H₂) Separation Using Composite Membrane. *Sustainability* **2019**, *11*, 703. [[CrossRef](#)]
72. Rahmad, B.; Raharjo, S.; Ediyanto, E.; Putra, G.P. Coal Gasification and Coal Microscopic Characteristics in Tanjung Baru, Lahat Regency, South Sumatera. In *Seminar Nasional Teknik Kimia Kejuangan*; UPN Veteran Yogyakarta: Yogyakarta, Indonesia, 2020; p. 5.
73. Chmielniak, T.; Dreszer, K. Technical and economical considerations of new coal processing technologies. *Chemist* **2010**, *64*, 222–247.
74. Deniz, I.; Vardar-Sukan, F.; Yüksel, M.; Saglam, M.; Ballice, L.; Yesil-Celiktas, O. Hydrogen production from marine biomass by hydrothermal gasification. *Energy Convers. Manag.* **2015**, *96*, 124–130. [[CrossRef](#)]
75. Calzavara, Y.; Jousot-Dubien, C.; Boissonnet, G.; Sarrade, S. Evaluation of biomass gasification in supercritical water process for hydrogen production. *Energy Convers. Manag.* **2005**, *46*, 615–631. [[CrossRef](#)]
76. Crocker, M. *Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals: Hydrothermal Processing of Biomass*; Savage, P.E., Levine, R.B., Huelsman, C.M., Eds.; USA: Royal Society Chemistry: London, UK, 2010; pp. 192–221.
77. Ge, Z.; Jin, H.; Guo, L. Hydrogen production by catalytic gasification of coal in supercritical water with alkaline catalysts: Explore the way to complete gasification of coal. *Int. J. Hydrogen Energy* **2014**, *39*, 19583–19592. [[CrossRef](#)]
78. Maćzka, T.; Pawlak-Kruczek, H.; Niedzwiecki, L.; Ziaja, E.; Chorażyczewski, A. Plasma Assisted Combustion as a Cost-Effective Way for Balancing of Intermittent Sources: Techno-Economic Assessment for 200 MW_{el} Power Unit. *Energies* **2020**, *13*, 5056. [[CrossRef](#)]
79. Yoon, S.J.; Lee, J.G. Hydrogen-rich syngas production through coal and charcoal gasification using microwave steam and air plasma torch. *Int. J. Hydrogen Energy* **2012**, *37*, 17093–17100. [[CrossRef](#)]
80. Liu, Q.; Hu, C.; Peng, B.; Liu, C.; Li, Z.; Wu, K.; Zhang, H.; Xiao, R. High H₂/CO ratio syngas production from chemical looping co-gasification of biomass and polyethylene with CaO/Fe₂O₃ oxygen carrier. *Energy Convers. Manag.* **2019**, *199*. [[CrossRef](#)]
81. Yoon, S.J.; Yun, Y.M.; Seo, M.W.; Kim, Y.K.; Ra, H.W.; Lee, J.G. Hydrogen and syngas production from glycerol through microwave plasma gasification. *Int. J. Hydrogen Energy* **2013**, *38*, 14559–14567. [[CrossRef](#)]
82. El-Shafie, M.; Kambara, S.; Hayakawa, Y. Hydrogen Production Technologies Overview. *J. Power Energy Eng.* **2019**, *7*, 107–154. [[CrossRef](#)]
83. Hong, Y.C.; Lee, S.J.; Shin, D.H.; Kim, Y.J.; Lee, B.J.; Cho, S.Y.; Chang, H.S. Syngas production from gasification of brown coal in a microwave torch plasma. *Energy* **2012**, *47*, 36–40. [[CrossRef](#)]
84. Vidaković-Koch, T. Editorial on Special Issue Electrolysis Processes. *Processes* **2020**, *8*, 578. [[CrossRef](#)]
85. Brauns, J.; Turek, T. Alkaline Water Electrolysis Powered by Renewable Energy: A Review. *Processes* **2020**, *8*, 248. [[CrossRef](#)]
86. Perez-Herranz, V.; Perez-Page, M.; Beneito, R. Monitoring and control of a hydrogen production and storage system consisting of water electrolysis and metal hydrides. *Int. J. Hydrogen Energy* **2010**, *35*, 912–919. [[CrossRef](#)]
87. Chanda, D.; Hnat, J.; Paidar, M.; Schauer, J.; Bouzek, K. Synthesis and characterization of NiFe₂O₄ electrocatalyst for the hydrogen evolution reaction in alkaline water electrolysis using different polymer binders. *J. Power Sources* **2015**, *285*, 217–226. [[CrossRef](#)]
88. Millet, P.; Grigoriev, S. Chapter 2—Water Electrolysis Technologies. In *Renewable Hydrogen Technologies. Production, Purification, Storage, Applications and Safety*; Gandia, L.M., Arzamendi, G., Dieguez, P.M., Eds.; Elsevier: Amsterdam, The Netherlands, 2013; pp. 19–41. ISBN 978-0-444-56352-1.
89. Fiegenbaum, F.; Martini, E.M.; de Souza, M.O.; Becker, M.R.; de Souza, R.F. Hydrogen production by water electrolysis using tetra-alkyl-ammonium-sulfonic acid ionic liquid electrolytes. *J. Power Sources* **2013**, *243*, 822–825. [[CrossRef](#)]
90. Hug, W.; Divisek, J.; Mergel, J.; Seeger, W.; Steeb, H. Highly efficient advanced alkaline electrolyzer for solar operation. *Int. J. Hydrogen Energy* **1992**, *17*, 699–705. [[CrossRef](#)]
91. Ando, Y.; Tanaka, T. Proposal for a new system for simultaneous production of hydrogen and hydrogen peroxide by water electrolysis. *Int. J. Hydrogen Energy* **2004**, *29*, 1349–1354. [[CrossRef](#)]
92. Costa, M.; La Villetta, M.; Piazzullo, D.; Cirillo, D. A Phenomenological Model of a Downdraft Biomass Gasifier Flexible to the Feedstock Composition and the Reactor Design. *Energies* **2021**, *14*, 4226. [[CrossRef](#)]
93. Ni, F.M.; Leung, D.Y.C.; Leung, M.K.H.; Sumathy, K. An overview of hydrogen production from biomass. *Fuel Process. Technol.* **2006**, *87*, 461–472. [[CrossRef](#)]
94. Nath, K.; Das, D. Hydrogen from biomass. *Curr. Sci.* **2003**, *85*, 265–271.
95. Asadullah, M. Barriers of commercial power generation using biomass gasification gas: A review. *Renew. Sustain. Energy Rev.* **2014**, *29*, 201–215. [[CrossRef](#)]
96. Park, S.-W.; Lee, S.-Y.; Jeong, Y.-O.; Han, G.-H.; Seo, Y.-C. Effects of Oxygen Enrichment in Air Oxidants on Biomass Gasification Efficiency and the Reduction of Tar Emissions. *Energies* **2018**, *11*, 2664. [[CrossRef](#)]

97. Xiao, X.; Wang, X.; Zheng, Z.; Qin, W.; Zhou, Y. Catalytic Coal Gasification Process Simulation with Alkaline Organic Wastewater in a Fluidized Bed Reactor Using Aspen Plus. *Energies* **2019**, *12*, 1367. [\[CrossRef\]](#)
98. Antoniou, N.; Monlau, F.; Sambusiti, C.; Ficara, E.; Barakat, A.; Zabaniotou, A. Contribution to Circular Economy options of mixed agricultural wastes management: Coupling anaerobic digestion with gasification for enhanced energy and material recovery. *J. Clean. Prod.* **2019**, *209*, 505–514. [\[CrossRef\]](#)
99. Duque-Acevedo, M.; Belmonte-Ureña, L.J.; Yakovleva, N.; Camacho-Ferre, F. Analysis of the Circular Economic Production Models and Their Approach in Agriculture and Agricultural Waste Biomass Management. *Int. J. Environ. Res. Public Health* **2020**, *17*, 9549. [\[CrossRef\]](#) [\[PubMed\]](#)
100. Castello, D.; Pedersen, T.H.; Rosendahl, L.A. Continuous Hydrothermal Liquefaction of Biomass: A Critical Review. *Energies* **2018**, *11*, 3165. [\[CrossRef\]](#)
101. Xu, C.; Hu, S.; Xiang, J.; Zhang, L.; Sun, L.; Shuai, C.; Chen, Q.; He, L.; Edreis, E.M.A. Interaction and kinetic analysis for coal and biomass co-gasification by TG–FTIR. *Bioresour. Technol.* **2014**, *154*, 313–321. [\[CrossRef\]](#) [\[PubMed\]](#)
102. Marcantonio, V.; Monforti Ferrario, A.; Di Carlo, A.; Del Zotto, L.; Monarca, D.; Bocci, E. Biomass Steam Gasification: A Comparison of Syngas Composition between a 1-D MATLAB Kinetic Model and a 0-D Aspen Plus Quasi-Equilibrium Model. *Computation* **2020**, *8*, 86. [\[CrossRef\]](#)
103. Werle, S. Obtaining gas fuel from unconventional biomass in the gasification process. *Instal* **2014**, *1*, 7–10.
104. Song, T.; Wu, J.; Shen, L.; Xiao, J. Experimental investigation on hydrogen production from biomass gasification in inter-connected fluidized beds. *Biomass Bioenergy* **2012**, *36*, 258–267. [\[CrossRef\]](#)
105. Ni, M.; Leung, M.K.H.; Sumathy, K.; Leung, D.Y.C. Potential of renewable hydrogen production for energy supply in HongKong. *Int. J. Hydrogen Energy* **2006**, *31*, 1401–1412. [\[CrossRef\]](#)
106. Uddin, M.N.; Daud, W.M.A.W.; Abbas, H.F. Potential hydrogen and non-condensable gases production from biomass pyrolysis: Insights into the process variables. *Renew. Sustain. Energy Rev.* **2013**, *27*, 204–224. [\[CrossRef\]](#)
107. Zhao, B.; Zhang, X.; Sun, L.; Meng, G.; Chen, L.; Xiaolu, Y. Hydrogen production from biomass combining pyrolysis and the secondary decomposition. *Int. J. Hydrogen Energy* **2010**, *35*, 2606–2611. [\[CrossRef\]](#)
108. Alvarez, J.; Kumagai, S.; Wu, C.; Yoshioka, T.; Bilbao, J.; Olazar, M.; Williams, P.T. Hydrogen production from biomass and plastic mixtures by pyrolysis-gasification. *Int. J. Hydrogen Energy* **2014**, *39*, 10883–10891. [\[CrossRef\]](#)
109. Pan, P.; Hu, C.; Yang, W.; Li, Y.; Dong, L.; Zhu, L.; Tong, D.; Qing, R.; Fan, Y. The direct pyrolysis and catalytic pyrolysis of *Nannochloropsis* sp. residue for renewable bio-oils. *Bioresour. Technol.* **2010**, *101*, 4593–4599. [\[CrossRef\]](#) [\[PubMed\]](#)
110. Lin, K.C.; Lin, Y.C.; Hsiao, Y.H. Microwave plasma studies of *Spirulina* algae pyrolysis with relevance to hydrogen production. *Energy* **2014**, *64*, 567–574. [\[CrossRef\]](#)
111. Maddi, B.; Viamajala, S.; Varanasi, S. Comparative study of pyrolysis of algal biomass from natural lake blooms with lignocellulosic biomass. *Bioresour. Technol.* **2011**, *102*, 11018–11026. [\[CrossRef\]](#) [\[PubMed\]](#)
112. Levin, D.B.; Chahine, R. Challenges for renewable hydrogen production from biomass. *Int. J. Hydrogen Energy* **2010**, *35*, 4962–4969. [\[CrossRef\]](#)
113. Kersten, S.R.A.; Potic, B.; Prins, W.; van Swaaij, W.P.M. Gasification of model compounds and wood in hot compressed water. *Ind. Eng. Chem. Res.* **2006**, *45*, 4169–4177. [\[CrossRef\]](#)
114. Reddy, S.N.; Nanda, S.; Dalai, A.K.; Kozinski, J.A. Supercritical water gasification of biomass for hydrogen production. *Int. J. Hydrogen Energy* **2014**, *39*, 6912–6926. [\[CrossRef\]](#)
115. Okajima, I.; Sako, T. Energy conversion of biomass with supercritical and subcritical water using large-scale plants. *J. Biosci. Bioeng.* **2014**, *117*, 1–9. [\[CrossRef\]](#)
116. Lu, Y.; Guo, L.; Zhang, X.; Yan, Q. Thermodynamic modeling and analysis of biomass gasification for hydrogen production in supercritical water. *Chem. Eng. J.* **2007**, *131*, 233–244. [\[CrossRef\]](#)
117. Lu, Y.J.; Jin, H.; Guo, L.J.; Zhang, X.M.; Cao, C.Q.; Guo, X. Hydrogen production by biomass gasification in supercritical water with a fluidized bed reactor. *Int. J. Hydrogen Energy* **2008**, *33*, 6066–6075. [\[CrossRef\]](#)
118. Miao, X.; Wu, Q.; Yang, C. Fast pyrolysis of microalgae to produce renewable fuels. *J. Anal. Appl. Pyrolysis* **2004**, *71*, 855–863. [\[CrossRef\]](#)
119. Miao, X.; Wu, Q. High yield bio-oil production from fast pyrolysis by metabolic controlling of *Chlorella protothecoides*. *J. Biotechnol.* **2004**, *110*, 85–93. [\[CrossRef\]](#)
120. Grierson, S.; Strezov, V.; Ellem, G.; Mcgregor, R.; Herbertson, J. Thermal characterisation of microalgae under slow pyrolysis conditions. *J. Anal. Appl. Pyrolysis* **2009**, *85*, 118–123. [\[CrossRef\]](#)
121. Hu, Z.; Zheng, Y.; Yan, F.; Xiao, B.; Liu, S. Bio-oil production through pyrolysis of blue-green algae blooms (BGAB): Product distribution and bio-oil characterization. *Energy* **2013**, *52*, 119–125. [\[CrossRef\]](#)
122. Giang, T.T.; Lunprom, S.; Liao, Q.; Reungsang, A.; Salakkam, A. Enhancing Hydrogen Production from *Chlorella* sp. Biomass by Pre-Hydrolysis with Simultaneous Saccharification and Fermentation (PSSF). *Energies* **2019**, *12*, 908. [\[CrossRef\]](#)
123. Zieliński, M.; Korzeniewska, E.; Filipkowska, Z.; Dębowski, M.; Harnisz, M.; Kwiatkowski, R. Biohydrogen production at low load of organic matter by psychrophilic bacteria. *Energy* **2017**, *134*, 1132–1139. [\[CrossRef\]](#)
124. Dębowski, M.; Korzeniewska, E.; Filipkowska, Z.; Zieliński, M.; Kwiatkowski, R. Possibility of hydrogen production during cheese whey fermentation process by different strains of psychrophilic bacteria. *Int. J. Hydrogen Energy* **2014**, *39*, 1972–1978. [\[CrossRef\]](#)

125. Zhang, H.; Li, J.; Zhang, Q.; Zhu, S.; Yang, S.; Zhang, Z. Effect of Substrate Concentration on Photo-Fermentation Bio-Hydrogen Production Process from Starch-Rich Agricultural Leftovers under Oscillation. *Sustainability* **2020**, *12*, 2700. [[CrossRef](#)]
126. Kapdan, I.K.; Kargi, F. Bio-hydrogen production from waste materials. *Enzym. Microb. Technol.* **2006**, *38*, 569–582. [[CrossRef](#)]
127. Kumar, N.; Das, D. Enhancement of hydrogen production by *Enterobacter cloacae* IIT-BT 08. *Process. Biochem.* **2000**, *35*, 589–593. [[CrossRef](#)]
128. Kumar, N.; Das, D. Continuous hydrogen production by immobilized *Enterobacter cloacae* IIT-BT 08 using lignocellulosic materials as solid matrices. *Enzym. Microb. Technol.* **2001**, *29*, 280–287. [[CrossRef](#)]
129. Wu, X.; Yao, W.; Zhu, J. Effect of pH on continuous biohydrogen production from liquid swine manure with glucose supplement using an anaerobic sequencing batch reactor. *Int. J. Hydrogen Energy* **2010**, *35*, 6592–6599. [[CrossRef](#)]
130. Fang, H.H.P.; Liu, H. Effect of pH on hydrogen production from glucose by a mixed culture. *Bioresour. Technol.* **2002**, *82*, 87–93. [[CrossRef](#)]
131. Kim, J.K.; Nhat, L.; Chun, Y.N.; Kim, S.W. Hydrogen production conditions from food waste by dark fermentation with *Clostridium beijerinckii* KCTC 1785. *Biotechnol. Bioprocess Eng.* **2008**, *13*, 499–504. [[CrossRef](#)]
132. Song, Z.X.; Dai, Y.; Fan, Q.L.; Li, X.H.; Fan, Y.T.; Hou, H.W. Effects of pretreatment method of natural bacteria source on microbial community and bio-hydrogen production by dark fermentation. *Int. J. Hydrogen Energy* **2012**, *37*, 5631–5636. [[CrossRef](#)]
133. Lanzilli, M.; Esercizio, N.; Vastano, M.; Xu, Z.; Nuzzo, G.; Gallo, C.; Manzo, E.; Fontana, A.; D'Ippolito, G. Effect of Cultivation Parameters on Fermentation and Hydrogen Production in the Phylum *Thermotogae*. *Int. J. Mol. Sci.* **2021**, *22*, 341. [[CrossRef](#)]
134. Fabiano, B.; Perego, P. Thermodynamic study and optimization of hydrogen production by *Enterobacter aerogenes*. *Int. J. Hydrogen Energy* **2002**, *27*, 149–156. [[CrossRef](#)]
135. Tenca, A.; Schievano, A.; Perazzolo, F.; Adani, F.; Oberti, R. Biohydrogen from thermophilic co-fermentation of swine manure with fruit and vegetable waste: Maximizing stable production without pH control. *Bioresour. Technol.* **2011**, *102*, 8582–8588. [[CrossRef](#)]
136. Xiao, B.; Liu, J. Biological hydrogen production from sterilized sewage sludge by anaerobic self-fermentation. *J. Hazard. Mater.* **2009**, *168*, 163–167. [[CrossRef](#)]
137. Chen, W.H.; Chen, S.Y.; Khanal, S.K.; Sung, S. Kinetic study of biological hydrogen production by anaerobic fermentation. *Int. J. Hydrogen Energy* **2006**, *31*, 2170–2178. [[CrossRef](#)]
138. Shin, H.S.; Youn, J.H.; Kim, S.H. Hydrogen production from food waste in anaerobic mesophilic and thermophilic acidogenesis. *Int. J. Hydrogen Energy* **2004**, *29*, 1355–1363. [[CrossRef](#)]
139. Kisielewska, M.; Dębowski, M.; Zieliński, M. Improvement of biohydrogen production using a reduced pressure fermentation. *Bioprocess Biosyst. Eng.* **2015**, *38*, 1925–1933. [[CrossRef](#)]
140. Saye, L.M.G.; Navaratna, T.A.; Chong, J.P.; O'Malley, M.K.; Theodorou, M.; Reilly, M. The Anaerobic Fungi: Challenges and Opportunities for Industrial Lignocellulosic Biofuel Production. *Microorganisms* **2021**, *9*, 694. [[CrossRef](#)]
141. Eroglu, E.; Gündüz, U.; Yücel, M.; Türker, L.; Eroglu, I. Photobiological hydrogen production from olive mill wastewater as sole substrate sources. *Int. J. Hydrogen Energy* **2004**, *29*, 163–171. [[CrossRef](#)]
142. Fan, Q.; Neubauer, P.; Lenz, O.; Gimpel, M. Heterologous Hydrogenase Overproduction Systems for Biotechnology—An Overview. *Int. J. Mol. Sci.* **2020**, *21*, 5890. [[CrossRef](#)] [[PubMed](#)]
143. Contreras-Angulo, J.R.; Mata, T.M.; Cuellar-Bermudez, S.P.; Caetano, N.S.; Chandra, R.; Garcia-Perez, J.S.; Muylaert, K.; Parra-Saldivar, R. Symbiotic Co-Culture of *Scenedesmus* sp. and *Azospirillum brasilense* on N-Deficient Media with Biomass Production for Biofuels. *Sustainability* **2019**, *11*, 707. [[CrossRef](#)]
144. Kim, M.S.; Baek, J.S.; Lee, J.K. Comparison of H₂ accumulation by *Rhodobacter sphaeroides* KD131 and its uptake hydrogenase and PHB synthase deficient mutant. *Int. J. Hydrogen Energy* **2006**, *31*, 121–127. [[CrossRef](#)]
145. Koku, H.; Eroglu, I.; Gündüz, U.; Yücel, M.; Türker, L. Kinetics of biohydrogen production by the photosynthetic bacterium *Rhodobacter sphaeroides* O.U. 001. *Int. J. Hydrogen Energy* **2003**, *28*, 381–388. [[CrossRef](#)]
146. Skjånes, K.; Andersen, U.; Heidorn, T.; Borgvang, S.A. Design and construction of a photobioreactor for hydrogen production, including status in the field. *Environ. Boil. Fishes* **2016**, *28*, 2205–2223. [[CrossRef](#)]
147. Limongi, A.R.; Viviano, E.; De Luca, M.; Radice, R.P.; Bianco, G.; Martelli, G. Biohydrogen from Microalgae: Production and Applications. *Appl. Sci.* **2021**, *11*, 1616. [[CrossRef](#)]
148. Khetkorn, W.; Rastogi, R.P.; Incharoensakdi, A.; Lindblad, P.; Madamwar, D.; Pandey, A.; Larroche, C. Microalgal hydrogen production—A review. *Bioresour. Technol.* **2017**, *243*, 1194–1206. [[CrossRef](#)] [[PubMed](#)]
149. Yetis, M.; Gündüz, U.; Eroglu, I.; Yücel, M.; Türker, L. Photoproduction of hydrogen from sugar refinery wastewater by *Rhodobacter sphaeroides* O.U.001. *Int. J. Hydrogen Energy* **2000**, *25*, 1035–1041. [[CrossRef](#)]
150. Oh, Y.K.; Scol, E.H.; Kim, M.S.; Park, S. Photoproduction of hydrogen from acetate by a chemoheterotrophic bacterium *Rhodospseudomonas palustris* P4. *Int. J. Hydrogen Energy* **2004**, *29*, 1115–1121.
151. Argun, H.; Kargi, F. Photo-fermentative hydrogen gas production from dark fermentation effluent of ground wheat solution: Effects of light source and light intensity. *Int. J. Hydrogen Energy* **2010**, *35*, 1595–1603. [[CrossRef](#)]
152. Laocharoen, S.; Reungsang, A. Isolation, characterization and optimization of photo-hydrogen production conditions by newly isolated *Rhodobacter sphaeroides* KCU-PS5. *Int. J. Hydrogen Energy* **2014**, *39*, 10870–10882. [[CrossRef](#)]
153. Sun, Y.; He, J.; Yang, G.; Sun, G.; Sage, V. A Review of the Enhancement of Bio-Hydrogen Generation by Chemicals Addition. *Catalysts* **2019**, *9*, 353. [[CrossRef](#)]

154. Kumar, G.; Shobana, S.; Nagarajan, D.; Lee, D.-J.; Lee, K.-S.; Lin, C.-Y.; Chen, C.-Y.; Chang, J.-S. Biomass based hydrogen production by dark fermentation—recent trends and opportunities for greener processes. *Curr. Opin. Biotechnol.* **2018**, *50*, 136–145. [[CrossRef](#)]
155. Manish, S.; Banerjee, R. Comparison of biohydrogen production processes. *Int. J. Hydrogen Energy* **2008**, *33*, 279–286. [[CrossRef](#)]
156. Nath, K.; Kumar, A.; Das, D. Hydrogen production by *Rhodobacter sphaeroides* strain O.U.001 using spent media of *Enterobacter cloacae* strain DM11. *Appl. Microbiol. Biotechnol.* **2005**, *68*, 533–541. [[CrossRef](#)]
157. Yokoi, H.; Mori, S.; Hirose, J.; Hayashi, S.; Takasaki, Y. H₂ production from starch by mixed culture of *Clostridium butyricum* and *Rhodobacter* sp. M-19. *Biotechnol. Lett.* **1998**, *20*, 895–899. [[CrossRef](#)]
158. Ghosh, D.; Sobro, I.F.; Hallenbeck, P.C. Optimization of the hydrogen yield from single-stage photofermentation of glucose by *Rhodobacter capsulatus* JP91 using response surface methodology. *Bioresour. Technol.* **2012**, *123*, 199–206. [[CrossRef](#)]
159. Keskin, T.; Hallenbeck, P.C. Hydrogen production from sugar industry wastes using single-stage photofermentation. *Bioresour. Technol.* **2012**, *112*, 131–136. [[CrossRef](#)] [[PubMed](#)]
160. Abo-Hashesh, M.; Ghosh, D.; Tourigny, A.; Taous, A.; Hallenbeck, P.C. Single stage photofermentative hydrogen production from glucose: An attractive alternative to two stage photofermentation or co-culture approaches. *Int. J. Hydrogen Energy* **2011**, *36*, 13889–13895. [[CrossRef](#)]
161. Seifert, K.; Waligorska, M.; Laniecki, M. Hydrogen generation in photobiological process from dairy wastewater. *Int. J. Hydrogen Energy* **2010**, *35*, 9624–9629. [[CrossRef](#)]
162. Anam, K.; Habibi, M.S.; Harwati, T.U.; Susilaningasih, D. Photofermentative hydrogen production using *Rhodobium marinum* from bagasse and soy sauce wastewater. *Int. J. Hydrogen Energy* **2012**, *37*, 15436–15442. [[CrossRef](#)]
163. Fang, H.H.P.; Liu, H.; Zhang, T. Phototrophic hydrogen production from acetate and butyrate in wastewater. *Int. J. Hydrogen Energy* **2005**, *30*, 785–793. [[CrossRef](#)]
164. Khanal, S.K.; Chen, W.H.; Li, L.; Sung, S. Biological hydrogen production: Effects of pH and intermediate products. *Int. J. Hydrogen Energy* **2004**, *29*, 1123–1131. [[CrossRef](#)]
165. Yokoi, H.; Saito, A.S.; Uchida, H.; Hirose, J.; Hayashi, S.; Takasaki, Y. Microbial hydrogen production from sweet potato starch residue. *J. Biosci. Bioeng.* **2001**, *91*, 58–63. [[CrossRef](#)]
166. Cheng, J.; Xia, A.; Liu, Y.; Lin, R.; Zhou, J.; Cen, K. Combination of dark- and photo-fermentation to improve hydrogen production from *Arthrospira platensis* wet biomass with ammonium removal by zeolite. *Int. J. Hydrogen Energy* **2012**, *37*, 13330–13337. [[CrossRef](#)]
167. Su, H.; Cheng, J.; Zhou, J.; Song, W.; Cen, K. Combination of dark- and photo-fermentation to enhance hydrogen production and energy conversion efficiency. *Int. J. Hydrogen Energy* **2009**, *34*, 8846–8853. [[CrossRef](#)]
168. Su, H.; Cheng, J.; Zhou, J.; Song, W.; Cen, K. Improving hydrogen production from cassava starch by combination of dark and photo fermentation. *Int. J. Hydrogen Energy* **2009**, *34*, 1780–1786. [[CrossRef](#)]
169. Levin, D.B.; Pitt, L.; Love, M. Biohydrogen production: Prospects and limitations to practical application. *Int. J. Hydrogen Energy* **2004**, *29*, 173–185. [[CrossRef](#)]
170. Zuorro, A.; García-Martínez, J.B.; Barajas-Solano, A.F. The Application of Catalytic Processes on the Production of Algae-Based Biofuels: A Review. *Catalysts* **2021**, *11*, 22. [[CrossRef](#)]
171. Show, K.Y.; Yan, Y.G.; Ling, M.; Ye, G.X.; Li, T.; Lee, D.J. Hydrogen production from algal biomass—Advances, challenges and prospects. *Bioresour. Technol.* **2018**, *257*, 290–300. [[CrossRef](#)]
172. Jiménez-Llanos, J.; Ramírez-Carmona, M.; Rendón-Castrillón, L.; Ocampo-López, C. Sustainable biohydrogen production by *Chlorella* sp. microalgae: A review. *Int. J. Hydrogen Energy* **2020**, *45*, 8310–8328. [[CrossRef](#)]
173. Liu, Y.; Min, J.; Feng, X.; He, Y.; Liu, J.; Wang, Y.; He, J.; Do, H.; Sage, V.; Yang, G.; et al. A Review of Biohydrogen Productions from Lignocellulosic Precursor via Dark Fermentation: Perspective on Hydrolysate Composition and Electron-Equivalent Balance. *Energies* **2020**, *13*, 2451. [[CrossRef](#)]
174. Tamburic, B.; Zemichael, F.W.; Maitland, G.C.; Hellgardt, K. Parameters affecting the growth and hydrogen production of the green alga *Chlamydomonas reinhardtii*. *Int. J. Hydrogen Energy* **2011**, *36*, 1–5. [[CrossRef](#)]
175. Oncel, S.; Vardar-Sukan, F. Photo-bioproduction of hydrogen by *Chlamydomonas reinhardtii* using a semi-continuous process regime. *Int. J. Hydrogen Energy* **2009**, *34*, 7592–7602. [[CrossRef](#)]
176. Rattanapoltee, P.; Dujjanutat, P.; Muanrukxa, P.; Kaewkannetra, P. Biocircular platform for third generation biodiesel production: Batch/fed batch mixotrophic cultivations of microalgae using glycerol waste as a carbon source. *Biochem. Eng. J.* **2021**, *175*, 108128. [[CrossRef](#)]
177. Laurinavichene, T.V.; Tolstygina, I.V.; Galiulina, R.R.; Ghirardi, M.L.; Seibert, M.; Tsygankov, A.A. Dilution methods to deprive *Chlamydomonas reinhardtii* cultures of sulfur for subsequent hydrogen photoproduction. *Int. J. Hydrogen Energy* **2002**, *27*, 1245–1249. [[CrossRef](#)]
178. Skjanes, K.; Knutsen, G.; Källqvist, T.; Lindblad, P. H₂ production from marine and freshwater species of green algae during sulfur deprivation and considerations for bioreactor design. *Int. J. Hydrogen Energy* **2008**, *33*, 511–521. [[CrossRef](#)]
179. Faraloni, C.; Ena, A.; Pintucci, C.; Torzillo, G. Enhanced hydrogen production by means of sulfur-deprived *Chlamydomonas reinhardtii* cultures grown in pretreated olive mill wastewater. *Int. J. Hydrogen Energy* **2011**, *36*, 5920–5931. [[CrossRef](#)]
180. Zhang, L.; He, M.; Liu, J. The enhancement mechanism of hydrogen photoproduction in *Chlorella protothecoides* under nitrogen limitation and sulfur deprivation. *Int. J. Hydrogen Energy* **2014**, *39*, 8969–8976. [[CrossRef](#)]

181. Liu, C.H.; Chang, C.Y.; Liao, Q.; Zhu, X.; Chang, J.S. Photoheterotrophic growth of *Chlorella vulgaris* ESP6 on organic acids from dark hydrogen fermentation effluents. *Bioresour. Technol.* **2013**, *145*, 331–336. [[CrossRef](#)] [[PubMed](#)]
182. Chader, S.; Hacene, H.; Agathos, S.N. Study of hydrogen production by three strains of *Chlorella* isolated from the soil in the Algerian Sahara. *Int. J. Hydrogen Energy* **2009**, *34*, 4941–4946. [[CrossRef](#)]
183. Lin, H.D.; Liu, B.H.; Kuo, T.T.; Tsai, H.C.; Feng, T.F.; Huang, C.C.; Chien, L.F. Knockdown of PsbO leads to induction of HydA and production of photobiological H₂ in the green alga *Chlorella* sp. DT. *Bioresour. Technol.* **2013**, *143*, 154–162. [[CrossRef](#)]
184. Amutha, K.B.; Murugesan, A.G. Biological hydrogen production by the algal biomass *Chlorella vulgaris* MSU 01 strain isolated from pond sediment. *Bioresour. Technol.* **2011**, *102*, 194–199. [[CrossRef](#)] [[PubMed](#)]
185. Guan, Y.; Deng, M.; Yu, X.; Zhang, W. Two-stage photo-biological production of hydrogen by marine green alga *Platymonas subcordiformis*. *Biochem. Eng. J.* **2004**, *19*, 69–73. [[CrossRef](#)]
186. Ji, C.F.; Yu, X.J.; Chen, Z.A.; Xue, S.; Legrand, J.; Zhang, W. Effects of nutrient deprivation on biochemical compositions and photo-hydrogen production of *Tetraselmis subcordiformis*. *Int. J. Hydrogen Energy* **2011**, *36*, 5817–5821. [[CrossRef](#)]
187. Oncel, S.; Vardar Sukan, F. Effect of light intensity and the light: Dark cycles on the long term hydrogen production of *Chlamydomonas reinhardtii* by batch cultures. *Biomass Bioenergy* **2011**, *35*, 1066–1074. [[CrossRef](#)]
188. Guo, Z.; Chen, Z.; Lu, H.; Fu, Y.; Yu, X.; Zhang, W. Sustained hydrogen photoproduction by marine green algae *Platymonas subcordiformis* integrated with in situ hydrogen consumption by an alkaline fuel cell system. *J. Biotechnol.* **2008**, *136*, S573. [[CrossRef](#)]
189. Kim, M.S.; Baek, J.S.; Yun, Y.S.; Sim, S.J.; Park, S.; Kim, S.C. Hydrogen production from *Chlamydomonas reinhardtii* biomass using a two-step conversion process: Anaerobic conversion and photosynthetic fermentation. *Int. J. Hydrogen Energy* **2006**, *31*, 812–816. [[CrossRef](#)]
190. Sun, J.; Yuan, X.; Shi, X.; Chu, C.; Guo, R.; Kong, H. Fermentation of *Chlorella* sp. for anaerobic bio-hydrogen production: Influences of inoculum/substrate ratio, volatile fatty acids and NADH. *Bioresour. Technol.* **2011**, *102*, 10480–10485. [[CrossRef](#)]
191. Cheng, H.H.; Whang, L.M.; Wu, C.W.; Chung, M.C. A two-stage bioprocess for hydrogen and methane production from rice straw bioethanol residues. *Bioresour. Technol.* **2012**, *113*, 23–29. [[CrossRef](#)] [[PubMed](#)]
192. Yun, Y.-M.; Jung, K.-W.; Kim, D.-H.; Oh, Y.-K.; Cho, S.-K.; Shin, H.-S. Optimization of dark fermentative H₂ production from microalgal biomass by combined (acid + ultrasonic) pretreatment. *Bioresour. Technol.* **2013**, *141*, 220–226. [[CrossRef](#)]
193. Liu, C.-H.; Chang, C.-Y.; Cheng, C.-L.; Lee, D.-J.; Chang, J.-S. Fermentative hydrogen production by *Clostridium butyricum* CGS5 using carbohydrate-rich microalgal biomass as feedstock. *Int. J. Hydrogen Energy* **2012**, *37*, 15458–15464. [[CrossRef](#)]
194. Xia, A.; Cheng, J.; Lin, R.; Lu, H.; Zhou, J.; Cen, K. Comparison in dark hydrogen fermentation followed by photo hydrogen fermentation and methanogenesis between protein and carbohydrate compositions in *Nannochloropsis oceanica* biomass. *Bioresour. Technol.* **2013**, *138*, 204–213. [[CrossRef](#)] [[PubMed](#)]
195. Batista, A.P.; Moura, P.; Marques, P.A.S.S.; Ortigueira, J.; Alves, L.; Gouveia, L. *Scenedesmus obliquus* as feedstock for biohydrogen production by *Enterobacter aerogenes* and *Clostridium butyricum*. *Fuel* **2014**, *117*, 537–543. [[CrossRef](#)]
196. Cao, G.L.; Zhao, L.; Wang, A.J.; Wang, Z.Y.; Ren, N.Q. Single-step bioconversion of lignocellulose to hydrogen using novel moderately thermophilic bacteria. *Biotechnol. Biofuels* **2014**, *7*, 1–13. [[CrossRef](#)]
197. Guo, Y.C.; Dai, Y.; Bai, Y.X.; Li, Y.H.; Fan, Y.T.; Hou, H.W. Co-producing hydrogen and methane from higher-concentration of corn stalk by combining hydrogen fermentation and anaerobic digestion. *Int. J. Hydrogen Energy* **2014**, *39*, 14204–14211. [[CrossRef](#)]
198. Wu, J.N.; Ein-Mozaffari, F.; Upreti, S. Effect of ozone pretreatment on hydrogen production from barley straw. *Bioresour. Technol.* **2013**, *144*, 344–349. [[CrossRef](#)] [[PubMed](#)]
199. Levin, D.B.; Islam, R.; Cicek, N.; Sparling, R. Hydrogen production by *Clostridium thermocellum* 27405 from cellulosic biomass substrates. *Int. J. Hydrogen Energy* **2006**, *31*, 1496–1503. [[CrossRef](#)]
200. Cui, M.J.; Shen, J.Q. Effects of acid and alkaline pretreatments on the biohydrogen production from grass by anaerobic dark fermentation. *Int. J. Hydrogen Energy* **2012**, *37*, 1120–1124. [[CrossRef](#)]
201. Li, Y.C.; Nissilä, M.E.; Wu, S.Y.; Lin, C.Y.; Puhakka, J.A. Silage as source of bacteria and electrons for dark fermentative hydrogen production. *Int. J. Hydrogen Energy* **2012**, *37*, 15518–15524. [[CrossRef](#)]
202. Cui, M.J.; Yuan, Z.L.; Zhi, X.H.; Wei, L.L.; Shen, J.Q. Biohydrogen production from poplar leaves pretreated by different methods using anaerobic mixed bacteria. *Int. J. Hydrogen Energy* **2010**, *35*, 4041–4047. [[CrossRef](#)]
203. Chen, C.C.; Chuang, Y.S.; Lin, C.Y.; Lay, C.H.; Sen, B. Thermophilic dark fermentation of untreated rice straw using mixed cultures for hydrogen production. *Int. J. Hydrogen Energy* **2012**, *37*, 15540–15546. [[CrossRef](#)]
204. Sikora, A. Hydrogen production in microbial processes. *Adv. Microbiol.* **2008**, *47*, 465–482.
205. Kim, D.H.; Kim, M.S. Hydrogenases for biological hydrogen production. *Bioresour. Technol.* **2011**, *102*, 8423–8431. [[CrossRef](#)] [[PubMed](#)]
206. Raj, R.; Kumari, M. Blue green algae (BGA) and its application. *J. Pharmacogn. Phytochem.* **2020**, *9*, 287–296.
207. Troshina, O.; Serebryakova, L.; Sheremetieva, M.; Lindblad, P. Production of H₂ by the unicellular cyanobacterium *Gloeocapsa alpicola* CALU 743 during fermentation. *Int. J. Hydrogen Energy* **2002**, *27*, 1283–1289. [[CrossRef](#)]
208. Aoyama, K.; Uemura, I.; Miyake, J.; Asada, Y. Fermentative metabolism to produce hydrogen gas and organic compounds in a cyanobacterium, *Spirulina platensis*. *J. Ferment. Bioeng.* **1997**, *83*, 17–20. [[CrossRef](#)]
209. Khetkorn, W.; Lindblad, P.; Incharoensakdi, A. Enhanced biohydrogen production by the N₂-fixing cyanobacterium *Anabaena siamensis* strain TISTR 8012. *Int. J. Hydrogen Energy* **2010**, *35*, 12767–12776. [[CrossRef](#)]

210. Khetkorn, W.; Lindblad, P.; Incharoensakdi, A. Inactivation of uptake hydrogenase leads to enhanced and sustained hydrogen production with high nitrogenase activity under high light exposure in the cyanobacterium *Anabaena siamensis* TISTR 8012. *J. Biol. Eng.* **2012**, *6*, 1–12. [[CrossRef](#)]
211. Khatoon, H.; Rahman, N.A.; Banerjee, S.; Harun, N.; Suleiman, S.S.; Zakaria, N.H.; Lananan, F.; Hamid, S.H.A.; Endut, A. Effects of different salinities and pH on the growth and proximate composition of *Nannochloropsis* sp. and *Tetraselmis* sp. isolated from South China Sea cultured under control and natural condition. *Int. Biodeterior. Biodegrad.* **2014**, *95*, 11–18. [[CrossRef](#)]
212. Yao, C.H.; Ai, J.N.; Cao, X.P.; Xue, S. Salinity manipulation as an effective method for enhanced starch production in the marine microalga *Tetraselmis subcordiformis*. *Bioresour. Technol.* **2013**, *146*, 663–671. [[CrossRef](#)]
213. Dudek, M.; Dębowski, M.; Zieliński, M.; Nowicka, A. Use of a wastewater after anaerobic pretreatment to microalgae *Platymonas subcordiformis* growth. *Ecol. Eng.* **2017**, *18*, 14–20.
214. Guo, Z.; Liu, Y.; Guo, H.; Yan, S.; Mu, J. Microalgae cultivation using an aquaculture wastewater as growth medium for bio-mass and biofuel production. *J. Environ. Sci.* **2013**, *25*, 85–88. [[CrossRef](#)]
215. Zhang, Y.; Fan, X.; Yang, Z.; Wang, H.; Yang, D.; Guo, R. Characterization of H₂ photoproduction by a new marine green alga, *Platymonas helgolandica* var. *tsingtaoensis*. *Appl. Energy* **2012**, *92*, 38–43. [[CrossRef](#)]
216. Xie, J.; Zhang, Y.; Li, Y.; Wang, Y. Mixotrophic cultivation of *Platymonas subcordiformis*. *Environ. Boil. Fishes* **2001**, *13*, 343–347. [[CrossRef](#)]
217. Ran, C.; Zhang, F.; Sun, H.; Zhao, B. Effect of culture medium on hydrogen production by sulfur-deprived marine green algae *Platymonas subcordiformis*. *Biotechnol. Bioprocess Eng.* **2009**, *14*, 835–841. [[CrossRef](#)]
218. Chinnasamy, S.; Bhatnagar, A.; Hunt, R.W.; Das, K.C. Microalgae cultivation in a wastewater dominated by carpet mill effluents for biofuel applications. *Bioresour. Technol.* **2010**, *101*, 3097–3105. [[CrossRef](#)] [[PubMed](#)]
219. Dasgupta, C.N.; Gilbert, J.J.; Lindblad, P.; Heidorn, T.; Borgvang, S.A.; Skjanes, K.; Das, D. Recent trends on the development of photobiological processes and photobioreactors for the improvement of hydrogen production. *Int. J. Hydrogen Energy* **2010**, *35*, 10218–10238. [[CrossRef](#)]
220. Tamburic, B.; Zemichael, F.W.; Crudge, P.; Maitland, G.C.; Hellgardt, K. Design of a novel flat-plate photobioreactor system for green algal hydrogen production. *Int. J. Hydrogen Energy* **2011**, *36*, 6578–6591. [[CrossRef](#)]
221. Saleem, M.; Chakrabarti, M.H.; Raman, A.A.A.; Hasan, D.B.; Daud, W.M.A.W.; Mustafa, A. Hydrogen production by *Chlamydomonas reinhardtii* in a two-stage process with and without illumination at alkaline pH. *Int. J. Hydrogen Energy* **2012**, *37*, 4930–4934. [[CrossRef](#)]
222. Oncel, S.; Kose, A. Comparison of tubular and panel type photobioreactors for biohydrogen production utilizing *Chlamydomonas reinhardtii* considering mixing time and light intensity. *Bioresour. Technol.* **2014**, *151*, 265–270. [[CrossRef](#)] [[PubMed](#)]
223. Oncel, S.; Sabankay, M. Microalgal biohydrogen production considering light energy and mixing time as the two key features for scale-up. *Bioresour. Technol.* **2012**, *121*, 228–234. [[CrossRef](#)]
224. Day, J.G.; Tsavalos, A.J. An investigation of the heterotrophic culture of the green alga *Tetraselmis*. *Environ. Boil. Fishes* **1996**, *8*, 73–77. [[CrossRef](#)]
225. Dudek, M.; Dębowski, M.; Zieliński, M.; Nowicka, A.; Rusanowska, P. Water from the Vistula Lagoon as a medium in mixotrophic growth and hydrogen production by *Platymonas subcordiformis*. *Int. J. Hydrogen Energy* **2018**, *43*, 9529–9534. [[CrossRef](#)]
226. Yao, C.; Ai, J.; Cao, X.; Xue, S.; Zhang, W. Enhancing starch production of a marine green microalga *Tetraselmis subcordiformis* through nutrient limitation. *Bioresour. Technol.* **2012**, *118*, 438–444. [[CrossRef](#)] [[PubMed](#)]
227. Cui, Y.; Wang, J.; Jiang, P.; Bian, S.; Qin, S. Transformation of *Platymonas (Tetraselmis) subcordiformis* (Prasinophyceae, Chlorophyta) by agitation with glass beads. *World J. Microbiol. Biotechnol.* **2010**, *26*, 1653–1657. [[CrossRef](#)]
228. Tamburic, B.; Zemichael, F.W.; Maitland, G.C.; Hellgardt, K. A novel nutrient control method to deprive green algae of sulphur and initiate spontaneous hydrogen production. *Int. J. Hydrogen Energy* **2012**, *37*, 8988–9001. [[CrossRef](#)]
229. Dębowski, M.; Zieliński, M.; Dudek, M.; Grala, A. Acquisition feasibility and methane fermentation effectiveness of biomass of microalgae occurring in eutrophicated aquifers on the example of the Vistula Lagoon. *Int. J. Green Energy* **2014**, *13*, 395–407. [[CrossRef](#)]
230. Ogbonna, J.C.; Tanaka, H. Night biomass loss and changes in biochemical composition of cells during light/dark cyclic culture of *Chlorella pyrenoidosa*. *J. Ferment. Bioeng.* **1996**, *82*, 558–564. [[CrossRef](#)]