



# **A Review on Advanced Processes of Biohydrogen Generation** from Lignocellulosic Biomass with Special Emphasis on Thermochemical Conversion

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**Abstract:** The utilization of lignocellulosic biomass as an alternative energy source presents a promising opportunity to achieve a future energy system that is clean and free from CO<sub>2</sub> emissions. To realize this potential, it is crucial to develop effective techniques for converting biomass and organic solid waste into secondary energy sources. Among the available options, hydrogen production stands out due to its numerous advantages, including its cleanliness, versatility in conversion and utilization technologies, high energy efficiency, and dense energy content per unit weight. This article offers a comprehensive overview of different conversion pathways and important technologies for generating hydrogen from biomass and organic solid waste. It specifically focuses on the thermochemical conversion processes are still in the developmental phase, utilizing organic biomass for hydrogen production is widely recommended due to its ability to yield higher amounts of end products and its compatibility with existing facilities. However, it should be noted that this method necessitates a substantial amount of energy due to its endothermic nature. This article also explores alternative hydrogen conversion technologies and their potential for utilizing organic biomass as a feedstock, while addressing the challenges and limitations associated with these methods.

Keywords: biohydrogen; thermochemical conversion; biomass; syngas; gasification

## 1. Introduction

The issue of energy crisis is now a major concern due to factors such as population growth, increased living standards, and industrialization [1]. Despite this, most of our energy production still depends heavily on non-renewable fossil fuels like coal, petroleum, and natural gas. However, the overuse of these fuels is leading to their depletion and rising prices. Additionally, the concern about global warming caused by the increase in greenhouse gas emissions due to the overconsumption of fossil fuel sources has resulted in a greater demand for finding clean and renewable energy sources [2]. The growing demand for clean energy sources due to industrial and economic development has led to recent developments in biofuels [3]. Hydrogen production from organic wastes is a promising and environmentally friendly alternative that has received global attention. Hydrogen has a high energy content and is versatile in its production and use, making it suitable for various applications. The term biohydrogen refers to hydrogen produced from biological sources, which is a promising alternative to conventional fossil fuels due to its clean combustion that produces only water [4]. Producing  $H_2$  from biomass as feedstocks has many environmental and economic advantages and has the potential to significantly meet the current fuel demand.



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Fossil fuels are responsible for the majority of hydrogen production, with 60% coming from primary hydrogen production plants. Around 71.27% of hydrogen is produced from natural gas, 27.27% from coal, 0.7% from petroleum, and 0.7% from water electrolysis. However, since the production process of hydrogen via fossil reformation results in a high number of greenhouse gas (GHG) emissions, it cannot be considered renewable or carbon-neutral [5]. There has been growing interest in waste-to-energy studies, which is influencing research in hydrogen production from waste materials. By generating biohydrogen from different types of organic wastes, this approach addresses the problems of both waste disposal and energy production at the same time. The term organic waste describes waste that is biodegradable in nature and may break down into carbon dioxide, methane, or simple organic compounds. A variety of organic wastes can be used to generate biohydrogen, including industrial waste, sewage sludge, solid waste, agricultural crops residue, poultry waste, and manure [6,7].

Biomass is considered the most abundant renewable resource on our planet and is estimated to have a global production of around  $2 \times 10^{11}$  tons. Numerous studies have explored the use of biomass to produce different types of solid, liquid, and gaseous fuels [4,8]. Out of all these fuel options, hydrogen is considered one of the cleanest because it does not emit any greenhouse gases during its combustion. Therefore, the utilization of hydrogen as a fuel has the potential to greatly support the objective of achieving a carbon-neutral world as outlined in the Paris Agreement. There are several pathways available for converting biomass into biohydrogen, primarily classified into two categories: biological pathways and thermochemical pathways.

A considerable amount of research has been undertaken to find the best route to suit local needs for the generation of hydrogen from lingo-cellulosic biomass. The collation of this information may help researchers to find the best route for further proliferation of these technologies. This article discusses the potential of hydrogen production using various routes, with special focus on the thermochemical conversion process.

#### 2. Biohydrogen Production Technologies

The biological production methods can be classified into two major categories, i.e., biological conversion and thermochemical conversion. The biological routes require the presence of a biohydrogen-producing enzyme for the production of hydrogen. These methods comprise mainly the fermentation, biophotolysis, and bio-electrochemical routes. The thermochemical conversion methods require a high temperature for biohydrogen production. Figure 1 categorizes various biohydrogen production routes by taking various past studies into consideration [9–12].

## 2.1. Fermentation

Fermentation is a process that uses microorganisms, such as nitrogenases, hydrogenases, and enzymes, to convert organic resources into energy. This process involves the oxidation of waste organic materials, and the outcome of the fermentation depends on the catalyst and organic substrate used, as well as the process parameters. Fermentation can occur in both aerobic and non-aerobic conditions, but anaerobic fermentation is preferred because it produces hydrogen, as well as acids and alcohols that are useful for industrial applications [13]. There are two types of biofermentation processes based on the light requirements of microorganisms: dark fermentation and photofermentation. In dark fermentation, cellulosic organic feedstock is broken down into hydrogen, alcohols, and acids without light and under aerobic conditions [14]. In contrast, photofermentation uses photosynthetic bacteria to convert organic substances into CO<sub>2</sub> and H<sub>2</sub> in the presence of sunlight and under anaerobic conditions [15]. Some studies have combined these two types of fermentation to improve the yield of biohydrogen production.



Figure 1. Various biohydrogen production pathways from biomass [9–12].

## 2.1.1. Dark Fermentation

Dark fermentation is a technology that helps microorganisms to produce biohydrogen in dark anaerobic environments [16]. This process is not considered as an advantageous process because the hydrogen yield is very low and many by-products are also formed. Equations (1) and (2) show the main reactions responsible for the production of biohydrogen in dark fermentation. Equations (3)–(5) depict the various pathways for hydrogen production from glucose.

$$2H^{+} + 2e^{-} = H_2 \tag{1}$$

$$C_6 H_{12} O_6 + 6 H_2 O = 6 C O_2 + 12 H_2$$
<sup>(2)</sup>

$$C_6H_{12}O_6 + 2H_2O = 2CH_3COOH + 2CO_2 + 4H_2O$$
 (Acetic Acid Route) (3)

$$C_6H_{12}O_6 = CH_3COOH + CH_3CH_2COOH + CO_2 + H_2$$
 (Propionic Acid Route) (4)

$$C_6H_{12}O_6 + 6H_2O = CH_3CH_2CH_2COOH + CO_2 + 2H_2$$
 (Butyric Acid Route) (5)

Equation (1) shows that hydrogen is generated through the reduction of protons by electrons, which are produced through the degradation of a carbon source. The [Ni-Fe]-hydrogenase and [Fe-Fe]-hydrogenase enzymes play a crucial role in this process [17]. Although theoretically (According to Equation (2)), a 12 mol/mol glucose yield of H<sub>2</sub> is expected, in practice, it is limited to 4 mol/mol glucose [18]. However, the yield of hydrogen can be improved in thermophilic fermentation. The low production of hydrogen in dark fermentation can be attributed to the generation of multiple by-products, including acetic acid, propionic acid, and butyric acid, in addition to hydrogen [19]. Agricultural waste, sewage water, food waste, and wastewater, which have different chemical compositions, are used as substrates for hydrogen production in dark fermentation [20]. Carbohydrate- or sugar-rich substrates have been found to produce more hydrogen than protein- or lipid-rich substrates, and there is a direct relationship between the production of hydrogen and the carbohydrate-richness of the substrate [21]. The pictorial representation of dark and photo fermentation is presented in Figure 2.



Figure 2. Pictorial representation of dark and photofermentation of biomass [20,21].

The pH level is a crucial factor in achieving a higher yield of hydrogen during dark fermentation because it affects the metabolic pathway and microbial activity of microorganisms, as well as the degradation of the substrate and production efficiency. Several studies have demonstrated the importance of maintaining an appropriate pH level at the beginning and throughout the process of dark fermentation. Xing et al. [22] investigated a range of pH levels from 4.0 to 12.0 for fermenting dairy manure and observed that a pH of 5.0 resulted in the highest hydrogen production (31.5 mL/g VS). However, the study also reported that no hydrogen production occurred at pH levels below 4.0 or above 12.0 [22].

In addition to this, stopping the production of hydrogen-consuming bacteria called hydrogenotrophic methanogens is one of the major steps in the production of biohydrogen because it is the reason for lower yields of biohydrogen. For increasing hydrogen-producing bacteria and decreasing hydrogen-consuming bacteria, pre-treatment with an inoculum is required. Aeration around the reactor can stop the production of methanogens because they are anaerobic microorganism, and thus, improve the yield of biohydrogen [23]. Furthermore, the impact of pH on methanogen production is a crucial factor. A study indicated that a pH range of 7–8, along with an optimal hydraulic retention time (HRT) of 15–20 days, enables methanogens to utilize hydrogen and generate methane [24]. Kumar et al. found that from a mixed microalgae biomass, the yield of hydrogen was 29.5 mL/g VS at a pH of 5.5 upon using a methanogenic inhibitor [25].

Biohydrogen production through dark fermentation using various organic wastes can employ different microorganisms, which are categorized into three groups based on their temperature requirements: thermophiles (45–65 °C), mesophiles (25–45 °C), and psychrophiles (0–25 °C). *Clostridium* and *Enterobacter* are the most frequently utilized mesophilic bacteria for biohydrogen production, whereas *Thermoanaerobium* is the most commonly reported thermophilic microorganism [22]. These microorganisms can be further categorized based on their metabolism in the presence of oxygen. Facultative bacteria such as *E. cloacae, Enerobacter aerogens,* and *Enterobacter asburiae* are able to perform both aerobic and anaerobic fermentation [26,27]. Obligate bacteria, such as *C. paraputrificum, Ruminococcus albus,* and *Clostridium beijerincki,* can only survive in the absence of oxygen. Gram-positive bacteria such as *Enterobacter* and *Clostridium* are often used for large-scale hydrogen production because they can multiply quickly and form endospores. According to research findings, a range of microorganisms have demonstrated favorable outcomes in generating biohydrogen through the process of dark fermentation. These microorganisms encompass lactic bacteria like *Klebsiella pneumoniae* and *Cellulomonas,* as well as thermophilic

archaea such as *Thermotoga neapolitana* and *Caldicellulosiruptor saccharo-lyticus*. The performance of these organisms has shown promising results in terms of biohydrogen production yield [28].

It was also found that fermenting different substrates together resulted in an increase in the yield of biohydrogen [29]. Furthermore, pre-treatment techniques such as acid treatment, base treatment, heat treatment, and pH neutralization have been observed to have a significant effect on biohydrogen yield [30,31]. Table 1 shows the optimum condition for hydrogen production from various agricultural wastes using the dark fermentation process.

Table 1. Hydrogen production from various types of biomass using dark fermentation process.

Feedstock	Preparation of Feedstock	Microorganism	pН	Temperature (°C)	H <sub>2</sub> Yield (mL/g VS)	Refs.
Dairy manure	Treatment with hydrochloric acid (0.2% concentration), boiling, and exposure to infrared radiation.	Mixed culture	5.0	36.0 ± 1	31.5	[22]
Poplar residue with sewage sludge	-	-	-	-	20.8	[32]
Rice straw	Drying at 80–100 °C	Activated sewage sludge	4.0-5.5	35.0	14.5 + 0.3	[33]
Rice straw	Size reduction of less than 2 mm, 1.0% alkali pre-treatment, cellulose hydrolysis	Clostridium pasteurianum	7.5	37.0 ± 2	2.6 (47.6 mL/g released sugar)	[34]
Sugarcane bagasse	Pre-treatment with H <sub>2</sub> SO <sub>4</sub>	Enterobacter aerogenes	6.8	30.0	1000.0	[35]
Wheat straw	Acetic acid pre-treatment followed by steam exposure at 190 °C for 10 min and enzymatic hydrolysis lasting 72 h	Caldicellulosiruptor saccharolyticus	$6.5\pm0.1$	70.0	134.0	[36]

VS = Volatile Solids.

#### 2.1.2. Photofermentation

The photofermentation method leads to the generation of hydrogen by breaking down organic acids in the presence of light-dependent sulfur and non-sulfur purple bacteria. In this process the bacteria can be classified into two categories: purple sulfur bacteria and purple non-sulfur bacteria (PNSB). The purple sulfur bacteria perform photosynthesis, which is a method they use to convert carbon dioxide into energy for their own sustenance, using sunlight. On the other hand, purple non-sulfur bacteria have the ability to produce hydrogen by breaking down various carbon-based substances such as biowastes, organic matter, carbohydrates, and organic acids. This means that PNSB can utilize these carbon substrates as a source of energy, and as a result, they generate hydrogen as a byproduct [37]. Generally, PNSB are also known as photobacteria. The chemical reactions for the production of hydrogen through the photofermentation of glucose and acetic acid are given in Equations (6) and (7), respectively. The photofermentive bacteria release hydrogen and carbon dioxide upon the oxidation of organic acids, such as lactic acid, propionic acid, acetic acid, butyric acid, and malic acid. Therefore, photofermentation is performed after the dark fermentation process to increase the hydrogen yield [38]. Adenosine triphosphate (ATP) generation during the photophosphorylation process further contributes to the energy required for the growth of microorganisms [39]. An artificial source of light and solar illuminations can also be employed for smooth operation of the batch- or continuous-type photofermentation process (Figure 3).

$$C_6 H_{12} O_6 + 6 H_2 O = 6 C O_2 + 12 H_2$$
(6)

$$2CH_3COOH + 4H_2O = 8H_2 + 4CO_2$$
(7)

The photofermentation process has the potential to produce high amounts of  $H_2$  from various sources such as wastewaters (e.g., olive mills, dairy, and brewery wastewater) and organic acid-rich wastes (e.g., dark fermentation effluent and hydrolyzed agricultural

waste) [11,20]. Some examples of these highly efficient purple non-sulfur bacteria include Rhodobacter capsulatus, Rhodobacter sphaeroides, Rhodovulum palustris, and Rhodopseudomonas sulfidophilum. These microorganisms have proven to be particularly effective in generating hydrogen as a result of photofermentation, which involves utilizing light energy to drive the production of hydrogen gas [40]. In addition to the previously mentioned purple non-sulfur bacteria, there are other types of bacteria that are utilized for hydrogen  $(H_2)$ production through different mechanisms. These bacteria include Chlorobium vibrioforme, Allochromatium vinosum, Desulfuromonas acetoxidans, Thiocapsa roseopersicina, and Chloroflexus aurantiacus. They employ processes such as nitrogenase activity and ATP production to generate hydrogen. These bacteria have been studied and harnessed for their ability to produce hydrogen gas through these specific biochemical pathways [26]. These bacteria use two different enzymes, hydrogenase and nitrogenase, to produce H<sub>2</sub> from organic acids using solar energy [41]. Nitrogenase is the primary enzyme responsible for  $H_2$  production in low-O<sub>2</sub> conditions. In large-scale production,  $N_2$  is typically converted to  $NH_3$  by nitrogenase [26]. However, in the absence of  $N_2$ , nitrogenase uses ATP and redundancy to generate  $H_2$ , as shown in Equation (8).

$$2H^{+} + 2e^{-} + 4ATP = H_2 + 4ADP + Pi$$
(8)

In recent years, there has been growing interest in using photofermentive processes for the production of hydrogen. Mirza et al. (2016) investigated the use of Rhodobacter capsulatus-PK, a PNSB extracted from paddy fields, for biohydrogen production from sugarcane bagasse. The study reported hydrogen yields ranging from 148 to 513 mL/L, with a maximum yield of 96 mol  $H_2$ /mol sugar achieved under conditions of pH 7.0, a 10% (v/v) inoculum size, a 30 °C temperature, and 120–150 W/m<sup>2</sup> light intensity. The Rhodobacter capsulatus-PK PNSB were also found to be effective in reducing the cost of the photofermentive biohydrogen production process [42]. García-Sánchez et al. (2018) studied the photofermentation of tequila vinasses (VT) using Rhodopseudomonas pseudopalustris and observed double the biohydrogen yield compared to that produced in synthetic medium. The study found that using nitrogen instead of hydrogen in the headspace resulted in three times higher growth of R. pseudopalustris and a higher biohydrogen yield ( $860 \text{ mL H}_2/\text{L}$ ) [43]. Laurinavichene et al. (2016) performed sequential dark photofermentation using PNS bacteria and an anaerobic saccharolytic consortium and obtained a maximum biohydrogen yield of 17.6 L/L of distillery waste [44]. Machado et al. (2017) utilized the PNS bacteria Rhodobacter capsulatus and Rhodopseudomonas palustris in a co-culture and studied the effect of glucose and milk whey permeates on hydrogen yield. They reported a maximum hydrogen yield of  $287.39 \pm 5.75$  mmol of H<sub>2</sub>/L day [45]. Keskin and Hallenbeck (2012) investigated the photofermentation process of beet, black strap, and beet molasses and obtained hydrogen yields of 14 mol  $H_2$ /mol sucrose, 8 mol  $H_2$ /mol sucrose, and 10.5 mol  $H_2$ /mol sucrose, respectively [46]. Table 2 provides a comparative analysis of different factors involved in biohydrogen production from photofermentive processes. It indicates that a temperature range between 28 and 32 °C provides the optimum operating conditions for photofermentation, and a neutral pH of approximately 7.0 results in the maximum biohydrogen yield. The photofermentation process is observed to have a longer hydraulic retention time (HRT) due to the slow metabolic activity of PNSB compared to the dark fermentation process. Light intensity also significantly affects the growth of microorganisms and biohydrogen yield.

Feedstock	Microorganisms	Enzyme	H <sub>2</sub> Yield	Refs.
Potato residue	Rhodospirillum rubrum, Rhodobacter capsulatus and Rhodopseudomonas palustris	Alpha-amylase	642 mL /(L h)	[47]
Bread waste	R. palustris	-	3.1 mol H <sub>2</sub> /mol	[48]
Corn stalk	Rhodospirillum rubrum, R. capsulata, R. pulastris, Rhodobacter sphaeroides, Rhodobacter capsulatus	Cellulose	23.96 mL/h H <sub>2</sub>	[49]
Fermented Waste food	Rhodobacter sphaeoides KD131	-	24% Substrate conversion efficiency (%)	[50]
Corncob	Rhodospirillum rubrum, Rhodobacter capsulatus, Rhodopseudomonas palustri	Cellulase	84.7 mL H <sub>2</sub> /g TS	[51]
Corn stover	HAU-M1	Cellulase	57.63 mL/g VS	[52]
Corn straw	Rhodospirillum rubrum, Rhodopseudomonas capsulate, Rhodopseudomonas palustris, Rhodobacter sphaeroides and Rhodobacter capsulatus	Cellulase	137.76 mL H <sub>2</sub> /g TS	[53]
Energy grass	Rhodospirillum rubrum, R. capsulata, R. pulastris, Rhodobacter sphaeroides, Rhodoba	Cellulase	$5.53 \text{ mL H}_2/(\text{h g TS})$	[54]

Table 2. Hydrogen production from various types of biomass via photofermentation process.

TS = Total Solids, VS = Volatile Solids.

#### 2.2. Biophotolysis

This route is identical to the photosynthesis process in plants and algae in which sunlight is directly converted into hydrogen. Biophotolysis, also known as water-splitting photosynthesis, is the process through which H<sub>2</sub> may be created, using just sunlight and water, by oxygenic photosynthetic microorganisms such as cyanobacteria and green microalgae. In this method, for the green microalgae application, FeFe-hydrogenase is required, and heterocystous cyanobacteria nitrogenase is employed [26]. The biophotolysis process can be classified into two categories, i.e., direct biophotolysis and indirect biophotolysis.

## 2.2.1. Direct Biophotolysis

In this process, green algae and cyanobacteria utilize solar energy within the 400–700 nm range for their growth. After absorbing sunlight, these microorganisms can produce hydrogen by employing nitrogenase or hydrogenase enzymes [55]. During this method, water is split using light energy at a wavelength of 680 nm, resulting in the creation of protons, electrons, and oxygen, as shown in Equation (9). The electrons generated in Equation (9) are then transferred through PS II and PS I until enough electrons are available for the reduction of ferredoxin (Fd). Equation (10) demonstrates that the hydrogenase enzyme reduces NADP+ (nicotinamide adenine dinucleotide phosphate) to NADPH (nicotinamide adenine dinucleotide phosphate) by utilizing the reduced Fd. This reduction process is crucial for the production of  $H_2$  [26].

$$2H_2O + light(h\nu) = O_2 + 4H^+ + 4e$$
(9)

$$2H^+ + 2Fd \text{ (reduction)} \leftrightarrow 2Fd \text{ (oxidation)} + H_2$$
 (10)

## 2.2.2. Indirect Biophotolysis

Indirect biophotolysis is a two-step photosynthetic process that converts light energy into chemical energy in the form of carbohydrate. In the first step, oxygen and carbohydrate are produced using light energy. In the case of green algae, starch and glycogen are produced [56]. Limiting N<sub>2</sub> during Equation (11) leads to a rise in carbohydrate production and a decline in O<sub>2</sub> quantity, which is beneficial for high hydrogen production. The next phase entails converting carbohydrate to  $CO_2$  and  $H_2$  using light energy in an anaerobic environment with less O<sub>2</sub>, as presented in Equations (12) and (13) [41]

$$6CO_2 + 12H_2O + light(h\nu) = C_6H_{12}O_6 + 6CO_2$$
(11)

$$C_6H_{12}O_6 + 2H_2O = 4H_2 + 2CH_3COOH + 2CO_2$$
(12)

$$CH_3COOH + H_2O light(hv) = 8H_2 + 4CO_2$$
(13)

Table 3 summarizes various studies that have been conducted to produce biohydrogen from green algae and cyanobacteria. Kossalbayev et al. conducted a study on four strains of cyanobacteria for biohydrogen production: (a) Desertifilum sp. IPPAS B-1220, (b) Synechocystis sp. PCC 6803, (c) Phormidium corium B-26, and (d) Synechococcus sp. The study measured the hydrogen production in moles of hydrogen per gram of chlorophyl (Chl) per hour. The highest H<sub>2</sub> accumulation of 0.037 mol H<sub>2</sub>/mg Chl/h after 120 dark hours was observed in Synechocystis sp. PCC 6803, while Desertifilum sp. IPPAS B-1220 produced 0.229 mol H<sub>2</sub>/mg Chl/h after 166 h of light incubation [57]. Hoshino et al. investigated the production of H<sub>2</sub> and O<sub>2</sub> in Chlamydomonas reinhardtii mutant strains utilizing PS I light. They observed the yield of hydrogen for 18 h of uninterrupted PS I light to be 220 dm<sup>3</sup>/kg for cbn 1–48 (a mutant with a deficiency of chlorophyll-b) and 176 dm<sup>3</sup>/kg for VHLR -S4 (a mutant with high light tolerance). The highest H<sub>2</sub> yield of 366 dm<sup>3</sup>/kg was found in cbn 1–48 when exposed to PS I-light for 1.5 h of light and dark cycle [58].

 Table 3. Hydrogen production from different microalgae via biophotolysis.

Microalgae/Cyanobacteria	Process Condition	Light Intensity (W/m <sup>2</sup> )	H <sub>2</sub> Production	Refs.
Nostoc PCC 7120	BG110 medium, supplied with a mixture of red and white light, altering 100% Ar and Ar/N2 (20/80)	18.8	6.2 mL/L/h	[59]
C. reinhardtii cbn 1–48	Tris-acetate-phosphate medium, 5% CO <sub>2</sub> , dark anaerobic adaptation	426.6	40.2 mL/kg	[58]
C. reinhardtii Dang 137+	TAP (Tris-acetate-phosphate) medium	34.1	6.0 mmol/L	[60]
Chlorella sp. IOAC707S	TAP-seawater medium	10.7	38.0 mL/L	[61]
<i>yngby</i> asp. (benzoate as a carbon source)	Basal medium, 600 mg/L benzoate at late exponential phase	31.6	17.1 µmol H2/g Chl a/h	[62]
C. reinhardtii (CC124)	sulfur-free TAP medium	64.0	$1.3\pm0.1~\mathrm{mL/L/h}$	[63]
C. reinhardtii CC-425 strain	TAP medium, TAP-sulfur	121.6	0.8 µmol/mg Chl /h	[64]

Chl = Chlorophyl, TAP = (Tris-acetate-phosphate).

#### 2.3. Biohydrogen Production using Microbial Electrolysis Cells (MECs)

Microbial electrolysis cells (MECs) are a new technology that has gained popularity for producing hydrogen from various substrates. MECs are composed of two electrodes, the cathode and anode, which can be placed in a single chamber or two separate chambers [65]. Two-chamber MECs are typically separated by a proton exchange membrane, while the anode chamber is filled with organic wastewater and the cathode chamber can be filled with different solutions [66,67]. Both types of MECs produce electrons through the oxidation of organic matter in the anode, which are then transported to the cathode to generate hydrogen when they combine with protons. However, MECs are sensitive to oxygen as they operate as an anaerobic system. Early MECs with two separate chambers produce high-purity hydrogen, but MECs require a small external potential of more than 0.110 V, in addition to the potential generated by microorganisms (-0.300 V), for hydrogen production [68]. While battery-powered external power sources are commonly used, renewable power from solar, wind, MEC, and waste heat can also be utilized. The chemical reactions involved in hydrogen production through MECs are depicted in Equations (14)–(16) [66,69].

Reactions at anode:  $CH_3COOH + H_2O = 2CO_2 + 8e^- + 8H^+$  (14)

Reactions at cathode: 
$$8e^- + 8H^+ = 4H_2$$
 (15)

Overall reactions:  $CH_3COOH + H_2O = 2CO_2 + 4H_2$  (16)

The technology of microbial electrolysis cells (MECs) has gained popularity for producing H<sub>2</sub> from various organic wastes, including butyrate, glucose, acetate, and glycol, as well as from different waste streams such as domestic wastewater, industrial wastewater, and waste-activated sludge [70–73]. Studies have shown that the H<sub>2</sub> yield can be improved by coupling MECs with anaerobic digestion and/or dark fermentation [74–77]. The performance of MECs is influenced by factors such as raw materials, temperature, pH, and operating voltage. MECs have been successfully used with wastewater within a temperature range of 0 to 45 °C, with better performance observed at temperatures between 10 °C and 20 °C. Increasing the external applied voltage has been found to increase the H<sub>2</sub> yield in MECs [70,78]. Electrogenic microorganisms such as *Shewanella* spp. and *Geobacter* spp. are used in MECs. Among these, *Shewanella oneidensis* and *Geobacter sulfurreducens* are the most commonly studied species [79,80]. Table 4 summaries the various studies conducted to generate biohydrogen using bio-electrochemical methods. Figure 3 represents the schematics of single- and double-chamber electrolysis cells [66,69].



**Figure 3.** Microbial electrolysis cells for conversion of biomass into Hydrogen. (**a**) Single-chamber microbial electrolysis cell. (**b**) Double-chamber microbial electrolysis cell [62,63].

**Table 4.** Biohydrogen production from different types of agricultural biomass using bioelectrochemical method.

Type of Waste	Type of MEC Reactor	Temperature (°C)	pН	External Voltage (V)	H <sub>2</sub> Yield (L/L/d)	Refs.
Swine manure + waste water	Two-chamber	$25.0\pm2$	7.0	1.2	5.1	[70]
Waste-activated sludge	Single-chamber	20.0	$7.0\pm0.2$	0.6	90.6	[78]
Waste of sugar beet juice	Two-chamber	25.0	7.2	0.4	306.0	[75]
Cornstalk wastewater	Two-chamber	$25.0\pm2$	7.0	1.0	3.9	[7]

## 2.4. Thermochemical Conversion of Biomass

# 2.4.1. Gasification

Biomass gasification is a viable method for converting carbon-based materials into useful gaseous products because it can accept a wide range of feedstocks. This endothermic process requires high temperatures (between 700 and 1200 °C) and a controlled oxidizing agent [81]. In the gasification process, biomass is initially dried to decrease its moisture

content before undergoing pyrolysis for thermal degradation. This leads to the formation of volatile products and char. Subsequently, these components undergo partial oxidation and reforming with the aid of a gasifying agent to produce syngas. Air, steam, oxygen, and carbon dioxide are commonly used as oxidizing agents in this process. The resulting syngas from biomass gasification consists of carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), hydrogen (H<sub>2</sub>), nitrogen (N<sub>2</sub>), methane (CH<sub>4</sub>), higher hydrocarbons, and minor contaminants [82]. To enhance the hydrogen (H<sub>2</sub>) content in syngas, it can undergo additional purification via steam reforming and water gas shift (WGS) reactions. Catalytic steam reforming is a two-stage process that not only improves the H<sub>2</sub>/CO ratio but also eliminates tar from the produced syngas. The chemical reactions involved in the gasification process are represented by Equations (17)–(21).

$$C + CO_2 = 2CO (-164.9 \text{ MJ kg-mole}^{-1})$$
 (17)

$$C + H_2O = CO + H_2 (-122.6 \text{ MJkg-mole}^{-1})$$
(18)

$$CO + H_2O = CO + H_2 (+42 \text{ MJkg-mole}^{-1})$$
 (19)

$$C + 2H_2 = CH_4 (+75 \text{ MJkg-mole}^{-1})$$
 (20)

$$CO_2 + H_2 = CO + H_2O (-42.3 \text{ MJ kg-mole}^{-1})$$
 (21)

## Air Gasification

Air is frequently employed as a gasifying agent for a diverse array of biomass sources due to its simplicity. However, its utilization can lead to reduced hydrogen  $(H_2)$  yields and varied gas compositions. This is primarily due to the heterogeneous nature of biomass compositions. Furthermore, the elevated nitrogen content in the medium can contribute to the production of syngas with a decreased heating value [83-86]. Pio et al. conducted research to investigate how the operating conditions influenced the producer gas generated from the direct gasification of residual forest biomass in a pilot-scale bubbling fluidized-bed (BFB) gasifier. The research revealed that reducing the equivalence ratio (ER) promoted the production of carbon monoxide (CO) and hydrogen ( $H_2$ ) as a result of a higher oxygen-tocarbon (O/C) ratio. However, it also led to a decrease in  $H_2$  yield due to lower reaction temperatures. Additionally, the study reported that higher temperatures were conducive to the generation of hydrogen (H<sub>2</sub>) [87]. In a study conducted by Inayat et al., the issue of tar formation during gasification was addressed by employing coal bottom ash as a catalyst in the direct gasification of palm kernel shell in a fixed-bed gasifier. The research revealed that temperature had the most significant impact on hydrogen  $(H_2)$  production, followed by catalyst loading and air flow rate. Under the conditions of an 850 °C temperature and a catalytic loading of 14.5 wt%, the study achieved a peak hydrogen ( $H_2$ ) content of 31.38 vol%. Additionally, lower yields of carbon dioxide (CO<sub>2</sub>) were observed [88].

#### **Oxy-Blown** Gasification

The elevated nitrogen content in producer gas resulting from air gasification can be enhanced through the implementation of an oxy-gasification process. In this alternative approach, pure oxygen is utilized instead of air to gasify biomass. This leads to higher temperatures and an increased production of hydrogen and carbon monoxide, while decreasing the yields of carbon dioxide and methane [89]. The utilization of pure oxygen in the gasification process eliminates the necessity for a nitrogen separator; however, it necessitates energy for the separation of oxygen from air. Oxy-gasification involves multiple reactions, including devolatilization, tar cracking, Boudouard, water–gas, water– gas shift, and methanation reactions. Elevated temperatures promote devolatilization and tar cracking reactions, resulting in increased hydrogen and carbon monoxide production and reduced carbon dioxide generation. Boudouard reactions enhance the efficiency of carbon conversion, and the utilization of a shift reactor with a catalyst enables the production of hydrogen-rich gas through the reaction of syngas with steam. Simulation studies have demonstrated that gasification with oxygen, followed by the CO shift reaction, can generate a gas stream containing up to 54.4% hydrogen content, with a hydrogen yield of 102 g/kg of biomass [90]. Bhattacharya et al. conducted experiments to investigate the use of oxy-blown gasification with rice straw as the biomass for hydrogen (H<sub>2</sub>) production. The study revealed that higher equivalence ratios (ERs) resulted in an improvement in H<sub>2</sub> yield and a reduction in CO<sub>2</sub> content. When utilizing 95% pure oxygen with an ER of 2.5, the producer gas contained approximately 102 g of H<sub>2</sub> per kg of wood [90]. Weiland et al. generated syngas by utilizing oxygen (O<sub>2</sub>) as the gasifying agent and pulp mill bark sourced from the pulp and paper industry. They achieved a maximum hydrogen (H<sub>2</sub>) yield of 15 mol/kg and carbon monoxide (CO) yield of 29 mol/kg from softwood. However, it is important to note that employing pure oxygen from air is energy-intensive due to the high energy consumption of the air separation unit (ASU). Moreover, the process requires elevated temperatures to produce substantial quantities of H<sub>2</sub> and CO [91].

## Steam-Blown Gasification

Using steam as a gasifying agent is more effective than air gasification for producing a medium-calorific-value gas without nitrogen, and it significantly enhances hydrogen yield. The products of biomass steam gasification include a gaseous fraction, which typically contains 30–50% hydrogen, 25–40% carbon monoxide, 8–20% carbon dioxide, and 6-15% methane [92]. There is also a heavier fraction known as tar, which is a complex mixture of aromatic hydrocarbons. The yields and properties of these products depend on various factors, including the configuration of the reactor, which affects the contact, mass, and heat transfer rates. Other factors include the initial characteristics of the biomass, operating conditions such as temperature and steam-to-biomass ratio, and the use of catalysts. Siedlecki and De Jong conducted research on the steam–oxygen gasification of biomass in a circulating fluidized-bed (CFB) gasifier. They discovered that using magnesite as a bed material led to an increase in hydrogen concentration in the product gas. Additionally, the use of magnesite resulted in a decrease in tar content in the syn gas, reducing it to approximately 2 gm<sup>-3</sup> [93]. Furthermore, adjusting the steam-to-biomass ratio within the range of 0.7 to 1.3 has been found to be effective in reducing tar and increasing hydrogen yield in the gasification process. As a result, numerous studies have been conducted with the goal of minimizing tar formation during gasification [94–96].

#### Supercritical Water Gasification

Supercritical water gasification is a hydrothermal process that involves using liquid water as a medium to gasify biomass. This process occurs at high temperatures and pressures, above the critical point of water, resulting in a supercritical state. The biomass is decomposed through various reactions, including pyrolysis, hydrolysis, condensation, and dehydrogenation, which produce gases such as hydrogen, carbon monoxide, carbon dioxide, and methane [97]. The process involves steam reforming, water–gas conversion, and methanation reactions. Unlike other gasification methods, supercritical water gasification does not require the biomass to be dried before processing, as water acts as both a reaction medium and a reactant [98]. This reduces energy consumption during the process. However, there are significant obstacles to implementing the supercritical water gasification process on a large scale. The pumping of feedstock is a technological challenge, as biomass must be converted into a pumpable slurry or solution. This limits the dry biomass content in the slurry to 20% by weight, depending on the type of biomass [98]. Additionally, long-term runs may result in plugging by char, tar, or alkaline catalysts, and these severe operating conditions can cause material corrosion problems. This process also requires a high amount of energy due to the need to maintain water at supercritical conditions. The limitations mentioned have impeded the ability to expand this process, and as a result, experiments on the supercritical gasification of biomass have been conducted mainly using batch reactors and, in some cases, using continuous-screw or fluidized-bed

**Type of Biomass Type of Gasification** H<sub>2</sub> Yield Refs. **Operating Conditions** S/B = 1.05 - 3.47Pine sawdust Steam-blown 55.87% volume [100]Temperature: 800–950 °C S/B = 0.18 - 1.32Wood chips Steam-blown 50.3% volume [101]Temperature: 800-950 °C S/B = 1.1 - 4.7Sawdust Steam- and oxy-blown ER = 0 - 0.3757.4% volume [102]Temperature: 750–950 °C ER = 0.20 - 0.34Lignocellulosic biomass Air 29.54% volume [3] Temperature: 600–1000 °C Temperature: 550 °C Sawdust [103] Supercritical water 10.40 mol/kg Pressure: 36–40 MPa Temperature: 745 °C Corn starch 55% volume Supercritical water [104]Pressure: 280 bar

 Table 5. Production of hydrogen from various types of biomass via gasification route.

reactors [99]. Table 5 provides the details of hydrogen yield with the gasification of various

## 3. Cleaning and Processing the Gas

types of biomass.

The need for the separation and purification of hydrogen depends on its intended use. In the case of using hydrogen as a fuel in fuel cells for automobiles, the International Organization for Standardization (ISO) issued the ISO 14687-2019 standard in 2012, which defines the requirements for hydrogen purity [105]. In 2015, the Society of Automotive Engineers (SAE) issued the SAE J2719-202003 standard, which defines the same requirements as the ISO standard [106]. The purity requirements for hydrogen specified by these standards are listed in Table 6.

Table 6. Requirements for the purity of hydrogen for transport [105].

Standard	ISO 14687-2019 SAE J2719-202003 [105]
Purity of hydrogen	99.97%
Total non-hydrogen gases	300 ppm
H <sub>2</sub> O	5 ppm
hydrocarbons without CH <sub>4</sub>	2 ppm
CH <sub>4</sub>	100 ppm
O <sub>2</sub>	5 ppm
He	300 ppm
N <sub>2</sub>	300 ppm
Ar	300 ppm
CO <sub>2</sub>	2 ppm
СО	0.2 ppm

As shown in Table 6, hydrogen that can be used as a fuel for automotive propulsion must meet strict purity requirements. The hydrogen produced from various sources is found in a mixture with other gases and impurities. Therefore, the separation of hydrogen from other gases and its subsequent purification constitute a significant part of hydrogen production technology. Various technologies have been developed for the separation and purification of hydrogen.

## 3.1. Producer Gas Reforming

The gas produced from the gasification of organic feedstocks is called producer gas or syn gas and it comprises various gases like CO,  $CH_4$ ,  $H_2$ ,  $CO_2$ ,  $NH_3$ ,  $H_2S$ , and  $N_2$  [107]. In addition to producer gas, the gasification byproduct includes a minor quantity of unreacted char and ash, along with a portion of long-chain condensable organic compounds referred to as tar [108]. This tar portion has a sticky and recalcitrant nature and it can choke the

supply line of the gas [109]. Gases like CO and  $H_2S$  are toxic in nature and can harm the environment. Consequently, it becomes crucial to conduct further purification of the gas in order to remove the tar compounds and other impurities like  $NH_3$ ,  $H_2S$ , and HCl. Moreover, additional processing of the producer gas is necessary to convert the remaining gases into hydrogen and  $CO_2$ , and to enhance the yield of hydrogen through purification methods. This process also generates a pure stream of  $CO_2$  that can be reused. Figure 4 illustrates the process flow of syn gas production from biomass and reforming of producer gas for better applicability [102,110].



Figure 4. Schematic of gasification process with integrated syn gas reforming process [102,110].

## 3.1.1. Steam Methane Reforming

The process known as Steam Methane Reforming (SMR) is used to produce hydrogen from methane. The equation representing the reaction involved in this process is shown in Equation (22). This reaction involves one mole of H<sub>2</sub>O and one mole of CH<sub>4</sub>, resulting in the production of three moles of hydrogen and one mole of CO. In practical applications, an excess of steam is employed during the reforming reaction, typically with a steam-to-carbon-molar ratio ranging from 2.5 to 3. This excess steam promotes a complete reaction and helps minimize catalyst deactivation caused by the formation of coke. A thermodynamic analysis of the reforming reaction indicates that high temperatures in the range of 700–900 °C are favorable for converting CH<sub>4</sub> and ensuring efficient chemical kinetics [111]. The catalysts commonly used in steam reforming include non-precious metals, particularly Ni-based catalysts, as well as noble metal-based catalysts like ruthenium, rhodium, palladium, and platinum.

$$CH_4 + H_2O + heat (206 \text{ kJ/mol}) \Leftrightarrow CO + 3H_2$$
 (22)

Ngo et al. conducted a separate investigation where they utilized a zeolite catalyst to boost the production of hydrogen and decrease the amount of tar produced during the steam reforming of producer gas derived from rice straw gasification. The reforming process was carried out at 400 °C. Following the process of steam reforming, the concentration of hydrogen in the resulting syngas rose from 7.31% by volume to 14.57% by volume, while the carbon monoxide content increased from 8.03% by volume to 17.34% by volume [110]. Furthermore, the researchers found that the process had 70–90% efficiency in removing tar. These studies have shown that by combining biomass gasification with downstream steam reforming, it is possible to greatly enhance the hydrogen content in the producer gas by transforming methane and other hydrocarbon compounds. This approach is particularly successful in producing a more favorable hydrogen-to-carbon monoxide ratio, which is beneficial for the subsequent water–gas shift reaction. As a result, both the cold gas efficiency and calorific value of the resulting syngas are enhanced [112,113].

#### 14 of 27

## 3.1.2. Dry Methane Reforming

Dry reforming (DR) is an endothermic reaction between methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) that produces a mixture of carbon monoxide (CO) and hydrogen (H<sub>2</sub>), also known as syngas [114]. The equilibrium of this reaction is governed by Equation (23).

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$$
 (23)

The dry reforming process is commonly executed at elevated temperatures (ranging from 800 to 1000 °C) and pressures (between 1 and 10 bar). These specific conditions are essential to counteracting the heat-absorbing nature of the reaction. Additionally, a catalyst like nickel or cobalt is typically introduced to enhance the reaction rate. A dynamic two-dimensional heterogeneous model was created to depict the biogas steam reforming process for producing hydrogen via catalysis. This model encompasses both the larger-scale and smaller-scale aspects of the system. To validate its accuracy, the model's predictions were compared with existing literature data. In terms of methane conversion, the model forecasted a hydrogen yield of 72.43% on a dry basis.

#### 3.1.3. Tri-Methane Reforming

The tri-reforming of methane is a process that combines three different methane reforming reactions into a single process. These process are depicted in Equations (24)–(26).

Steam reforming (SMR): 
$$CH_4 + H_2O \rightarrow CO + 3H_2$$
 (24)

Partial oxidation (POX): 
$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$$
 (25)

Dry reforming (DRM): 
$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$
 (26)

The tri-reforming procedure offers several benefits compared to alternative methods of hydrogen generation. Initially, it boasts notable efficiency, potentially yielding as much as 90% hydrogen from methane. Secondly, the process presents the capacity to seize and utilize carbon dioxide, a significant greenhouse gas. Lastly, the tri-reforming process can generate syngas, a versatile resource that is applicable in the production of diverse fuels and chemicals. Mesoporous Ni-Al<sub>2</sub>O<sub>3</sub> catalysts, varying in Ni weight percentages of 5 to 15, were synthesized, analyzed, and evaluated for their potential in methane tri-reforming (TRM). The analysis outcomes demonstrate that the metal loading influences the interaction between the metal and support within the catalysts. Under TRM conditions at 600 °C, the conversions and yields experienced enhancement as Ni loading increased, with no detection of carbon byproducts. Elevating the metal loading from 5 wt% to 15 wt% led to an escalation in CH<sub>4</sub> conversion from 70.5% to 82.4%, and in CO<sub>2</sub> conversion from 10.2% to 19.7% [115].

#### 3.1.4. Water–Gas Shift Reaction

Although the hydrogen content in the producer gas is increased by the steam reforming reaction, carbon monoxide still remains in the gas. The water–gas shift (WGS) reaction can be used to further transform CO into H<sub>2</sub> and CO<sub>2</sub>. The water–gas shift (WGS) reaction finds extensive use in hydrogen production from natural gas and in adjusting the ratio of hydrogen to carbon monoxide in syngas conditioning. It is commonly employed in the downstream conditioning of syngas for hydrogen production processes, including the reforming of fossil fuels and biomass gasification [116]. This reaction is characterized as a reversible redox reaction and can be expressed by the following equation.

$$CO + H_2O \Leftrightarrow H_2 + CO_2 + heat (40.9 \text{ kJ/mol})$$
(27)

The water–gas shift (WGS) reaction is commonly conducted using a two-reactor system, with the first reactor operating at high temperatures and the second reactor operating at low temperatures. The purpose of the lower-temperature reactor is to promote the production of hydrogen and carbon dioxide by utilizing the heat released during the reaction. However, the reaction rate tends to be slow at lower temperatures [117]. To address this, the high-temperature water–gas shift reaction (HT-WGS) is employed in the first reactor to facilitate faster reaction rates [118]. Subsequently, the low-temperature water–gas shift reaction (LT-WGS) takes place in the second reactor, promoting the conversion of reactants such as carbon monoxide (CO). HT-WGS is conducted at temperatures ranging from 310 to 450 °C and pressures of 25 to 35 bar. Catalysts employed in this process include Fe and Cu, which are further enhanced by promoters such as Ni, Cr, Zn, Al, Mn, Co, and Ce [119]. On the other hand, the low-temperature water–gas shift reaction (LT-WGS) is carried out at temperatures between 200 and 250 °C. Catalysts commonly used for LT-WGS include Cu-Zn, Cu-Mn, and Cu-Fe, with additional promotion by Pd, Pt, and Al [120]

Numerous studies have explored the water–gas shift (WGS) reaction in producer gas derived from biomass gasification to boost the hydrogen content by converting CO in the gas [119–121]. In a study conducted by Patra et al. [122], the influence of water–gas shift (WGS) reaction temperature on the conversion of carbon monoxide (CO) was experimentally examined. The study utilized a typical producer gas obtained from biomass gasification, with air as the gasification agent. The composition of the producer gas consisted of 15.95% hydrogen (H<sub>2</sub>), 15.74% carbon monoxide (CO), 12.41% carbon dioxide  $(CO_2)$ , 5% methane  $(CH_4)$ , and 50.90% nitrogen  $(N_2)$ . The findings demonstrated that with an increase in water-gas shift (WGS) reaction temperature from 300 to 375 °C, the conversion of carbon monoxide (CO) escalated from 53.88% to a maximum of 78.99% at 375 °C. Furthermore, there was an increase in the levels of hydrogen (H<sub>2</sub>) and carbon dioxide ( $CO_2$ ), with the H<sub>2</sub> content rising from 24.21 vol.% to 27.29 vol.% and the  $CO_2$ content increasing from 21.59 vol.% to 24.65 vol.%. In contrast, the concentration of carbon monoxide (CO) decreased from 7.35 vol.% to 3.35 vol.% as the water-gas shift (WGS) reaction temperatures varied (300 °C, 325 °C, 350 °C, and 375 °C), while maintaining a constant steam-to-CO ratio of 8.

#### 3.2. Separation and Purification of Hydrogen

The different biomass-to-hydrogen conversion processes produce a gas mixture that cannot be directly used as renewable energy due to the presence of CO<sub>2</sub>, and other trace gases, along with hydrogen. Therefore, there is a need to purify the hydrogen to make it compatible for use as renewable energy. The purification process involves purifying, compressing, and storing the impure hydrogen gas at a high density to match the energy values of other gases like gasoline and natural gas. Regarding the purification of producer gas, numerous methods exist for eliminating impurities from syngas at various temperatures, aiming to meet the specifications outlined in Table 5. Figure 5 shows different approaches to purifying syn gas [123].

#### 3.2.1. Removal of Tars

Various technologies are available to successfully eradicate tar. Generally, methods for removing tar can be divided into two categories: physical techniques, including cyclones, scrubbers, fabric filters, or porous sorbet, and thermo-chemical conversion methods. The second process enables the conversion of tar into a usable gas product, thereby enhancing the overall efficiency of the gasification process [124]. Consequently, these techniques have garnered significant interest. Within the thermo-chemical conversion techniques, the process of thermally cracking tar at high temperatures helps break down large-chain hydrocarbon into smaller, non-condensable gases. However, this particular method is not popular due to its reliance on thermal energy and the production of soot [125].



Figure 5. Different approaches to the purification of producer gas [124].

Removal of Tar Using Catalysts

There have been numerous research studies dedicated to investigating catalysts specifically for the purpose of tar removal. These studies have yielded valuable insights that help determine the most suitable catalyst to utilize. When making the selection, it is crucial to consider several key characteristics [126]. Firstly, the porosity of the material must be taken into account. Furthermore, the catalyst must exhibit efficient performance even when exposed to high concentrations of  $H_2$ , CO, CO<sub>2</sub>, and  $H_2$ O, within a temperature range of 650 to 950 °C. Another important characteristic to consider is the catalyst's capability to reform methane. Moreover, it must be capable of delivering the suitable Hydrogen-to-carbon monoxide ratio required for the procedure. The catalyst's ability to withstand deactivation, which can occur due to carbon fouling, sintering, and poisoning, particularly from sulfur, is also an essential aspect to take into account. Lastly, the catalyst's ease of regeneration is an important consideration in the selection process. The most popularly used catalyst for tar elimination is natural or activated dolomite. Natural calcinated dolomite is known for its affordability and its ability to achieve a tar conversion rate of 95% or more [127–129]. In a study conducted by Pinto et al. [130], the effectiveness of various catalysts, such as dolomite, olivine, and lime catalysts, was investigated. Among all of these natural catalysts, dolomite was observed to be the most effective catalyst for tar reduction in syn gas. Additionally, the presence of dolomite resulted in the highest gas yield and a greater heating value (HHV) of the syngas. As a result, it can be concluded that dolomite is a highly promising catalyst. In an experiment conducted by Roche et al. [131], dried sludge was subjected to a BFB gasifier operating at 800 °C and an S/B (Steam/Biomass) ratio of 1. The scientists showed that the catalytic properties of dolomite were enhanced when steam was employed as the oxidizing substance. In particular, by substituting dolomite and pure air with a mixture of dolomite and air-steam, the ratio of H<sub>2</sub> to CO increased by more than double, i.e., from 1.1 to 2.6. Multiple research studies have consistently confirmed that using calcined dolomite (CaO-MgO) is the most efficient method for eliminating tar. These studies highlighted that the improved mass transfer was attributed to both the enhanced pore volume and pore diameter of the calcined dolomite [132–135].

Removal of Tars via Physical Methods

There are two main types of physical cleaning methods: dry cleaning and wet cleaning. Dry cleaning is typically performed at temperatures ranging from 200 to 500 °C and sometimes at even higher temperatures of 600 to 800 °C [136,137]. On the other hand, wet cleaning is carried out after cooling down to approximately 20 to 60 °C [122]. Table 6 displays the main techniques employed for both dry and wet cleaning, along with the temperatures at which they are operated and their effectiveness in removing tar.

The application of ceramic filters placed inside a gasifier, combined with in-bed gas cleaning using a catalyst, demonstrates a highly effective method for tar removal. This approach operates within a temperature range that closely aligns with the gasification process, further enhancing its tar removal efficiency. Rapagna et al. [138] showcased that the inclusion of dolomite as a sorbent in a bubbling fluidized-bed (BFB) reactor, operating at around 800 °C, along with olivine, resulted in a significant reduction in tar in the produced syngas. The reduction in tar levels varied between 50% and 80% when compared to parallel experiments conducted without the presence of dolomite. Additionally, the inclusion of a catalytic filter candle within the gasifier further contributed to this tar reduction; the produced syngas exhibited negligible tar content and was entirely devoid of dust particles.

Savuto et al. [139] conducted a study in which they focused on a catalytic filter that is readily available on the market. The study examined three different test conditions: an unfilled candle, a catalyst-filled candle with a capacity of up to 50%, and a candle entirely filled with catalyst pellets. The test results clarified that the scenario in which the candle was filled to 50% capacity closely aligned with the anticipated thermodynamic values. This finding suggests that the catalyst plays a significant role in facilitating the steam reforming of hydrocarbons, demonstrating its effectiveness. The overall concentration of tar, including benzene, was notably reduced from  $5.8 \text{ g/Nm}^3$  to an average of  $0.4 \text{ g/Nm}^3$ . The purified tar mainly consisted of single-ring compounds, with toluene being the dominant component, along with the two-ring compound naphthalene, averaging  $37 \text{ mg/Nm}^3$  or 7 parts per million (ppm). In addition, there were minimal traces of higher-ring tars detected. It is anticipated that the combination of dolomite and olivine will further decrease tar concentrations. When almond shells were used as the feedstock for gasification, relatively low levels of tar were observed. On the other hand, when municipal solid waste was gasified, the tar concentrations tended to be 1 to 2 times higher compared to using wood as the exclusive feedstock. Table 7 provides the major technologies available for tar removal in dry and wet conditions.

Table 7. Different methods of tar cleaning.

S.No	Technology	Type of Cleaning Method	Tar Removal Efficiency (%)	Operational Temperature (°C)	Rank	[Ref.]
1.	Cyclonic separator	Dry	30-70	100-900	10	[140]
2.	Fabric filter	Dry	0-50	Up to 600	12	[140]
3.	Sand bed filter	Dry	50-90	20	6	[140]
4.	Bio-oil scrubber	Wet	60	50	11	[141]
5.	Quartz filter	Dry	75–95	650-770	5	[142]
6.	Activated carbon as adsorbent	Dry	80	20	4	[141]
7.	Electrostatic precipitator	Wet	40-70	20-30	9	[143]
8.	Permeable catalytic filter disk (aluminum oxide (2.5 wt%); nickel (1.0 wt%); magnesium (0.5 wt%))	Dry	77–99	800 900	3	[144]
9.	Permeable catalytic filter disk (nickel (1 wt%)/calcium oxide (0.5 wt%))	Dry	96–98	900	1	[145]
10.	Impinger	Wet	70	50	8	[146]
11.	Three impingers in series	Wet	>95	50	2	[146]
12.	Washing tower	Wet	10-25	50-60	14	[140]
13.	Venturi scrubber	Wet	50-90	20-100	6	[147]
14.	Packed bed scrubber	Wet	75	300	7	[148]
15.	Water scrubber	Wet	22	20-100	13	[147]

## 3.2.2. Removal of Sulfur

The process of eliminating sulfur at elevated temperatures concentrates on either sulfur dioxide  $(SO_2)$  or hydrogen sulfide  $(H_2S)$ . In the past, the conventional approach to sulfur removal at high temperatures involved "scrubbing" the emitted SO<sub>2</sub> resulting from combustion. But nowadays, more studies are focused on the removal of H<sub>2</sub>S instead of SO<sub>2</sub>. The majority of sulfur removal technologies employ physical or chemical adsorption. The desirable qualities for an optimal desulfurization adsorbent include a significant adsorption capacity, leading to a reduced requirement of adsorbent quantity and smaller process equipment. It should also exhibit rapid adsorption kinetics, where the desulfurization process primarily depends on the first-order reaction rate of  $H_2S$ . Additionally, a high equilibrium constant, affordability, efficient and cost-effective regeneration capability, and ideally, reusability are considered important attributes [149]. Husmann et al. [150] utilized various in-bed sorbents within a BFB steam gasifier and found that dolomite reduced the  $H_2S$  concentration by 60%, limestone by 70%, and lime by 55%. A comparison of the most commonly used metal oxides for desulfurization can be found in Table 6. Currently, zinc-based sorbents are considered the most suitable option for  $H_2S$  removal [151], as they can effectively eliminate nearly all H<sub>2</sub>S at temperatures of 400 °C. Higher temperatures lead to the devolatilization of zinc, resulting in a decrease in adsorption capacity. Apart from zinc-based sorbents, only cerium-based or copper-based sorbents have the ability to reduce  $H_2S$  levels below 1 ppm [151,152]. Generally, the  $H_2S$  removal capability of different oxides can be ranked as follows: Ni < Fe < M < Co < Zn < Cu and Ce [108]. Table 7 outlines the key characteristics of the most commonly used metal oxides for H<sub>2</sub>S removal. Slimane and Abbasian developed CuO sorbents with varying copper and manganese content, achieving remarkable desulfurization efficiency (H<sub>2</sub>S concentration below 1 ppmv.) within temperature ranges of 500 to 600 °C for the sorbent IGTSS-179 and 450 to 600 °C for sorbent the IGTSS-326A [153]. The results of the study conducted by Zheng et al. [154] revealed that CeOn (where n < 2) exhibited superior desulfurization capacity in comparison to CeO<sub>2</sub>. It successfully reduced the concentration of H<sub>2</sub>S to 10 ppmv at 850 °C and 1 ppmv at 700 °C. Moreover, during the regeneration process of the sulfide product, Ce<sub>2</sub>O<sub>2</sub>S, using SO<sub>2</sub>, elemental sulfur was produced directly. This direct production of elemental sulfur eliminates the concern of sulfur control in the diluted SO<sub>2</sub> regeneration product gas, which is associated with zinc-based sorbents. Table 8 provides the different sorbents and their operating conditions for hydrogen sulfide removal from the syn gas.

Table 8. Properties of different sorbents for H<sub>2</sub>S elimination.

Sorbent	Ideal Sorption Capacity (g S/g Sorbent)	<b>Operating Temperature (°C)</b>	Rank	Ref.
Cerium oxide	0.093	500–700	7	[155]
Copper oxide	0.224	540-700	6	[155]
Zinc copper ferrite	0.398	540-680	3	[155]
Zinc oxide	0.395	450-650	4	[156]
Manganese oxide	0.400	400-900	2	[155]
Iron oxide	0.245	450-700	5	[157]
Lime powder	0.571	815–980	1	[158]

#### 3.2.3. Removal of Chlorine

Chlorine is frequently present in biomass, and although chloride salts can be formed in specific circumstances, a significant amount is released as hydrogen chloride (HCl). When it comes to cold gas cleaning, HCl, along with alkali, tars, and particulate matter, is typically eliminated. On the other hand, in hot gas cleaning, a sorbent is commonly used to primarily remove HCl [159]. An effective method for the removal of HCl involves the use of alkalibased sorbents, primarily sodium and potassium compounds. Typically, investigations on CaO or CaCO<sub>3</sub> sorbents are conducted for applications at temperatures above 500 °C. Verdone et al. confirmed that Na<sub>2</sub>CO<sub>3</sub> sorbents exhibited the highest HCl removal efficiency

within the temperature range of 400 to 500 °C [160]. Ohtsuka et al. conducted experiments to assess the effectiveness of NaAlO<sub>2</sub> as an HCl sorbent. Their findings showed that NaAlO<sub>2</sub> successfully reduced the HCl concentration in simulated syngas from 200 ppm to below 1 ppm at 400  $^{\circ}$ C. The researchers emphasized that NaAlO<sub>2</sub> exhibited a higher HCl capture efficiency compared to Na<sub>2</sub>CO<sub>3</sub>. Furthermore, both NaAlO<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> demonstrated the capability to capture HCl in the presence of  $H_2S$  [161]. In a separate study, Krishnan et al. investigated nahcolite (NaHCO<sub>3</sub>), a naturally occurring carbonate mineral that undergoes a transformation into porous Na<sub>2</sub>CO<sub>3</sub> when exposed to temperatures exceeding 150 °C. The sorbent based on nahcolite effectively decreased HCl concentration from 1750 ppm to below 1 ppm within the temperature range of 400 to 600  $^{\circ}$ C [162]. Dou et al. [163] demonstrated that nahcolite (NaHCO<sub>3</sub>) is a highly suitable alkali-based sorbent, effectively reducing the HCl concentration to below 1 ppmv within the temperature range of 526 to 650 °C. Ren et al. conducted experimental investigations to examine the effectiveness of an alkali-based potassium carbonate sorbent for HCl adsorption. They observed reductions of 54%, 51%, and 32% in HCl concentration at temperatures of 500 °C, 300 °C, and 20 °C, respectively. The adsorption of hydrogen chloride by Na<sub>2</sub>CO<sub>3</sub> was found to be thermodynamically favorable at moderate temperatures, while higher temperatures favored kinetics until reaching the decomposition limit of the alkali chloride salt [164]. In a separate study, Baek et al. [165] analyzed the performance of both unprocessed and processed potassium-based CO<sub>2</sub> sorbents for HCl removal. They utilized a micro-fluidizedbed reactor and a bench-scale bubbling fluidized-bed reactor, operating at temperatures of 300 °C and 540 °C, respectively, and at a pressure of 20 bar. Their findings revealed a decrease in HCl concentration from 150 to 900 ppmv to 5 ppmv, and from 130 to 390 ppmv to 1 ppmv.

## 4. Energy Efficiency and Green House Gas Emission Footprints of Different Hydrogen Production Routes

When evaluating the sustainability of various conversion methods, it is crucial to take into account the effectiveness with which each route transforms input energy into valuable output energy, along with its GHG emission potential. In this review, both biological and thermochemical hydrogen routes are compared on the basis of data available in the literature for energy consumption, GHGs emission, and hydrogen yield. Table 9 compares the energy efficiency and GHGs emission potential of each conversion pathway. As depicted, the thermochemical conversion process, while consuming the maximum non-renewable energy, also has the highest energy efficiency. Both photofermentation and the two-stage process exhibit comparable efficiencies, although they are less efficient than the dark fermentation process. In contrast, thermochemical conversion ranks as the least efficient option for biohydrogen production due to its higher demand for electricity or fossil energy during gasification and reforming. However, all the biohydrogen processes analyzed in this study are environmentally friendly, reducing greenhouse gas emissions and saving non-renewable energy. The dark fermentation process shows the highest potential, primarily because it produces a larger quantity of valuable by-products.

**Table 9.** Energy efficiency and greenhouse gas emissions of different hydrogen production routes (per kg of H<sub>2</sub>).

Pathway	Conventional Energy Use (MJ)	Energy Efficiency (%)	GHGs Emission (kg CO <sub>2</sub> eq)	Ref.
Thermochemical Conversion	256.8	43-70	2.14	[166]
Dark Fermentation	61.7	1–10	-87	[12]
Photofermentation	40.1	1–25	-21.9	[12]
Dark + Photofermentation	39.3	27.2	-19.5	[167]
Microbial Electrolysis	64.8	6–26	-17.5	[167]

## 5. Comparison between Different Biohydrogen Production Methods

The potential of utilizing biomass and organic solid waste for hydrogen conversion is highly recognized. However, as the technologies mentioned above are still in their research and development phase, there are several obstacles that must be addressed, including technological and economic challenges [9]. Table 10 provides an overview of the advantages and challenges currently associated with each biohydrogen conversion pathway. Generally, the thermochemical approach exhibits a significantly higher rate of hydrogen production compared to the biological method. Dry thermal gasification, pyrolysis, and steam reforming are the most developed and readily available technologies, capable of generating up to 190 g  $H_2/kg$  feedstock [168]. Although catalysts can enhance the conversion rate, their utilization presents challenges such as regeneration and recovery, particularly when by-products like char and tar are involved [85]. Furthermore, the incorporation of a catalyst can increase production costs, especially if it necessitates the use of expensive materials [84,155]. In contrast, biological conversion approaches offer advantages such as operating at lower temperature and pressure conditions and requiring minimal energy input, especially in the case of dark fermentation and enzyme-free photobiological processes. These biological methods are well-suited for materials abundant in liquid and organic content, like molasses and raw food waste [4]. However, they often necessitate pre-treatment procedures to enhance their conversion efficiency. Considering the energy efficiency and technical feasibility of all the methods, the thermochemical conversion of biomass to biohydrogen shows the merit of the large-scale production of hydrogen [84].

**Table 10.** Comparison of different biohydrogen production process.

H <sub>2</sub> Production Processes	Advantages	Constraints	Refs.
Dark fermentation	<ul> <li>Different wastes can be utilized.</li> <li>High rate of hydrogen production.</li> <li>Simple reactor design.</li> </ul>	<ul> <li>The product contains both H<sub>2</sub> and CO<sub>2</sub>; therefore, separation of gases is required.</li> <li>High BOD level in the effluent.</li> <li>In the case of certain types of biomass, pretreatment of biomass is required.</li> </ul>	[35]
Photofermentation	<ul> <li>The rate of COD (chemical oxygen demand) removal is significant.</li> <li>Higher H<sub>2</sub> yield.</li> </ul>	<ul> <li>Light source is necessary.</li> <li>Slow rate of production.</li> <li>Minimum light conversion efficiency is needed.</li> <li>Only suitable for waste with high concentrations of volatile fatty acids (VFAs).</li> </ul>	[35,169,170]
Biophotolysis	<ul> <li>High light H<sub>2</sub> conversion efficiency (microalgae with FeFe hydrogenase).</li> </ul>	<ul><li>Specialized photobioreactor is necessary.</li><li>Hydrogen production is minimal.</li><li>External light source is needed.</li></ul>	[168,171]
MEC	<ul> <li>More H<sub>2</sub> production.</li> <li>Works efficiently at room temperature.</li> </ul>	<ul><li>Rate of hydrogen production is lower.</li><li>External power source required.</li></ul>	[171]
Gasification	<ul> <li>More H<sub>2</sub> production.</li> <li>Suitable for all lignocellulosic biomass.</li> </ul>	<ul> <li>The product contains H<sub>2</sub>, CO, CH<sub>4</sub>, and CO<sub>2</sub>; therefore, separation of gases is required.</li> <li>High tar content.</li> </ul>	[85,168]

#### 6. Conclusions

Hydrogen is considered a highly promising source of energy for the future, and much research has been conducted over the past few decades to explore various methods for producing it. One potential method is the use of biomass, which is a reliable energy resource that is renewable, abundant, and easy to use. Different kinds of waste materials, including wastewater, residues from agriculture and forestry, sewage sludge, food waste, and solid waste from cities, have been employed as resources for producing hydrogen. Among these waste materials, various types of wastewater have been extensively investigated in fermentation and microbial electrolysis cell methods, while wood waste has predominantly been studied in gasification processes. Moreover, agricultural residual materials rich in lignocellulosic content and municipal solid waste have also been frequently utilized in fermentation and gasification studies, respectively. The effectiveness of hydrogen generation varied considerably depending on the type of waste material used, where the carbohydrate content had a more significant impact on production efficiency compared to the lipid and protein content. Additionally, the operational parameters specific to each technology process had a substantial influence on hydrogen efficiency. By optimizing these operational parameters, it becomes possible to maximize hydrogen production while minimizing waste. The current research indicates that dark fermentation exhibits a high rate of hydrogen production but a low production yield, while photofermentation and microbial electrolysis cell technology have a relatively slower production rate but a higher production yield. Therefore, it is advisable to consider integrating different technologies rather than relying solely on a single approach to achieve efficient hydrogen production.

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