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Review

Thermochemical Production of Hydrogen from Biomass: Pyrolysis and Gasification

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Abstract: Today, hydrogen is one of the best options for generating electrical energy, for both industrial and residential use. The greatest volume of hydrogen produced today derives from processes that utilize petroleum. Although hydrogen has numerous benefits, continuing to produce it by these means is undesirable. This document presents a review of the literature on biohydrogen production based on an analysis of over 15 types of terrestrial and marine biomasses. The fundamental components of different production systems are described, with a focus on the thermochemical processes of pyrolysis and gasification, which have been identified as two of the most effective, practical ways to produce hydrogen from biomass. It also discusses catalysts, solid residues, and residual water that are used in the thermochemical production of biohydrogen. The article ends with an analysis of hydrogen and its benefits as an energy option with great potential in the short term to participate in the transition from fossil fuels.

Keywords: hydrogen; biomass; pyrolysis and gasification; methods of generating H_2

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1. Introduction

Several industries, including the chemical, petrochemical, metallurgical, alimentary, electronic, and energy sectors, employ hydrogen gas (H_2) as a raw material [1]. This gas can be made from various sources, including non-renewable ones like hydrocarbons derived from petroleum (today, 95% is produced by this method). However, the most common technologies employed to produce hydrogen from fossil fuels generate significant carbon dioxide emissions (CO_2) that are incompatible with current concerns for global environmental sustainability. Water can be used as a raw material in processes like electrolysis, thermolysis, and photolysis to produce hydrogen from renewable sources as well. Of these, electrolysis is perhaps the best-developed technique at the commercial level, but another option for capturing H_2 utilizes distinct kinds of waste materials, such as substrates for biophotolysis, dark fermentation, and photofermentation. The reformulation of biomethane is also gaining ground, for it uses the same technology as the natural gas reforming process [2,3]. Finally, but equally as significant, H_2 and synthesis gas can be produced utilizing a variety of biomass through thermochemical processes including pyrolysis (Tables 1 and 2), gasification (Table 3), or combustion [2,3]. Figure 1 illustrates this process.

Table 1. Hydrogen yield of various lignocellulosic biomasses: pyrolysis [4–10].

Biomass	≈Max. Yield H_2 (%)	≈Max. Temperature (°C)
Palm shell	34	900
Olive stalk	16	850
Walnut shell	22	850
Corn cob	16	850
Wheat straw	54	750
Sunflower	17	850
Cellulose	15	700
Bagasse	38	600
Corn stover	17	700
Palm kernel	21	700
Casava pulp	28	800
Coconut shell (CS)	57	800
Rice husk (RH)	10	550
Chestnut (Ch)	18	800
Sugar bagasse	30	700
CS + rhenium carbide	57	800
RH + silver	14	550
Ch + iron	32	800

Table 2. Synthesis gas (syngas) yield of various lignocellulosic biomasses: pyrolysis [11–18].

Biomass	≈Max. Yield Syngas (%)	≈Max. Temperature (°C)
Lignin	45	850
Rice straw	40	800
Sawdust	46	800
Cherry	22	600
Calophyllum inophyllum	40	500
Sugarcane leaves	55	650
Rubber shell seed	25	600
Corn cob	40	700
Corn stalk	30	700
Palm shell	65	900
Cellulose	22	700
Coffee husk	34	450
Salsola collina	45	500
Pine wood	27	700
Palm kernel	25	800
Casava	35	800
Crofton weed	46	800
Jatropha waste meal	22	500

Table 3. Hydrogen yield of various lignocellulosic biomasses: gasification [10,19–30].

Biomass	≈Max. Yield H_2	≈Max. Temperature (°C)
Pine needle + CaO	68%vol	850
Pine wood	6%wt	850
Pine sawdust	38%vol	950
Woodchips	52%vol	900
Pine wood pellets	2%wt	820
Almond shells+Olivine/Al_2O_3/NiO	15%wt	813
Corn straw	58%vol	950
Palm kernel shell	49 mol/kg	750
Sewage sludge	52%vol	450
Beech wood	22 mol/kg	1300
Green macroalgae	11 mol/kg	600
Sugarcane bagasse+Ni-Al_2O_3	39 mol/kg	1050

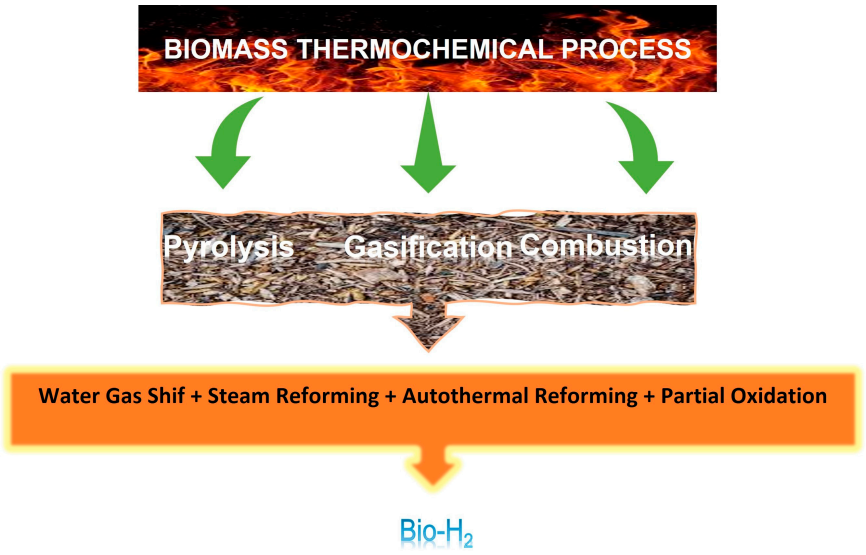


Figure 1. Forms of biohydrogen generation.

In light of the above, we analyze obtaining hydrogen from renewable sources as a short-term option for replacing traditional raw materials, due to the low level of carbon dioxide emitted, the absence of direct emissions of greenhouse gases, and the potential to generate hydrogen with a relatively low dependence on fossil fuels [31]. Since H_2 produced by these means is easily stored and transported, it can contribute greatly to creating safer energy systems.

Harnessing hydrogen energy emerged as a promising direction for future development in international economies in the mid-1970s. Four decades ago or so—after the 1973 oil crisis—it was defined as a "critical, indispensable element of a sustainable. decarbonized energy system" that would provide safe, profitable energy that respects the environment [32,33], suggesting that it was set to become the energy of the future [34]. Development of hydrogen energy has accelerated since the early 21st century. As part of national policies, many nations and regions have been successful in promoting the growth of the hydrogen energy generation sector. The world market for hydrogen has expanded, especially in nations like Japan, the United States, China, and across Europe, where important hydrogen energy projects have received support. In 2020, China's National Development and Reform Commission and Ministry of Justice published the document "Opinions on the acceleration of the establishment of regulations and policies for green production and consumption". That text includes a commitment to "Study and formulate standards, norms, and support policies for developing new energy sources like hydrogen energy", listed among 27 priority goals [35]. Most nations worldwide have a growing interest in developing hydrogen energy, and Russia is no exception [33].

Industrially developed countries visualize achieving the so-called "hydrogen economy", a term coined in 1970 by U.S. scientists John Bockris and Lawrence Walter Jones based on the idea of partially or totally replacing hydrocarbons with hydrogen to significantly reduce greenhouse gases [36]. Technological and economic studies have demonstrated that although hydrogen is a secondary energy vector and is more costly than natural fuels, its use is economically feasible in today's world. Therefore, hydrogen energy is a high-priority area of science and technology that is receiving greater financial support from both the public and private sectors [37]. Natural gas is one of the most important energy sources in the U.S., accounting for almost 100% of hydrogen production. Alternative energy sources are also applied in other countries for hydrogen generation, but they are so few that the amounts generated are considered insignificant. Regarding production via nuclear energy, research is still in the experimental stage. The U.S. and other countries (e.g., Russia), are searching for new technologies that will permit producing hydrogen using all kinds of energy sources, including nuclear, but Japan, Germany, and France have abandoned this

out of safety concerns, especially after the accident at Fukushima. Companies prefer to invest in conventional energy sources because they are more dependable from a business standpoint, which adds another complexity. However, opting for renewable energy sources may give companies access to substantial subsidies and earn them public and political support [38]. The objective of this review article is to show the potential of some terrestrial and marine biomasses for the generation of green hydrogen, including agroforestry and lignocellulosic materials, such as residues, seeds, and nuts, which represents the novelty of this work.

2. Thermochemical Processes: Pyrolysis and Gasification

Today, thermochemical processes are a viable option for converting biomass into high value-added products (Figure 1) [39,40]. Thermochemical conversion of biomass is among the technologies most often utilized today to generate hydrogen and other gases that may contain significant amounts of this gas [41]. The principal processes applied are pyrolysis and gasification. Although liquefaction is another method for generating hydrogen, it is deemed unfavorable due to the operating conditions required and limited productivity [42]. Combustion of biomass produces heat or steam that can drive generators or turbines that generate electrical energy. Gasification processes are utilized to convert biomass into fuel or syngas that is used to drive combined cycle or high-efficiency turbines, or to produce liquid biofuels. Biomass can also be transformed by pyrolysis into an oil that is relatively easy to store and transport for later use in generating electrical energy [43]. Pyrolysis offers the advantage of generating usable products from a broad range of waste materials simply by adjusting process parameters. As a result, it is now sparking greater interest [44].

2.1. Generating Biohydrogen from Pyrolysis of Terrestrial Biomass

This thermal process, also called destructive distillation, is carried out in an inert atmosphere (e.g., nitrogen and argon), unlike the process that uses oxygen (complete combustion). Pyrolysis makes it possible to obtain diverse volatile substances (Figure 2) important for industry, such as oil, carbon, gases, hydrocarbon chains (e.g., methane), aromatic compounds and, of course, hydrogen, which is usually obtained industrially in the form of syngas. It is important to mention that as a result of this process, kinetic studies are currently being carried out with the objective of optimizing the energy yield of the biomass (Figure 2). Pyrolysis generally requires temperatures of 400–600 °C and a pressure of 1–5 Bar [45]. Considering hydrogen's efficiency, and the potential for obtaining it from biomass, various researchers have taken up the challenge of optimizing the acquisition process, given that the amount of H_2 generated depends on four key factors: type of biomass, the mechanism and type of catalysis, temperature range, and the time the biomass is held at a certain temperature [46]. One variant of pyrolysis is called "fast pyrolysis". In this approach, gaseous products are obtained by increasing the process temperature and, simultaneously, the hydrogen yield. Assays conducted in a temperature range of 377–752 °C, for example, have reported average yields of 55, 40, 48, 50, 48, and 50% in biomass derived from walnut, cotton, and residues from tea, olive, and beech and fir wood production, respectively [47]. Sunflower oil and beef fat (triglycerides) have also been used in studies of pyrolysis for hydrogen production, where yields of 8.5–30%, for the former, and 9.4–32%, for the latter, have been reported for a temperature range of 975–1175 K. There are also reports of greater carbon monoxide production of 21–27% at temperatures of 802–902 °C [48]. Fast, high-temperature pyrolysis has also been performed with the ionized gas process to generate H_2 from natural gas or hydrocarbons, with no problems of CO_2 production. In that case, methane derived from natural gas is divided into carbon and hydrogen [49]. Some studies report 100% of hydrogen production with no traces of CO_2 emissions [50]. High-temperature pyrolysis has been reported in assays at 950 °C using steam reforming [51,52].

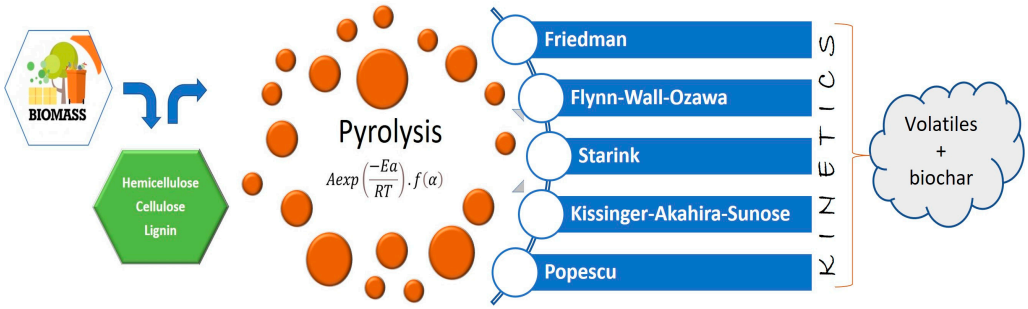


Figure 2. Kinetics of the pyrolysis process. Where Friedman, Flynn–Wall–Ozawa, Starink, Kissinger–Akahira–Sunose, and Popescu represent some of the kinetic models.

A study in Pakistan analyzed 1.4×10^6 tons of rice residue (*Oriza sativa*), 35.8×10^6 tons of wheat waste (*Triticum aestivum*), and 16.3×10^6 tons of sugarcane bagasse per year (*Saccharum officinarum*) as biomass to calculate the amount of hydrogen that could be produced by pyrolysis. The authors performed catalysis with dolomite ($MgCa(CO_3)_2$) and a mixture of 10% by weight of nickel-dolomite. The hydrogen yields reported were only 2.12, 2.07, and 2.22 mmol/g, respectively, for the rice, sugarcane, and wheat biomass, but these levels increased to 23.71, 21.18, and 21.59 mmol/g, respectively, with steam reforming in all three cases. When that experiment was performed with nickel-dolomite (10% by weight of nickel), no important changes in hydrogen yields were detected (25.44, 25.41, and 24.47 mmol/g, respectively) for these biomasses, but production from the rice residue was marginally higher. Significantly, deposits of 1.3–10.13% by weight of graphitic and amorphous carbon were produced [53].

Exploitation of olives has also spurred researchers' interest in hydrogen production. The residues of this biomass—pit, peel, and flesh—have all been analyzed by the steam reforming method with catalysis carried out with carbon obtained from the pyrolytic process of olive residue (OPC) at a temperature of 700 °C. The materials tested were OPC treated with acid (W-OPC), OPC treated with added nickel (Ni/OPC), brown carbon without nickel (CoC), with nickel added (Ni (10% by weight)/CoC), and with a mixture of iron (Fe (10% by weight)/CoC). The total mass used in that experiment was 50 g. The amounts of hydrogen calculated were approximately 250, 120, 320, 100, 250, and 200 mLgas/gbiomass, respectively, for the OPC, W-OPC, Ni/OPC, CoC, Ni/Coc, and Fe/CoC catalysts. Clearly, although nickel acts as an accelerant in the deposition of carbon in the pores of the material, the largest amount of hydrogen obtained was with the Ni/OPC catalyst [54]. Hydrogen production from pyrolysis has also included seeds, for example, it has recently been published that the *Azadirachta indica* species, native to Iran, commonly known as Neem seed, has a H_2/CO ratio of up to 65% [55].

2.1.1. Catalysts for Generating Biohydrogen via Pyrolysis

While the hydrogen yields cited above are relatively good, they fall short of satisfying current commercial and energy needs. For this reason, one option that has been explored is using catalytic pyrolysis with rice residue by means of such metallic oxides as chrome (Cr_2O_3), sodium (Na_2CO_3), or calcium carbonates ($CaCO_3$). Here, Cr_2O_3 has been reported as the best catalyst for optimizing hydrogen production [56]. Nickel (Ni) and aluminum (Al) have also been utilized in catalytic pyrolysis in a ratio of 1:2. That study used pine shavings as the biomass at a particle size of 150–350 µm, with 10% humidity. The elemental analysis revealed H_2 percentages as high as 6.45. The study concluded that the calcination temperature (750–850 °C) and the hydrogen's flow velocity were two variables that determine the final behavior of the gas produced. Yields improved when the catalysts were subjected to reducing phases [57].

Turning to the liquid product called "bio-oil", another variant of fast pyrolysis utilizes steam reforming in a reactor to produce H_2. Adding catalysts allows the reaction to occur at a lower temperature (500–800 °C), considering that ABO_3-type perovskites can optimize

hydrogen generation. Studies in this area are exploring the catalytic capacity of the material $La_{0.8}K_{0.2}MnO_3$ (K = 0.2), which has made it possible to achieve hydrogen yields as high as 72.5%, greater than those attained with commercial catalysts like 14 wt% Ni/ZrO_2. The material used in that work in China was bio-oil from pine shavings. It is important to mention that during their experiments the authors observed a catalytic deactivation they attributed to a concentration of carbon residues during the reaction [58]. It should be noted that perovskite-structured materials are not only used to generate hydrogen, today they are also used for the oxidation and reduction of this gas in anode and cathode electrodes of a solid oxide fuel cell (see Figure 3), which generates electricity using bio-hydrogen as fuel. Hardwoods have also been employed in analyses of steam reforming with catalysts to produce hydrogen from bio-oil, as in the case of the *DynaMotiva* company (Vancouver, Canada). Their results showed a hydrogen yield of 8.4% according to its elemental composition, with a theoretical yield as high as 13.8 g of hydrogen per 100 g of bio-oil. In contrast to the anterior study, the catalysts used were, on the one hand, commercial, the material C11-NK, a nickel-based catalyst known for its ability to reform naphtha, and on the other, four formulations fabricated in a laboratory. Because they have applied for a patent for their research, the authors do not indicate the exact nature of the catalysis they developed, but they obtained good results for stoichiometric yield—up to 80%—and losses due to attrition as high as 0.15%/h [59]. That group has also conducted experiments with pine shaving bio-oil, poplar wood, and, as in the aforementioned study, C11-NK as the catalyst. Compared to theoretical H_2 production, they achieved a yield of 80% via pyrolysis of bio-oil, which represented as much as 6 kg of H_2 per 100 kg of biomass. The researchers mention that this can be increased to 90% by considering the conversion of carbon monoxide through steam stripping [60]. Catalysis reformed with nickel has also been tested with the oxide La_2O_3-αAl_2O_3 to generate hydrogen. This requires two steps: first, bio-oil from pine shavings (from Spain) was used for thermal treatment by pyrolysis (pyrolytic lignin) with steam reforming; second, performing catalytic reforming where, in addition to hydrogen, carbon monoxide, carbon dioxide, methane, and hydrocarbons (C_2-C_4) are obtained. Results indicated that a temperature of 700 °C was needed to obtain complete conversion of the bio-oil and a gas rich in hydrogen, above 66% in volume, but it is important to note that after 7 h of this process, yield decreased due to catalytic deactivation [61]. In other attempts to reduce the phenomenon of catalytic deactivation, researchers have added various compounds to nickel, including zirconium oxide (ZrO_2). The compound Ni (16 wt%)/ZrO_2 permitted a higher hydrogen yield by preventing the reduction of carbon deposits and presenting lower activity toward the formation of secondary phases. However, those deposits tended to increase with greater nickel concentrations up to a maximum of 23% by weight, and with working temperatures around 500 °C. Note that the proportions of methane and carbon monoxide also impacted the reaction [62]. The zirconium oxide used in that study has also been employed with lanthanum trioxide added to form the mesoporous material La_2O_3-ZrO_2 using the sol-gel synthesis method. Given that bio-oil from lignocellulosic biomass has a variation of 17–65% by weight [63,64], and that significant amounts of hydrogen can be derived from it, that experiment was conducted with steam reforming at temperatures of 550–700 °C. Optimal results were found for the composition 15Ni/La_2O_3-ZrO_2, as it produced up to 89.27% of hydrogen and 80.41% of carbon dioxide during a 20/hour test period [65].

Studies have also been carried out to improve hydrogen yields based on the comparative acetic acid (AcAc) bio-oil model. Like the works cited above, this recent work used nickel, but at concentrations of 23, 28, and 33% according to the other materials utilized (Ni/(Ni+Al)). The best hydrogen yield (g/g acetic acid) (0.118) with carbon monoxide (at 0.130) and carbon dioxide (at 1.109) was obtained with 28% of nickel at 650 °C [66]. Other materials that have been employed to enhance catalysis when using steam reforming of CH_3COOH are of the hydrotalcite type ($CH_{24}O_{23}Mg_6Al_2$). For example, using the co-precipitation method and nickel-magnesium-aluminum precursors with diverse molar proportions—03NiMg, 04NiMg, 05NiMg, and 06NiMg—those researchers determined that,

due to the lower velocity of the formation of carbon deposits (3.51 mg C/g cat. h. g_{AcAc}) and greater hydrogen yield (1.89 mol-H_2/mol-acetic acid), the 04NiMg composition was the best option [67].

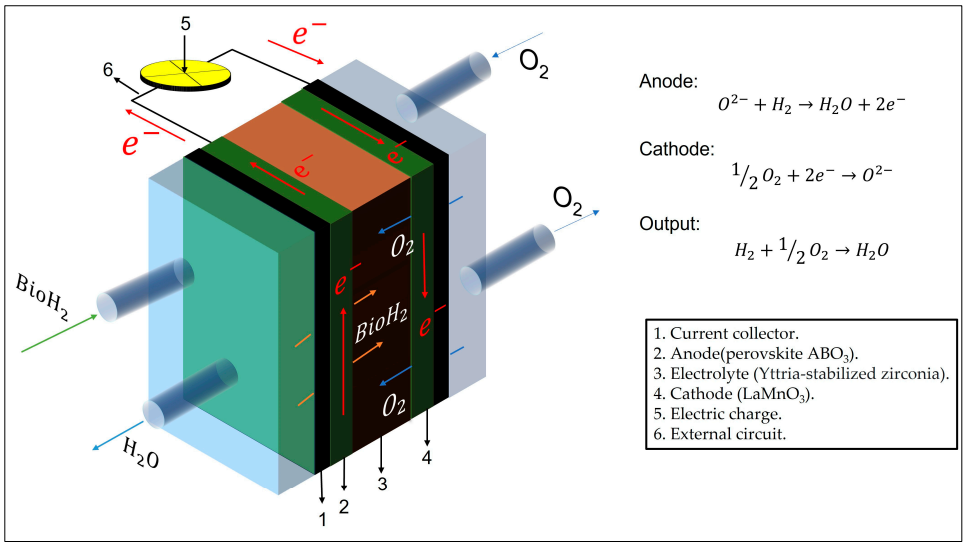


Figure 3. Use of biohydrogen in a solid oxide fuel cell.

With respect to calcium, some researchers have developed a viable catalyst based on this element by adding catalytic material of the Ni-MgAl type to produce hydrogen in a fixed bed reactor. The biomass chosen was wood shavings, but the species was not identified. Results showed that hydrogen content increased significantly, producing yields of 10.4–18.2 mmol of gas/gram of biomass due to the adsorption of carbon dioxide. While this approach improved hydrogen yield during pyrolysis of the biomass, the amount of calcium in the catalyst must be monitored to reduce carbon deposits that can cause deactivation of the catalyst as much as possible [68]. Aluminum and nickel have been implemented as catalysts in the form of porous nanoplates to produce syngas rich in hydrogen. In that case, the biomass was rice husk, while the method for preparing the catalyst was coprecipitation of the hydrolysis of urea. Findings showed a hydrogen yield around 8–17 mmol of gas/g of husk. The H_2/CO relation maintained an approximate ratio of change of 2–3 [69].

Some elements have the capacity to break carbon bonds and improve hydrogen and CO_2 yields, though with low ethylene (C_2H_4) production at relatively low temperatures around 400 °C [70]. In this regard, cobalt has been used to generate H_2 via steam reforming of acetic acid. Studies have tested adding nickel supported in oxide lanthanum (Ni-Co/La_2O_3), compounds obtained by the impregnation method at 500–700 °C, considering an acetic acid flow of 0.36 mL/min. Acetic acid conversion was reported as high as 84.5% using the material Ni-Co/La_2O_3 with reduced carbon deposits and, hence, enhanced hydrogen selectivity [71]. Another case that used cobalt involved the bimetallic union with nickel. The catalytic capacity of that union has been studied at various molar proportions of Ni:Co (1:0.5, 1:1, 0.5:1, 0.25:1, and 0.1:1), with the 0.25:1 ratio producing the best yield. That study reported a complete conversion of the acetic acid and results for hydrogen, CO_2, and methane selectivity as high as 96.3, 98.1, and 0.7%, respectively. Up to 60 ppm of CO was detected as well [72].

In addition to the elements mentioned above, lanthanum (La) and potassium (K), have been examined in studies of the catalysis of the steam reforming of biomass as a function of acetic acid, but focusing on how they affect the character of basicity in the yield. Studies have analyzed the material Ni/γ-Al_2O_3, with results showing that La and K markedly increased the basic character to approximately 31 and 94%, respectively, thus promoting acetone formation. That work included magnesium, which fosters a selectivity of almost

100% of hydrogen at 450 °C [73]. As can be seen, nickel is used in most commercial catalysts to obtain hydrogen from acetic acid. However, its application at the industrial level is limited due to such factors as low stability, resistance to the formation of carbon deposits, and relatively easy deactivation. A biomass formed of ash from corn residue consists of diverse oxides, such as silicon, calcium, potassium, aluminum, magnesium, sodium, and iron, all of which have important catalyzing properties. Recent studies have employed these materials—in addition to nickel—and examined their effects to improve hydrogen yields from the acetic acid in biomass. Yields at temperatures of 600, 700, 800, and 900 °C were approximately 15, 20, 25, and 28%, while the figures for carbon monoxide were 10, 20, 35, and 20%. These yields were calculated as a function of the theoretical quantification of moles of hydrogen and carbon monoxide generated. Note that carbon deposits decreased by approximately 50% between 600 and 900 °C [74]. Regarding hydrogen yields derived from the conversion of acetic acid, it is important to mention that some clays added to the nickel for use as catalysts have produced excellent results. These include attapulgite (palygorskite), a phyllosilicate of aluminum and hydroxylated/hydrated magnesium usually obtained by the precipitation, impregnation, or mechanical alloy methods. It has obtained yields of around 85% at 650 °C [75]. Another clay is olivine, a silicate made up of iron and magnesium that has been analyzed with nickel and cerium oxide (Ni-CeO_2-MgO) to study the catalysis and steam reforming of acid as a support model for bio-oil. In this case, a hydrogen yield as high as 75% was achieved in a period of 70 h with no sign of catalytic deactivation [76]. Ruthenium is another element that has been evaluated as a catalyst to produce hydrogen from biomass. One example is the material Ru/γ-Al_2O_3 with zinc added, prepared by impregnation, and utilized for the catalysis of the thermal process of the biomass of bagasse chips from Iran. The hydrogen and CO yields reported were around 16 and 8 mmol of gas/g of bagasse, respectively [77].

2.1.2. Residual Water and Solid Residues to Generate Biohydrogen through Pyrolysis

Nowadays, residual water from cities is difficult to treat and expensive. Landfilling or combustion is generally an option for handling such waste, although in the long run it can generate more problems for the environment. Researchers have suggested thermal treatment as a solution, not only to solve the problem, but also to obtain energy benefits. However, in the case of combustion, it brings with it some health hazards to society, for example, the impact that toxic volatile compounds can have. Pyrolysis, used at low temperature, is a viable alternative for better treatment of wastewater and its volatile compounds [78]. An example of this is the fast pyrolysis of wastewater residues obtained from containers [79]. In this case, it could be observed that the hydrogen yield depends on the amount of bio-oil, water, and the kind of biomass subjected to study. Residual water (called sludge) has been analyzed for this purpose using pyrolysis. Here, the use of fast pyrolysis has achieved bio-oil yields of 50.9% with dehydrated digested sludge, and as high as 57.5% with activated sludge, which obtained a high calorific value while consuming a very small amount of water of 25 MJ/kg and 10%, respectively. It is important to mention that phenol, derived from the oil of pyrolysis, is one of the compounds that researchers have attempted to obtain from residual water, though due to its diverse corrosive properties for the environment, the aim is to leave it in disuse [80]. It is important to mention that due to the ash content as well as its calorimetric properties, residual water incineration may not be considered feasible. Among the main problems to be solved for its treatment are the formation of coke that promotes the deactivation of the catalyst used, the possibility of poisoning, and of course the hydrogen yield.

2.1.3. Influence of the Reaction System

The configuration of the reactors used in pyrolytic processes to obtain hydrogen influences the kinetics of secondary reactions and hydrogen formation, which depends on the temperature–time profile used [81,82]. Depending on the type of biomass and the heating mode, the pyrolytic reactor can be adapted in such a way that a thermochemical conversion

of biomass into hydrogen and non-condensable gases is generated in a maximum amount. The type of feedstock and the dimensions of the different reactor types, such as fluidized bed, fixed bed, cyclone, rotary, screw conveyor, etc., are determining factors in the main reactor conditions, such as the external heat transfer coefficient. Many of the end products of biomass pyrolysis will depend on the reactor design and the operating conditions of the reactors, so proper reactor selection based on the type of biomass to be used is key to obtaining desirable products. Another key factor in reaction systems is the involvement of a carrier gas, which aims to remove volatile compounds from the pyrolysis environment during the biomass pyrolysis process. Generally N_2, CO_2, steam, and hydrogen are usually used during pyrolysis. The residence time of pyrolysis products have a relationship with the purge rates of carrier gases such as N_2 and feedstock; if the purge rate is high, pyrolysis volatiles escape from the reaction zone, while lower residence time increases the formation of liquid oil, decreasing the gas formation [83].

2.2. Generating Biohydrogen by Gasification

Gasification is another method of important expectations in the thermal transformation of biomass [84]. In this case, solid biomass is converted into a combustible gas through a series of high-temperature chemical reactions (750–900 °C) using air, oxygen, water steam, or a mixture of these materials as oxidizing agents [85]. This explains why this procedure is gaining popularity [40]. This process permits obtaining gases with calorific values of 4–6 MJ/m^3 that can be utilized for direct combustion as fuel in gas motors and turbines, or as a raw material in the production of other chemicals, such as syngas, which allows production of methane, hydrogen, biogasoline, and biodiesel, all of great importance for the future of fuels [86]. Gasification mainly produces gas, so in hydrogen production it can, in some cases, provide more favorable results than pyrolysis. Like pyrolysis, the efficiency of gasification processes is affected by numerous operative parameters [87,88] including raw material composition, operating temperature, particle size, the composition of the entrance gas, and the equivalence and steam/biomass ratios [89,90]. It has been proven that steam reforming maintains a positive effect due to the fact that it promotes the increase in the final amount of hydrogen. The gasification process may also be more effective when the biomass utilized has humidity content values of <35% [91].

2.2.1. Generating Biohydrogen from Gasification of Terrestrial Biomass

Currently, a broad range of biomasses are being used in studies of gasification and analyses to determine hydrogen generation (Table 3). A study of walnut and pistachio shell (particle size = 0.5–2 mm) utilized silica sand as the support material for both kinds of biomass at a gasification temperature of 770 °C, with two gasification agents: air and steam. The H_2 concentration generated by gasification with air reported values of 3.1–5.6% and 3.2–8.4%, respectively, accompanied by high nitrogen content (66.4%–55.5%) for pistachio shell, and 64.6–54.9% for walnut shell. When gasification was performed with steam, the concentration of H_2 increased to 51.6–30.4% for walnut and 54.2–19.4% for pistachio shell. Increased generation of CO and CO_2 was also reported, indicating that better results are obtained using steam as the gasification agent to generate hydrogen [92]. These values are higher than those reported using wood briquettes (44%) or almond husks (39%) [93,94].

Experiments with gasification of biomass from orange peel and pine shavings produced hydrogen yields of 34.35 and 24.31 mol/kg, respectively, values which indicate that the former produces more hydrogen than the latter under such conditions. According to the authors, gasification of orange peel achieved greater stability than pine shavings because it reached a maximum equilibrium when all the carbon content in the biomass was converted into CO_2. It is important to note here that H_2 constituted the largest proportion in the syngas, at 57.70 and 58.53%, respectively, for the pine shavings and citric biomasses. Analyses of the gasification products showed that H_2 yield and the conversion coefficient of carbon in the orange peel were approximated to 35 mol/kg and 67%, respectively, figures higher than those for the pine shavings (24.31 mol/kg, 48.5%). Parallel to this, the way in

which synthesis gas behaves indicated that the reaction velocity in the gasification of orange peel was significantly greater than with pine shavings. Thus, the authors concluded that orange peel is more adequate for gasification than pine shavings under their experimental conditions [95].

Derived from the production of virgin or extra virgin olive oil, and as in the pyrolysis process, gasification studies have included olive pomace and the fats, pits, and skin of this biomass. One type of olive pomace analyzed was from a factory in Izmir, Turkey, an important olive oil-producing country with up to 263×10^3 tons produced (2017–2018) [96]. The gasification agents used were dry air and pure oxygen. The highest hydrogen yield (53%) occurred at 900 °C in pure oxygen (0.01 L/min). The amount of methane generated was low (10%) compared to the value of 20% at 700 °C in a dry air atmosphere (0.1 L/min) [97].

Similar to the case of olives, residue from coffee production has been explored as a potential energy source using gasification with a view to generating hydrogen. For example, coffee from Brazil has been tested by gasification utilizing three types of atmospheres: oxygen, nitrogen, and carbon dioxide with hydrogen. The combination O_2/N_2 proved to be optimal for producing H_2 and CO_2 in steam, generating up to 70 and 18%, respectively [98]. Cotton plant stalks are another kind of biomass that has been assessed for its potential to obtain hydrogen. In one study, a simultaneous conversion process using gasification–pyrolysis produced a hydrogen yield of 65 g/kg with a total gas yield of approximately 1.6 Nm^3/kg from this material [99]. In a 2016 study, researchers used rice husk from Jiangsu as the source of biomass fuel with natural acerin as the oxygen carrier. Results showed that the hematite accelerated gasification of the biomass and improved the carbon conversion rate. Hematite, then, might raise the heat carrying capacity of materials in a continuous reactor. The H_2 yield reported was around 45%. Syngas reached a maximum of 0.64 Nm^3/kg at 850 °C, an ideal temperature for gasification [100].

The yield of hydrogen and other gases (CO, CO_2, CH_4) from the gasification of rice husk provided by the Association of Farmers of the Taichung District, has been studied as a function of such key parameters as temperature, the steam/biomass ratio, and the ideal alimentation point. In contrast to the previous study, a decrease in H_2 was observed by 42%, though CO, CO_2, and CH_4 increased their approximate percentages and calorific power rose 3.0 kJ/g-rice husk [101].

An experiment using wood splinters, wood pellets, and pellets of herbs in a fixed-bed reactor fluidized at 800 °C reported acceptable efficiency values for generating hydrogen as a fuel. For the splinters, H_2 and CO content was approximately 17 and 20%, respectively. Similarly, the values for the wood pellets were around 17 and 19%, respectively. Another important parameter considered in the analyses of gas composition was the equivalence radius. In this case, the best value was obtained for the wood splinters at 0.16 at 800 °C, where conversion reached 75%. However, the same success was not attained for the gasification of the herb pellets due to agglomerations and the low carbon conversion in this biomass. The authors concluded that herb pellets are not a good source of biomass for alimentation in gasification processes designed to produce hydrogen [102].

In an attempt to improve hydrogen production by gasification, some researchers have implemented a double-stage process that requires a premixture of air-gas. One example of this involved biomass from acacia wood, which produced up to 9% greater general energy efficiency compared to the conventional form of a one-stage gasification process. Note that the high calorific power obtained (6.415 MJ/Nm^3) was due to the amount of hydrogen generated [103].

2.2.2. Generating Biohydrogen via Gasification of Marine Biomass

While it is true that terrestrial biomass has significant advantages for hydrogen generation, marine biomass is another promising option (Table 3). This is the case of algae (micro and macro forms), which exist in immense quantities (e.g., sargasso) and can be transformed thermally into usable forms relatively simply. One important difference from

terrestrial biomass is the proportion of lignin and sugars, elements that are easily hydrolyzed and promote rapid decomposition. Another key aspect is the yield from this kind of biomass, which is higher than that achieved with biomass from terrestrial plants [104]. Furthermore, there is no need to grow marine macroalgae on land because they may be grown in seawater without nitrogen-based fertilizers. These plants grow quickly and have a high capacity to fix CO_2 [105]. Algae constitute one kind of lignocellulosic biomass that can be used to produce syngas and, as a subproduct, hydrogen, generated by gasification. Due to high productivity and photosynthetic efficiency, macroalgae generate large amounts of carbohydrates (25–60%), proteins, hemicelluloses, and lipids [106,107], though it is important to emphasize that high humidity (~90%) is problematic for thermal gasification processes. Studies have tried to solve this problem and optimize energy efficiency by up to 40% through various stages of drying, gasification, and combined cycles. One example is the use of the alga *Laminaria digitata*, preferred for its high carbohydrate (64.1%) but low ash content (21.1%) [108].

The two primary economies that gain from increases in the effectiveness of producing biohydrogen from macroalgae that promote macroeconomic growth and hasten the development of the biohydrogen industry are Malaysia and India. One recent study of macroalgae (*S. Japonica*) obtained a production velocity of H_2 of 0.34 L/L/h and 8.16 L/L/d [109]. The gasification of microalgae has also been conducted in conjunction with biomass like rice husk and palm leaves. For example, utilizing CO_2, the gasification of microalgae to generate hydrogen showed a higher H_2/CO ratio (1.35) than with palm leaves (1.23) or rice husk (1.04). Regarding the percentage of hydrogen generated from the biomass in that study, the values obtained were 31.3, 30.4, and 31.7% at temperatures of 800, 1000, and 1200 °C, respectively. These results demonstrate the high potential of microalgae [110].

Like the thermal pyrolysis process, gasification has been studied with oxides that act as catalysts to favor the gasification reaction during hydrogen generation. Another study of microalgae (*Chlorella vulgaris* and *Spirulina*) evaluated the catalytic capacity of calcium oxide (CaO) with nickel and yttrium oxide to produce syngas and, hence, hydrogen. The hybrid material type Ni-CaO-Y_2O_3 has been used in assays of this kind. Temperatures in that study ranged from 350 to 500 °C. After performing the analysis in triplicate, the authors reported an approximate yield of 440 mL/g of hydrogen from the residue of the microalga *Chlorella vulgaris*. That case considered 40% by weight of the catalyst (CaO). For the residue of *Spirulina*, the yield was a little lower, approximately 320 mL/g, with the same percentage of catalyst. It is worth mentioning that the purity of the hydrogen obtained had a variation of around 50 and 40 for the *Chlorella vulgaris* and *Spirulina* biomasses, respectively [111]. Another recent study with that catalyst (CaO) obtained good results by adding nickel by impregnation. In that case, gasification was carried out in a fixed-bed reactor with citric peel biomass and steam as the gasification agent. Findings showed that utilizing 10% of nickel allowed an acceptable catalytic yield and a hydrogen yield of around 37 mmol/g of biomass. That report indicated high carbon conversion efficiency at approximately 85%. The authors stated that the behavior observed was due to the generation of crystalline structures in the Ni material (111), detected by X-ray diffraction [112]. A separate study, this one with *C. vulgaris*, based on GAMS software modeling and considering a constant pressure of 220 bar, contemplated supercritical gasification, that is, the thermal conversion of biomass without previous drying. Those researchers concluded that temperatures of 627–727 °C improved the autothermal conditions for generating hydrogen by approximately 50% [113].

2.2.3. Generating Biohydrogen from Gasification–Torrefaction

Compared to untreated biomass, biomass treated by torrefaction has lower humidity, greater hydrophobicity, and improvements in the amount of energy obtained. Specifically, the grindability of the biomass improves markedly with torrefaction, allowing the treated solids to become more spherical, thus notably enhancing their uniformity and stability during alimentation [114,115]. In recent decades, extensive research has focused on the

viability of drag flow gasification of unprocessed biomass, but few studies have explored the effects of torrefaction pretreatment and the amount of hydrogen produced. For example, rice husk, wood shavings, and camphor wood (usually considered an exotic wood) have been studied. Considering the composition of the gas, reports indicate that the maximum percentage by volume of hydrogen was 50% for rice husk and wood shavings, but the figure for camphor wood was lower, at just 30% [116]. A similar study with pine wood shavings showed that pretreatment by torrefaction greatly reduces the amount of volatile matter and the amount of soot, while improving energy density and the grindability of the biomass. Moreover, with torrefaction the authors obtained larger amounts of H_2 and CO_2, approximately 15 mmol/g at 280 °C [117].

Another important product for industry that has been analyzed for hydrogen generation by torrefaction is the argan nut from the *Argania Soinosa* (L.) *Skeels* tree, native to southwestern Morocco (Essaouira). Some 4000 tons of argan nut oil have been quantified, and this material has been found to have diverse uses in the alimentary and cosmetics industries. Researchers have studied the possibility of utilizing the residue from the fabrication of this product to obtain hydrogen. For example, a process using gasification with added steam obtained a yield of 9.7–11% by volume of hydrogen gas with a steam/carbon ratio of 0.5. The torrefaction (220–250 °C) carried out showed a lower hydrogen yield (6.9% vol) [118].

2.2.4. Generating Biohydrogen from Thermal Plasma Gasification

One variant of the gasification of biomass uses thermal plasma as the heat source required to trigger the, essentially endothermic, reactions of gasification. Advantages of this method include greater process velocity, smaller amounts of reagents, and, especially, improvement of gaseous characteristics (produced gas). While it is true that this process achieves a better quality of gas for use in devices such as a turbine, it has some disadvantages. One important drawback is its high electrical consumption [119]. In 2020, a simulation of the thermal plasma gasification process used three biomasses: sugarcane bagasse from Cuba, rice husk, and wood shavings. Researchers developed a model with a thermochemical equilibrium focus to explore the operating zones using the graphic technique. The bagasse and rice husk were of agro-industrial origin, while the wood shavings came from firewood. The best result of these biomasses was for the wood shavings, as they generated the largest amount of hydrogen, up to 97 gr/kg of biomass. However, it is important to note that producing this amount of H_2 required high electrical consumption (2.23 kWh/kg of biomass) because of the plasma torches used. The values for the sugarcane bagasse and rice husk were lower (m H_2/m biomass) at 83 and 54 g/kg, respectively. Electrical consumption for these materials was 1.95 and 1.48 kWh/kg of biomass, respectively. The authors mentioned obtaining a gas rich in hydrogen with maximum averages of 2.8, 2.37, and 2.81 NM^3/kg (based on a molar ratio of H_2/CO = 2) from the bagasse, rice husk, and wood shavings, respectively. Note that these values represent lower electrical consumption per kilogram of hydrogen compared to the water hydrolysis process, which showed averages as high as 55 kWh/kg of H_2 [120]. Oxygen flow is another important parameter of this process since observations show that hydrogen efficiency decreases as oxygen increases. A study with wood pellets found this behavior at temperatures of 700 and 900 °C, though increasing oxygen can reduce the amount of electrical energy supplied to the system [121]. It is worth mentioning that plasma gasification is not exclusive to terrestrial biomass; studies have also been conducted on marine biomass, for example, Enteromorpha algae, which has shown hydrogen yields of approximately 34%, which is higher compared to that generated by sargassum (24%) [122].

2.2.5. Catalysts for Generating Biohydrogen by Gasification

Some oxides can be used as catalysts in gasification processes. Iron-based catalysts are one option for biomass conversion, for example, the oxide Fe_2O_3. A simulation using the ReaxFF software (reactive force field) analyzed hydrogen yield and the efficiency of the gasification of lignin and soda black liquor, two residues of the process employed to obtain

cellulosic pulp. This catalyst has shown acceptable behavior for generating hydrogen but, depending on the state of oxidation of the iron—low or high—carbon monoxide or dioxide may form [123]. The effect of catalysts on hydrogen generation by gasification has also been analyzed using the residue called soda black liquor derived from paper manufacturing. Studies have examined the catalytic capacity for producing hydrogen from numerous oxides: zinc, titanium, tin, vanadium, tungsten, molybdenum, iron, manganese, chrome, cerium, copper, zirconium, and cobalt. The best hydrogen yields were obtained from those of cobalt (Co_2O_3) and zinc (ZnO) with approximate values of 22 and 21 mol/kg, respectively [124]. Clearly, catalysts can have a significant impact on hydrogen generation. Catalysts of perovskite structure have been proposed for this purpose, combined with marine biomass (microalgae). For example, the material with added calcium ($La_{0.8}C_{0.2}FeO_3$) that has been utilized in the selective fabrication of NH_3 generates hydrogen during the process after partial oxidation of the perovskite. In this case, the yield of syngas was approximately 20 mmol/g-microalga, equivalent to an H_2/CO ratio of 2.5 [125]. Due to their ability to disintegrate the biomass structure, zeolites are another material that has been studied for hydrogen generation (80 mol%) from methane co-gasification (5–10%). Such is the case of the catalytic materials 0.5% Fe 4%Mo-ZSM-5 and 1.5% Fe-4%Mo-ZSM-5 used in biomass pallets (hardwood), although it is not clearly indicated which wood species has been used. Iron and molybdenum act as promoters for the activation of carbon-hydrogen bonds. According to the authors, the high hydrogen yield is mainly due to the oxophilic nature of the elements involved (Fe-Mo) [126]. Biomass sawdust char has also been the subject of study in relation to its conversion by carbon bi-oxide. As in the research mentioned above (zeolites), the wood species used is not indicated. In this case the catalysts synthesized were 5%K-5%Fe, 5%K-5%Ni, 5%K-5%Co, and 5%K-5%Ce, obtaining the best catalytic yields with cobalt of up to 99% in a time of 83.59 min [127]. As can be seen, iron is an element widely used as part of the catalysts used in biomass gasification. In order to obtain synthesis gas, recently this element has also been used together with nickel and activated carbon for the gasification of pine biomass, wheat, corn straw, peanut shells, and cotton stalk, obtaining the best hydrogen yields, approximately 3 L, for corn straw and pine wood. In this experiment, up to 5 g of the catalyst (Fe-Ni/activated carbon) was considered and the conditions of temperature, gas flow, and time were 750 °C, 1 mL/min, and 20 min, respectively. Under these conditions, a ratio H_2/CO of approximately 2 was obtained [128]. The use of Chinese pine sawdust is one more attempt for hydrogen recovery, as well as the possibility of absorbing the greatest amount of CO_2 through the use of calcium oxide (CaO) as a catalyst in gasification processes and promoting the reduction of greenhouse gases. It is worth mentioning the low amount of hydrogen produced. The use of CaO had an impact of up to a maximum of 10% in the generation of H_2 and synthesis gas [129]. Wood chips, also from China, have been used for the same purpose, although without an improvement in the reduction of the amount of CO_2, which increased in parallel with the higher amount of H_2 obtained. This analysis was carried out with the use of natural cement as the catalyst. The results showed an approximate increase of between 40–50% in hydrogen volume, this last value was obtained with 9% by weight of cement [130]. In addition to cement, some researchers have chosen to include catalysts such as dolomite and limestone, for example, in the gasification of palm residues where good yields of syngas (≈39%) and methane (≈20%) were obtained at a temperature of 900 °C [131]. In addition to dolomite, gamma alumina (γ-Al_2O_3) has been applied as a catalyst in the gasification of pine (pinus insignus) biomass residues, observing an increase in hydrogen by approximately 50% [132]. Contrary to pine sawdust, oil palm leaves have been a highly recommendable option for obtaining hydrogen by gasification, although the catalyst is of vital importance. For example, with 0.3 g of biomass and a time of 8 min, the 20ZnO/MgO type catalyst has promoted a yield of up to 118 mmol/mL of hydrogen and a molar ratio (H_2/CO_2) of approximately eight [133]. The above biomass, oil palm, has also been considered in similar gasification studies, but with the catalysts $Mg_{0.80}Ni_{0.20}$ [134] and $Mg_{0.80}Zn_{0.20}O$ [135], obtaining an increase in hydrogen yield of approximately 362% (194 mL/g) and 438% (214 mL/g), respectively. Such

results are attributed to the catalytic and basic properties of the nanomaterials employed. Many of the abovementioned biomasses are composed of raw materials such as hemicellulose (15–25%), which is the second most abundant polymer [136]. This component has also been studied in the gasification process, for example, in sawdust from *Populus alba L.* wood (15% hemicellulose). The catalyst in this study was K_2CO_3, achieving an approximate yield of 85% of the gas at a temperature of 600 °C. In relation to hydrogen, a maximum value of approximately 29% was obtained [137]. Other oxides derived from zirconium, aluminum, and silicon have also been used as catalysts for biomass residues. Such is the case of soybeans of Canadian origin, where a yield of 8.1, 7.0, 6.7, 5.6, 5.1, and 3.5 mmol/g of hydrogen by using the catalysts 10Ni/ZrO_2, 10Ni/Al_2O_3, 10NiCNT (carbon nanotubes), 10Ni/SiO_2, and 10Ni/Al_2O_3-SiO_2, respectively [138]. Turkey is a country that produces thousands of tons of nut residues, such as hazelnut (≈600,000 Tn), walnut (≈180,000 Tn), and almond (≈55, 000 Tn), which have also been studied for obtaining hydrogen by using catalysts such as trona [$Na_3(CO_3)(HCO_3)\cdot 2H_2O$], dolomite [$CaMg(CO_3)_2$], and borax [$Na_2B_4O_7\cdot 10H_2O$]. In the case of hazelnut shells and in the presence of the trona catalyst, the highest yield of approximately 82% was obtained, followed by walnut residues (≈74%). For almond biomass, a lower but not very low yield of 40% was visualized. These results may be related to the lignin content, since, generally, the higher the lignin content, the higher the amount of hydrogen will be as presented in these three biomasses: hazelnut (lignin ≈ 40%) > walnut (lignin ≈ 35%) > almond (lignin ≈ 30%) [139].

2.2.6. Use of Residual Water and Solid Residues to Generate Biohydrogen by Gasification

Solid municipal residues are another object of study due to the possibility of obtaining hydrogen from syngas by gasification. This is the case of a simulation conducted with a mixture of plastic, wood products (splinters, pellets), copper, and lead (heavy metals) in a nitrate-type solution. Results showed a hydrogen content as high as 32% molar compared to syngas, calculated at 900 °C [140]. Recently, residual water from the process of olive exploitation in Spain was analyzed in a low-temperature gasification study designed to generate hydrogen and methane. Findings for these two gases were approximate yields of 17 and 11 mol/kg of biomass, respectively. The authors affirmed that the yields of hydrogen and methane were related directly to carbon (38%) and oxygen (55%) content [141]. Finally, it is important to point out that, in addition to pyrolysis and gasification, other methods have the potential to produce hydrogen, including biochemical processes [142] like direct and indirect photolysis [143,144] and dark fermentation [145].

3. Challenges and Future Prospects

Hydrogen production still presents major challenges. In order to ensure its long-term environmental sustainability, hydrogen production must be based on renewable and carbon-neutral resources. In this context, lignocellulosic biomass presents itself as the main feedstock that meets these conditions, thanks to its abundance and low cost. Progress in the development of hydrogen production processes is focused on the optimization of the processes considering all the factors that limit efficiency, and the implementation of technologies that have been developed in recent years. This article has studied the potential of pyrolysis and gasification of terrestrial and marine lignocellulosic biomass for hydrogen generation. Despite the benefits presented by each of them, it is important to mention some of the challenges to be overcome, for example, with respect to pyrolysis, the need to be able to use the oil produced instead of petroleum; to be able to explain in more detail the synergistic effect of co-pyrolysis of biomass; to solve the problem of carbon deposits in the catalysts that are deactivated due to excess coke; and to investigate in greater depth the problem of how to control pyrolysis (use of catalysts) and co-pyrolysis. In relation to gasification, there is a need to solve some problems to improve hydrogen production such as porosity (plugging) caused by some elements such as calcium, which can reduce gas propagation and carbon dioxide production. As in pyrolysis, it is imperative to reduce the coke deposits that deactivate the catalyst used, which can eventually generate huge

economic losses in the process. Another major challenge is to eliminate or at least minimize the amount of tar generated (steam-sorption). Finally, it has to be mentioned that it is necessary to implement actions in the future to reduce the high maintenance costs in gasification processes.

4. Conclusions

The processes of pyrolyzing and gasifying biomass to generate hydrogen offer important advantages, such as relatively low costs and the existence of abundant sources of biomass that, in some cases, may be available free because they consist of "waste" materials like straw and wood shavings from agricultural and forest exploitation that are easily stored. There are, however, some disadvantages for instance, hydrogen yields can vary widely as a function of the biomass available since different kinds of raw material may be accessible in larger or smaller quantities in certain times of the year. As a result, pyrolysis gives lower hydrogen production, though catalysts can be added to improve yields. This is one of the best options for converting acetic acid derived from bio-oil. In this regard, alloys with nickel are an excellent option, as long as it is possible to reduce certain disadvantages: low stability, resistance to the formation of carbon deposits, and relatively easy deactivation. The formation of carbon during thermal processes like pyrolysis and gasification can be reduced by adiabatic pre-reforming or processes that facilitate the evaporation of mixtures of liquid hydrocarbons.

Gasification is also an effective process for generating hydrogen. In addition to terrestrial biomass, marine biomass, especially algae, has uniquely adequate characteristics for this purpose. According to recent research, hydrogen yields from the thermal processing of biomass vary as a function of time of residence, heating velocity, the maximum final temperature at which the experiment is performed, the origin of the biomass, and its composition due to differences in cellulose content. In addition to reducing greenhouse gases such as CO_2, economic aspects, and availability, the gasification process offers as its main advantage the possibility of generating synthesis gas, mixing with natural gas such as methane, propane, etc. In addition, the transportation of this gas is relatively feasible (pipelines). One of the main advantages of this gas is the alternative to obtain hydrogen and methane, which can be used for the generation of electric energy through one of the available fuel cells, for example, the solid oxide fuel cell (Figure 3). Despite such advantages, gasification also presents some major problems that can become very serious, for example, the blockage of filters and pipes of the generated fuel due to the generation of tar.

Finally, it is important to consider that mechanical pretreatment of the biomass is often a prerequisite for its use in these processes, given the minimum effort needed to obtain good yields. Developing efficient pyrolysis and gasification to generate hydrogen will benefit macroeconomic growth and permit development of the biohydrogen industry to produce alternative energy sources.

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