Review

Production of Hydrogen from Lignocellulosic Biomass: A Review of Technologies

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Abstract: Hydrogen is considered one of the most important forms of energy for the future, as it can be generated from renewable sources and reduce CO_2 emissions. In this review, the different thermochemical techniques that are currently used for the production of hydrogen from biomass from plantations or crops, as well as those from industrial or agro-industrial processes, were analyzed, such as gasification, liquefaction, and pyrolysis. In addition, the yields obtained and the reactors, reaction conditions, and catalysts used in each process are presented. Furthermore, a brief comparison between the methods is made to identify the pros and cons of current technologies.

Keywords: hydrogen; gasification; liquefaction; pyrolysis; biomass

1. Introduction

The growth in the world population generates significant increases in fossil fuel consumption, leading to an increase in anthropogenic emissions of greenhouse gases and global warming. According to the 2015 World Energy Statistical Review report, almost 85% of energy consumption mainly depends on these reserves, resulting in environmental problems, energy crises, and depletion of sources [1]. For these reasons, one of the main challenges today is to address the growing global demand for energy and discover ways to meet this demand through sustainable and environmentally friendly energy solutions [2]. To substitute fossil fuels, researchers are exploring new alternative sources of renewable fuels with environmental safety in mind [3]. Among the promising renewable energy resources are biodiesel, bioethanol, and hydrogen. According to Zhang et al., biodiesel is considered a stable, biodegradable, non-toxic, and environmentally friendly renewable energy source with excellent acid catalytic activity, ideal in the field of biorefinery [4]. It is also easy to store/transport and is technically and economically accessible [5,6]. It can be produced from fatty acids, various edible oils, and non-edible oils with small-chain alcohol by esterification/transesterification over an acid/base catalyst [7]. Biodiesel shows a similar combustion performance to fossil diesel [8]. There are also several studies related to the production of bioethanol; for instance, different biomasses have been evaluated, such as sorghum biomass, Delonix regia pods, waste date palm fruits, etc., to obtain bioethanol through enzymatic hydrolysis processes, using different biomasses and processes applying acid hydrolysis, followed by fermentation with yeasts [8–11]. In addition to studies on the production of biodiesel and bioethanol, there are several studies related to hydrogen, which is considered one of the most important forms of energy for the future due to its cleanliness and high calorific value. As a result, it has become a focus of renewed interest in many parts of the world [12]. It has been proposed as a high-yield potential energy vector—it has the highest energy density of all fuels and energy carriers with a yield of 122 $MJKg^{-1}$. It is believed to be an effective replacement for gasoline because 9.5 kg of hydrogen is enough

to replace 25 kg of gasoline. Its properties of high energy density, fast burning, high octane number, and zero damage potential, will soon make it the fuel of choice [13]. Even when comparing hydrogen with electricity, which can also be produced by renewable sources, electricity has the disadvantages of transmission and heat losses caused by high voltages and electrical resistance, while hydrogen offers some advantages, such as high conversion efficiency of energy, abundant sources, ability to be created with zero emissions from water, and long-distance transportation [2]. As for the cons of hydrogen as a biofuel, its storage is challenging. As the lightest molecule, hydrogen gas has a very low density: 1 kg of hydrogen gas occupies more than 11 m^3 at room temperature and atmospheric pressure, and pure hydrogen has flammable and explosive characteristics [14]. Thus, for hydrogen storage to be economically viable, its storage density must be increased. Various storage methods are currently being investigated [15]. However, expensive equipment is required to liquefy hydrogen, as well as to transport the liquid hydrogen [16]. In addition, biomass conversion techniques (e.g., gasification and pyrolysis) have some limitations and are very energy intensive [17].

The predominant method for hydrogen production is based on natural gas or other fossil fuel sources that require abundant energy and result in the emission of a significant amount of CO_2 into the atmosphere [18]. An alternative to obtaining hydrogen is the use of biomass energy, which is considered a green source with almost zero carbon emissions. Unlike solar energy, biomass has no time limit. This energy source contains significant amounts of carbon and hydrogen, making it favorable for producing fuels and chemical products [19]. In addition, lignocellulosic biomass is broadly accessible as a low-cost renewable feedstock with a nonreactive nature [20]. It has a high potential for the production of bio-oil and other chemical products [21] and is considered the fourth largest energy source available [22]. Residues are obtained from forestry and agriculture, although biomass grown in Europe is significantly more expensive than biomass grown in Latin America [23]. Forestry residues generated by wood extraction operations have traditionally been considered products of low economic value [24].

Different methods of converting biomass into hydrogen have been developed, and thermochemical and biochemical conversion is the most recommended. Alongside biomass thermochemical conversion processes, other methods include gasification, pyrolysis, and liquefaction, with steam gasification considered the most promising to produce hydrogen-rich synthesis gas. In this route, the use of steam as a gasifying agent not only provides H_2-rich synthesis gas but also causes minimal environmental impact, especially preventing NO_x formation with low CO_2 generation, making the hydrogen obtained to be considered "green" [25,26]. However, the wide varieties of biomass have different physical characteristics and chemical compositions, which always result in different steam gasification efficiencies [27]. Biomass containing less sulfur in the fuel reduces acid rain. As a result, the use of biomass fuel instead of fossil fuel causes a decrease in GHG (greenhouse gas) emissions [28]. In this review, the different thermochemical techniques that are currently used for the production of hydrogen from biomass from plantations or crops, such as gasification, liquefaction, and pyrolysis, are described. Complete monitoring of the process is carried out, from the characterization of the most widely used types of biomass to its transformation into hydrogen. The yields obtained from both hydrogen and different by-products are described and a brief comparison is made between methods to identify the pros and cons of current technologies. In this way, a source of useful information is provided that details advances in research toward the production of new energy sources.

2. Biomass

Biomass refers to organic materials derived from living entities, such as plants and animals. A variety of agricultural and forestry residues, household, commercial, and industrial waste, as well as particular energy crops, are examples of raw materials for bioenergy. The structure of biomass may vary depending on the feedstock types [29].

Lignocellulosic biomass is the most abundant type of biomass, considered to be any organic substance derived directly or indirectly from the photosynthesis process that is available in a renewable way and can be used as an energy source [24,25,27]. Generally, lignocellulose biomass can be categorized into four main sources: agricultural residues, forestry residues, energy crops, and cellulosic waste. As a wide category of biomass, agro-industrial biomass incorporates both food-based and non-food-based portions of crops [30]. Its composition is very diverse, with its main components being cellulose, hemicellulose, and lignin [29,31].

From the point of view of chemical and structural composition, cellulose $(C_6H_{10}O_5)_x$ is a linear polymer consisting of a D-glucose chain linked by β-(1,4)-glucosidic bonds. Approximately two-thirds of cellulose's mass is organized in an ordered structure to form stable crystallization zones, and high-density hydrogen bonding in crystallization zones makes cellulose less soluble and recalcitrant in conversion. Therefore, cellulose is insoluble in water and most organic solvents [32]. Hemicelluloses $(C_5H_8O_4)_m$ are heterogeneously branched biopolymers containing a variety of polysaccharides, including xylan, glucuronoxylan, arabinoxylan, glucomannan, and xyloglucan. They are relatively easy to hydrolyze. Lignin $[C_9H_{10}O_3(OCH_3)0.9 - 1.7]_n$ is an aromatic polymer synthesized from phenylpropanoid precursors. It confers rigidity to the cell wall, in addition to protecting cellulose and hemicellulose from hydrolytic attack by plant pathogens. The structural composition is presented in Figure 1.

Due to their different compositional characteristics, there is no single way to classify biomass, so they can be grouped differently according to their purpose and scope. The most used classifications are as follows [33]:

Wood and woody biomass: mainly composed of carbohydrates and lignin. Generally, this category consists of materials such as trees and residue roots, bark, and leaves of woody shrubs.

Herbaceous biomass: Herbaceous biomass comes from plants that have a non-woody stem and that die back at the end of the growing season. This category includes pasture, grain, or seed crops from the food-processing industry and their by-products, such as cereal straw.

Aquatic Biomass: This category includes macroalgae, microalgae, and emergent plants. It is considered the ideal feedstock for the production of third-generation biodiesel, as it does not compete with food crops, along with the advantage of producing considerably higher amounts of biomass per hectare compared to terrestrial crops.

Biomass from human and animal waste: The most common sources are bones, meat meal, various types of animal manure, and human manure.

Mixed biomass: In some cases, when several substrates belonging to the different classes mentioned above are found in hybrid form, they are classified in this category.

Globally, biomass sources are available in various categories, but the top four sources that benefit energy industries are crops, agricultural residues (crop residues), forestry residues, and municipal solid waste [34]. Forest and agricultural residues represent the most abundant natural biomasses in the natural world with an approximate yield of around 200 billion tons. In China, the annual yield of agricultural residues can reach 900 million tons, followed by Brazil (600 million tons), India (550 million tons), Indonesia (165 million tons), and Argentina (129 million tons). The countries with annual production between 5 and 10 million tons are Malaysia, Zambia, Mozambique, the Czech Republic, Sri Lanka, Kenya, and Bulgaria, while the countries with potentially less than 5 million tons/year are Rwanda and Niger [35,36].
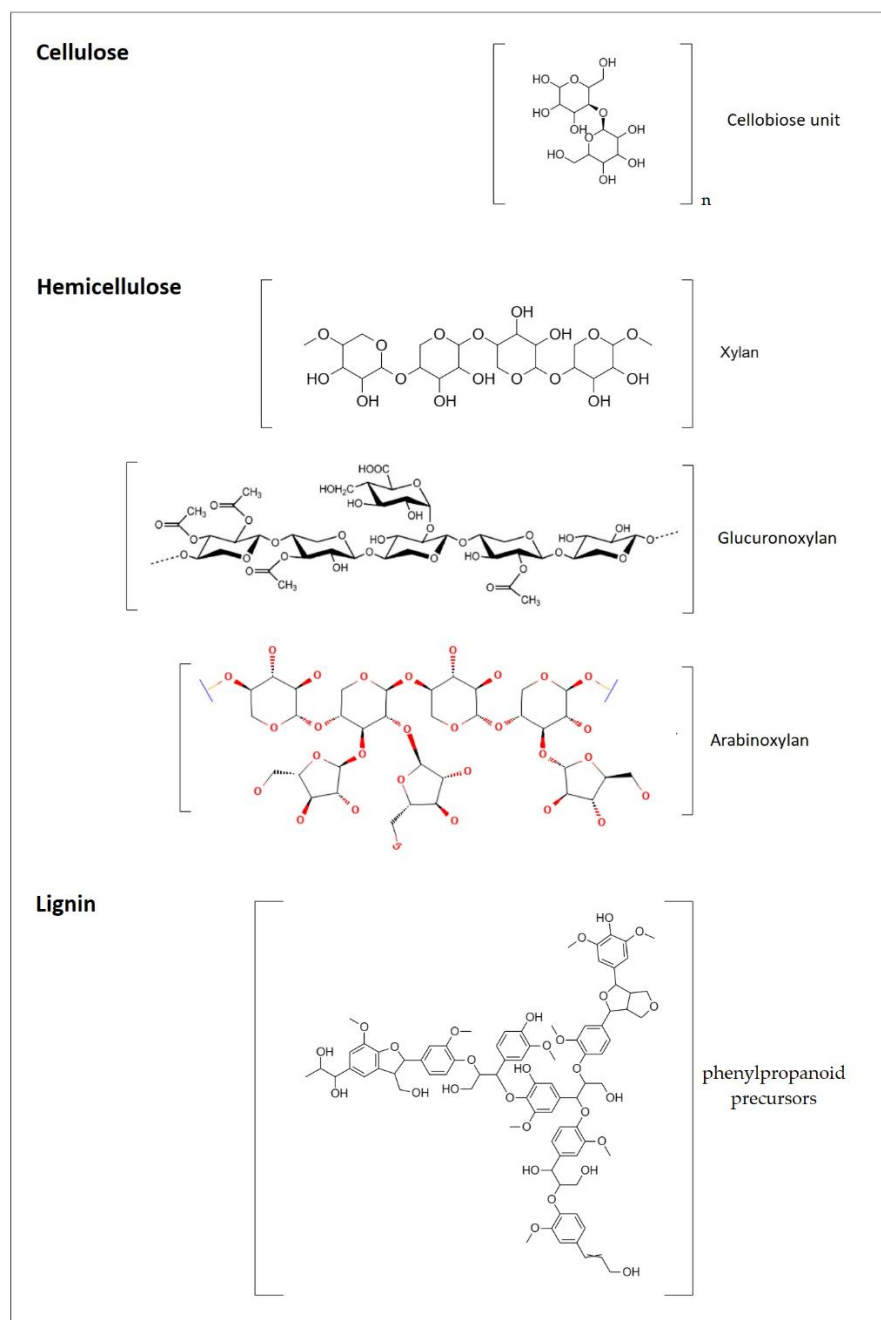
Figure 1. Structure of biomass.

We can consider the elemental composition of different types of biomasses and their calorific value. The most investigated residues are sugarcane bagasse, wood sawdust, different parts of banana plants, bamboo wood, etc. The amount generated depends on the agricultural production of each country and the country's processing industries. These crop remnants are generally left in the ground after harvesting or milling and can potentially be used as biomass or an energy source. Of the types of biomass presented in Table 1, those with the highest hydrogen content and lowest ash content are wood sawdust, banana pseudostem, and Chlorella vulgaris. These are considered suitable for hydrogen production according to their physicochemical characteristics.

Table 1. Lignocellulosic biomass characteristics for hydrogen production.

Biomass	Elemental Analysis					High Calorific Power (Kcal/kg)	% Ash	% Humidity	Ref.
	% C	% H	% N	% S	% O				
Woods and woody biomass									
Bamboo	39 ± 3	6.1 ± 0.2	0.6 ± 0.3	0.018 ± 0.006	54 ± 3	4359–4568	1.4–3.0	44.51	[37,38]
Oil palm frond biomass	41.9	7.2	-	0.6	49.8	-	4.3	67	[39,40]
Sawdust agricultural waste materials	44.75	6.31	1.68	0.05	46.87	3155.30–4411.48	1.03	59.38	[41–43]
Palm empty fruit bunch	40.8	4.1	-	0.52	52.8	4633.6	1.6	75.60	[44]
Herbaceous biomass									
Rice husk and dust	39.8–41.1	5.7 ± 6.1	37.4 ± 36.6	-	0.5–0.6	4301.10–4573.50	16.21	9.53	[45,46]
Banana peels	35.65 ± 0.21	6.19 ± 0.07	1.94 ± 0.16	0.020 ± 0.0955	45.94 ± 0.17	4533.3	13.44	89.09	[27,47]
Banana pseudo-stem	42	5.62	1.08	-	51.30	3702.11	1.4–3.0	91.3 ± 0.5	[48–50]
Palm kernel shells	45–55	5.70	-	0.05–0.20	30–45	3854.97	2–5	44–55	[19]
Olive pits	44.81	6.40	-	-	47.93	-	2	12	[22]
Peanut shells	47.52	5.67	1.59	0.13	34.94	3907.52	11.5	10.1	[51,52]
Sunflower husk granules	52.1	5.8	0.7	0.14	37.2	4394.76	2.8	5.68	[52]
Bagasse	58.10	6.54	S/V	0.19	34.57	2388.46–2627.3	7.91	10.21	[53]
Corn	85.35	1.69	S/V	S/V	12.12	7237.03	1.92	10.01	[54]
Aquatic Biomass									
Chlorella vulgaris	52.8	7.24	4.81	0.35	28.2	5181.64	5.93 ± 0.81	6.8 ± 1.11	[55]
Phaeodactylum tricornutum	51.1	6.80	2.75	0.207	27	4945.03	-	-	[55]
Synechococcus elongatus	48.8	6.88	10.1	0.069	25.2	4600.86	-	-	[55]

The selection of the best process to use depends on the physicochemical properties of the biomass. Residues with high moisture content, such as herbaceous plants, lend themselves to a "wet/aqueous" conversion process, which involves biologically mediated reactions, while "dry" biomass, such as wood chips, is more economically suitable for gasification, pyrolysis, or combustion. Aqueous processing is used when the moisture content of the material is such that the energy required for drying would be excessively large compared to the energy content of the product formed [56]. In addition to moisture, other properties are analyzed, such as ash calorific value, fixed and volatile carbon proportions, metal/residue content, alkali metal content, and cellulose/lignin ratio. For dry biomass conversion processes, the first five properties, including moisture, are of interest, whereas, for wet biomass conversion processes, the first and last properties are the most important [57].

3. Hydrogen Production from Biomass

Based on the process of gas generation, the direct production of hydrogen from biomass can be achieved by two routes: thermochemical methods and biochemical processes using microorganisms. The former include gasification, pyrolysis, and liquefaction and are considered the most effective methods for producing hydrogen-rich gases from biomass. These processes define all biomass into liquid and gaseous biofuels, which are then synthesized into the required chemical. Otherwise, they can be used directly as a transportation fuel. Thermal gasification is a known thermochemical method, producing a temperature of 800 to 1000 °C and involving partial oxidation of biomass in the presence of gasifying agents, such as steam or oxygen and air that provide O_2 in amounts less than stoichiometric amounts [48]. In the case of gasification with air, energy for the process is produced by partial combustion of the fuel, whereas for gasification with steam, energy

from an external source is required to generate steam and is, therefore, more challenging. Syngas (a mixture of CO and H_2) and biofuels are the main products of gasification and pyrolysis, respectively. Biofuels are also determined in the synthesis of gas through some specific conversion techniques, such as bio-oil reforming, bio-oil gasification, online pyrolysis reforming, etc. [58,59]. Pyrolysis or co-pyrolysis is another promising technique for hydrogen production. In this technique, the heating and gasification of organic matter take precedence in a temperature range of 500–900 °C at a pressure of 0.1–0.5 MPa. Although the pyrolysis process is considered the precursor to gasification, it differs significantly. The primary products of pyrolysis comprise condensable gases and solid carbon. Condensable gases can be further decomposed into CO, CO_2, H_2, and CH_4, liquid, and char through homogeneous gas-phase reactions and heterogeneous thermal gas–solid-phase reactions. In addition, non-condensable gases, such as H_2, CO, CO_2, and LHG (light hydrocarbon gas), are formed due to the cracking of condensable vapor through gas-phase reactions. Another thermochemical process is gas liquefaction, which is a highly complex process that consumes a lot of energy [60]. Liquid hydrogen is produced by cooling, purifying, converting ortho to hydrogen, expanding, and liquefying hydrogen feed gas from atmospheric temperature to approximately 20 K [61].

There are also several biohydrogen production routes that use the biochemical processes of microorganisms, such as, depending on the type of dark substrate and the microorganism, biophotolysis, indirect photolysis, fermentation, and photofermentation. The biophotolysis process is similar to the photosynthesis process in that a water molecule is used by the microbial photosynthesis mechanism to transfer solar energy to molecular hydrogen. Scenedesmus spp., Chlorococcum spp., and Chlorella spp are considered to be algal strains that produce inefficient hydrogen cells using this route of hydrogen production. At the end of biophotolysis, two protons are released from the water molecule. Hydrogen is formed by the presence of hydrogenase or by the reduction in CO_2 [62] Indirect photolysis is the process in which many cyanobacteria and microalgae can be used to produce hydrogen from starch or glycogen. Two steps are involved in indirect biophotolysis: the synthesis of carbohydrates using light energy and the production of hydrogen from the synthesized carbohydrate using the cell's metabolism under dark and photodecomposition conditions [20,62]. Dark fermentation is considered the most promising technique for biohydrogen generation through biomass conversion. It has a net energy ratio equivalent to 1.9, while for steam-reforming methane, it is only 0.64. Hydrogen production can be carried out by anaerobic bacteria, which is grown in a substrate rich in carbohydrates or a dark substrate. In this method, in addition to obtaining hydrogen, acetic, butyric, lactic, and propionic acids are produced, as well as solvents such as ethanol, methanol, and acetone. Photofermentation involves the production of hydrogen from the conversion of organic substrates by photosynthetic microorganisms. In this process, anoxygenic photosynthetic bacteria, especially purple bacteria without sulfur, are capable of reducing H^+ ions to gaseous H_2 by reducing the power obtained from the oxidation of organic compounds. It is estimated that the yield of H_2 is around 9–49 gKg^{-1} of raw material [63].

### 3.1. Hydrogen Production from Catalytic Biomass Gasification

A reliable method of using biomass is gasification to produce syngas. However, more studies are currently required to eliminate the technical barriers to this process, such as the formation of tar and the accumulation of ash. Tar can cause serious operational problems in downstream equipment, such as coolers, filters, and channels, that impose a high cost on the system. These problems require the removal of at least part of the produced tar before using the produced gas. Therefore, tar control and removal are vital issues for the development of biomass gasification on an industrial scale. One of the most promising methods for tar removal that provides multiple benefits is catalytic gas cleaning [64].

Hydrogen production through biomass gasification varies in performance due to different factors, such as the use of catalysts. The desired properties of the catalyst include high catalytic efficiency, low cost, and high practical value [65]; according to Mastuli,

factors such as dispersion, basicity, and binding strength play more important roles in the biomass gasification of biomass in supercritical water to produce hydrogen [66], as well as in reaction conditions, taking into account some critical parameters, such as the equivalence ratio, metallic catalysts, temperature variations, and gasification agents in hydrogen production.

The partial temperature and rate of heat have an important effect on the performance of gasification, as well as on the composition pressure and the yield of the gaseous products. During the gasification process, some unwanted components, such as tar, are also produced, and these are the cause of many problems, such as blocking downstream equipment and increasing operating costs. High heating rate and gasification temperature could increase syngas (H_2 and CO) production and decrease tar production. However, in situ catalytic tar reduction is the most reasonable and effective strategy to remove tar and convert it to useful product gas [67]. The investigation of catalysts in the gasification process is a very important aspect because the right catalyst can rapidly increase the efficiency of gasification and hydrogen production, as well as decrease the formation of unwanted components [54].

The content of H_2 and CH_4 during gasification increases significantly as the temperature increases; thus, CO content increases by 10% (650 °C to 850 °C) and CO_2 content decreases slightly [65]. Scheme 1 shows the gasification process, along with the chemical reactions that occur in the process.
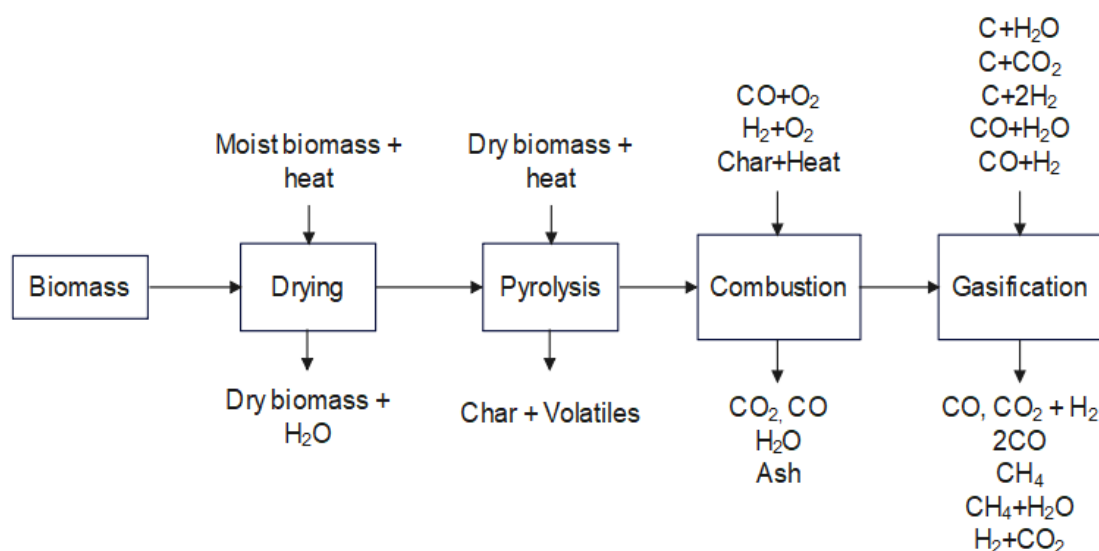
Scheme 1. Gasification process.

Table 2 shows the main reaction conditions applied, the type of reactor, the catalysts used in the gasification reaction, and the yields achieved in terms of hydrogen production.

Hydrogen Production from Non-Catalyzed Biomass

According to a study by Rauch, the sorption-enhanced gasification of biomass is highly advantageous, as it can produce hydrogen-rich syngas with a relatively high hydrocarbon content, especially methane, as a source of energy and syngas [68]. Decomposition without a catalyst at high temperatures presents an almost complete conversion of methane. Partial oxidation can be used in this context, presenting advantages over other reforming methods, including fuel flexibility, fast response time, simplicity, long useful life [69], long service life, and a wide range of operating conditions for various feedstocks. It also yields catalyst-free single-stage reforming of natural gas. Catalyst-free operation allows natural gas to be reformed in a wide range of operating conditions [70].

According to Agarwal et al., the production of H_2 from non-catalyzed pyrolysis shows that the yield of H_2 was directly proportional to the time and temperature of pyrolysis, increasing energy expenditure compared to the catalytic reaction [71]. However, Ioannidou

reports that the presence of a catalyst seems to increase the quality of both the liquids and the gases produced, showing an increase in H$_2$% and its calorific value compared to non-catalytic reactions in corn pyrolysis [72].

As can be seen in Table 2, the reaction temperature ranges from 300 °C to a maximum value of 950 °C. The most common reactors are fixed-bed and fluidized-bed reactors. Fixed-bed reactors can have countercurrent mass flow and, in this case, the biomass and reactant flow in opposite directions. While in fluidized-bed gasification systems, the flow direction is the same. Bubbling and circulating, differing with respect to speed and fluidizing agent, are the most common effects in the reviewed investigations of water vapor and nitrogen gas. In some special cases, argon carrier gas and oxygen vapor are also used. Figure 2 shows the gasification process.
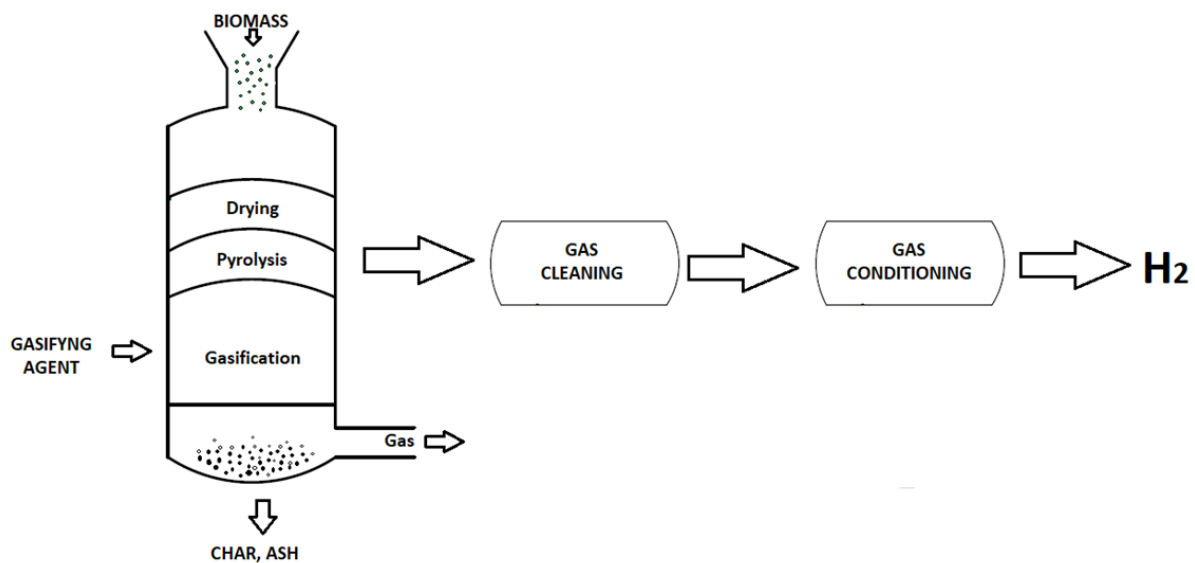

Figure 2. Gasification system scheme.

Table 2. Operating conditions and results obtained using the gasification method.

Biomass	Reactor	Gasification Agent	Reaction Conditions	Catalyst	H$_2$	Ref.
Pine sawdust	RLF	Water steam	T = 800–950 °C. t = 6.4–4.5 s.	Porous ceramic : MgO, Fe$_2$O$_3$, Na$_2$O, K$_2$O, CaO, TiO$_2$ y BaO.	24,985 mmol g^{-1}	[41]
Rice husk	FBR–bubbly	Air	T = 950 °C	CaMg(CO$_3$)	45.9% vol with temperature rise to 950 °C	[64]
Banana peel	FBR quartz	Water steam	S/C: 21.7; T = 1023 K	—	3.42 mmol g^{-1}	[73,74]
Rice husk	FBR	Steam plus silica sand	T = 600 °C; P = atmospheric t = 24 h; S/B = 0.4.	CaO samples; (Mg, K, Na)	17.5–20.5 mmol g^{-1}	[21]
Oil palm	SCWG reactor batch	Water steam	T = 380 °C; P = 22.1 Mpa	20NiO/MgO, 20CuO/MgO and 20ZnO/MgO	35.4 mmol mL^{-1}	[39]
Oil palm	SCWG reactor discontinuous	Water steam	T = 400 °C P = 25 Mpa t = 30 min	Zn doped with MgO nanometric	118.1 mmol mL^{-1}	[39]
Corn straw	RLF	Water steam with oxygen	T = 800–950 °C, t = 10 min	Biochar with (KOH, K$_2$CO$_3$, NaOH y Na$_2$CO$_3$).	197.8 mmol g^{-1}	[54]
A mixture of banana peel, Japanese cedar, and rice husk	RLF	Argon carrier gas	T = 650–850 °C, t = 2 h, v = 50 cm^3/min	K$_2$CO$_3$ y CaO	66.8% when the temperature rises to 850 °C.	[12]

Table 2. *Cont.*

Biomass	Reactor	Gasification Agent	Reaction Conditions	Catalyst	H$_2$	Ref.
Palm kernel shells	ADG	Water steam	T = 800 °C, 5–10 Kpa	NiO/MD	H$_2$ + CO = 80.4%	[19]
Wood sawdust	FBR	Steam and N$_2$	T = 700 °C v = 35 °C/min.	Fe/CaO	38.21 mmol g^{-1}	[75]
Cotton stall, rice husk	-FPBO -RLF two stages	Water steam	T = 600–700 °C v = 0.1 g/min	CaO	11.55 mmol g^{-1}	[76]
Sugar cane bagasse	RDS		T = 500–800 °C	Nickel nanocatalysts (Ni/CNT) supported on carbon nanotubes	21.8 mmol mL g^{-1}	[53]
Banana pseudostem	Reactor SCWG	Water steam win N$_2$	T = 300–600 °C t = 60 min, P = 22 and 25 Mpa	with metal (Ni/Fe/Ru)	11.1 mmol mL g^{-1}	[40]
Wheat straw	RDS	Water steam	T = 300, 400, 500 °C, P = 23–25 Mpa, t = 15, 30 and 45 min	Nickel catalysts	5.78 mmol mL g^{-1}	[77]
Oil palm	Reactor WGS	Steam	T = 800 °C atmospheric pressure		59.25% by volume to 800 °C, CGE (cold gas efficiency) maximum of 84%.	[78]
Sorghum	RLF	Steam	T = 773 K v = 11,8 K/min. t = 90 min. P = 9.6–29.6 Mpa	K$_2$CO$_3$ and Na$_2$CO$_3$	11.9 mmol g^{-1}	[79]
Pinewood	FBR	Water steam	T = 650–850 °C	Dolomite, olivine, and magnesite	15.8%	[65]
Cane bagasse	RDS	Water steam	P = 25 Mpa, T = 800 °C	KOH	75.6 mmol g^{-1}	[80]
Nutshell	Batch microreactor	Water steam	T = 600 °C t = 30 min P = 220 bar	KOH y Na$_2$CO$_3$	4.63 mmolg^{-1}	[81]
Palm shell	FBR	Water steam	T = 900 °C P = 5 Mpa t = 16.3 min	Sodium on Pt/Al$_2$O$_3$	31.5 mmol g^{-1}	[28]
Rice husk	Reactor WGS	Water steam	T = 700 °C P = 1 atm	CaO	6.58 mmol g^{-1}	[76]
Pine sawdust	RLF	Water steam	T = 730 °C P = 1.5 Mpa t = 6 h	NiO/Dolomite	22.95 mmol g^{-1}	[82]
Wood	Reactor: Ryield and Rgibbs	CO$_2$, water steam	T = 750 °C P = 1 atm t = 6 h	CaO/C	85.55 mmol g^{-1}	[83]
Banana peel	RLF	N$_2$–air	T = 320 °C t = 25 min	-	32.71 mmol g^{-1}	[73]
Rice straw	FBR	Steam	T = 650 °C P = 1 atm t = 5–7 h	CaO	24.63 mmol g^{-1}	[84]

RLF: fixed-bed reactor; FBR: fluidized-flow reactor; RDS: discontinue reactor; SCWG: supercritical water gasification; SWG: critical water gasification; FPBO: fast pyrolysis bio-oil; ADG: allothermal downdraft gasifier.

Another important aspect of the development of the reaction is the use of catalysts. Catalytic gasification reactions show evidence of greater efficiency in the process and better results are obtained when a catalyst is added. The most widely used catalysts are metallic ones, such as Ni, Fe, Ru, Na, and K, followed by Al$_2$O$_3$, CaO, MgO, CO$_3$, zeolite, and dolomite, as can be seen in Table 2. The Ni-based catalyst shows high tar removal efficiency in the range of 50% to 70% and an improvement in H$_2$ production linked to residence time. In the 45 min it takes to increase from 2.8 to 5.78 mmol/g, a volume fraction of synthesis gas was obtained in a percentage of 48.2% H$_2$, 28.2% CO, 15.9% CO$_2$, and 7.6% CH$_4$ and a calorific value of 11.5 MJ/Nm^3. By adding nickel nanocatalysts (Ni/CNT) supported on carbon nanotubes, the yield is 21.8 mmol H$_2$/g of biomass, while catalysts with CaO support present a yield of 256.81 mL/g of biomass and a 67% reduction in tar from 550 °C to 700 °C. By adding Fe on a CaO support, the synthesis gas yield was 38.21 mol/kg of biomass, the H$_2$ yield was 26.40 mol/kg of biomass, LHV values were 8.69 MJkg^{-1}, and gasification efficiency was 49.15% with a ratio of Fe/CaO = 5% being the optimized mass. The gasification reactions with catalysts with both aluminum silicate, CaO, zeolite, and dolomite present an equivalent ratio of 0.235, 1.94 m^{3}kg^{-1} of synthesis gas yield, 57.4% cold gas efficiency, and a low calorific value of 4.61 MJm^{-3}.

Gao et al. carried out an experimental study using a fixed-bed gasifier with a steam reformer with a porous ceramic packing layer, which acts as a catalyst and is composed of SiO_2, Al_2O_3, MgO, Fe_2O_3, and Na_2O + K_2O + CaO, TiO_2 + BaO + NiO in a percentage of 26, 60, 11, 1, 1.1–1.5, and 0.8, respectively. This porous ceramic reformer showed good performance in the tar cracking process, not only avoiding its production in the organic phase but also not presenting the deactivation problem that typically occurs when using a catalyst for reforming [41]. Another study in which unconventional catalysts were presented is that of Ning et al., who used catalytic steam from corncob char to obtain hydrogen-rich synthesis gas. Using a laboratory-scale fixed-bed gasifier, the method of char-absorbing catalysis was used to load the catalyst, using four alkaline salts KOH, K_2CO_3, $NaOH$, and Na_2CO_3. The results showed that KOH and $NaOH$ exhibited higher catalytic behavior, reaching a maximum hydrogen yield of 197.8 g Kg^{-1} char. In addition, the CO_2 concentration decreased with the increase in KOH concentration and the CO concentration increased from 24% to 29.5% [54]. Studies such as that of Guozhao Zhang show that the use of calcined dolomite improves catalytic activity, offers improvements in synthesis gas production, and decreases tar production and steam reforming of light hydrocarbons.

Other factors, such as the effect of the steam/biomass ratio, have an influence on the synthesis gas obtained, as well as on the formation of undesirable products, which also depend on the application given to the synthesis gas; additional purification steps are necessary, for example, a higher H_2/CO ratio is needed for fuel cells, while the ratio of 2 is more appropriate for the Fisher–Tropsch process, so it is important to consider this in future experimental processes.

3.2. Hydrogen Production from Pyrolysis of Biomass

According to Vuppaladadiyam, pyrolysis is a thermochemical conversion to obtain value-added products [85]. It can convert biomass into fuel gas, liquid oil, and solid coal efficiently in the absence of oxygen [86,87], which occurs at relatively low temperatures (between 350 and 700 °C). This process involves the heating and drying of a biomass particle, as well as the release of volatiles. It could be considered a very attractive process because the hydrogen produced is clean and free of contaminants, that is, CO and CO_2 [88]. The fast pyrolysis of solid biomass is of particular interest as it produces a significant yield of liquid that can be used as a fuel. Various types of pyrolysis reactors are known, such as the fluidized-bed flash pyrolyzer, the Auger reactor, the rotating cone reactor, and the vacuum pyrolysis reactor [87]. Scheme 2 shows the pyrolysis process, along with the chemical reactions that occur in the process.
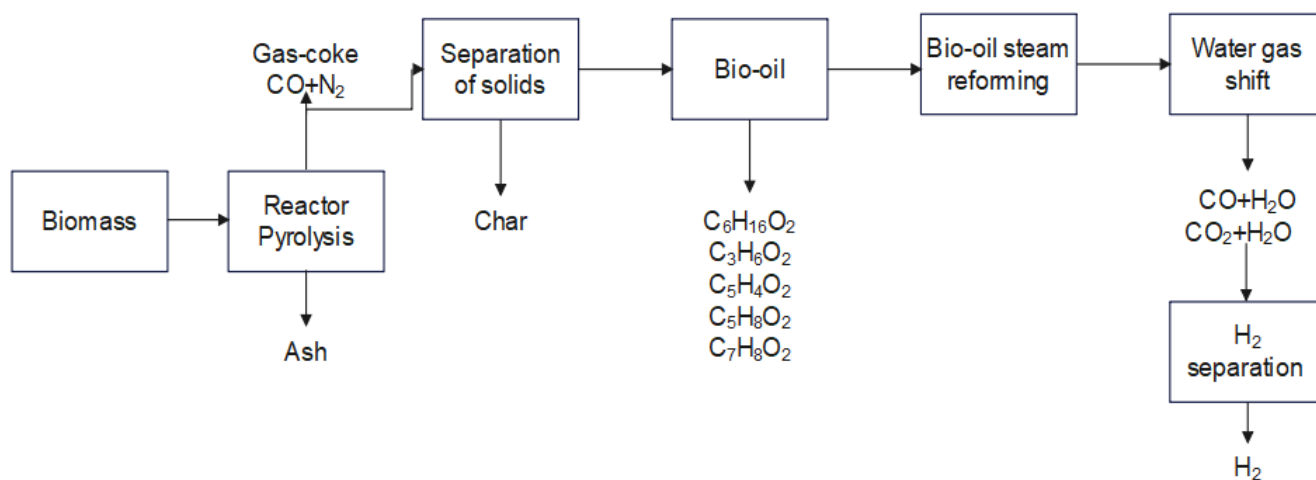
Scheme 2. Pyrolysis process.

According to Table 3, it can be seen that the temperature ranges up to a maximum value of 900 °C. An increase in temperature affects the yield of hydrogen production, which

is more common between 500 and 600 °C, and the residence time of the reactions occurs in a relatively short time, which yields lower costs and better results. The yields are above 40% in weight. Catalysts play a very important role in the production of synthesis gas, and it can be seen that nickel-based catalysts are the most used because they improve the efficiency and productivity of the gas and the removal of tar. More promising due to its performance and low cost, alumina is also a highly regarded catalyst. The fixed-bed reactor is considered within the study as the most used in the pyrolysis process. Figure 3 shows the pyrolysis process.

Table 3. Operating conditions and results obtained using the pyrolysis method.

Biomass	Reactor	Gasification Agent	Reaction Conditions	Catalyst	Results	Ref.
Baggase	Double-bed microreactor	Ar-H_2	T = 850 °C P = 1 atm t = 30 min	Ni and Fe nanocatalysts	Yield H_2 = 35.32 mmol g^{-1} biomass	[53]
Pine Tree	RLF	Air	T = 550 °C t = 17 min	Zeolites-quartz sand	Yield H_2 = 18% in weight	[85]
Wood chips	RLF	Water steam	T = 700 °C	Ni/Char	109.848 mmol g^{-1} biomass	[89]
Sewage sludge	Quartz RLF	Water steam	T = 600 °C v = 100 mL/min t = 20 min	CaO	Yield = 42.59% 12.07 mmol g^{-1} biomass	[84]
Sawdust	RLF	Water steam	T = 650 °C P = 101.325 KP v = 30 mL/min t = 20	Ni − Fe/CaO	Yield H_2 = 18.29% 20.40 mmol g^{-1} biomass	[90]
Guangxi black skin bagasse	Quartz FPBO	Argon atmosphere	T = 250 °C P = 0.28 MPa v = 40 mL/min t = 5 min	Ni/SiC	19.065 mmol g^{-1} biomass	[91]
Pine and fir wood	FPBO of two steps	-	T = 500 °C P = 0.28 MPa v = 0.2 L/min t = 5 min	$NiAl_2O_4$/Al_2O_3	Yield H_2 = 48.12% 9.34 mmol H_2g^{-1} biomass	[92]
Rice husk	FPBO continue flow	N_2	T = 700 °C	Al_2O_3	Yield H_2 = 47.9%	[93]

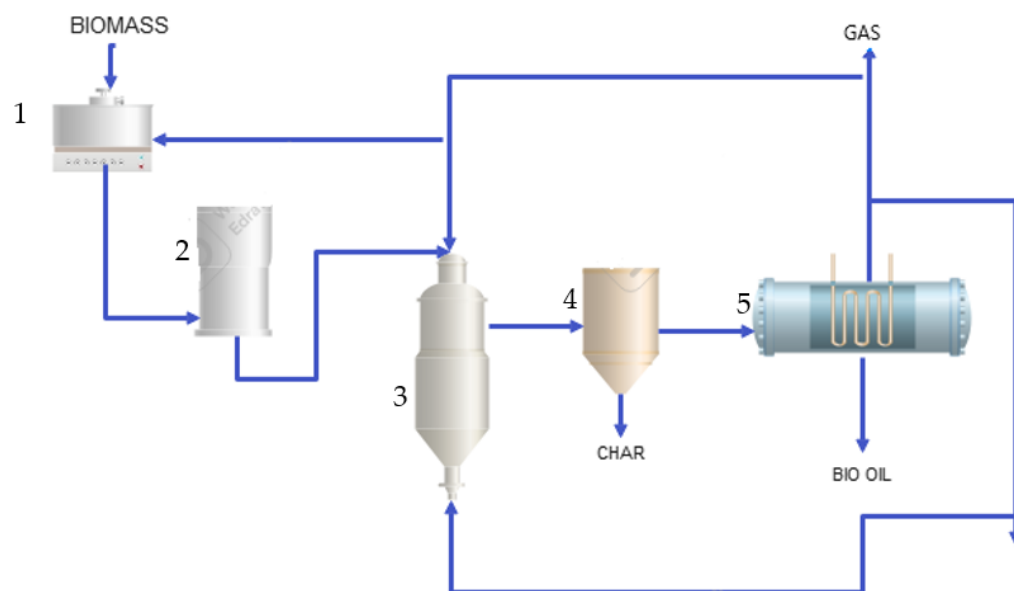RLF: fixed-bed reactor; FPBO: fast pyrolysis bio-oil.

Figure 3. Pyrolysis reactor scheme, own source based on the diagrams in [94,95]. 1. Dry; 2. Grind; 3. Pyrolysis reactor; 4. Cyclone 5. Cool and collect.

3.3. Hydrogen Production by Liquefaction

Liquefaction is an emerging potential route for hydrogen production, still in the early stage of investigation. Distinct from gasification and pyrolysis, the main product of biomass liquefaction is bio-oil, and it operates at low temperatures (250–325 °C) and high pressure (20 MPa). This can be classified into two processes: direct liquefaction and hydrothermal liquefaction. Hydrothermal liquefaction of wet biomass is normally operated at moderate

temperatures (250–370 °C), high pressures (4–22 MPa), and preferably in the presence of a catalyst to break down the polymeric structure of the biomass. It has an advantage over the pyrolysis process in that it is not necessary to perform biomass drying pretreatment, which implies energy savings. For this reason, this process is highly desirable for the processing of aquatic biomass, garbage, and organic sludge; however, it presents some disadvantages, such as the severe reaction conditions and the low yield of hydrogen from the reformation of the oil produced as a result of hydrothermal liquefaction because the main products of this process are a liquid biocrude oil together with a gas stream, an aqueous phase, and a solid waste by-product. Scheme 3 shows the process. To address these challenges, some researchers have proposed coupling hydrothermal liquefaction with aqueous phase reforming, which is a catalytic process capable of converting oxygenates dissolved in water into a hydrogen-rich gas that can be used to upgrade biocrude [96,97]. The reactors used can be batch or continuous. Although continuous reactors give a higher conversion of raw material, most of the studies focus on batch conditions. Due to these facts, no plant has been implemented on a commercial scale so far, and it is necessary to explore many factors, such as the reaction mechanism, thermal and kinetic behavior, optimization of process parameters, reactor design, and economic analysis [98,99]. Figure 4 shows the liquefaction process.
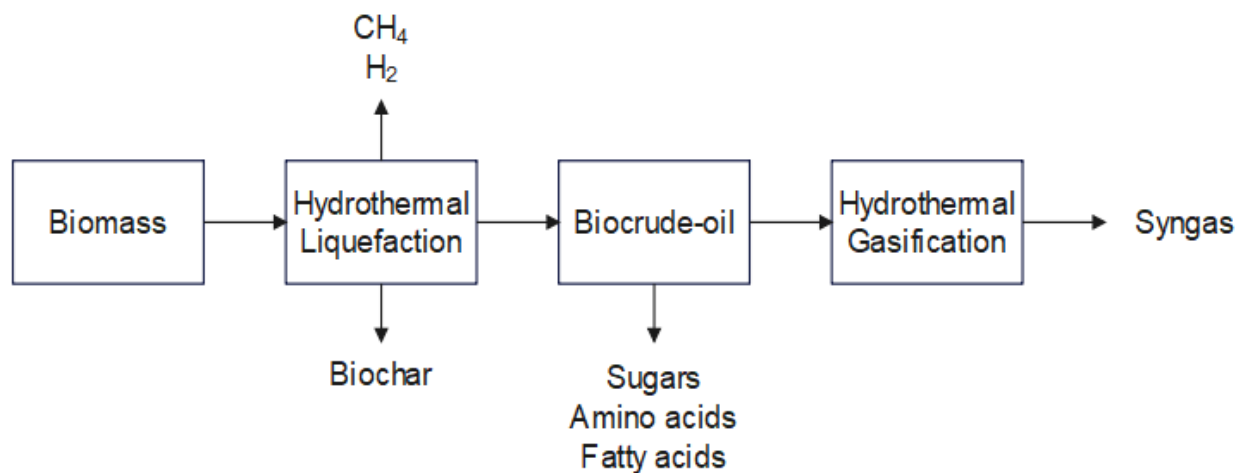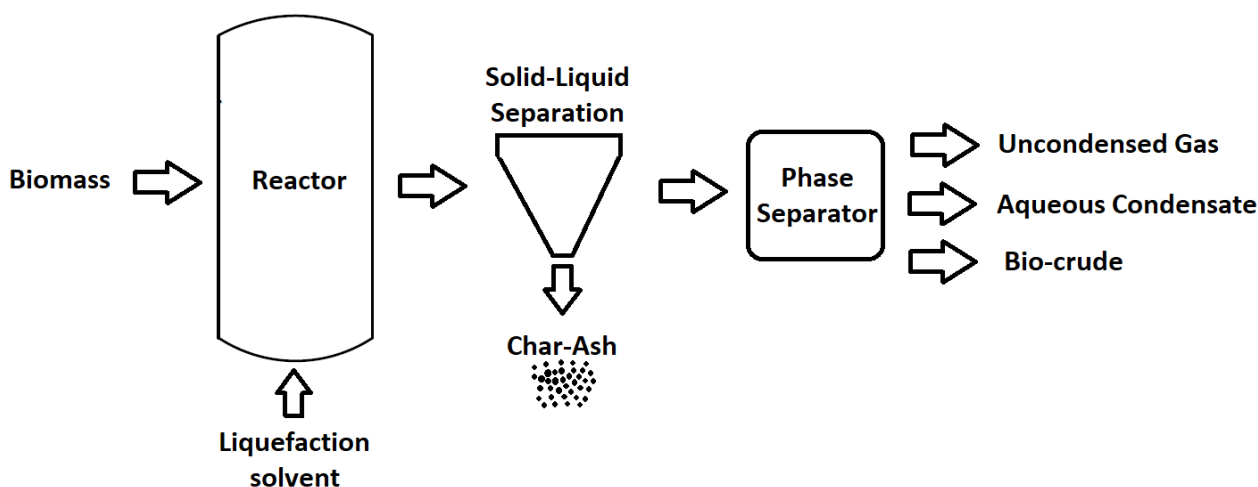

Scheme 3. Liquefaction process.

Figure 4. Liquefaction system scheme, own source based on the diagrams in [106,107].

In Table 4, it can be seen that the effect of process parameters, such as temperature, pressure, catalyst, type of parameter, and reaction time are significantly important for

the production of H_2. In addition, liquefaction is mainly focused on the production of liquid fuels, and additional processes such as gasification are needed for the production of hydrogen. The best yields were obtained using Chlorella vulgaris and fruit pulp. It is also observed that all investigations were carried out in batch reactors, so a study of the economic and environmental feasibility of this method should be carried out.

Table 4. Operating conditions and results obtained through biomass liquefaction.

Biomass	Reactor	Reaction Conditions T (°C)/P (Mpa)/t (min)	Catalyst	H_2, mmol g^{-1}	Ref.
Coconut shell	Tubular batch	600 °C/ 23–25 Mpa	K_2CO_3	4.8	[77]
Fruit pulp	Batch	600 °C/ 25 Mpa	RU/activated charcoal	54.8	[100]
Microalgae	Batch	385 °C/ 26 Mpa	——	4	[101]
Chlorella Vulgaris	Non-stirred batch	350 °C/35 Mpa/ 30 min	——	30	[102]
Chlorella Vulgaris	Batch	350 °C/ Atmosphere /0–60 min	——	38–72	[103]
Scenedesmus obliquus	Batch	240–320 °C/ 5 Mpa/ 60 min	CaOH	5.55	[104]
Household waste	Batch	240–320 °C/5 Mpa/ 60 min	Bentonite/ $Nb - tTiO_2$	3.9	[105]

4. Technical and Economic Evaluations

Climate change and global warming have garnered a lot of interest due to the need to reduce anthropogenic emissions of greenhouse gases, which is why the low-carbon economy contributes to implementing new and profitable energy systems [108]. Therefore, renewable energy technologies, such as solar, wind, hydro, biomass, geothermal, and hydrogen, have been introduced to generate electricity to overcome the current environmental crisis [109]. An official report from the International Energy Agency (IEA) states that the demand for the use of fossil fuels to generate electricity has begun to decrease since 2019 [110]. Hydrogen is a very interesting energy carrier with an energy yield of 122 KJg^{-1}, which is 2.75 times more than the fossil fuels [111]. Solid biomass in the United States was estimated to be able to supply 48 million metric tons (MMT) of hydrogen per year [112].

Research shows that the cost of renewable energy has an indirect effect on attitudes towards the use of renewable energy through the associated impact on the perception of ease of use and perceived usefulness [110]. To optimize processes, biomass must be as cheap as possible according to Klein and Lepage, as conditions have a significant impact on cost, including energy to increase temperature and pressure, electricity used for equipment or reactions, and catalyst type and cost. Cost estimates are also affected by external factors, such as fluctuating fossil fuel prices, variations in a given country's biofuel policies, and emissions [113,114]. Biomass gasification represents an effective and promising conversion technology for different energy carriers/chemicals, it has promising potential to offer high energy-conversion efficiency (in the range of 57 to 59%), lower energy costs, and decarbonization penalties (around 2.2 to 3.5 net), and present negative carbon emissions [108]. One of the key characteristics of biomass-based sources is their potential renewability. The overall efficiency of power generation from biomass is low (15–30%) [115]. The gasification life cycle cost was 35% lower than a single gas system. For systems with large biomass gasification, the capital cost is considered to be around USD 700/kW of hydrogen. The results show that forestry-residue-derived hydrogen is economically competitive (USD 1.52–2.92/kg H_2) compared to fossil-derived hydrogen [116].

Studies on the techno-economics of the fast pyrolysis of corn stover to hydrogen production demonstrate a production cost of USD 2.1–3.09/kg of H_2 [85]. The cost of producing hydrogen gas should typically be near to USD 0.3/kg H_2, which is equivalent

to the cost of gasoline (USD 2.5/GJ) [111]. The biogas production cost of these types of processes should be considered. These expenditures, therefore, cause the production cost of hydrogen using biomass materials to be in the range of USD 1.2–2.4/kg, while natural gas reforming can produce hydrogen with a cost of less than USD 0.8/kg [113].

5. Main Remarks and Conclusions

Hydrogen is considered the fuel of the future; however, obtaining it still presents great challenges. In order for it to be environmentally sustainable in the long term, it must be generated from resources that are renewable and carbon neutral. In this sense, the main raw material that meets these conditions is lignocellulosic biomass, which is characterized by its abundance and low cost. It is considerably cheaper than crude oil in energy terms. From the thermochemical methods reviewed in this study, it can be observed that the types of biomasses mostly used are wood and woody biomass. This is due to the fact that they have a lower moisture content and a greater amount of lignin compared to herbaceous biomass, which would imply a lower energy cost in drying processes; however, there are also various studies for different types of algae.

Tables 2–4 present the different biomasses used for the production of hydrogen as well as the reaction conditions and the results obtained with the main thermochemical methods that have been developed. The pyrolysis and gasification methods are those that have seen the most research and are considered in the literature as economically viable and competitive with the conventional method of natural gas reforming. The product obtained in gasification with steam is 1–6 g without the application of a catalyst and 6–8 g with a catalyst for every 100 g of biomass, which makes evident the necessity of a catalyst in this process, managing to improve the performance of H_2, as well as energy costs, due to the decrease in the conditions of both temperature and reaction time. Additionally, the biggest drawback of gasification is the production of tar because it causes serious problems for the subsequent use of synthesis gas; therefore, the optimization of the catalyst is essential to improve this method. Another important aspect is the type of reactor used. Performance improvements can come from new designs, such as catalytic membrane reactors, which improve syngas conversion by changing the equilibrium of the reaction. Regarding the results obtained in the biomass pyrolysis-reforming process in two steps, they are encouraging as an alternative form of biomass gasification. The main advantage of this process is that a tar-free product is obtained, which is the biggest challenge of gasification; however, the deactivation of the catalyst, especially its stability, must be taken into account for future studies so that this method can be scaled. For its part, the liquefaction process is still under investigation, with studies using only batch reactors. This method is promising because it does not require biomass pretreatment, which implies a lower energy cost corresponding to drying processes. Because this method is still under investigation, the reaction conditions are not optimized, being very severe and with very low yields.

In the future, the conversion of biomass to hydrogen will largely depend on many factors, including the availability of biomass, technological development, measures taken to solve the problems mentioned above, and political regulations on clean fuels.

Author Contributions: Writing—original draft preparation, L.J.-C.; and M.A.-G.; writing—review and editing, V.P.-V. and L.J.-C. All authors have read and agreed to the published version of the manuscript.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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