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Review

Advances in Bio-Hydrogen Production: A Critical Review of Pyrolysis Gas Reforming

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Abstract: Supplying the growing energy demand of emerging economies by utilizing available biogenic streams will be a key challenge in the coming years. Hydrogen is a promising alternative energy carrier to support the transition of the energy sector and other industries. In recent years, the use of biomass as a renewable energy source for bio-based hydrogen production has gained significant attention due to its potential to reduce environmental impact. Among the various thermochemical processes, biomass pyrolysis can be used to produce hydrogen, though the current use of this process is limited. Reforming the volatile fraction of biomass pyrolysis products has been only marginally explored, differently from gasification; the reforming of pyrogasses can then be seen as a viable method to enhance hydrogen yield. This review explores the key factors influencing hydrogen yield, including operating conditions and the role of catalysts. It is noteworthy that most of the studies evaluated in this review are in the laboratory and pilot scales, and the focus of this study is on the slow pyrolysis process in the first stage. Findings indicate that hydrogen production can be significantly improved with the proper choice of catalysts, with metal-based and nonmetal-based catalysts among the most effective. The outcomes of this review highlight the key effect of increasing the reforming temperature and steam-to-biomass ratio to enhance hydrogen production.

Keywords: hydrogen production; biomass pyrolysis; volatile reforming; catalysts; steam reforming; decarbonization

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1. Introduction

Energy demand has increased considerably all over the world during recent decades and it originates from different reasons such as the increasing population, changing lifestyles due to technological advancement, economic development, and rising life standards [1]. Hence, providing required energy while securing supply is currently an important challenge, for many regions in the world. Fossil-based fuels are still the primary energy resource; recently published data show that the share of fossil fuels in primary energy consumption worldwide was about 81.5% in 2023 [2]. At the same time, environmental concerns related to the use of fossil-based resources for energy production are growing. The use of fossil-based fuels is associated with a considerable amount of greenhouse gas (GHG) emissions [3]. Considering the current use of fossil fuels globally, the importance of pushing for sustainable alternatives has been stressed over recent decades. As a result of policies aiming at curbing the environmental impact of energy production, the share of renewable and sustainable fuels increased consistently during these years: the share of renewable energy in primary energy consumption from 2012 to 2023 increased from 9.42% to 14.56%, worldwide [4].

Among the potential substitutes for fossil fuels, hydrogen has been identified for its potential to be a carbon-free energy carrier. As an innovative energy carrier, hydrogen can perform a vital role in environmental decarbonization, when sustainably produced [5]. A key function of the hydrogen economy is the possibility to support the implementation of the growing contribution of renewable resources such as wind and solar energy, by addressing the critical aspect of their intermittent nature [6]. Furthermore, hydrogen can play a key role in the decarbonization of hard-to-abate industrial sectors, like steel and cement making [7]. These convincing advantages stimulate experts to research the various aspects of the hydrogen value chain, including production, transport, storage, etc. Hydrogen can be produced by using different kinds of resources. It must be mentioned that hydrogen production from fossil fuels accounted for 96% of total production in 2021, and renewable sources had only a 4% share of global production [8]. Reforming oil and gas is the main technology for hydrogen production, covering 78% of the total [9]. However, large-scale clean hydrogen production methods have gained interest during these past years. The increasing trend of renewable energy production, such as wind, solar, and biofuel energy, provides a great opportunity to develop clean and environmentally friendly routes to produce hydrogen [10].

The water electrolysis process can be implemented to produce hydrogen by decomposing water, and the electricity produced by renewable energies such as wind and solar can be used for this purpose. A polymer electrolyte membrane (PEM) electrolyzer is one of the technologies that can be used for water electrolysis. Producing high-purity hydrogen (99.99%), a compact design, and enabling fast responses during load variation are the advantages of this technology [11,12]. Alkaline electrolyzers are another technology for water electrolysis and they can also reach high purity levels. This technology has the capability to produce hydrogen in a few hundred MW, although gas permeation caused by using a diaphragm is one of the significant drawbacks of it. It must be noted that the operation temperature of PEM electrolyzers and alkaline electrolyzers is relatively low [12,13]. A solid oxide electrolyzer (SOE) is another electrolysis technology with an operating temperature higher than 500 °C, which results in an efficiency increase. Also, an oxygen ion can be used for steam decomposition, which operates up to 1000 °C. However, this temperature leads to some problems, such as degradation and challenges in selecting materials for electrodes and catalysts [14,15]. Although the technology readiness levels (TRLs) of alkaline and PEM electrolyzers are 9 and 8, respectively [14], there is still room for improving materials' life-time and energy efficiency [16]. Existing challenges of hydrogen production by water electrolysis, such as high production costs, the cost of some rare materials, and corrosive environments, have led to other production methods being considered [17].

Hydrogen production using biomass has attracted much interest in recent years [18–20], as biomass resources can play a crucial role in reducing GHG emissions. Energy crops, agricultural residues, industrial and municipal waste, and forestry waste are examples of different types of biomass that can be used as feedstock to produce energy [21]. Based on the IRENA's renewable energy map, the predicted share of biomass among renewable resources in total final energy consumption in 2050 will be 30% [22]. Converting biomass feedstocks to heat or power is one of many possible routes to produce energy; other processes can convert biomass to secondary energy sources and energy carriers, such as hydrogen [23].

Thermochemical and biological processes are the main routes for hydrogen production using biomass as feedstock. The thermochemical pathway is much faster than biological processes and the hydrogen yield is typically higher [24]. Conversely, biological conversion processes are typically considered more robust and technologically mature [25]. Thermochemical processes include gasification, pyrolysis, and hydrothermal liquefaction (HTL).

The gasification process is designed to convert biomass to a combustible gas mixture in the controlled presence of oxidation agents, such as oxygen, air, or steam, and the high temperature of this process increases hydrogen yield [24,26,27]. The main products of this process include CO, H_2, H_2O, CO_2, CH_4, and other hydrocarbons [23], and the temperature range for gasification is between 600 °C and 1200 °C [28]. Many research studies at different scales have investigated H_2 production using the gasification method. The steam gasification of pine sawdust at the laboratory scale was performed by Luo et al. to assess hydrogen production [29]. The temperature range was considered between 600 °C and 900 °C to assess its effects on hydrogen production. Results demonstrated that increasing temperature raised hydrogen production, and the maximum hydrogen yield was 7.3 wt% at 900 °C. Fremaux et al. [30] investigated hydrogen production via the steam gasification of waste wood as a feedstock on a bench scale with a 2.5 kg/h capacity. The reaction temperature and steam-to-biomass ratio were set to 900 °C and 1, respectively. The obtained results showed a 5.9 wt% hydrogen yield. Also, the results of pine wood pellets' steam gasification at 800 °C at a pilot plant showed 1.8 wt% hydrogen production [31]. However, there are some disadvantages in this process which conversely affect hydrogen production. The need for additional catalytic processes to increase hydrogen production by gasification is another disadvantage of this route. Also, one of these drawbacks is catalyst deactivation by sintering at high temperatures [28].

Pyrolysis is a thermochemical process that converts biomass into various types of products in the absence of oxygen; process outputs include liquid oils (bio-oil), solids (biochar), and non-condensable gasses. While the condensable part is also referred to as bio-oil, and contains complex organic compounds, the non-condensable part includes gasses, such as carbon monoxide, carbon dioxide, hydrogen, and methane. The composition of pyrogas in different studies are shown in Table 1. The main components of biomass include cellulose, hemicellulose, and lignin, which are decomposed at different temperatures; 200 °C to 327 °C, 327 °C to 450 °C, and 200 °C to 550 °C are the mass loss temperature ranges of hemicellulose, cellulose, and lignin, respectively [32]. Also, depolymerizing lignin components is more challenging due to its composition, which is mostly constituted by aromatic polymers [33]. The main products of decomposing lignin are hydrogen and methane [34]. It must be mentioned that the share among the products is significantly affected by the operating conditions for the pyrolysis process, such as temperature, residence time, and pressure. The heating rate (°C/s) is used to classify the pyrolysis process as slow, intermediate, and fast [23,35]. Also, there are other conditions that are typically common in different types of pyrolysis process, such as residence time and hot vapor residence time [36]. In recent decades, pyrolysis has received considerable attention because of its advantages, such as energy efficiency and the possibility for direct biomass conversion into a wide range of products. Additionally, the lower operating temperature and pressure than those in gasification and HTL are other advantages often referred to in relation to pyrolysis [37]. A comparison of different hydrogen production processes is shown in Table 2.

Different research studies related to hydrogen production via pyrolysis can be categorized based on the investigated production routes. While some of these studies have only one pyrolysis stage, other methods, including catalytic reforming, contain additional steps to increase hydrogen yield [28]. Reforming pyrolysis volatiles is one of the most interesting routes for hydrogen production which has attracted a lot of interest in recent years. Although there are many studies related to hydrogen production from gasification processes, the advantages of reforming pyrolysis volatiles compared to biomass gasification, such as the complete conversion of volatiles, avoiding catalyst deactivation by sintering, and more suitable conditions for optimizing processes in two separate reactors, highlight the importance of assessing this thermochemical method [28]. However, the existing body of knowledge lacks comprehensive and extensive reviews to assess its impacts on hydrogen yield compared to those of pyrolysis processes. Also, with a detailed observation of recent research studies, it can be inferred that there is a gap in the identification of effective factors and their impacts on hydrogen yield in the catalytic reforming of pyrolysis volatiles and its comparison with pyrolysis processes. The aim of this study is to fill existing gaps by covering all new studies about hydrogen production by the two-stage catalytic reforming of pyrolysis volatiles. This paper compares this technological option with hydrogen yield in standard pyrolysis processes to explore the possible advantages of this two-stage process. Also, important factors affecting hydrogen production are evaluated in this study to understand their role in this process and optimize it to maximize hydrogen yield. It is worth mentioning that the focus of this review is on the slow pyrolysis process for reforming pyrolysis volatiles, although a few studies relevant to other types of pyrolysis are also evaluated. The assessment of this process can play a key role in increasing hydrogen production and pave the way for large-scale economical hydrogen production from biomass feedstock.

Table 1. Pyrogas composition in different studies.

Pyrolysis Process Type (Temperature)	Feedstock	H_2 (vol%)	CO (vol%)	CO_2 (vol%)	CH_4 (vol%)	C_{2+} (vol%)	N_2 (Vol%)	O_2 (vol%)	Ref.
Slow (650)	Waste wood	7	30.5	44.7	14.7	3.1			[38]
	Cardboard	13.4	36.6	32.4	15.3	2.3			
	Textile	5.4	34.7	35.6	19.2	5.1			
Slow (500)	Neem seed	6.89 ± 1	0.46 ± 0.3	7.16 ± 1	15.87 ± 2			18.46 ± 2	[39]
	Pigeon pea	4.66 ± 1	1.60 ± 1	8.93 ± 1	21.57 ± 2			14.58 ± 1	
	Yellow pea	0.15± 0.1	1.30 ± 1	11.23 ± 1	24.77 ± 2			15.56 ± 2	
	Ground nut shell	5.02 ± 1	10.16 ± 1	6.97 ± 1	13.21 ± 1			10.93 ± 1	
	Channa straw cicer	4.36 ± 1	14.02 ± 1	6.94± 1	19.93 ± 2			10.58 ± 1	
	Soyabean Straw Glycine	8.29 ± 1	13.85 ± 1	7.80± 1	18.53 ± 2			10.60 ± 1	
	Wheat straw	7.05 ± 1	7.51 ± 1	5.62 ± 1	18.70 ± 2			13.38 ± 1	
	Sawdust	7.11 ± 1	6.26 ± 1	4.93± 0.5	22.25 ± 2			15.40 ± 2	
Slow (600)	Olive stone	29.47	31.48	14.1	20.5	3.65		0.8	[40]
Fast (550)	Sawdust	4.54	34.49	16.8	4.41		35.55	4.25	[41]
Fast (550)	Woody biomass	7.01	24.13	36.35	4.41	28.1			[42]

Table 2. Comparison of different hydrogen production processes [43–45].

Process	Advantages	Disadvantages	Efficiency (%)
Steam methane reforming	Mature technology, low production cost	GHG emissions, fossil fuel resource depletion	74–85
Partial oxidation	Proven technology	GHG emissions, fossil fuel resource depletion	60–75
Electrolysis	Mature technology, no emissions, cheap and available feedstock, O_2 byproduct	Low overall efficiency, high capital cost, corrosion challenges	40–60
Biomass pyrolysis	Cheap feedstock, CO_2-neutral	Tar formation, seasonal availability of and impurities in feedstock	35–50
Biomass gasification	Cheap feedstock, CO_2-neutral	Tar formation, seasonal availability of and impurities in feedstock	35

2. Hydrogen Production by Using Pyrolysis Process

Different types of pyrolysis processes, including slow, intermediate, fast, and flash ones, have been used to produce hydrogen. Many studies in the literature report the composition and yield of pyrolysis gas and hydrogen content, considering different conditions in the pyrolysis process, such as the temperature, residence time, and heating rate.

Experimental results of cotton stalk slow pyrolysis at 300 °C, 400 °C, and 500 °C showed the product compositions and distribution. The heating rate and residence time of this process were set to 10 °C/min and 1 h. While the maximum char yield was 58.54 wt% at 300 °C, maximum gas and bio-oil production was achieved at 500 °C, which yielded 36.6 wt% and 25.25 wt%, respectively. Analysis of the pyrolysis gas showed that it mainly contained carbon dioxide and hydrogen, in the range of 0.26, 0.35, and 0.54 wt% at 300 °C, 400 °C, and 500 °C, respectively [46]. A slow pyrolysis experiment of waste wood with a 30 °C/min heating rate was performed at different temperatures, and the main components of the pyrolysis gas composition were measured. Hydrogen production results showed that it slightly increased between 500 °C and 700 °C, but it was enhanced considerably in the 700–800 °C temperature range. The hydrogen concentration at 800 °C increased to 42.7 vol% [47].

Rice straw slow pyrolysis was explored to evaluate the effect of temperature on product yield distribution and product compositions. The results of pyrolysis gas composition showed a low increasing trend in hydrogen from 300 °C to 500 °C, which was enhanced from 1.9% to 9.08%, and after that, it increased up to 17.72% by increasing the pyrolysis temperature from 500 °C to 600 °C [48]. The pyrolysis of wood sawdust at 500 °C was performed to explore the product's distribution and composition, and the results of the pyrolysis gas composition (mol) showed 6.7% hydrogen [49]. Hydrogen production was investigated using the pyrolysis process with rice straw and sawdust at 500 °C, 750 °C, and 850 °C. The obtained results demonstrated that increasing the pyrolysis temperature enhanced gas product distribution by up to 40.6%. Also, the results showed that the hydrogen yield by pyrolyzing the rice straw and sawdust at 500 °C was 41.2 wt% and 40.6 wt% of pyrolysis gas, respectively. Additionally, the highest hydrogen yield for the pyrolysis of sawdust and rice straw was 47 and 48.2 mmol/g, respectively [50].

Rice husk slow pyrolysis results considering the temperature range between 400 °C and 600 °C demonstrated that hydrogen yield increased up to 15 vol% at 600 °C, and the minimum hydrogen yield was less than 5 vol% at 400 °C. Also, these results show the beneficial effect of increasing temperature on hydrogen yield in the slow pyrolysis process [51]. Sugar cane bagasse slow pyrolysis showed that hydrogen volume in produced volatiles was increased considerably from 9.6 vol% to 28.8 vol% by increasing temperature from 480 °C to 680 °C. Also, pyrolysis gas yield was enhanced from 25.1 wt% to 35.67 wt% in this temperature range. Additionally, fast pyrolysis results for sugar cane bagasse were reported in this study. While these obtained results showed that hydrogen volume in the produced syngas increased dramatically from 8.7 vol% to 45.3 vol% in the mentioned temperature range, a slight increase in pyrolysis gas yield was observed [52]. An experiment was performed by Guizani et al. to investigate the effects of woody biomass fast pyrolysis on product distribution and mass balance. The pyrolysis gas composition showed that the hydrogen concentration in the pyrolysis gas was enhanced from 1.7 vol% to 12.7 vol% by increasing temperature from 450 °C to 600 °C. Also, the pyrolysis gas yield increased by 45.4 wt% in this temperature range [53]. The fast pyrolysis of 14 live and dead plant species was performed to collect related data on pyrolysis product distribution, composition, and concentration. Average light gas composition data showed 1.7 wt% and 1.5 wt% hydrogen yields for the live and dead species, respectively [54].

3. Hydrogen Production by Catalytic Reforming of Pyrolysis Volatiles

Using two-stage pyrolysis and catalytic reforming to produce hydrogen has been gaining momentum because of its advantages compared to other biomass-to-hydrogen routes. Under this approach, the pyrolysis of biomass takes place in the first step, where the feedstock is converted into pyrolysis volatiles, including condensable and non-condensable fractions, and biochar. In the following step, pyrolysis volatiles may be reformed in the catalytic reformer. Figure 1 shows the concept of a two-stage process to reform pyrolysis volatiles.

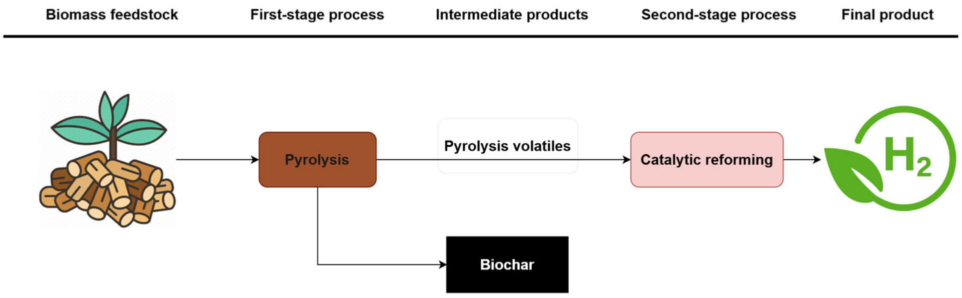

Figure 1. Catalytic reforming of biomass pyrolysis volatiles.

This two-stage configuration has the advantage of a considerable increase in gas production and a decrease in bio-oil production. The advantage of the two-stage approach is related to the opportunity to convert pyrolysis volatiles in the second reactor, including the non-condensed bio-oil fraction. For instance, in comparing gas product distribution between pyrolysis and the reforming of pyrolysis volatiles for palm kernel shell, performed by K. Akubo et al. [33], a 66.1% increase in gas yield could be observed. The results of another research study showed that gas distribution increased by 7.64% without any catalyst. Also, Ni-based and Co-based catalysts with 10% loading enhanced gas production (wt%) by 25% and 43.76% compared to the pyrolysis process, respectively [55]. Additionally, based on the literature, an increase in hydrogen yield is another important result of reforming pyrolysis volatiles. In the case of palm kernel shell, hydrogen yield was enhanced from 6.62 mmol/g to 25.35 mmol/g by reforming pyrolysis volatiles [33]. Figures 2 and 3 show the effects of reforming pyrolysis volatiles on hydrogen yield and gas product distribution compared to the single pyrolysis process.

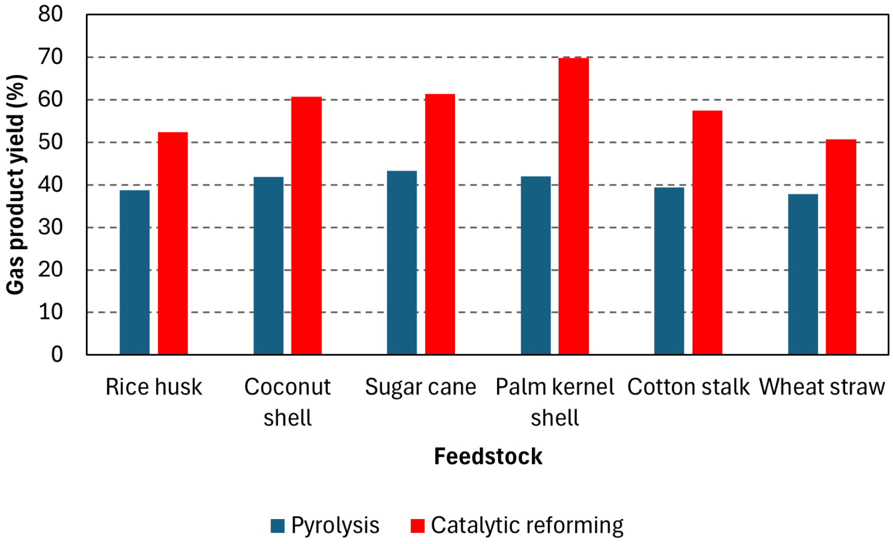

Figure 2. Comparing gas product yield between processes of pyrolysis and reforming of pyrolysis volatiles [33].

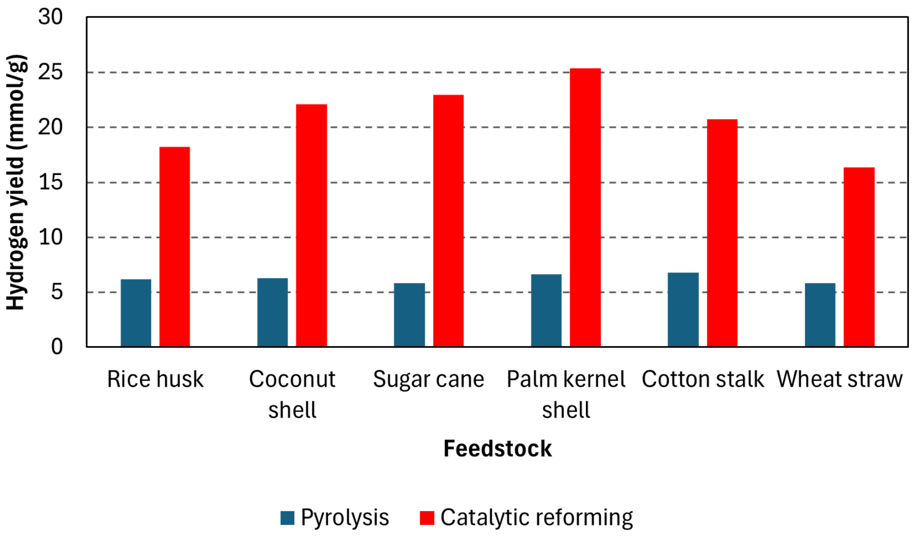

Figure 3. Comparing hydrogen yield between processes of pyrolysis and reforming of pyrolysis volatiles [33].

The separation of pyrolysis and reforming steps provides an opportunity to control and optimize these processes more efficiently [56]. This configuration has the additional advantage of avoiding direct contact between the feedstock impurities and the reforming catalyst [57]. Additionally, preventing catalyst sintering and achieving the full conversion of pyrolysis volatiles using highly active reforming catalysts, such as the commercial Ni catalyst, are other significant advantages of this configuration [28,58,59]. Moreover, considering the process description and the possibility of using a highly active reforming catalyst to achieve complete conversion, there is no need to condense pyrolysis products and design complicated steps to cope with them. Additionally, the simplicity of scaling up this two-stage process with continuous feed is its most significant advantage [28]. Producing syngas by consuming greenhouse gasses (CO_2 and methane) in the dry reforming process is another significant advantage of it [60]. A two-stage fixed-bed reactor was used for experimental studies of this process on a laboratory scale [33,61,62] and the schematic of the pyrolysis and catalytic reforming process is shown in Figure 4.

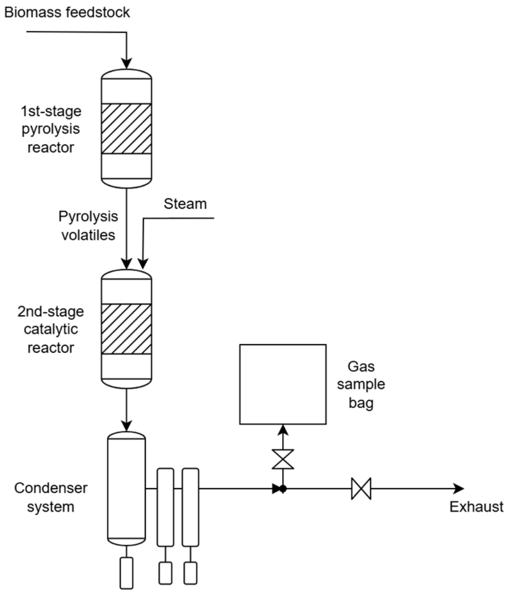

Figure 4. Commonly used configuration of reactor to reform pyrolysis volatiles [33].

Different reactions take place in this process, such as pyrolysis, the catalytic reforming of hydrocarbons and tars, the catalytic cracking of tar, char gasification, etc. Table 3 shows the most significant reactions occurring in the two-stage process of reforming pyrolysis volatiles.

Table 3. All possible reactions in the process of reforming pyrolysis volatiles [33].

Reaction	Description
Biomass $\rightarrow H_2O + H_2 + CO + CO_2 + C_xH_yO_z + C_xH_y +$ char	Biomass pyrolysis
$C_xH_yO_z \rightarrow H_2O + H_2 + CO + CO_2 + CH_4 + C_nH_m$	Catalytic tar cracking
$C_xH_yO_z + H_2O \rightarrow H_2 + CO$	Tar steam reforming
$C_nH_m + H_2O \rightarrow H_2 + CO$	Hydrocarbon volatile steam reforming
$C_xH_yO_z + CO_2 \rightarrow H_2 + CO$	Tar dry reforming
$C_nH_m + CO_2 \rightarrow H_2 + CO$	Hydrocarbon volatile dry reforming
$CO + H_2O \rightarrow CO_2 + H_2$	Water gas shift
$C + H_2O \rightarrow CO + H_2$	Char steam gasification
$C + CO_2 \rightarrow 2CO$	Char CO_2 gasification

Considering the existing literature, different factors affect this two-stage process, such as the heating rate, the pyrolysis temperature, and catalysts. Identifying and analyzing these factors and their effects play a vital role in better and more accurately understanding the process. This literature review shows that slow, intermediate, and fast pyrolysis processes can be considered for the first stage of this process. Pyrolysis type is used in this study to create a categorization for this two-stage process and evaluate the effects of different factors.

3.1. Slow Pyrolysis

Slow pyrolysis is characterized by a slow heating rate and typically high residence times, and it is one of the common processes used in the first stage of the process [63–66]. The following section investigates the impacts of different factors on the two-stage process of reforming slow pyrolysis volatiles.

3.1.1. Pyrolysis Temperature

Pyrolysis temperature can be considered a key operating condition in the two-stage catalytic reforming and pyrolysis process. Generally, increasing pyrolysis temperature has a beneficial effect on gas yield. The impacts of increasing wood sawdust pyrolysis temperature were investigated in a research study performed by Olalaye et al. [67] to compare numerical modeling results with experimental results. The obtained experimental results showed that increasing the pyrolysis temperature from 300 °C to 600 °C and reforming pyrolysis volatiles at 800 °C increased gas distribution considerably, so the gas yield increased from 21.65 wt% to 58.04 wt%. Furthermore, the hydrogen yield increased from 4.24 mmol/g to 11.01 mmol/g in this temperature range [67]. A comparison of two studies using waste wood as a feedstock for the catalytic reforming of pyrolysis volatiles at 800 °C in the presence of a Ni-based catalyst showed that the hydrogen yield was enhanced from 10.5 mmol/g up to 27.52 mmol/g by increasing the pyrolysis temperature from 600 °C to 800 °C [61,62]. Increasing pyrolysis temperature can beneficially affect gas production and hydrogen yield in the two-stage process. The effect of pyrolysis temperature on hydrogen yield in the catalytic reforming of woody biomass pyrolysis volatiles is reported in Figure 5.

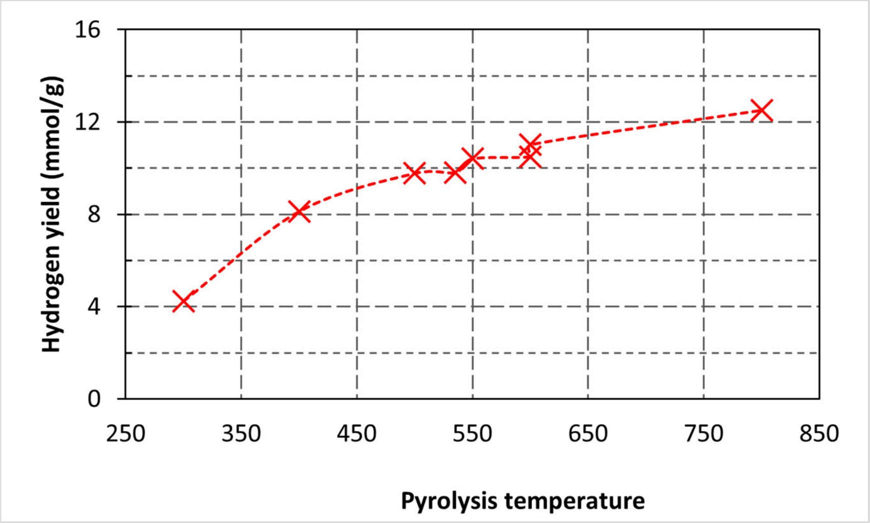

Figure 5. Effect of pyrolysis temperature on hydrogen yield and its trendline [61,67–70].

3.1.2. Reforming Temperature

Different research studies show that reforming temperature is among the most relevant factors impacting hydrogen yield. Rjeily et al. [71] investigated the two-stage pyrolysis and catalytic reforming of oak wood. The temperature range of the catalytic reforming was from 700 °C to 800 °C, and three different catalysts were used in this experimental study. The results proposed by the authors showed that using the nickel catalyst, the hydrogen production volume increased from 34.1% to 41.7% when the reforming temperature increased from 700 °C to 750 °C. Also, it could be seen that the hydrogen production volume was decreased by 0.6% by additionally increasing the reforming temperature from 750 °C to 800 °C. Moreover, the results indicated that the hydrogen production volume using a cobalt catalyst at 700 °C, 750 °C, and 800 °C was 22.7%, 31.1%, and 32.1%, respectively. Based on the results, the hydrogen concentration with the Ni and Co-Ni catalysts was maximized at 750 °C [71].

Jaffar et al. [62] analyzed syngas production using biowaste as a feedstock and a three-stage process including pyrolysis, catalytic steam reforming, and catalytic hydrogenation. Waste wood sawdust was used as a feedstock in this study and the selected catalyst for the first two steps of the process was a 10 wt% Ni catalyst loaded on an Al_2O_3 support. It must be mentioned that the weight of the biomass sample and catalyst for the steam reforming step was 1 g. The temperature range for catalytic reforming in this study was 600–900 °C. The results showed that increasing the reforming temperature from 600 °C to 900 °C led to an increase in the hydrogen yield from 26.8 to 28.94 mmol/g of biomass. Also, the hydrogen volume percentage was decreased from 72% to 60.4% by increasing the reforming temperature in this range. Also, the results of the experiments revealed that the H_2/CO ratio was decreased by 108.8% by increasing the reforming temperature from 600 °C to 900 °C [62]. The effect of reforming temperature on syngas and hydrogen gas yield was also evaluated by Wang et al. [66]; they performed an experiment by using a two-stage fixed-bed reactor to study the influence of different factors on syngas yield. Using a 10 wt% Ni/char catalyst to reform poplar wood pyrolysis gas, they showed that increasing the temperature from 600 °C to 700 °C increased the hydrogen yield from 23.186 mmol/g to 26.767 mmol/g.

Zhao et al. [72] also used the pyrolysis and catalytic reforming process to produce hydrogen-rich gas from corncob feedstock and natural limonite ore as a catalyst. In their experiments, the reforming temperature increased from 400 °C to 750 °C, and results showed that the hydrogen yield increased by 191.7 percent over this range. Moreover, the maximum hydrogen yield was observed between 400 °C and 500 °C, when the hydrogen yield increased by 73 percent to 31.4 mmol/g. The obtained results also showed that the hydrogen yield was not significantly affected by increasing the reforming temperature above 700 °C, as they reported that this value increased only 1.15 percent to reach 52.8 mmol/g. The presented results also demonstrated that the hydrogen volume concentration was 59.2 vol% at 400 °C, and increasing the reforming temperature to 750 °C resulted in increasing the hydrogen volume up to 71 vol% [72]. Figure 6 shows the effect of reforming temperature on hydrogen yield in different research studies. There are considerable differences between hydrogen production in these three studies, and they originate from the various conditions of these experiments, such as the pyrolysis temperature, catalyst, and feedstock. In this case, hydrogen production at 700 °C was significantly higher for the Zhao et al. study because the pyrolysis temperature of this experiment was 900 °C [72], and it was the main factor that led to higher hydrogen production compared to that in the other two studies. It is worth mentioning that the pyrolysis temperatures of X. Xiao et al.'s and Al-rahbi and Williams's studies were 700 °C and 500 °C, respectively [70,73], indicating the reason for the difference in hydrogen production.

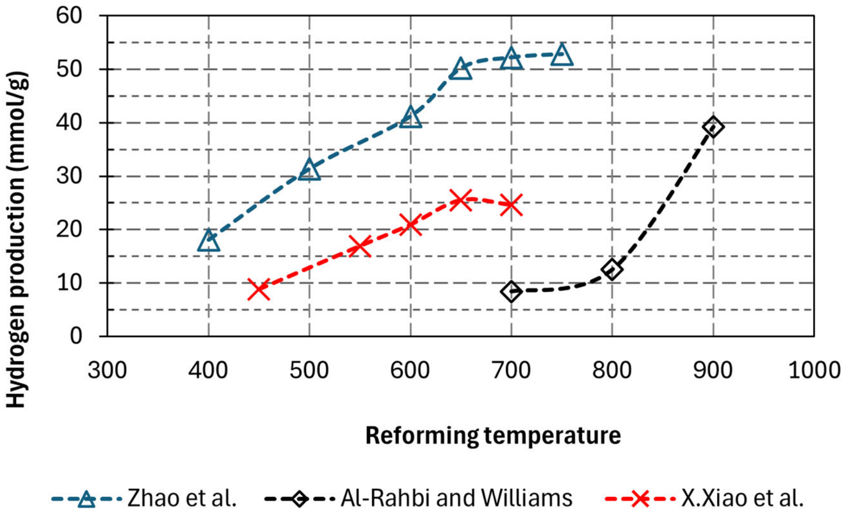

Figure 6. Effect of reforming temperature on hydrogen yield [70,72,73].

3.1.3. Steam-to-Biomass Ratio

Steam is one of the most common reforming agents and can be used for reforming pyrolysis volatiles. The use of steam has important advantages, as highlighted by many authors [73,74]. Promoting the reforming process and limiting coke deposition on the catalyst surface are among the main reported advantages of using steam in this step of the process [73,75]. According to research performed by Wang et al. [76], reforming corncob pyrolysis volatiles at 650 °C over nickel with a Shenli lignite char catalyst showed that introducing steam as a reforming agent increased the gas yield up to 85.1 mmol/g, and this amount was twice as great compared to that of the gas yield in the reforming process without steam. While the hydrogen yield was 21.3 mmol/g without using steam as an agent in the reforming process, hydrogen production was enhanced by 279.8% and reached 61.9 mmol/g [76]. Another research study performed by Cao et al. [77] assessed the effects of using steam and a Ni–exchanged resin char catalyst on reforming corncob pyrolysis volatiles at 650 °C. Gas yield results demonstrated that the steam reforming process produced 84.5 mmol/g of gas, 80% more than the reforming process without steam. In addition, the hydrogen yield increased to 61.2 mmol/g, which was 37 mmol/g more than that supplied by the non-steam reforming process [77].

The impact of the steam-to-biomass (S/B) ratio is another important factor investigated in the literature. This ratio was considered between 1.8 and 6 for the reforming of wood pellets pyrolysis volatiles at 900 °C using tire-derived char as a catalyst. According to the results of the study, increasing the S/B ratio from 1.82 to 3.32 led to a 28% gas yield increase. Also, hydrogen production was enhanced from 17.2 mmol/g to 33.6 mmol/g in this range. However, the results of increasing the S/B ratio from 3.32 to 4.32 and then up to 6 demonstrated its negligible effects on gas yield. Hydrogen yield was also evaluated in this range, and the results showed that it was 33.6 mmol/g, 35.1 mmol/g, and 42.8 mmol/g at ratios of 3.32, 4.32, and 6, respectively. Therefore, a higher S/B ratio led to producing more hydrogen, although it did not have a considerable effect on the total gas yield [70]. Taking into account these results, optimizing the S/B ratio performs a key role in designing feasible processes from technical and economic points of view.

3.1.4. Space Velocity

Space velocity is another operating factor affecting product distribution in the two-stage pyrolysis and catalytic reforming process. Decreasing space velocity, which is equal to increasing residence time in the reforming process, has a beneficial impact on catalytic reactions in the catalyst bed, tar reduction, and enhancing gas yield [73,77]. Cao et al. [75] investigated the effects of increasing space velocity from 4000 h^{-1} to 8000 h^{-1} during the reforming of sewage sludge pyrolysis products at 650 °C. Their results showed that hydrogen production decreased considerably, taking into account the increasing space velocity trend. Also, carbon deposition was enhanced when space velocity was doubled. The gas yield results with space velocity decreasing from 7200 h^{-1} to 3600 h^{-1} and 2400 h^{-1} during the catalytic reforming of corncob pyrolysis volatiles demonstrated the beneficial influences of decreasing space velocity such that hydrogen yield increased from 14.2 mmol/g to 19 mmol/g and 24.8 mmol/g, respectively. Furthermore, the carbon monoxide yield was increased when the space velocity was reduced in the range of 7200 h^{-1} to 2400 h^{-1} [76]. Another experimental research study investigating the reforming process of corncob pyrolysis volatiles over natural limonite as a catalyst demonstrated the effectiveness of space velocity on gas yield and carbon balance [72]. The results showed that the gas yield increased from 36.22 mmol/g to 41.61 mmol/g when the space velocity decreased from 7200 h^{-1} to 3600 h^{-1}. However, a slight change in the gas and hydrogen yield could be seen with the space velocity decreasing to 2400 h^{-1} [72] These results from different research studies are very well aligned with the study performed by Uddin et al. [78], which indicates that lower space velocity and longer residence time are favorable for tar reforming and gas production.

3.1.5. Catalyst Type

Selecting the appropriate catalyst clearly has a significant role in designing the two-stage pyrolysis and reforming process, in order to achieve hydrogen-rich gas. Reviewing existing research articles shows that different types of metal-based catalysts such as Ni, Co, Pt, Fe, or Rh can be used for this process. Efika et al. investigated the effects of different catalysts, including NiO/Al_2O_3, $NiO/CeO_2/Al_2O_3$, and NiO/SiO_2. The obtained results showed that hydrogen productions of 44.4 vol%, 43.1 vol%, and 37.6 vol% were achieved by using NiO/Al_2O_3, $NiO/CeO_2/Al_2O_3$, and NiO/SiO_2, respectively [79]. Koike et al. also evaluated the effect of a $12Ni/MnO_xAl_2O_3$ catalyst on hydrogen production using a two-stage process. Their results demonstrated a 46.5 vol% hydrogen concentration [80]. The impacts of $Ni/CaAlO_x$ catalysts with various Ca/Al ratios on hydrogen production were assessed by Chen et al. Based on their results, a maximum hydrogen yield of 15.57 mmol/g was achieved using a 1:2 ratio, and the lowest hydrogen production of 12.97 mmol/g was achieved by a 1:2 ratio of Ca/Al [64]. Moreover, Jin et al. examined the effect of adding calcium to Mg-AlO_x-supported Ni catalysts. The results showed that adding calcium increased hydrogen production from 10.45 mmol/g to 18.2 mmol/g. Also, they evaluated the effect of using different calcium ratios on the two-stage process of reforming pyrolysis volatiles, and hydrogen production was maximized up to 21.4 mmol/g by using a 0.3 ratio of calcium [69]. From the analysis of the literature, it emerges that low-cost metal-based catalysts, e.g., Ni and Co catalysts, are the most used ones. Ni/Al_2O_3 is one of the most commonly used catalysts in experimental studies. Zhao et al. [72] assessed the effect of a Ni/Al_2O_3 catalyst on a two-stage process. Corncob was used as a feedstock, and the pyrolysis and catalytic reforming temperatures were set to 900 °C and 650 °C, respectively. The results of the catalytic steam reforming process showed a 51 mmol/g hydrogen yield. The impact of using Ni/Al_2O_3 as a catalyst was evaluated for the dry and steam reforming of pyrolysis volatiles of sewage sludge at 900 °C. Based on the obtained results, using a Ni/Al_2O_3 catalyst at 650 °C increased hydrogen production in the dry and steam reforming processes to 28 mmol/g and 53 mmol/g, respectively [75]. K. Olaleye et al. [67] performed an experimental study to assess the pyrolysis and catalytic reforming process. This study used 1 g of raw wood sawdust and 0.5 g 10 wt% Ni/Al_2O_3 as a catalyst to perform the experiment. The pyrolysis temperature range was considered between 300 °C and 600 °C, and the reforming temperature was set to 800 °C. The obtained results demonstrated that the hydrogen yield increased up to 11.01 mmol/g at 600 °C.

Moreover, other types of Ni-based catalysts, prepared by mixing nickel with other types of metals and non-metal materials, have been used in the literature to assess their effects on hydrogen yield in the two-stage process of reforming pyrolysis volatiles. The feasibility of using a novel catalyst by loading nickel on lignite char for the reforming of corncob pyrolysis volatiles was evaluated by Wang et al. [76], considering 900 °C and 650 °C for the pyrolysis and reforming temperatures, respectively. The results of using this catalyst showed that the gas yield increased by 209.1% and reached up to 44.2 mmol/g. The hydrogen yield also increased from 4.1 up to 21.2 mmol/g. Waheed et al. [63] investigated the effects of using a 10 wt% Ni–dolomite catalyst on the two-stage pyrolysis and steam reforming process. The pyrolysis and reforming temperatures were set to 950 °C, and three different feedstocks, including rice husk, sugar cane, and wheat straw were selected for this experimental study. Hydrogen production, by reforming pyrolysis volatiles and using the Ni–dolomite catalyst, was raised up to 23.71, 21.18, and 21.59 mmol/g for the rice husk, sugar cane bagasse, and wheat straw, respectively [63]. Ni–exchange resin char was another catalyst used to investigate the two-stage pyrolysis and reforming process of corncob, considering 900 °C and 650 °C for the pyrolysis and reforming temperatures, respectively. Gas composition analysis showed a significant gas yield increase due to using the Ni–exchange resin char of 3.32 times compared to that of the non-catalytic reforming. The obtained results showed that the hydrogen yield was increased up to 25 mmol/g using Ni–exchange resin char [77]. A research study performed by Dong et al. [68] evaluated the effects of nanosized $NiZnAlO_x$ catalysts on hydrogen production in two-stage pyrolysis and steam reforming. While the ratio of gas yield to wood sawdust when using a sand bed was 33 wt%, adding the $NiZnAlO_x$ catalyst with a 5% Ni molar ratio increased the gas yield to 49.3%. Also, the hydrogen yield, by using this catalyst, was increased from 2.4 mmol/g to 8.2 mmol/g. It is worth mentioning that hydrogen production, due to using $NiZnAlO_x$ with a 35% Ni molar ratio, increased to 20.1 mmol/g, which was about 737.5% more than that from the process without using a catalyst [68]. Figure 7 shows the effects of various catalysts on hydrogen yield.

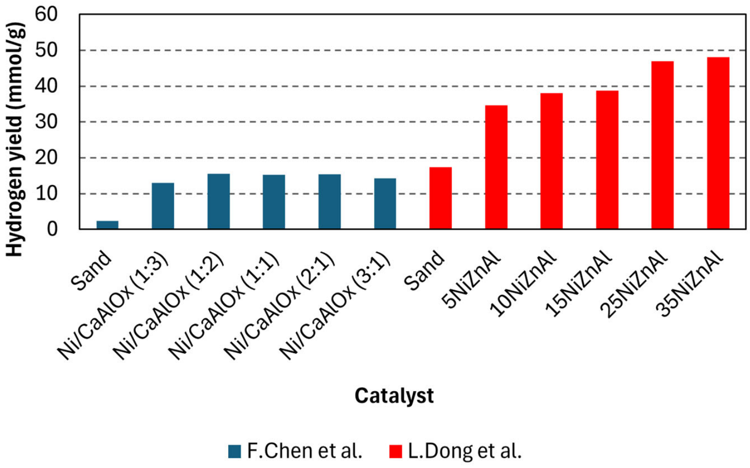

Figure 7. Effect of using different catalysts on hydrogen yield [64,68].

The impacts of using other types of materials as catalysts have been investigated by research studies. Tire char, which can be produced by the pyrolysis of waste tires, is one of the materials used as a catalyst for the reforming pyrolysis of wood pellet volatiles. While the pyrolysis temperature was set to 500 °C, a reforming temperature range between 700 °C and 900 °C was considered. Also, the acid treatment of tire char by HCl was performed to examine the effects of ash on this two-stage process. Results for the hydrogen yield showed that it could be enhanced by up to 39.2 mmol/g by increasing the reforming temperature to 900 °C in the presence of the tire char catalyst. Although the hydrogen yield increased considerably due to using the acid-treated tire char, the results showed the negative effect of tire char treatment on the hydrogen yield. For instance, the hydrogen yield, due to using acid-treated tire char, was reduced by 5.7 mmol/g, 3.9 mmol/g, and 8.7 mmol/g at reforming temperatures of 700 °C, 800 °C, and 900 °C, respectively [70]. Hydrogen yield results with various types of catalysts are shown in Figure 8.

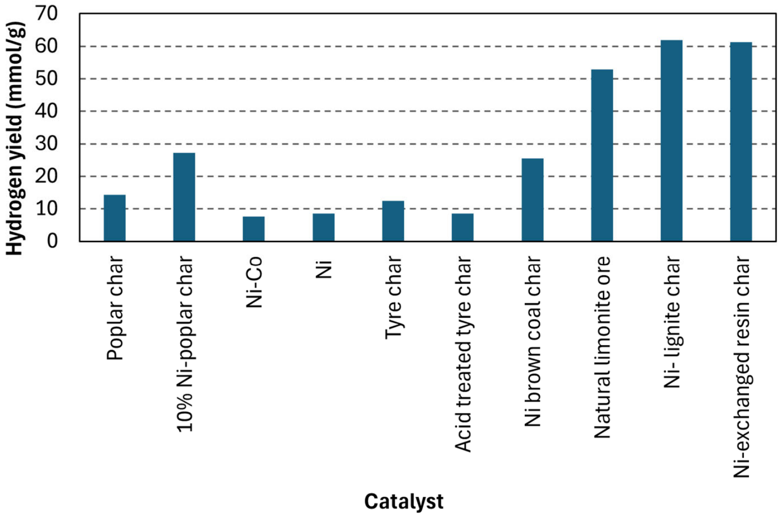

Figure 8. Effect of different catalysts on hydrogen yield [66,70–73,76,77].

An experimental research study performed by Wang et al. [66] assessed the feasibility of using biochar as a catalyst and poplar wood, catalpa wood, elm wood, and pine wood as feedstocks, and the pyrolysis and reforming temperatures were set to 700 °C and 650 °C, respectively. Product yield results showed that hydrogen production, due to using catalpa char, poplar char, pine char, and elm char, increased to 17.1 mmol/g, 14.4 mmol/g, 14.4 mmol/g, and 15.7 mmol/g, respectively. Another section of this experimental study examined the effects of using Ni/biochar as a catalyst with different nickel loadings. The results of using 5% Ni/poplar char, 10% Ni/poplar char, and 15% Ni/poplar char as catalysts for the two-stage pyrolysis and reforming process showed 21.4 mmol/g, 27.2 mmol/g, and 18.9 mmol/g hydrogen yields, respectively [66]. Natural limonite ore is another material used to catalyze the reforming process of corncob pyrolysis volatiles. Results for the hydrogen yield of pyrolysis volatile steam reforming showed that it could be enhanced up to 50.2 mmol/g at 650 °C using a limonite-reduced catalyst, which was only 0.8 mmol/g less than that with the condition of using a commercial Ni-based catalyst [72]. Waste ash materials were also used to investigate their impact as catalysts on the two-stage process of steam reforming pyrolysis volatiles. Ash residues from the combustion of coal, refuse-derived fuel (RDF), and waste tire were used as catalysts to reform pyrolysis volatiles of waste wood pellets. The results demonstrated that the gas yield increased up to more than 59 wt%, although the gas yield was 39.9 wt% using clean quartz instead of a catalyst. The maximum hydrogen production, which was 7.9 mmol/g, was achieved using the RDF ash catalyst and this amount was 133% higher than that under the condition of using quartz and sand. Also, the impact of ashes as a catalyst support in Ni–ash catalysts was assessed. The Ni–tire ash catalyst had the best performance in increasing gas production and hydrogen yield and using this increased the hydrogen yield to 10.5 mmol/g. Also, a volumetric increase is a common effect of using different types of ashes as a catalyst or catalyst support [61]. The stability of a catalyst is an important subject related to evaluating catalyst performance; there are relevant experimental studies that have quantified this aspect. Yang et al. suggested new catalyst strategies, including using a tandem biocarbon + NiAlO spinel + biocarbon, which showed efficient and stable performance in 15 continuous cycles [81]. Table 4 shows the impacts of using different types of catalysts on hydrogen yield.

Table 4. The effect of using different catalysts on hydrogen yield.

Feedstock	Catalyst	H_2 Yield (mmol/g)	Ref.
Corncob	Ni/Al_2O_3	51	[72]
Sewage sludge	Ni/Al_2O_3	53	[75]
Wood sawdust	Ni/Al_2O_3	11.01	[67]
Corncob	Ni/Al_2O_3	21.2	[76]
Rice husk	Ni–dolomite	23.71	[63]
Sugar cane		21.18	
Wheat straw		21.59	
Corncob	Ni–exchanged resin char	25	[77]
Poplar wood	Poplar char	14.4	[66]
Catalpa wood	Catalpa char	17.1	
Elm wood	Elm char	15.7	
Pine wood	Pine char	14.4	
Poplar wood	5% Ni/poplar char	21.4	
Poplar wood	10% Ni/poplar char	27.2	
Poplar wood	15% Ni/poplar char	18.9	
Corncob	Natural limonite ore	50.2	[72]

3.2. Intermediate and Fast Pyrolysis

Other types of pyrolysis used in the two-stage catalytic process of reforming pyrolysis volatiles are intermediate and fast pyrolysis. The assessment of different routes to produce hydrogen and biocarbon using the intermediate pyrolysis process of the Envigas plant in Sweden was performed by Zaini et al. [82]. An electrically heated screw reactor was used for the intermediate pyrolysis process, and an electrically heated reformer was considered for the reforming process. It is worth noting that two possible configurations were considered to produce biocarbon and hydrogen. While pyrolysis volatiles were used as feedstocks for the reforming process in the first scheme, a condenser was used in the second suggested configuration to separate condensable materials from the pyrolysis volatiles, and these processes were modeled in Aspen Plus software version 9.0. The flow rate of forest waste biomass as a feedstock was 1000 kg/h, and the pyrolysis and reforming temperatures were set to 550–650 °C and 850 °C, respectively. Ni-based catalysts were also used in the reforming process. Another important point that should be mentioned is the requirement to use a water–gas shift reactor after the reforming process because of high carbon monoxide production. Implementing a water–gas shift reactor is vital in increasing hydrogen yield. The final results of first suggested configuration showed a hydrogen yield of 93.5 kg/h, equal to 10 wt% of the dry biomass input. However, the hydrogen production was 43.8 kg/h in the second suggested configuration. The main reason for this difference was using a condenser in the second configuration to collect the bio-oil as a product. The results of this study should be considered important since the feedstock flow rate of this study was on the industrial scale, and it reflects the merits and energy efficiency of this process in large-scale capacities [82].

Fast pyrolysis was also considered a process for the first step of reforming pyrolysis volatiles, and the impacts of using this were examined in a research study. The experimental results of reforming pyrolysis volatiles produced by the fast pyrolysis of pine wood sawdust showed hydrogen yields with different reforming temperatures. Hydrogen production at 550 °C was 64 g/kg of biomass, which was enhanced up to 110 g/kg at a reforming temperature between 600 °C and 700 °C [83]. Waste wood was used as a feedstock in a two-stage fast pyrolysis and steam reforming process to produce syngas, and four different Ni-based catalysts were used in this experiment. The pyrolysis temperature, heating rate, and reforming temperature of this experimental study were set to 500 °C, 40 °C/s, and 760 °C, respectively. Product distribution results showed that using a NiO/SiO_2 catalyst maximized the gas product yield by increasing this amount up to 54 wt%. Also, gas composition analysis demonstrated the beneficial effects of catalytic steam reforming to increase hydrogen concentration. The steam reforming of pyrolysis volatiles without using any catalyst yielded 18.2 vol% of hydrogen, and introducing Ni-based catalysts increased this amount considerably. Among four different catalysts, NiO/Al_2O_3 had the most positive effect on hydrogen yield, which increased hydrogen production from 18.2 vol% to 44.4 vol% [80]. Producing hydrogen using biowaste was investigated by considering three different feedstocks: pine wood, citrus waste, and rice husk. Gas product yields showed that hydrogen, CO, and CO_2 were the main gas compounds, and the hydrogen yield for these feedstocks was in the range between 93.5% and 96.4%. Additionally, the hydrogen concentration of all feedstocks was around 66 vol% of the produced gas [84].

4. Main Results

This literature review of the two-stage catalytic reforming of pyrolysis volatiles demonstrates that this approach can significantly enhance hydrogen production, when compared to the single pyrolysis process. This significant increment in hydrogen production originates from two reasons: first, reforming pyrolysis volatiles, including condensable and non-condensable components, increases gas products and allows tuning the component distribution; second, the possibility to use different types of reactors for the reforming gives additional flexibility for increasing the hydrogen concentration in the products. The main findings of studies about the two-stage reforming of pyrolysis volatiles process are summarized in Tables 5 and 6, respectively. It is worth remarking that the reported studies in Table 6 were conducted at the laboratory scale.

Table 5. Hydrogen yield reported in different research studies of pyrolysis process.

Feedstock	Pyrolysis Temperature °C (Heating Rate °C/min)	Scale	Total Gas Yield (wt.%)	H_2 Yield (vol%)	Ref.
Slow pyrolysis					
Pine	1600 (50)	Lab scale	55	41.7	[85]
Cypress wood	600 (30)	Lab scale	11	14.4	[86]
Sugar cane bagasse	480 (20)	Lab scale	25	9.6	[52]
	780 (20)		36	28.8	
Waste wood	500 (30)	Lab scale	63	40.6	[47]
	550 (30)		63.4	47.8	
	600 (30)		65.6	52.5	
	650 (30)		67.8	54.2	
	700 (30)		71.3	53.6	
	750 (30)		74.3	53.4	
	800 (30)		76.5	52.5	
Rice husk	800 (2)	Lab scale	25.5	8.6	[87]
Olive stone	600	Lab scale	44.17	29.47	[40]
Intermediate pyrolysis					
Agricultural residue	500 (50)	Lab scale	32	2.5	[88]
Brewers spent grain	450 (100)	Lab scale	21	1.6	[89]
Fast pyrolysis					
Sugar cane bagasse	480 (120)	Lab scale	14.12	8.7	[52]
	580 (120)		15.46	15.2	
	680 (120)		17.94	45.3	
Beach wood	350 (1000)	Lab scale	10	0.9	[90]
	400 (1000)		18.4	1.4	
	450 (1000)		10.1	0.8	
	500 (1000)		17.7	2.3	
	550 (1000)		20.5	3.4	
	800 (1000)		56.9	13.8	
Pine	550 (1000)		17.9	6.9	
Bamboo	500 (1000)		19.1	1.5	
Pine wood	440 (N.A)	Pilot scale	61.5	4.2	[91]
	460 (N.A)		62.6	4.9	
	480 (N.A)		65.9	6.1	
	510 (N.A)		64	7	
	525 (N.A)		63.4	9.1	
	565 (N.A)		61.5	15.1	
Sawdust	400 (N.A)	Lab scale	23.7	10	[92]
	450 (N.A)		22.1	20	
	500 (N.A)		15.2	24	
	550 (N.A)		22.7	21	
	600 (N.A)		26.7	19	
Flash pyrolysis					
Palm kernel shell	600 (N.A)	Lab scale	5	18.5	[93]
	900 (N.A)	Lab scale	32	26.6	

Note: N.A: not available.

Table 6. Hydrogen yield reported in different research studies of process of two-stage reforming of pyrolysis volatiles.

Feedstock	Pyrolysis Temperature °C (Heating Rate °C/min)	Reforming Temperature °C	Catalyst	H_2 Concentration (vol%)	H_2 Yield (mmol/g)	Ref.
Rice husk	950 (20)	950	10 wt % Ni–dolomite	59.32	25.44	[63]
Sugar cane bagasse				57.4	25.41	
Wheat straw				58.3	24.47	
Rice husk	550 (20)	750	10 wt% $NiAl_2O_3$	57.63	18.22	[33]
Coconut shell				58.21	22.11	
Sugar cane				59.23	22.96	
Palm kernel shell				57.36	25.35	
Cotton stalk				57.95	20.74	
Wheat straw				54.06	16.38	
Lignin				64.02	25.25	
Cellulose				56.43	19.72	
Xylan				58.77	20.54	
Corncob	900 (10)	650	Ni–exchanged resin char (Ni/RC)	72.5	61.2	[77]
Wood pellets	500 (40)	700	Tire char	34.6	10.2	[70]
		800	Tire char	38.2	15.1	
		900	Tire char	51.8	47.6	
		700	Acid-treated tire char	14.3	3.11	
		800	Acid-treated tire char	28.3	10.2	
		900	Acid-treated tire char	47.1	36.7	
Wood sawdust	550 (40)	800	Blank	23.2	6	[69]
			Ni-Ca-Mg-Al (1:1:1:1)	52.3	18.2	
			Ni-Mg-Al	35.1	10.4	
Wood sawdust	500 (40)	800	Sand	17.5	2.4	[65]
			Fe-Zn/Al_2O_3 (1:1)	40.6	9.65	
			Fe-Zn/Al_2O_3 (1:2)	35.1	7.25	
			Fe-Zn/Al_2O_3 (1:3)	35.6	6.79	
			Fe-Zn/Al_2O_3 (1:4)	35.1	6.59	
Waste wood	500 (2400)	760	Sand	18.2	N.A	[80]
			NiO/Al_2O_3	44.4	N.A	
			NiO/SiO_2	38.7	N.A	
			$NiO/CeO_2/Al_2O_3$	43.1	N.A	

Note: N.A: not available.

Conclusions

This review of the existing literature allows deriving that pyrolysis temperature is a key operating condition directly influencing hydrogen yield. Although a higher reaction temperature can enhance hydrogen yield, the associated increase in process energy demand must be carefully assessed when scaling up plants.

Reforming temperature is another operating condition that strongly affects hydrogen yield. This literature review demonstrates that increasing reforming temperature enhances hydrogen yield. However, the positive effect of increasing temperature shows a maximum around 700 °C and 800 °C. Considering the main findings of the reviewed studies, while increasing pyrolysis and reforming temperatures leads to increased hydrogen production, energy consumption contextually increases. Also, catalyst sintering is another challenge when increasing reforming temperature. So, optimizing pyrolysis and reforming temperatures should be performed by considering energy consumption limitations and preventing catalyst sintering. It has to be stressed that reforming at higher temperatures requires more energy and more complex plants, so the optimum reforming temperature should be a balance between hydrogen yield and energy requirements. Also, the results show the positive effect of using steam as a reforming agent in enhancing hydrogen yield. Similarly, increasing the steam-to-biomass ratio leads to increasing hydrogen yield in the two-stage reforming of pyrolysis volatiles. Space velocity can also affect hydrogen yield. This literature review shows that lower space velocity and longer residence time have beneficial effects on tar reforming and gas production.

The analysis of these studies, mostly performed at the lab scale, shows that feedstock type and composition strongly affect hydrogen production in the two-stage process of reforming pyrolysis volatiles. Also, catalyst deactivation is another important factor influencing hydrogen production, and implementing methods to reduce or avoid this effect can significantly increase hydrogen output. This issue is one of the most important technical challenges that has to be resolved for scaling this approach to the commercial scale. The regeneration strategies of catalysts are another important factor that can be taken into account when developing industrial-scale plants. Also, it is important to note that mixing plastic waste with biomass feedstock allows for a significant increase in hydrogen production; this is another interesting approach that has attracted attention in the past few years and it should be carefully evaluated in detail in future studies.

It can be concluded that reforming pyrolysis volatiles with a two-stage approach can significantly enhance the potential for hydrogen production from the pyrolysis process. Clearly, optimizing operating conditions is key to producing high hydrogen yield. Increasing pyrolysis and reforming temperatures increases hydrogen yield, although energy requirements may be carefully considered in the overall balance. The possibility of using commercial, low-cost, metal-based catalysts and biochar-based materials offers a chance to find appropriate solutions and ensure that the process is economically feasible. Overall, the availability of a wide range of choices for all effective factors provides an opportunity for the optimization of the techno-economic design of reforming pyrolysis volatiles, allowing the production of hydrogen from biowaste feedstock.

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Abbreviations

The following abbreviations are used in this manuscript:

GHG	Greenhouse gas
PEM	Polymer electrolyte membrane
SOE	Solid oxide electrolyzer
TRL	Technology readiness level
HTL	Hydrothermal liquefaction
S/B	Steam to biomass
RDF	Refuse-derived fuel

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