hydrogen

Review

# Hydrogen from Waste Gasification

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**Abstract:** Hydrogen is a versatile energy vector for a plethora of applications; nevertheless, its production from waste/residues is often overlooked. Gasification and subsequent conversion of the raw synthesis gas to hydrogen are an attractive alternative to produce renewable hydrogen. In this paper, recent developments in R&D on waste gasification (municipal solid waste, tires, plastic waste) are summarised, and an overview about suitable gasification processes is given. A literature survey indicated that a broad span of hydrogen relates to productivity depending on the feedstock, ranging from 15 to 300 g $H_2$/kg of feedstock. Suitable gas treatment (upgrading and separation) is also covered, presenting both direct and indirect (chemical looping) concepts. Hydrogen production via gasification offers a high productivity potential. However, regulations, like frame conditions or subsidies, are necessary to bring the technology into the market.

**Keywords:** hydrogen production; waste gasification; thermochemical conversion

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## 1. Introduction

Environmentally benign fuels, which can replace today's fossil-based fuels, such as oil, natural gas, and coal for combustion, either in stationary or traction applications, are of the utmost importance. One such fuel is hydrogen, which is the fuel of the future. Hydrogen is an energy carrier and energy storage medium, maintaining potential applications in many industrial processes and power generations. Hydrogen has gained momentum in recent years as a potential fuel for aviation, vehicles, and domestic heating requirements, either by direct combustion or in so-called "cold combustion" in fuel cells to realize a sustainable world. The introduction of hydrogen in our societies would mean a paradigm shift in the use renewable energy sources, leading principally to the decarbonization of the energy sector and ecosystem and, hence, a substantial decrease in greenhouse gases. Owing to its abundance bound in the form of compounds and complexes, it is estimated that over 75% of the mass of the universe is primarily hydrogen [1]. The combustion product of hydrogen practically being water makes it strategically important for clean and sustainable energy production. The calorific value for hydrogen combustion is 120 MJ/kg (LHV), showing its superior quality compared to gasoline [2]. However, currently, 96% of the global hydrogen production relies mainly on industrial processes derived from fossil fuel feedstocks [3]. Biomass with its huge sources and diverse compositions, waste products, and water have been considered as an alternative source of hydrogen production by thermolysis, biolysis, photolysis, and electrolysis. Hydrogen produced by valorization of waste materials provides both a clean energy vector and sustainable waste management compared to landfill and incineration methods [4]. Thus, waste-to-energy (WtE) and/or waste-to-hydrogen (WtH) processes or syngas have the potential to be utilized as a reliable transition from fossil fuel, globally emitting 900 Mt $CO_2$ associated with hydrogen production [5]. Currently, there are several different "colors" of hydrogen, which give the production pathway and, indirectly, the sustainability of the produced hydrogen. They are summarised in Table 1. Hydrogen from waste does not have its own color but can be classified as green hydrogen.

**Table 1.** Types of hydrogen.

| Color | Production Pathway | Byproducts |
|---|---|---|
| black | Gasification of coal | $CO_2$ |
| grey | Steam reforming of natural gas without CCS * | $CO_2$ |
| blue | Steam reforming of natural gas with CCS * | - |
| turquoise | Pyrolysis of natural gas | Elemental carbon |
| white | Naturally occurring | - |
| pink | Electrolysis of nuclear power | $O_2$ |
| green | Electrolysis of renewable energy | $O_2$ |
| | Conversion of biomass | Carbon negative with CCS * |

* CCS = carbon capture and storage.

Waste management, as one of the most crucial societal challenges with the ever-growing discharge of municipal solid waste (MSW), waste products from industries, agroresidues, sewage sludge, and animal manure, is closely related to welfare, hygiene, health, and bionomical issues. With the global surge of population, economic development, and standard of living, there is a remarkable increase in and disposal of MSW from cities and towns, plastics, and tires, with enormous impacts on health, economy, and environment.Thus, annual generation and production increased to 2.01 billion tons of global waste and 460 million tons of plastic in 2019 [6,7]. A significant volume of these waste products is poorly managed and ends up in landfills, leading to the resistance of biological and chemical degradation or emission of leachate and gases as well as the requirement of huge acreages with large-scale environmental concerns. At the global scale, only a quarter of the MSW, 15 wt% of plastics, and 17 MT of tires were collected and recycled for the respective years, showing the magnitude of waste management [7,8]. Though waste with its inhomogeneity is composed of biodegradable and non-degradable contents, its organic fraction as an economic and renewable resource has great potential for energy recovery technologies in the form of heat, power, and chemicals. EU Directive 2008/98/EC establishes a legal framework of waste hierarchy for (i) prevention, (ii) reuse, (iii) recycling, (iv) recovery (energy, etc.), and (v) disposal in a bid to protect the environment and human health. Therefore, appropriate policy measures and interventions are key roadmaps for the utilization of waste as useful and sustainable fuel and products with considerable effects on the circular economy and, at the same time, decreasing the negative role on living organisms and the environment.

Biomass and its derivatives in the form of organic waste are readily converted to their final products by a set of different technologies, including mechanical, chemical, biochemical, and thermochemical processes. Among these, thermochemical methods by combustion, pyrolysis, gasification, and liquefaction have gained increased attention for the conversion of biomass and waste, with a high proportion of hydrocarbon content in renewable fuel for energy and product retrieval [9–15]. These technologies differ substantially in reactor configurations, particle size of feedstock, heating rate, residence time, type and yield of product, reactor temperature intervals and pressures, product treatment and enrichment, type of reactant, and use of catalyst. Although the combustion of biomass and solid waste to $CO_2$ and $H_2O$ has shown to effectively reduce the mass and volume of the MSW by 80–95% to be used in power and heat generations, it is essentially associated with emissions of toxic substances, such as furans, dioxins, NOx, SOx, and particulate matter, compared to gasification [16–18]. The pyrolysis and gasification of wastes (municipal, tires and plastics) are among the most mature technologies, showing different reaction products and operating at different temperatures, as shown in Figure 1.

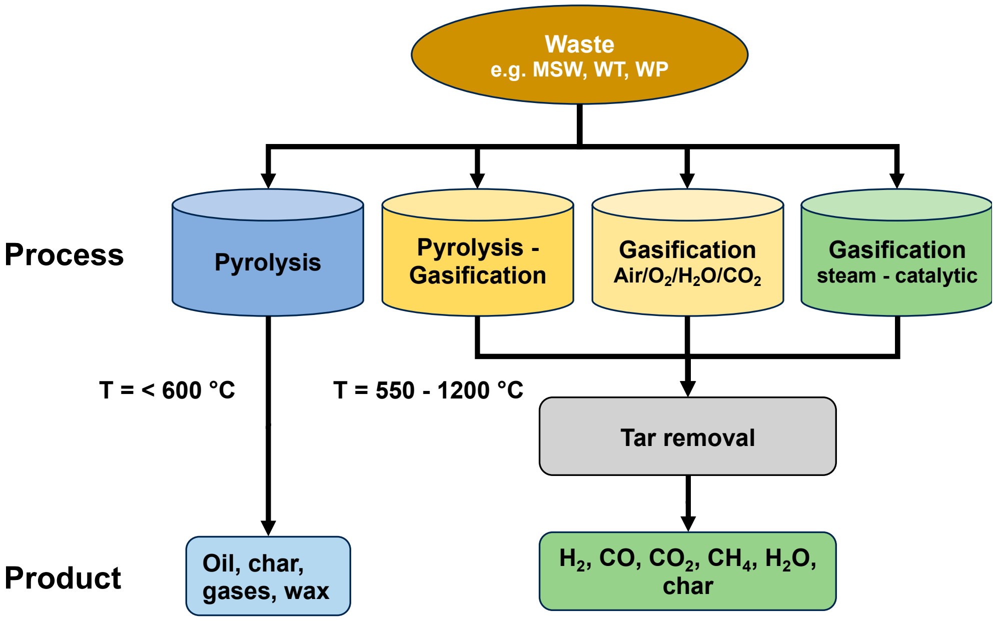

**Figure 1.** Schematic diagram of thermochemical recycling of municipal solid waste (MSW), waste tires (WTs), and waste plastics (WPs).

Although gasification is a mature technology with large-capacity plants generating syngas/fuel gas in many countries [12], its successful implementation for the production of WtH or syngas as an alternative and renewable fuel is closely related to the release of byproducts, such as ash, sulfur, alkali metals, particulates, and tar, and the subsequent product cleanup systems. Tar as condensable organic molecules is especially challenging, affecting operational and environmental problems during gasification by settling in filters and downstream flow in equipment, resulting in interruptions [19–21]. Different approaches for the containment of tars and related byproducts are used in the form of physical, thermal, and catalytic processes for achieving high-purity hydrogen and/or syngas. The present work focuses on the available literature for the generation of hydrogen, i.e., waste to hydrogen (WtH) or syngas, as a valuable source replacing the current fossil fuel-based production. It is a primary aim of this coverage not only to dwell on municipal waste but also on plastics and tires by implementing the gasification technology for conversion and valorization of the waste products generated in huge amounts as renewable sources for sustainable energy use. Although plasma gasification has been shown to be a viable technology to convert MSW, plastics, and rubber with various challenges remaining to be addressed [22], the focus of this review is mainly on conventional gasification technologies.

## 2. Gasification to produce Hydrogen from Waste

### *2.1. Gasification Basics*

Gasification is a process where solid carbonaceous materials are converted to combustible gases ($H_2$, CO, $CH_4$, and $CO_2$) in a reaction with a co-reactant (gasification agent/medium) in a temperature range of 550–1000 °C [23]. However, byproducts of tar as a mixture of high-molecular-weight aromatic and oxygenated hydrocarbons, $C_2$–$C_3$ hydrocarbons, solid residues of char, ash with metals, and minerals are formed [19,20,23]. Depending on the gasifying agent, the producer gas heating values can vary significantly, being 4–7 $MJ/Nm^3$ for air due to dilution with nitrogen, 10–12 $MJ/Nm^3$ for pure oxygen, and 15–20 $MJ/Nm^3$ for steam [13]. $CO_2$ is also used as an agent for gasification and has resulted in reduced energy input to the reactor with efficient gasification of the solid fuel [23,24]. The product gas can be upgraded to a syngas (mainly, CO and $H_2$ but sometimes also $CO_2$) used for synthesis processes or further upgraded to, e.g., pure hydrogen gas.

The gasification of biomass and solid waste occurs often not delineated in a reactor through a set of complex endothermic and exothermic reactions, consisting of (i) dehydration by drying the biomass with its inherent moisture, (ii) pyrolysis (thermal decomposition) in the absence of oxidant, (iii) partial oxidation or gasification, and (iv) reduction zone [25]. The set of complex heterogeneous and homogeneous reactions is shown in Table 2 [18,26]. Gasification involves reactions with different phases, such as gas–liquid, gas–solid, liquid–solid, and gas–gas, where diverse phenomena such as chemical reactions and transport phenomena (heat, mass and momentum transfer) between the gasification agent and feedstock take place.

**Table 2.** Main reactions in gasification reactions [18,26].

| Reaction | $\Delta H_R$ (kJ/mol) | Equation |
|---|---|---|
| $C + ½\,O_2 \rightarrow CO$ | −111 | (1) |
| $C + O_2 \rightarrow CO_2$ | −394 | (2) |
| $C + 2\,H_2 \rightleftharpoons CH_4$ | −85 | (3) |
| $CO + ½\,O_2 \rightarrow CO_2$ | −283 | (4) |
| $CO + H_2O \rightleftharpoons H_2 + CO_2$ | −41 | (5) |
| $CO + 3\,H_2 \rightleftharpoons CH_4 + H_2O$ | −206 | (6) |
| $C + CO_2 \rightleftharpoons 2\,CO$ | +173 | (7) |
| $H_2 + ½\,O_2 \rightarrow H_2O$ | −242 | (8) |
| $CH_4 + ½O_2 \rightarrow 2\,H_2 + CO$ | −110 | (9) |
| $C + H_2O \rightarrow H_2 + CO$ | +131 | (10) |
| $CH_4 + CO_2 \rightleftharpoons 2\,CO + 2\,H_2$ | +247 | (11) |
| $C_xH_y + x\,H_2O \rightarrow (x + y/2)\,H_2 + x\,CO$ | Endothermic | (12) |
| $C_xH_y + x\,CO_2 \rightarrow (y/2)\,H_2 + 2x\,CO$ | Endothermic | (13) |
| primary and secondary tars → CO, $H_2$, $CO_2$, C, $C_xH_y$ * | Endothermic | (14) |

* $C_xH_y$ = hydrocarbons.

In most processes for increased hydrogen or syngas production, steam is the most preferred gasifying agent for increased hydrogen or syngas production, albeit the energy requirement is high, as shown by Equations (6) (reverse), (10), and (12). In Table 2, the oxidation (1, 2, 5, 8, and 9) and methanation (3) reactions are exothermic, implying that reactor temperatures beyond 900 °C can maintain the autothermal reactions of the gaseous products within the reactor regime, validating Le Chatelier's principle of favorable reactants and products in exothermic and endothermic reactions, respectively. Steam addition as an agent allows the tars to react via steam reforming, as shown in Equation (13). Tars can also decompose by increasing the equivalence ratio (ER-oxygen used for gasification), higher temperatures, and gas residence time as well as by using catalysts for higher-purity hydrogen or syngas production.

### 2.2. *Gasification Research on Waste to Hydrogen*

To increase the combustible part and, thus, also the energy content, unsorted waste such as MSW passes a mechanical and biological treatment installation (MBT) to recover recyclable materials separating inert and wet organic wastes to a fuel termed RDF (refuse-derived fuel). There is, however, no quality requirement for RDF, and, therefore, the gasification research presented below is for MSW. As special waste types, tires and waste plastics are also included [14,27,28].

#### 2.2.1. Municipal Solid Waste

MSW with typical physical compositions varies significantly according to geographical location, socioeconomic factors, and society, where more than half of the organic waste is generated across all regions, except for Europe, Central America, and North America having higher portions of dry waste [6]. These waste products contain different combustible materials with high energy content, including polymeric materials, rubber, cardboard, paper, textiles, food waste, and biomass as their main components [14,29]. The physicochemical characterizations by proximate and ultimate analyses of various studies [22,27,29–35] according to standard methods are presented in Table 3 showing the non-uniformity of the MSW samples, deriving from various proportions of the residual source.

**Table 3.** Representative proximate (P) and ultimate (U) analyses of MSW samples.

| **P-U/Ref.** | **[27]** | **[29]** | **[30]** | **[31]** | **[32]** | **[33]** | **[36]** | **[34]** | **[35]** |
|---|---|---|---|---|---|---|---|---|---|
| Moisture content (wt% wb) | 20.86 | 5.46 | 5.06 | - | 4.69 | 3.82 | 14.3 | 1.5 | - |
| Volatile matter (wt% db) | 69.03 | 64.76 | 59.34 | 82.28 | 60.28 | 83.31 | 47.0 | 86.6 | 77.52 |
| Fixed carbon (wt% db) | 3.27 | 6.44 | 8.36 | 11.79 | 8.5 | 8.64 | 8.5 | - | - |
| Ash (wt% db) | 6.87 | 23.34 | 27.24 | 5,93 | 26.53 | 4.23 | 44.6 | 8.3 | 7.12 |
| C (wt% db) | 40.49 | 61.13 | 48.61 | 51.81 | 57.86 | 65.25 | 46.3 | 69.7 | 49.51 |
| H (wt% db) | 5.81 | 6.78 | 6.01 | 5.76 | 6.70 | 9.1 | 5.2 | 10.1 | 6.42 |
| O (wt% db) | 31.53 | 30.28 | 12.49 | 30.22 | 33.62 | 20.74 | 44.8 | 10.0 | 31.86 |
| N (wt% db) | 0.61 | 0.89 | 3.87 | 0.26 | 0.81 | 0.44 | 2.9 | 0.57 | 0.78 |
| S (wt% db) | - | 0.92 | 0.33 | 0.36 | 1.01 | 0.16 | 0.86 | 0.054 | 0.48 |
| LHV (MJ/kg) | 16.02 | - | 18.59 | 21.306 | - | - | 10.0 | - | 19.99 |

wb: wet basis; db: dry basis.

The status of MSW in gasification technology is mostly used for CHP, power, fuel gases, and biofuels, except for hydrogen generation from plastics by Showa Denko in Japan [12]. MSW gasification technology to produce hydrogen has been researched in various studies looking into different reactor configurations and process parameters, such as temperatures, gasifying agents with or without co-mixtures, particle sizes, heating rate, and residence time.

The moisture content is usually removed by heating at temperatures above 100 °C as this influences the overall calorific value of the feedstock and must be suppressed for increasing the conversion efficiency. However, the presence of high moisture content without a high input of steam is regarded as beneficial for in situ downstream gasification and hydrogen and syngas production [37,38]. The volatile matter is an indication of the formation of syngas (CO, $H_2$, $CH_4$, $CO_2$), $H_2O$, and tar after the devolatilization step in the pyrolysis zone [39]. The fixed carbon or char and total carbon originate with more than half as biogenic and the rest as fossil-based, which together with hydrogen defines the usable heating value of the fuel, while the fuel reactivity of the fuel increases with the contents of hydrogen and oxygen [40,41]. The fuel during gasification has an ash content related to the fuel quality and the quantity of the volatile matter along with the presence of inorganic materials. The oxygen contained in the fuel is part of the gasification process and, as such, also defines the important parameter of the equivalence ratio (ER) (actual air/fuel ratio to the stoichiometric air/fuel ratio) for syngas production. The mass fraction of hydrogen has high relevance regarding hydrogen production, as 6–7 wt% in biomass is equivalent to 0.67–0.90 $Nm^3$ gaseous hydrogen in 1 kg biomass [42,43]. Thus, any increment or reduction in the fuel hydrogen content in MSW or any waste influences the yield of hydrogen gas and/or syngas.

A summary of operating process conditions with the respective gasifier type and hydrogen and CO production of MSW is given in Table 4. Most experiments were performed at bench-scale, from micro to batch level fixed-bed reactors, except a few with a continuous fluidized bed and pilot plant, with a feed capacity of feedstock at 100 kg/h. Steam gasification has shown increased $H_2$ concentration and yield (g/kg MSW), primarily due to the set of gas-phase reactions involving Equations (5), reverse (6), (10), (12), and (14). Higher temperatures would also entail the discharge of $H_2$ of the rather hard-to-crack endothermic reactions of char and tars, with high carbon conversion efficiency [44]. Thus, the increase in the syngas yields of $H_2$ and CO as a building block for the application in chemical processes from an indigenous resource of municipal solid waste as a fuel source has significant bearing capacity. This applies to improving pollution in cities by 'green' strategies across societies by mitigating climate change, increasing national revenues through the introduction of innovative technologies, replacement of fossil-derived fuels and independency from unstable regions, and insecurity on energy supply. The implementation of gasification technology on MSW by harnessing $H_2$ production fulfils the bulk of the UN 2030 Agenda for Sustainable Development.

**Table 4.** $H_2$ and CO production of MSW by gasification.

| Reactor Type | Agent | ER | T (°C) | $H_2$ (vol%) | CO (vol%) | $H_2$ (g/kg MSW) | LHV (MJ/Nm$^3$) | Ref. |
|---|---|---|---|---|---|---|---|---|
| Downdraft fixed bed | Air | 0.4 | 900 | 36.51 | 26.23 | 21.6 | 14.59 | [27] |
| Bubbling fluidized bed | Air | 0.4 | 900 | 35.7 | 36.79 | 24.1 | 12.57 | [27] |
| Tube | Air | - | 703.5 | 45.79 | 33.33 | 27.69 | 9.96 | [29] |
| Drop tube | $CO_2$/steam | - | 1000 | 43.44 | 28.85 | 37.69 | 12.41 | [30] |
| Fixed bed | Steam | - | 950 | 53.29 | 16.92 | 77.28 | 9.36 | [31] |
| Tube | Air | 0.241 | 758 | 41.36 | 28.46 | 32.0 | 12.48 | [32] |
| Fluidized bed | Air/$O_2$ | 0.2 | 900 | 9.57 * | 31.56 * | 19.24 |  | [33] |
| Bubbling fluidized bed | Air | 0.34 | 770 | 10.2 * | 12.4 * | 11.03 | 3.70 | [36] |
| Fixed bed | Steam | - | 800 | 70.0 | 7.0 |  |  | [34] |
| Fixed bed | Steam | - | 850 | 59.0 | 15.0 | 98.15 | 9.34 | [35] |
| Fixed bed | Steam | - | 750 | 49.42 | 13.0 | 24.8 |  | [38] |
| Fixed bed | Steam | - | 900 | 53.22 | 25.72 | 86.05 | 9.0 | [31] |
| Downdraft fixed bed | Air | 0.2 | 800 | 10.2 * | 14.1 * |  | 6.8 | [45] |
| Fixed bed | Steam | - | 900 | 58.2 | 13.7 |  |  | [46] |
| Fixed bed | Steam | - | 900 | 54.22 | 22.72 | 84.72 |  | [44] |
| Fixed bed | $O_2$ | - | 600 | 50.65 | 34.0 |  |  | [47] |
| Fluidized bed | Steam | - | 900 | 49.6 | 22.0 | 80.0 |  | [48] |
| Fluidized bed | Air/$CO_2$ | 0.25/0.4 | 900 | 39.8 | 50.0 | 81.7 |  | [11] |

ER: equivalent ratio; * $N_2$ included.

Ma et al. [32] studied MSW by varying the temperature in a range of 700–900 °C, ER 0.2 to 0.3, and residence time of 10 to 30 min and found out that the maximum yield of $H_2$ was 41.36 mol% (~32 g/kg MSW) in conditions of 757.7 °C, 0.241, and 22.26 min for temperature, ER, and residence time, respectively. This study was based on response surface methodology (RSM) as central composite design (CCD) to optimize the effect of process variables on the final product. Ying et al. [30] varied temperatures at 1000–1100 °C and the $CO_2$/steam ratio in a range of 0.5–3, with the $CO_2$ derived from gasification and reused. The experiments showed that the Boudouard reaction (Equation (7)) dominates above 700 °C, where $CO_2$ reacts with the solid char to produce CO. An optimal $CO_2$/steam ratio of 2.5 at 1000 °C resulted in a $H_2$ yield of 37.7 g/kg MSW and 338.9 g/kg MSW of CO. Seo et al. [27] carried out a comparative study of gasifiers with downdraft fixed bed (DFB) and bubbling fluidized bed (BFB) performed in terms of ER in a range of 0.2 to 0.6, gas yield, and composition as well as the important parameters of carbon conversion efficiency (CCE) and cold gas efficiency (CGE). CGE is expressed as total reacted carbon in the system (kg)/total carbon fed into the system and CCE as LHV of fuel gas × fuel gas production/LHV feed [31,49]. The results obtained in BFB showed a higher syngas composition of 72.53 mol% ($H_2$ + CO), 63.70% CCE, and 67.31% CGE at ER 0.4 and at 900 °C. Ma et al. [27] utilized experimental validation using statistical methods to analyze the effects of temperatures (700, 800, 900 °C), particle sizes in mm (1, 2.5, 3.5), and heating rates in °C/min (5, 1, 15). They were able to obtain optimum $H_2$ production of 45.8 mol% with $H_2$ + CO of 72.8 mol% with lower tar and char contents at 703.49 °C, particle size of 3.21 mm, and a heating rate of 5 °C/min. The $H_2$ production rate was believed to increase with the reaction temperatures from 700 to 900 °C by both steam-reforming (reverse Equation (6)) and water-gas shift (WGS) (Equation (5)) and the endothermic reaction of Equations (8) and (10). Campoy et al. [36] compared various wastes (orujillo, meat, and bone meal, dried sewage sludge (DSS) and MSW) in a 100 kW$_{th}$ fluidized-bed pilot plant and showed that the $H_2$ content of MSW was greater than the other wastes, depending on process parameters.

One of the approaches receiving increased attention without the need for increased temperature, displaying selectivity for tar removal by catalytic cracking, steam reforming of hydrocarbons, and absorption of byproducts during gasification of MSW, is catalysts and sorbents. He et al. [31] studied steam gasification of MSW in a bench-scale downstream fixed-bed reactor, using a calcined dolomite ($CaMg(CO_3)_2$) as a catalyst. The tar decomposition was complete at a temperature of 950 °C with a $H_2$ yield of 77.3 g/kg MSW but achieved a maximum potential yield of 140.4 g $H_2$/kg MSW at 900 °C. This high yield was attributed to the catalytic effect of dolomite in steam gasification of both tar and char, where the steam-to-MSW ratio was held at 0.77 for a weight hourly space velocity of 1.29 $h^{-1}$. Likewise, dolomite as a catalyst was studied, where the influence of the steam-to-MSW ratio was varied between 0.39 and 1.04 and weight hourly space velocity in the range of 1.22–1.51 $h^{-1}$ at 900 °C by He et al. [31]. The highest $H_2$ content of 53.2 mol% and hydrogen yield of 86 g/kg MSW with a hydrogen potential yield of 119.8 g/kg MSW was at the level of 1.04 steam-to-MSW ratio.

CaO has been applied both for in situ $CO_2$ adsorption and as a catalyst in MSW gasification. MSW containing four main components, plastics (43 wt%), paper (37 wt%), wood (12 wt%), and textiles (8 wt%), was studied in steam gasification using different mass ratios of CaO-to-carbon in MSW in a temperature range of 650 to 850 °C for hydrogen production [38]. The results show that in situ carbon capture increased the $H_2$ concentration to 49.42 vol% and a $H_2$ yield of 24.8 g/kg MSW at 750 °C and a Ca/C ratio of 0.7. A recycle looping system formed of $CaCO_3$ and tar was used to regenerate into CaO, converting the tar into non-condensable gases in a heating chamber to be fed into the gasifier.

In a study by Zhou et al. [34], steam gasification in a batch-type fixed bed using the CaO additive at different CaO/MSW ratios at temperatures of 700–900 °C was investigated. At 800 °C, an optimum production of $H_2$ is achieved during both the devolatilization and char gasification stages by more than 10% compared to gasification without CaO. However, the effect of CaO seems to be reduced by an increase in temperature to 900 °C.

Nickel-supported catalysts and their combinations with other metals are commonly known for their high catalytic effect and stability for steam reforming reactions of hydrocarbons with high conversions at relatively high temperatures and have been applied for MSW gasification reactions. In a study by Li et al. [46], three different reaction conditions, without catalyst, calcined dolomite and nano NiLaFe/$\gamma$-$Al_2O_3$ at 750–900 °C, catalyst particles, catalyst to MSW, and steam to MSW ratios were varied and compared in a combined fixed-bed reactor. The investigation showed that the most important factor was temperature at 900 °C and at a steam-to-MSW ratio of 1.33, rendering a significant increase in $H_2$ by 59 mol%. % of a total of 2.40 $Nm^3$/kg MSW for the supported tri-metallic catalyst. The effects of catalyst type (NiO/$\gamma$-$Al_2O_3$ or calcined dolomite), reactor temperature, and steam-to-carbon (S/C) ratio were investigated by Luo et al. [50]. At a temperature of 900 °C, catalytic steam gasification, performed in a fixed-bed reactor, contributes to a $H_2$ content of 54.2 mol% and gas yield of 1.75 $Nm^3$/kg MSW for the active $\gamma$-$Al_2O_3$ catalyst, S/C ratio of 2.41, and a higher CCE of 84.87%, with $H_2$ dominating in the syngas production. Nano-catalysts of Ni/$\gamma$-$Al_2O_3$ and Cu/$\gamma$-$Al_2O_3$ were prepared by Gao et al. [47] for steam gasification in a micro-FB system in a temperature range of 650 to 800 °C with varying catalyst loadings for reforming reactions and char conversion. A higher yield of 32 g/kg MSW was obtained at 800 °C for 4 g loading of Ni/$\gamma$-$Al_2O_3$ with 97% conversion of char, showing the activity of the catalyst. NiO on modified dolomite was compared with NiO/$\gamma$-$Al_2O_3$ and studied for a period of 10 h to observe the lifetime test for tar reduction at different reactor temperatures [35]. The effective conversion of 99% with an increased hydrogen yield of 80.7 g/kg MSW and CCE of 76.8% was achieved with no deactivation of the catalyst at 850 °C and steam-to-MSW ratio of 1.23. Couto et al. [11] investigated MSW gasification in a semi-industrial fluidized-bed gasifier using NiO on modified dolomite. The effects of ER, rector temperature, $CO_2$-to-MSW and steam-to-MSW ratios were investigated with mathematical modelling and experimental validation. The results show that at operating ER 0.25, steam-to-feed ratio of 1 at 900 °C and $CO_2$-to-MSW ratio of 0.4, the $H_2$ yield was 81.7 g/kg MSW with a $H_2$ and CO content of 39.8 mol% and 50 mol%, respectively. It is interesting to note, however, that the effect of $CO_2$ leads to higher concentrations of CO and $CO_2$ with decreased $H_2$ content due to reverse WGS reactions (Equation (5)) and

Boudouard (Equation (8)), while a significant amount of the gasifying agent leaves the reactor unreacted, as observed by the authors.

Co-gasification with other biomass residues of wheat straw is another way to enhance the production of $H_2$, as in a study by Zhao et al. [33]. The study shows an overall incremental increased $H_2$ production of 14% when the oxygen concentration increases by 5% in the range of ER 0.2–0.5 and between 600 and 900 °C. Moreover, a ratio of 1:1 of wheat straw to MSW increased the $H_2$ yield by 6.4%, mainly due to the reduced availability of plastics in the MSW and the presence of alkali metals ($K^+$, $Na^+$, $Ca^{2+}$) as inherent catalysts for enhancing char oxidation [49]. However, gasification with oxygen enrichment shows a moderate increase in $H_2$ content as more combustibles are exposed to oxidation reactions, resulting in higher concentrations of $CO_2$. Co-gasification of switchgrass with MSW was performed by varying the ratios in a commercial-scale downdraft gasifier to increase the syngas compositions, yield, and heating values by Bhoi et al. [45]. The results show that the co-gasification ratios of 0, 20, and 40 wt% of MSW show variations in the syngas yield from 1.6 to 1.4 $Nm^3/kg$, with 10 mol% $H_2$ and 17 mol% CO, respectively.

### 2.2.2. Waste Tires (WTs)

Tires contain non-decomposable and non-biodegradable components, which, upon disposal in landfills or incineration, create toxic chemicals, solid residues, particulate matter, heavy metals, and pyrolytic oils containing polycyclic aromatic hydrocarbons, causing environmental and health issues [51]. Many countries and regions have strict regulations and legislation regarding scrap tire management and harnessing used tires in energy and material recovery. According to ETRMA (European Tire and Rubbers Manufacturers' Association), in 2018, 91% of end-of-life tires were collected and treated for material recycling (2 Mt, 61.75%) for reuse in secondary materials and 1.25 Mt (32.85%) for energy recovery in cement kilns, urban heating, and power plants [52–54]. Moreover, scrap tires have also found applications as rubber powder in small amounts as flooring in sport courts, children's playgrounds, shoe soles, gaskets, shims, ribbons, transport belts, motorway barriers, filler in asphalt for roads, artificial reefs, breakwaters, reclaim rubber, etc. [52,53]. However, considering the voluminous production rate of tires and their properties as durable and difficult to degrade with minor recycling/recovery levels, alternative routes for utilization have been considered as viable energy sources being abundant with carbon and hydrogen.

Tires have diverse contents and are composed of elastomers of natural rubber (NR), styrene-butadiene rubber (SBR), cis-polyisoprene or synthetic rubber (SR), carbon black, zinc oxide, textiles, additives, and sulphur [51,55]. Typical tire substances with different results depending mainly on the type and brand, characterized by corresponding authors of the proximations and analyses, are shown in Table 5. The sulphur content, typically 1–3 wt%, is vulcanized with raw rubber to cross-link for hardening with ZnO as an activator compounding together with carbon black to improve elasticity, thermal resistance, conductivity, support, and strengthening the abrasion resistance of the rubber. Steel cords, textiles, ZnO, S, rubber extender oils, and carbon black are blended during the tire manufacturing process. The scrap tires are treated and removed of the heavier parts, followed by shredding, grinding to be reduced and sifted to different particle sizes, and to be used as tire-derived fuel (TDF). The moisture and ash contents are relatively low, the C higher, and the FC several folds higher than in MSW. Waste tires have calorific values higher than a range of biomass (15–22 MJ/kg) [56] and different coal samples (13.49–24.88 MJ/kg) [57], making them suitable for the potential recovery of energy by waste to hydrogen, syngas, and liquid feedstock.

**Table 5.** Representative proximate (P) and ultimate (U) analyses for waste tires.

| P-U/Reference | [58] | [59] | [60] | [61] | [62] | [63] | [8] | [64] | [65] |
|---|---|---|---|---|---|---|---|---|---|
| Moisture content (wt% wb) | 0.76 | 1.62 | ns | 1.21 | 0.68 | ns | 0.8 | 0.82 | 0.75 |
| Volatile matter (wt% db) | 63.04 | 63.41 | 67.7 | 65.1 | 65.1 | 61.8 | 62.4 | 62.7 | 64.97 |
| Fixed carbon (wt%) | 32 | 21.86 | 25.5 | 8.8 | 28.95 | 33.8 | 29.4 | 32.31 | 30.08 |
| Ash (wt% db) | 4.2 | 13.21 | 6.8 | 4.9 | 46.63 | 4.4 | 7.4 | 4.17 | 4.16 |
| C (wt% db) | 83.34 | 80.46 | 77.3 | 67.9 | 79.55 | 85.2 | 87.1 | 81.2 | 83.92 |
| H (wt% db) | 6.56 | 8.14 | 6.2 | 6.6 | 7.99 | 7.3 | 7.7 | 7.2 | 6.83 |
| O (wt% db) | 2.78 | 6.9 | 7.1 | 17.4 | 2.53 | 0.5 | 3.1 | 8.7 | 7.55 |
| N (wt% db) | 0.79 | 0.82 | 0.6 | 1.9 | 0.15 | 0.4 | 0.4 | 0.8 | 0.78 |
| S (wt% db) | 1.33 | 3.68 | 1.8 | 1.28 | 2.47 | 2.3 | 1.7 | 2.1 | 0.92 |
| LHV (MJ/kg) | - | 36.34 | - | 29.5 | 37.4 | 37.1 | 35.8 | - | 38.6 |

wb: wet basis; db: dry basis.

Pyrolysis and gasification as thermochemical conversion technologies of WT have been extensively studied for obtaining various products. Several review papers and studies [58,59,65–68] have recently covered the research progress on the pyrolysis of waste tires for the optimization of important factors in the process and the products of char, oil, and gases. Although pyrolysis has its own advantage in lower-temperature operations for the products, it is a primary focus of this work to dwell on the gasification of WT for product yields of non-condensable gases of hydrogen and other syngases, including CO. Currently, there are no large-scale gasifiers operating using TDF as a feedstock, with most research being conducted at laboratory scale [69].

The fundamental chemical reactions taking place during the gasification of WT are valid, like those described in Table 2. However, as rubber is a thermosetting polymer with different physicochemical properties, it is initially decomposed into heavy and light hydrocarbons (waste tire → heavy and light hydrocarbons + char), subsequently followed by secondary and tertiary reactions (heavy hydrocarbons → light hydrocarbons + $H_2$ + CO + $CO_2$; light hydrocarbons → hydrocarbons + $H_2$ + CO) [70].

Table 6 shows the results of gasification of WT and/or combined pyrolysis–gasification, as given in the references. The types of reactors from a laboratory-scale fixed bed to rotary kilns to fluidized-bed pilot plant, where the feed varies in particle sizes from 0.14 mm to 2 cm, a temperature range of 500–1300 °C, with or without gasification agents, are key among the studies. Furthermore, dual-purpose two-stage fixed-bed reactors with different catalysts [64,71–73] and steam gasification and reforming reactor [63] with increased hydrogen concentration were obtained. Steam, catalysts, and high-temperature gasification seem to show promising results for hydrogen and CO production, with lower char content, implying increased tar and char reactions. The char and tar yields may depend on the optimum operating conditions of ER and tire particle sizes for higher syngas yield, gas HHV/LHV, and energy recovery ratio [52]. The use of catalysts for both reforming and shift reactions for a combined system of pyrolysis and gasification is mainly interesting for the high-rate conversion of tire products into hydrogen. However, the presence of sulphur in the fuel feed and tars makes the catalysts prone to poisoning and coke deposition on the active sites, leading to deactivation [64,71–73].

**Table 6.** $H_2$ and CO production of WT by gasification.

| Reactor Type | Agent | ER | T (°C) | $H_2$ (vol%) | CO (vol%) | $H_2$ (g/kg MSW) | LHV (MJ/Nm$^3$) | Ref. |
|---|---|---|---|---|---|---|---|---|
| Rotary kiln | Steam | - | 1000 | 65.0 | 17.25 | 100.1 | 25.0 | [60] |
| Tube | Steam | - | 625 | 46.7 | 5.2 | 39.44 | - | [61] |
| Bubbling fluidized bed | Air | 0.15 | 805 | 20.0 $^b$ | 3.52 $^b$ | - | 7.03 | [62] |

**Table 6.** *Cont.*

| Reactor Type | Agent | ER | T (°C) | $H_2$ (vol%) | CO (vol%) | $H_2$ (g/kg MSW) | LHV (MJ/Nm$^3$) | Ref. |
|---|---|---|---|---|---|---|---|---|
| Rotary kiln | Steam | - | 750 | 73.3 | 21.5 | - | 17.74 | [63] |
| Hybrid filtration | Air | - | 1294 | 3.3 [b] | 4.1 [b] | - | 10.26 | [8] |
| Rotary kiln | Steam | - | 850 | 57.0 | 17.7 | - | 22.56 [a] | [74] |
| Fixed bed | Air | 0.07 | 500 | 30.4 | 8.2 | 32.0 | 6.0 | [52] |
| Fixed bed | Steam | | 787 | 50.0 | 9.8 | 30.37 | 22.0 | [70] |
| Fixed bed | Steam | | 800 | 48.81 | 3.89 | - | 15.21 | [75] |
| Fixed bed | Air/Steam | | 800 | 22.63 | 4.88 | - | 7.34 | [75] |
| Two-staged fixed bed | - | | 600/800 | 57.47 | 16.06 | 36.32 | - | [64] |
| Two-staged fixed bed | - | | 500/800 | 60.8 | 9.7 | - | - | [72] |
| Two-staged fixed bed | Steam | | 500/900 | 56.8 | 15.0 | - | - | [73] |
| Two-staged fixed bed | - | | 500/800 | 56.0 | 11.0 | - | - | [71] |
| Fixed bed | Air | | 700 | 2.8 [b] | 4.0 [b] | - | 7.5 | [76] |

[a] MJ/kg; [b] $N_2$ included.

Based on a thermodynamic modelling study for tire oil composed of mainly limonene ($C_{10}H_{12}$), Mastral et al. [53] found that an appreciable hydrogen yield of 158 g/kg compared to what was achieved for those represented in Table 5 is also far from the maximum theoretical amount of $H_2$ available in WT, estimated to be 387 g/kg [68]. Donatelli et al. [74] showed both in a numerical model and through experimental results of energy balance on syngas production that the available energy by combustion of gases produced compared to experimentally required energy for gasification of 1 kg of WT was 32.5 MJ. In a recent study [77] using models for WT gasification with steam and the other steam-integrated steam methane reforming unit, Ahmed et al. showed that the cost of hydrogen lies between 5.57 and 4.46 EUR/kg.

Considering the highly extractable and inexhaustible resource from the ever-increasing vehicles with pneumatic tires in traction, the high H/C ratio, and environmental remediation, WT can be potentially utilized by conversion into WtH and/or syngas for the further production of fuels and chemicals. The product distribution of gas, liquid, and appreciable amounts of char, whose high carbon content and surface areas can be used as activated carbon for different adsorption processes, catalyst support, and power sources, has a supply chain in the circular economy. Thus, there is a great incentive to dwell on research orientations for process optimizations of WT along with tar-free higher heating value fuels for sustainable value-added products for industrial processes and power generation as well as pollution and emission control by thermochemical methods.

### 2.2.3. Waste Plastics (WPs)

Plastics, polymers with different functional groups of monomers consisting mainly of carbon, and hydrogen chains with or without additives have become an indispensable commodity product for everyday use due to their performance, low cost, and various application areas. The production and consumption rates of plastics have shown an upsurge, culminating in 368 Mt in 2019, with a nearly 20% increase in the last 5 years. Typical sources of plastic wastes generated may encompass both low-density (LD) and high-density (HD) polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC). The release of plastics due to a lack of proper management and strategy has led to serious problems for marine and terrestrial ecosystems. An estimated 8 Mt of plastic litter has entered the world's oceans, degrading into microplastics and nanoplastics and causing impairments for marine living organisms and humans [78–80]. Therefore, a multifaceted solution is needed to utilize these abundant polymeric materials by collection, treatment, and recycling through re-polymerization, energy, and chemical application.

Table 7 shows the proximate and ultimate analyses by those given in the references. The volatile contents of the samples and calorific values are by far the highest among those previously reported for MSW and WT in Tables 3 and 5, respectively. The ash content is, likewise, low, resulting in high conversion of the feedstock for increased gas concentrations and high quality of char. There is variation among the pure polymers, often obtained from a supplier, but they are treated under different conditions of the analytical and combustion method used. However, the mixed plastics can usually be blends of pure polymers or collected from MSW mixtures and are, therefore, contaminated from the raw solid, showing higher ash contents than those of the pure plastic materials, while the oxygen content shows not-too-high deviations.

**Table 7.** Representative proximate (P) and ultimate (U) analyses of different waste plastics.

| Type | MC (wt% wb) | VC (wt% db) | FC (wt% db) | Ash (wt% db) | C (wt% db) | H (wt% db) | O (wt% db) | S (wt% db) | N (wt% db) | Cl (wt% db) | LHV (MJ/kg) | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PE | 0.02 | 99.85 | 0 | 0.15 | 85.81 | 13.86 | 0 | 0.06 | 0.12 | - | - | [31] |
| | 0.01 | 99.9 | 0 | 0 | 85.60 | 13.72 | 0.68 | 0 | - | - | - | [81] |
| | 0 | >99 | - | <0.01 | 85.84 | 14.07 | <0.01 | 0 | 0.09 | - | 43.38 | [82] |
| | 0.08 | 99.92 | 0 | 0 | 85.29 | 14.51 | 0.20 | 0 | 0 | - | 43.30 | [83] |
| PET | 0 | 87.96 | 12 | 0.04 | 62.8 | 4.3 | 32.79 | 0.04 | 0.07 | - | 22.77 | [84] |
| | 0.21 | 94.69 | 5.1 | 0 | 60.97 | 4.25 | 32.82 | 0 | 0.03 | - | 21.97 | [85] |
| PP | 0 | 100 | 0 | 0 | 86 | 14.0 | 0 | 0 | 0 | - | - | [84] |
| | 0.4 | 99.6 | 0 | 0 | 85.18 | 14.39 | 0.43 | 0 | 0 | - | - | [85] |
| | - | >99 | - | <0.1 | 85.86 | 13.91 | 0.13 | 0 | 0.10 | - | 43.42 | [82] |
| | 0 | 99.0 | - | 0.94 | 85.25 | 14.71 | 0 | 0 | 0.04 | - | - | [86] |
| | 0.1 | 96.7 | 3.2 | 0.03 | 84.3 | 13.8 | 1.7 | - | 0.6 | - | 45.1 | [87] |
| PS | 0 | 84.6 | 14.4 | 0.97 | 46.87 | 6.06 | 45.48 | 0 | 0.62 | - | 18.09 | [64] |
| LDPE | 0.1 | 99.9 | 0 | 0 | 92.3 | 7.4 | 0.2 | 0 | 0 | - | 40.3 | [88] |
| | - | - | - | - | 85.38 | 14.62 | 0 | 0 | 0 | - | - | [88] |
| HDPE | 0 | 99.7 | 0.3 | 0 | 85.71 | 14.29 | 0 | 0 | 0 | - | 43.10 | [64] |
| | 0 | 99.1 | 0.01 | 0 | 85.4 | 14.6 | 0 | 0 | 0 | - | - | [89] |
| PVC | 0.1 | 66.6 | 29.0 | 4.3 | 50.1 | 6.2 | 22.3 | 0 | 0 | 20.5 | - | [87] |
| MP | - | 96.3 | 1.1 | 2.6 | 77.1 | 11.5 | 11.2 | - | 0.2 | - | - | [90] |
| | 0.47 | - | - | 2.04 | 76.54 | 12.84 | 7.91 | - | 0.2 | - | 39.7 | [91] |
| | 0.3 | - | - | 1.3 | 84.4 | 14.0 | 0 | 0 | 0 | - | 45.5 | [92] |
| | 0.4 | 98.9 | - | 2.7 | 82.3 | 12.3 | 5.0 | 0.1 | 0.3 | - | 42.2 | [93] |
| | 4.4 | 86.73 | 4.1 | 9.2 | 68.85 | 8.89 | 21.3 | 0.14 | 0.4 | 0.32 | 24.68 | [94] |
| | 4.4 | 82.91 | 3.9 | 8.8 | 62.52 | 8.07 | 19.34 | 0.13 | 0.36 | 0.37 | 24.68 | [95] |
| | 0.51 | 62.35 | 18 | 19.1 | 65.18 | 15.61 | 9.15 | 0.11 | 0.16 | 2.98 | - | [96] |
| | - | - | - | - | 77.1 | 11.5 | 11.2 | - | 0.2 | - | - | [90] |
| | - | 93.2 | 3.5 | 3.3 | 68.9 | 12.8 | 14.3 | 0.2 | 0.5 | - | 35.2 | [97] |
| | 0.38 | 94.71 | 4.37 | 0.54 | 82.41 | 13.42 | 2.86 | 0 | 0.18 | 1.13 | 43.17 | [98] |

wb: wet basis; db: dry basis; MC: moisture content; VC: volatile content; FC: fixed carbon; MP: mixed plastics = not specified.

The disposal of waste plastics in landfills or by incineration for energy recovery is widely implemented around the world, though both systems contributing to leakage and emissions of toxic substances, impacting health and the environment. The status of plastic waste treatment in the EU is that 42.6% is used for energy recovery, 24.9% landfilled, and 32.5% recycled, with the aim, in the latter case, to increase it to 55% by the year 2030, as stipulated by the European Green Deal [99]. Thermochemical recycling by pyrolysis and gasification of waste plastics is among the most effective methods for the recovery of liquid compounds, solid residues, and gases. Advanced microwave-assisted reactors for the production of gasoline, jet fuel by subsequent catalysis, and other valuable products are reported in the literature [100–105]. Gasification offers a flexible means to handle mixed plastic waste blended with other mixtures of biomass and municipal waste to valorize for chemicals and other energy as well as reductions in environmental pollution [106,107].

Table 8 summarizes the hydrogen and CO production together with the operating conditions and gasifier types for some studies using waste plastics.

Wilk et al. [82] investigated different types of plastic materials in a dual-fluidized bed by superheated steam in a 100 kW gasification pilot plant with olivine as the bed material at 850 °C. Depending on the monomer used for the specific plastic (polyethylene (PE), polypropylene (PP), PE + polyethylene terephthalate (PET), PE + polystyrene (PS) and PE + PP), different reaction products were observed, yielding different rates of tars, primarily for PE, PP, and PE + PET in the range of 44 to 60 g/$Nm^3$, while this was less pronounced for PE + PP, where alkanes and alkenes are converted during the reforming reactions. The $H_2$ and CO concentration distributions for the various plastics, however, were in the order of PE + PS > PE + PP > PE > PP > PE + PET. A small-scale fluidized-bed pilot plant with dolomite and olivine at a gasification temperature of 850 °C and ER of 0.32–0.36 was performed on PP, with the objective of effective tar removal [86]. It was asserted that dolomite was more active in tar elimination than olivine but produced particulates purged together with the reaction products plugging downstream devices. The use of olivine showed promising results, with a tar content of 2 g/$Nm^3$.

A two-stage gasifier comprising a fluidized bed supplied by steam and a tar cracking reactor with active carbon (AC) was assembled for the gasification of PE [85]. A tar content in gas of 0 mg/$Nm^3$ was obtained in the presence of the high-surface-area active carbon (BET surface area 1126 $m^2$/g) compared without AC, with a tar yield of 8.4 g/$Nm^3$. The effect of a steam-to-feed ratio in the range of 1.5–2.5 seems not to change the syngas concentration significantly, with an almost constant $H_2$ concentration of 65 vol%. The in situ regeneration of active carbon with steam, however, showed that the recovery rate of the surface area and total pore volume were 63% and 64%, respectively, after seven runs of gasification and tar cracking operations. PET gasification was conducted using a two-stage gasifier in a fluidized bed at ER = 0.27 at a temperature of 778 °C and a tar cracking reactor of 844 °C filled with active carbon, resulting in a minimum 7 mg/$Nm^3$ gas [85]. The syngas production of $H_2$ and CO was between 17–22 vol% and 18–27 vol%, respectively, compared without the presence of active carbon having 3 vol% $H_2$ and 15 vol% CO. However, regeneration due to pore plugging of the porous structure of the active carbon might hamper long-term use for tar removal. Air gasification of PVC in a two-stage reactor comprising a fluidized-bed reactor with a tar cracking reactor and chlorine removal was studied in the presence Ni/AC and calcined Ca-based additives [87]. The temperatures for both reactors were kept at 800 °C and an ER for the gasifier at 0.32. Effective tar-free and higher HCl removals in producer gases were obtained with activated carbon and Ca from oyster shells. Furthermore, Ni as an active catalyst showed an increase in $H_2$ content through steam reforming reactions. A conical spouted-bed reactor (SBR) was used to study the effects of temperature (800–900 °C), steam plastic ratio (0–2) with olivine, and $\gamma$-$Al_2O_3$ as bed materials and catalysts for tar removal for the gasification of HDPE. The $H_2$/CO ratio of 2.2 with olivine having 4.8 wt% tar less than $\gamma$-$Al_2O_3$ and sand at 900 °C shows the effective use of the SBR for high heat transfer rates by steam gasification.

He et el. [108] studied the effect of temperature on the gasification of waste PE in the presence of steam using NiO/$\gamma$-$Al_2O_3$ as a catalyst to induce tar cracking. Catalytic gasification at lower temperatures instead of the high-temperature decomposition of tars containing different compounds can be an effective method for tar removal and reactions. Comparisons of $H_2$, CO, $CO_2$, $CH_4$, $C_2H_4$, and $C_2H_6$ contents for pyrolysis, catalytic pyrolysis, steam gasification, and catalytic steam gasification showed a marked output for $H_2$, while the concentrations of $CH_4$ $C_2H_4$, $C_2H_6$, tar, and char decreased substantially due to steam reforming and water–gas shift reactions. At a reaction temperature of 900 °C, stable performances of the catalyst with all the gaseous reaction products were observed. Similarly, Yang et al. [81] studied the gasification of waste PE and PP in a fluidized-bed reactor at ER = 0.1, with sand particles at 600 °C for the production of hydrocarbons, followed by a fixed-bed catalytic reactor with Ni/$Al_2O_3$ for the co-production of hydrogen and carbon nanotubes (CNTs). Among the various Ni/$Al_2O_3$ catalysts, the one calcined under a reductive hydrogen atmosphere with nanocatalysts of Ni showed the highest $H_2$ and CO contents, with $H_2$ and CNT yields of 68 g/kg WP and CNT 30.5 wt%, respectively. The increase in $H_2$ and CO and decrease in $CO_2$ and hydrocarbons are due to the dry reforming of methane (Equation (11)) and hydrocarbons (Equation (13)).

Different types of $Al_2O_3$ supports having 30 wt% Ni catalyst loadings were studied in fixed-bed reactors for the gasification of HDPE with ER 0.2 in a catalyst bed reactor for enhanced hydrogen production [89]. Air contributes to the combustion reaction at the sub-stoichiometric level by pyrolysis. High $H_2$ generation was observed when <50 nm sized $Al_2O_3$ was used as a support for Ni catalysts in the other structures of $Al_2O_3$. The differences in product selectivity might be attributed to the dispersion of the active catalysts on the support and textural properties of the support. However, coke deposition due to the breakup of the tars of unsaturated compounds on the catalyst and support is considered to have an impact on the long-term activity for hydrogen production. The pyrolysis and gasification of PP, PS, HDPE, and their mixtures and plastic wastes were studied at a pyrolysis temperature of 500 °C and a gasification temperature of 800 and 850 °C in the presence of Ni-Mg-Al catalysts [90]. The effect of the catalysts in the decomposition hydrocarbons ($C_1$–$C_4$), steam reforming, and water–gas shift reactions is enhanced. However, due to the structural properties with different monomers of the plastics, different $H_2$ contents were obtained, as shown in Table 8.

Coke deposition in the form of filamentous carbon was found in samples for the pyrolysis–gasification system of PP, HDPE, and the plastic waste mixture. A chemical looping tar cracking–gasification process of simulated plastic waste products was investigated to produce $H_2$ and syngas by pyrolysis with Ni-Fe-Al catalysts at a cracking temperature of 800 °C [109]. The catalysts were regenerated due to coke formation by steam. Among the catalysts tested, the coke removal efficiency was found to decrease in the following order: NiFeAl > $NiFeAl_2$ > $NiFeAl_4$ > $NiFeAl_{10}$.

Arena et al. [91] carried out experiments on two plastic wastes, one mainly with poly-olefins and the other with a plastics-to-biomass ratio of 4:1 in a pilot-scale bubbling fluidized-bed reactor, with a feedstock capacity of 100 kg/h, a maximum thermal output of 400 kW with ER of 0.2–0.3, and a temperature of 840–930 °C. Olivine was used as a bed material for tar removal but showed a reduced tar cracking performance with 59 $g/Nm^3$ and 34 $g/Nm^3$ for plastics only and mixed with biomass, respectively. The results show that carbon particles and heavy condensable hydrocarbon compounds are correlated to the compositions and structures of the fuel feedstock, giving rise to particulate matter for the one blended with biomass and larger quantity of tars for plastics. The results also showed that a high-quality producer gas with 76–86% carbon conversion efficiencies seem possible.

Co-gasification on a mixture of pine sawdust and HDPE was carried out in a two-stage pyrolysis–gasification system with pyrolysis at 550 °C and a gasification temperature of 700 °C using Ni-Fe@CNF/porous carbon as a tar cracking catalyst [110]. The catalytic performances and syngas production were optimized by varying the operating temperatures and biomass/plastic ratios. The synergistic effect on gas yield from the combinations of the system shows that the tar yield was reduced with the increase in the ratio of the plastic added, with the plastic being a source of $H_2$ and $CH_4$, while the decrease in the biomass feedstock reduced the CO and $CO_2$ contents due to the decrease in oxygenated compounds. The biomass/plastic ratio of 1:2 showed a positive effect, resulting in a high $H_2$/CO ratio of 5.63. Higher-temperature operation implies that reactions (Equations (4), (5) and (11)–(13)) take place both thermally and catalytically. It was found that at 550 °C, the tar yield was 83.01 mg/g feed but was suppressed to 5.22 mg/g feed at 750 °C, a decrease of more than 90%. The effects of feedstock ratio, pyrolysis temperature, reforming temperature, water flow rate on co-pyrolysis, and gasification of pine saw dust and LDPE on Ni + CaO/C at different temperatures were studied by Gao et al. [88]. A feedstock ratio of 5:5, a flow rate of 5 mL/h, and pyrolysis and reforming temperatures of 700 and 600 °C, respectively, were found optimal for maximizing the generation of $H_2$. The results also showed that the use of Ni for reforming and CaO for $CO_2$ adsorption promote high $H_2$ content and yield. The co-gasification of low-sulphur-containing lignite and waste plastics gathered from MSW was studied in a gasifier with $H_2O/CO_2$ as gasifying agents at 700–750 °C and a thermal tar reformer unit at 1200 °C [93]. The composition of the gas produced shows that the $H_2$ and CO contents decrease from 55 vol% for lignite alone to 51.87 vol% for the 20% WP mixture and CO from 19.54 vol% to 15.55 vol%, while $CO_2$ increases from 21.44 vol% to 27 vol% for the same cases. It was concluded from the chars analyzed by Raman spectroscopy that the ratio of disordered carbon to ordered carbon is higher for char emanating from lignite than for the mixtures of lignite and WP with disorder to be more reactive than the ordered one. Table 8 shows a review of the results obtained in studies regarding $H_2$ and CO production via WP gasification.

**Table 8.** $H_2$ and CO production of WP by gasification.

| Reactor Type | Agent | ER | T (°C) | $H_2$ (vol%) | CO (vol%) | $H_2$ (g/kg MSW) | LHV ($MJ/Nm^3$) | Ref. |
|---|---|---|---|---|---|---|---|---|
| Fluidized bed/Fixed bed | Air | 0.1 | 600/750 | 36.85 | 35.91 | 65 | - | [81] |
| Dual fluidized bed | Steam | - | 850 | 51.2 | 23.3 | 86.94 | - | [82] |
| Fluidized bed/Tar cracker | Steam | - | 800/850 | 66.02 | 9.78 | 150 | 12.23 | [83] |
| Fluidized bed/Tar cracker | Air | 0.27 | 778/844 | 22.2 [b] | 25.3 [b] | 46 | 7.27 | [85] |
| Bubbling fluidized bed | Air | - | 850 | 9.72 [b] | 8.6 [b] | 49.16 | 5.8 | [86] |
| Fluidized bed/Tar cracker | Air | 0.32 | 796/805 | 29.8 [b] | 15.5 [b] | - | 7.8 | [87] |
| Two-stage fixed bed | - | - | 550/750 | 53.0 | 11.5 | 73 | - | [110] |
| Fixed bed | Air | 0.2 | 700 | 36.25 | 24.7 [b] | - | - | [89] |
| Two-stage fixed bed | Steam | - | 500/850 | 66.18 | 28.6 | 241 | - | [90] |
| Two-stage fixed bed | Steam | - | 850 | 60.0 | 33.18 | 196 | - | [90] |
| Two-stage fixed bed | Steam | - | 850 | 65.45 | 25.19 | 303 | - | [90] |
| Bubbling fluidized bed | Air | 0.248 | 850 | 6.3 [b] | 6 [b] | - | 6.6 | [91] |
| Fluidized bed | Air | 0.2 | 850 | 8.63 [b] | 5.2 [b] | 16.12 | 7.78 | [92] |
| Fluidized bed | Steam/$CO_2$ | - | 900 | 55.73 | 24.21 | - | 11 | [93] |
| Bubbling fluidized bed | Air/Steam | 0.25 | 800 | 36.4 | 34.8 | 11.5 | 16.3 | [94] |
| Bubbling fluidized bed | Air/Steam | 0.25 | 900 | 7.0 [b] | 16.5 [b] | 13.5 | - | [95] |
| Two-stage fixed bed | Steam | - | 500/700 | 68 | 22 | 258 | - | [90] |
| Bubbling fluidized bed | Air/Steam | 0.28 | 800 | 27.25 [b] | 7.15 [b] | - | 6.11 | [98] |
| Fixed bed | - | - | 800 | 86.8 | 5.1 | - | - | [109] |
| Bubbling fluidized bed | Air | 0.25 | 750 | 3.29 | 7.53 | 126 | 5.61 | [111] |
| Two-stage fixed bed | Steam | - | 600/800 | 53.8 | 26.4 | 90 | - | [112] |
| Spouted bed | Steam | - | 900 | 61.6 | 27.8 | 184 | 15.5 | [113] |

[b] $N_2$ included.

In summary, depending on the monomers and physicochemical properties of the feedstock in the form of waste plastics, there is a varying degree of alterations in gasification product quality and distribution with different gasifying agents, pyrolysis stage, steam and catalytic reforming, bed material and catalysts for tar purification, and temperature interval used. Thermochemical recycling using different operating conditions has shown potential perspectives for the production of high concentrations of $H_2$ and syngas purity along with the high heating values (5.6–16 $MJ/Nm^3$) to be used for further chemical upgrading through synthesis (DME, ammonia, methanol, F-T diesel, fuel, etc.). The works shown in Table 8 imply the feasible application of gasification technology for small- and large-scale applications. However, high contents of volatiles suggest challenges in the final product due to tar formations, which inevitably needs in situ tar cracking beds and catalysts of dolomite, olivine, activated carbon, CaO, and supported and unsupported metals.

Han et al. [114] utilized thermodynamic modelling for simulating the potential of $H_2$ production from different plastic waste (HDPE, PP, PS, PET, PVC) and compared the obtained results against experimental findings. All the simulation results were in agreement with experimental findings, with the $H_2$ production being sensitive to the operating conditions applied (mainly the gasification temperature being positively correlated to $H_2$ production, whereas pressure was negatively correlated to CGE and $H_2$ production). $H_2$ productivity ranged from 1.3 g/kg of feedstock to 23 g/kg feedstock, with PP being the most efficient.

Gasification has also shown its flexibility when different feedstock mixtures of plastics or plastics with lignite and biomass are used, improving the heat and mass transfer characteristics. Thus, valorization through thermochemical means establishes the circular economy and environmental sustainability of the exceedingly high-rate production and consumption of waste plastics.

### 2.3. Gasification Processes

The advantage of gasification-based processes, compared to conventional combustion-based systems used today, is its ability to convert a solid fuel in such a way that specific chemical compounds can be isolated, e.g., CO and hydrogen, for use as a basis for the synthesis of chemical products or upgrading and separation to pure hydrogen. As waste contains numerous amounts of impurities, it is evident there is need for gas cleaning and upgrading, ranging from a few to several process steps, depending on the requirements of the application of the produced gas. Table 9 shows selected data for contaminants in raw product gas from waste gasification together with gas cleaning requirements related to different applications.

**Table 9.** Selected data for raw product gas content and gas cleaning requirement related to different applications [115–118].

| Contaminants/Applications | Raw Product Gas | Gas Engine | Gas Turbine | Fuel Cell | Syngas |
|---|---|---|---|---|---|
| Particles (mg/Nm$^3$) | 100–50,000 | <50 | <10 | <0.1 | <1 |
| Tar (mg/Nm$^3$) | 20–100,000 | <50 | <10 | n.a. | 0.1–1 |
| Sulfur species (ppmv) | 50–5000 | <20–50 | <20 | SOFC < 0.06–10<br>PAFC < 50<br>MC < 0.5 | <0.01–1 |
| Nitrogen species (ppmv) | 100–20,000 | <80 | <50 [a] | Not limited | <0.02–1 |
| Alkali species (ppmv) | 10–1000 | <0.025–0.1 | <0.025–0.1 | Not specified | <0.01 |
| Halides (Cl + F + Br) (ppmv) | 5–1000 | <100 | <1 | <1 | <0.01 |

[a] Emission limited.

Figure 2 shows an example of a gas cleaning and purification train for upgrading to a synthesis gas. Note that the gas may be separated at different stages of cleaning for different application purposes and that some of the steps are optional depending on the needs for gas cleaning. Also, in the case of hydrogen production steps for upgrading by, e.g., WGS (Equation (5)), the separation of hydrogen should be added.

Prior to operation in the gasifier, the different types of waste including MSW must be prepared, sorted, and pretreated as they contain heterogeneous degradable and non-degradable mixtures in the form of food waste, yard waste, paper and cardboard, plastics, rubber, glass, electronic waste, metal, inert, and miscellaneous refuse [16,119]. Therefore, it is, in many cases, important to process the waste into structured forms of small pellets, fluffs with small particle sizes for increased bulk, and energy densities of the fuel, i.e., so-called RDF or SRF.

The next step is gasification, where the solid feedstock is converted to a combustible gas in a gasifier (various gasifier technologies are described in the subsequent section) followed by certain gas cleaning steps to convert tar and, if also needed, all other hydrocarbons, particulates, and alkali-, chloride-, fluoride-, and nitrogen-containing species. At this stage of cleaning, the produced gas may be used for heat and electricity production by, e.g., direct combustion in a boiler or in a gas engine.

In gas purification, the gas is further purified to meet the requirements of the final use of the gas by removal of trace levels of hydrocarbons, mainly aromatics, tars, and heavy metals, such as mercury, sulphur compounds, and HCN.

Figure 2 clearly shows that upgrading a raw gas, produced in waste gasification, to hydrogen is rather costly and adds significantly to the plant investment and operating costs.

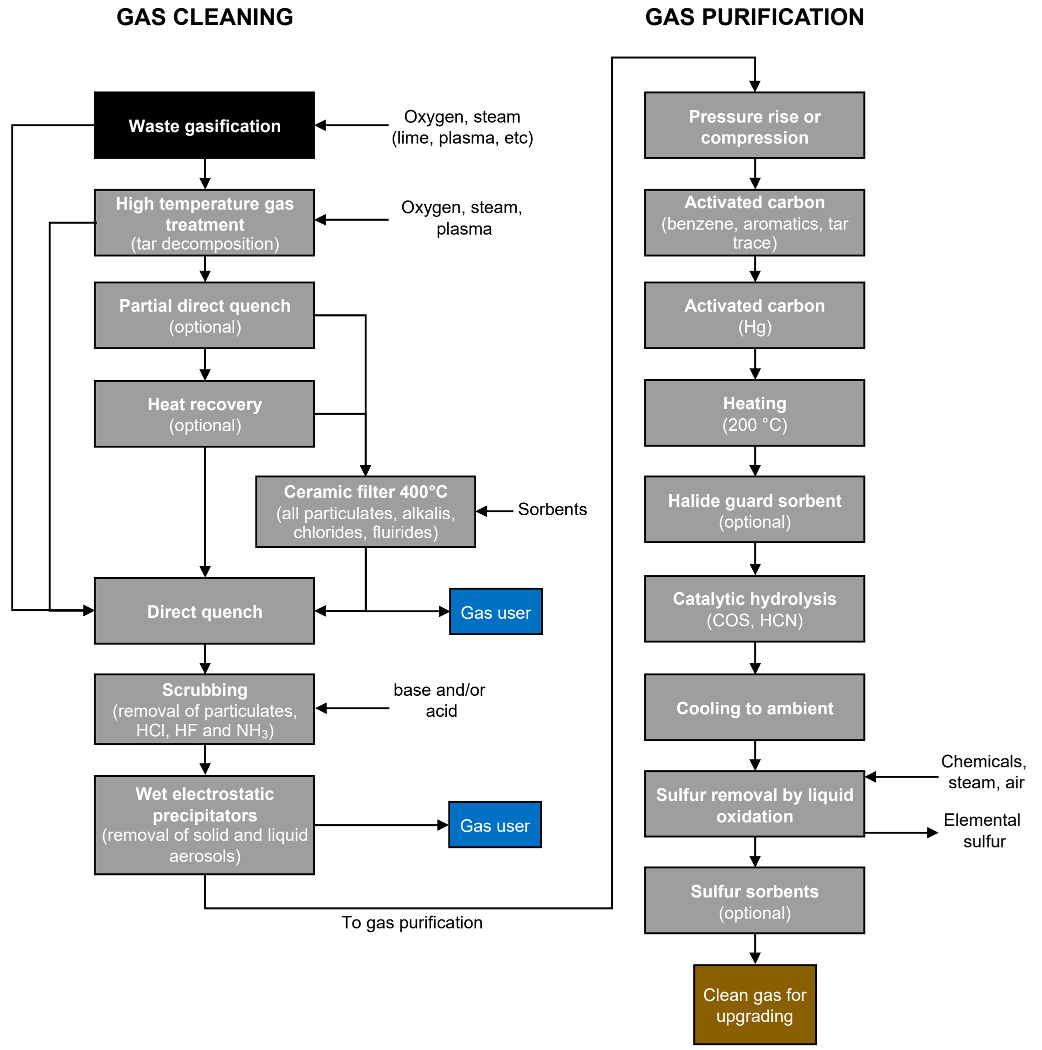

**Figure 2.** Example of a waste gasification process for production of a clean synthesis gas. Adapted from [120]. Reproduced with permission from L. Waldheim, IEA Bioenergy, Paris, France 2019.

Another option for the purification of the hydrogen is indirect processes, also called "chemical looping". Here, the raw syngas is used to reduce a metal oxide to the metal and, in a subsequent step, the metal is then oxidized by steam, producing clean hydrogen. Several groups are working on this so-called steam–iron process, like TU Graz [121], who recently realized a 10 kW unit, or [122] demonstrated this for 250 kW or [123] 25 kW. Chemical looping for hydrogen production is based on very old methods of producing hydrogen, where one of the first patents were examined in 1911 [124]. The principle is that the fuel is gasified to a lean reducing gas, containing carbon monoxide and hydrogen. This gas reacts with iron oxides (hematite $Fe_2O_3$, magnetite $Fe_3O_4$, wuestite FeO) to produce a reduced form of iron oxide (wuestite FeO, iron Fe). The reduced iron oxide is re-oxidized with steam to form magnetite and hydrogen. In this way, very clean hydrogen can be produced from raw synthesis gas and dilution by inert gases, like nitrogen does not constitute a problem. An ongoing project in Austria converts biogas to hydrogen in the scale of 10 kW [125].

### Gasifiers

There are several literature sources describing gasifier technologies and their features, and in the present review, we do not intend to be inclusive and only summarize based on information from selected sources [21,120,126,127].

Since most reactions occurring in the gasifier are endothermic, with the main exception being the oxidation of char (Equations (1) and (2)) or combustible gases (Equations (4),

(8) and (9)) by oxygen, WGS (Equation (5)) and pyrolysis, which in certain temperature windows is exothermic, there is a need to supply or generate heat within the gasifier to balance the overall process. Gasifiers providing the needed heat by adding an oxidation agent, such as oxygen or air, to achieve partial oxidation of the fuel are called autothermal gasifiers or direct gasifiers. Thus, the heat produced is directly in the reactor. In case the heat is provided separately from a source outside the gasifier, it is referred to as allothermal gasifiers or indirect gasifiers. This means the heat consumed in a gasifier, where the fuel is gasified, is separated from the source of heat. Allothermal gasifiers can be divided into two main types: processes using a heat carrier, such as sand, circulating between a gasifier and combustion reactor; transfer of heat via an indirect heat exchanger where heat in, e.g., a hot flue gas, is transferred in the form of radiation and convection to the gasifier. There are certain disadvantages and advantages of the two types, as briefly outlined in Table 10.

**Table 10.** Advantages and disadvantages of autothermal and allothermal gasifiers [120,126,127].

| Autothermal Gasifiers | Allothermal Gasifiers |
|---|---|
| One reactor | Two reactors or a separate heating system |
| Simpler design | More complex design |
| One gas stream to clean | Cleaning of two streams often needed. |
| Oxygen or steam/oxygen as gasifying agent for syngas production | Gasification by steam/$CO_2$, so air separation unit is not necessary |
| Generally lower tar content in the produced gas due to higher temperature. | High tar content in the produced gas due to lower temperature. |

In addition to pure autothermal and allothermal gasifiers, hybrid gasifiers also exist, as exemplified by indirect plasma gasifiers where heat from electricity is transferred via an injection of a plasma gas (most often air) as a heat carrier to the gasifier.

The type of gasifier used for the conversion greatly impacts the distribution and yield of the main reaction products of the raw product gas. Gasifiers are typically classified into three main groups viz. fixed-bed gasifiers, fluidized-bed gasifiers, and entrained-flow gasifiers, as shown in Figure 3. Table 11 shows selected characteristics for the main types of gasifiers.

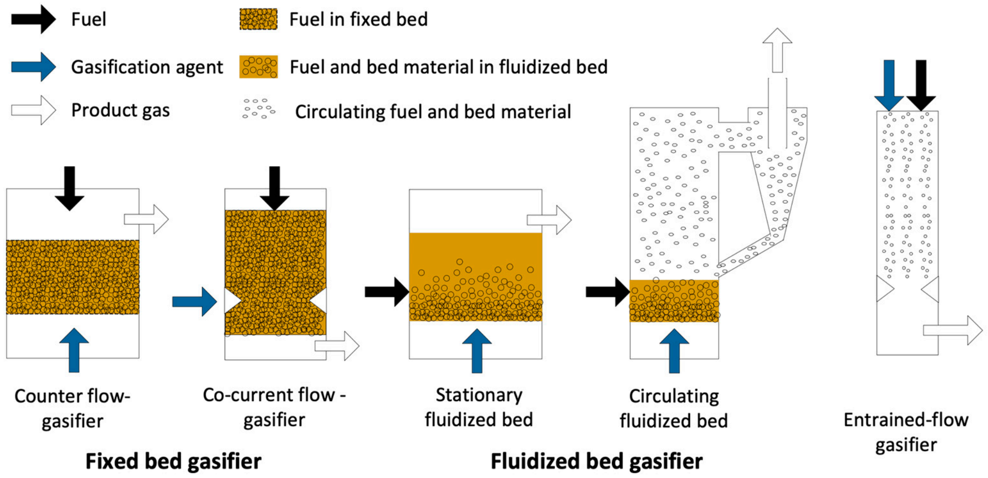

**Figure 3.** Fixed-bed gasifiers (counter and co-counter flow), fluidized-bed gasifiers (stationary/bubbling and circulating) and entrained-flow gasifier [128]. Reproduced with permission from J. Hrbek, IEA Bioenergy, Paris, France, 2016.

Fixed-bed or moving-bed gasifiers including updraft and downdraft configurations have been used for waste gasification (Figure 3). The configuration relates to the input of feedstock and the gasifying agent. In the case of an updraft gasifier, the gasifying agent and the feedstock enter the bottom and the top of the reactor, respectively. Hot gases produced from oxidation in the bottom of the gasifier flow through the reduction zone (gasification, pyrolysis, and drying zone during its way out at the top of the reactor). This results in a subsequent decrease in the gas temperature, from high in the oxidation zone to low at the top and, as a consequence, a product gas with a high tar content (Table 11) as the tar-laden pyrolysis gas, produced in the pyrolysis zone, never passes through the high-temperature zone. The high tar content as well as the low product gas temperature are limiting factors, selecting this technology for the production of clean syngas or hydrogen as extensive tar decomposition mitigations are needed. The restricted capacity of <10 MW (Table 11) is mainly related to heat transfer and flow issues in the bed [120]. In downdraft gasifiers, the input of a gasifying agent is on the side or top of the gasifier, resulting in a different flow pattern compared to updraft gasifiers. This results in a lower tar content in the product gas as the gas passes through the high-temperature oxidation zone on its way out of the reactor. Although several studies report the use of this technology for various types of waste [129], a limiting factor is the potential capacity limited to <1 MW (Table 11). The limiting factor is the throat section of the gasifying agent inlet, where a scale up results in a bad mixing over the cross-section, causing channeling in the bed due to a less-uniform movement in the bed [120]. Waste used in moving-bed gasifiers needs be relatively uniform without too many fines and with sufficient mechanical strength to avoid the breakdown of fuel particles, caused by the weight of the bed. This is important as the bed porosity needs to be maintained to keep a realistic pressure drop.

**Table 11.** Selected characteristics for the main gasifier types. Adapted from [120]. Reproduced with permission from L. Waldheim, IEA Bioenergy, Paris, France, 2019.

| Characteristic/Gasifier Type | Fixed Bed | BFB | CFB | Entrained Flow |
|---|---|---|---|---|
| Capacity range MW thermal (Typical operation pressure) | Downdraft < 1<br>Updraft < 10<br>(mainly atmospheric) | 10–50<br>(atmospheric)<br><200<br>(<3 MPa) | 20–150<br>(<3 MPa) | 100–400<br>(1–8 MPa) |
| Bed particle size (mm) | none | 0.1–1 | 0.1–0.4 | None |
| Fuel particle size (mm) | 10–100 | 1–100 | 1–100 | <1 |
| Operating temperature (°C) | 800 | 800–950 | 800–950 | 1400–1500 |
| Gas superficial velocity (m/s) | 0.1–0.5 | 0.5–1.5 | 4–8 | 15–25 |
| Solids mixing | Very low | High, complex | High complex | Low |
| Tar content in gas (g/Nm$^3$) | Downdraft < 1<br>Updraft >> 10 | >10 | >10 | <<1 |
| Particles in gas (g/Nm$^3$) | 0.1–0.2 | 0.1–1 | 2–20 | 1 |

BFB: bubbling (stationary) fluidized bed; CFB: circulating fluidized bed.

Fluidized-bed gasifiers are mainly divided into bubbling (stationary) or circulating fluidized beds based on the principles of fluidization, where a fluidizing medium (generally a gas stream of air, steam of steam/oxygen mixtures in case of gasification) with a high enough gas velocity causes a bed material (inert or catalytically active) with a fuel to behave like a fluid. The fluidized bed provides high rates of heat and mass transfer and good mixing of the solids. This means that the temperature is relatively constant throughout the bed and that chemical reactions proceed at high rates. In the case of bubbling fluidized-bed gasifiers, the gas velocity is rather low and between 1 and 3 m/s to keep the bed material suspended by the gas. A freeboard (an enlargement in the reactor cross-section area) is used to separate particles, ejected by erupting bubbles, back to the bed. For a circulating fluidized bed, the gas velocities are much higher, 3–10 m/s, resulting in different hydrodynamics, where the solids are dispersed all over the tall riser. This allows for a long residence time for both the gas and the fine particles. The particles are, thereafter, separated from the gas in a cyclone and recycled back to the bottom of the reactor. Direct fluidized-bed gasifiers with large capacity are possible, as exemplified by the atmospheric biomass CFB gasifier at Vaskiluodon Voima in Vaasa, Finland, with a capacity of 140 MW thermal [130], but CFB boilers at even higher thermal capacities are also available. Dual-bed fluidized-bed gasifiers, as illustrated in Figure 4, are allothermal examples where two fluidized beds, any type, are combined, one acting as a gasifier and the second as a combustor [131]. They work in the same way as direct fluidized beds, but no oxidant is used in the gasifier; only steam and the heat required is supplied by hot bed material transferred from the combustor reactor. Fluidized-bed technologies have all been used for waste, but there are some specific requirements for the waste feedstock to be used. The feedstock particle size of any kind must have characteristics, such as particle size and density, to be able to sustain floating properties in the dense bed. For example, fines in the feedstock are entrained and leave the bed. In the case of waste, pre-treatment to RDF quality removing glass, metal, and other large inorganic objects is required.

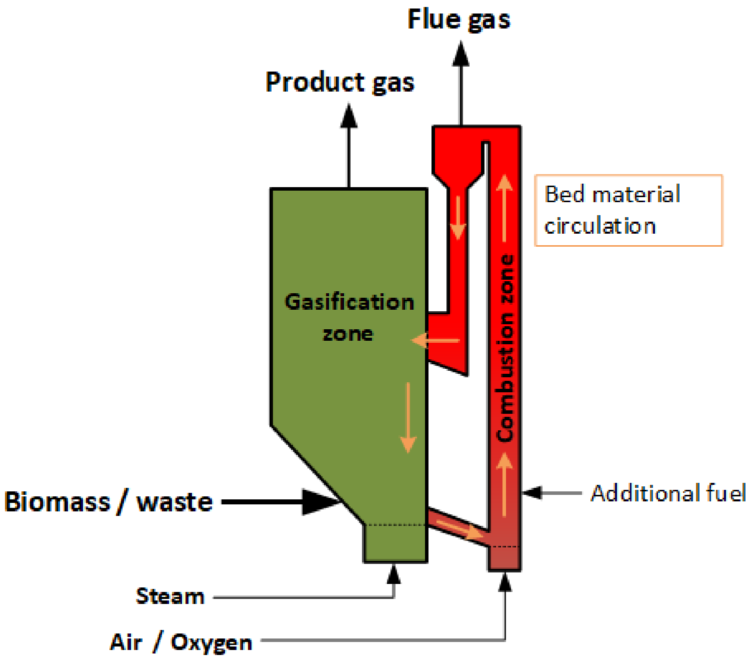

**Figure 4.** An example of an indirect dual-fluidized-bed gasifier.

Entrained-flow or suspension gasifiers are generally used for pressurized industrial large-scale coal (Table 11) gasification because of its higher availability, higher throughput, and better product gas quality [132]. In the case of coal, pulverized fuel (<1 mm) is injected together with the oxidant in a burner. The high temperatures used result in a very low content of tar and condensable gases, with methane composition close to the equilibrium. Entrained-flow gasifiers are generally not suitable for waste gasification, as either pumpable, atomizable liquid, or fine-powdered solid homogeneous feedstock is required. This restricts entrained-flow gasifiers to waste oils or potentially plastic wastes.

Other than the main gasifier types, there is also a number of other gasifier types, such as grate [133] and rotary kiln gasifiers [134], typically classified as moving-bed gasifiers, as illustrated in Figure 5. Grate and rotary kiln gasifiers are more suitable for non-uniform, compared to updraft and downdraft moving-bed gasifiers, as the movement of the bed is caused by mechanical work, improving the fuel mixing. Other examples are plasma gasifiers, which is not a basic type of gasifier but is a way to supply the heat at very high temperature to a gasifier or a downstream post-treatment reactor. The plasma is, in many cases, used in the updraft moving-bed gasifier type, where a carrier gas, e.g., air, steam, $CO_2$, is ionized, generating a plasma in an electric arc at high temperature [133]

There are several aspects to consider when selecting a gasifier suitable for converting a solid feedstock to a gas suitable for further upgrading to chemicals or hydrogen. As waste is a fuel consisting of a variety of components, such as food waste, paper, plastic, rags, metal, glass, etc., a selected technology either needs to be able to handle the inhomogeneous waste feedstock as is, or different degrees of extensive pre-treatment of the waste are needed prior to feeding into the gasifier. There are pros and cons in both cases, as the former implies extensive gas cleaning and purification after the gasifier compared to the latter case, where some of the impurities may be mitigated in the pre-treatment process. In principle, costs related to investments in process or operation either end up before or after the gasifier. In any case, it is beneficial if both the feeding system and the gasifier can handle both course and fine materials and a varying degree of fuel quality.

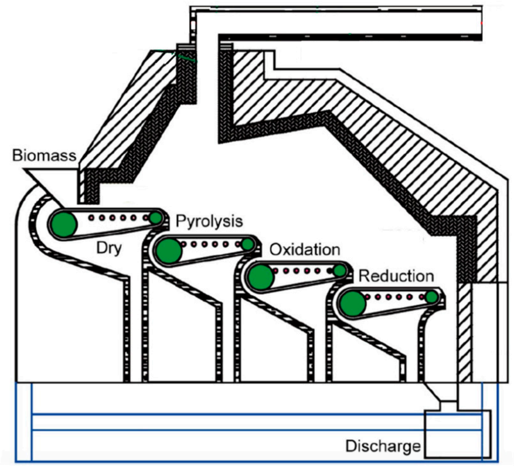

**Figure 5.** An example of a grate gasifier [133]. Reproduced with permission from J. Cai, Process Saf. Environ. Prot., 2021.

Of special concern in the gasification of waste are the inorganics, particularly metallic compounds, such as heavy metals. They tend to evaporate at high temperatures and leave as aerosol particles [135]. Preferentially, they should be recovered in, e.g., the bottom ash, and this is one of the reasons many so-called waste gasifiers are operated at 400–600 °C, compared to biomass gasifiers operating at 800–900 °C [135]. However, a high gasification temperature benefits the thermal cracking of tars and hydrocarbons [44]. In any case, even when a high-grade pre-treatment of the waste is used, the non-combustible "ash" content is still higher compared to a typical biomass fuel, and, therefore, the capacity to extract ash and to control the ash inventory is important.

## 3. Opportunities and Risks

### *3.1. Potential of Hydrogen from Waste*

Approximately 96% of hydrogen ($H_2$) is currently produced by transforming fossil fuels (48% from natural gas, 30% from heavy oils and naphtha, and 18% from coal), which leads to $CO_2$ emissions equivalent to 1.7% of the global energy-related $CO_2$ emissions. Only 4% of the globally produced hydrogen stems from water electrolysis [136]. The $H_2$ market is projected to grow by 50–82 metric tons by 2050 or approximately 5–10% per year [137].

The use of different feedstocks, primarily from biomass sources and wastes, would allow the full benefits of $H_2$ to be realized as a clean, versatile, and efficient fuel, with new hydrogen-related policies emerging by 2030 [4,137]. The handling of waste as a likely source of $H_2$ generation has attracted interest for its sustainable nature and for opening new opportunities for the comprehensive use of renewable energy sources [138]. Significant amounts of waste are produced in the agricultural, household, and industrial sectors that could be used in the production of $H_2$ [139]. These wastes are categorized as organic wastes from food processing, crop residues, forest residues, industry, animal manure, agricultural wastes, household, and community wastes (municipal solid wastes, wastewater, etc.) [138]. Approximately 40–50 kg of hydrogen can be produced per ton of dry waste. In contrast, the amount of hydrogen can vary between 30 kg and 120 kg, depending on whether the waste mixtures contain water or moisture [140,141].

The potential of a wide variety of gaseous, liquid, and solid carbonaceous wastes has been investigated as a renewable source for hydrogen gas formation using various technologies (biological and thermochemical) [142]. Thermochemical processes such as gasification have been widely studied as promising processes for hydrogen production. Table 12 presents further results of potential hydrogen production from waste gasification using different reactors and gasifying agents.

**Table 12.** Potential for hydrogen production from waste gasification on dry basis.

| Biomass Type | Reactor | Gasifying Agent | $H_2$ Production | Reference |
|---|---|---|---|---|
| Sewage sludge | Semi-batch | Steam | 0.07 g $H_2$/g | [143] |
| Pine sawdust | Fixed bed (updraft) | Steam | 79.91 g $H_2$/kg | [144] |
| Wood chips | Dual fluidized bed | Steam | 39.7 g $H_2$/kg | [145] |
| Municipal solid waste | Tubular batch reactor | Air | 26.53 g $H_2$/kg | [29] |
| Municipal solid waste | Allothermal fixed bed downdraft gasifier | Air<br>Mixture of air and steam<br>Steam | 157 g $H_2$/kg<br>165.3 g $H_2$/kg<br>199.6 g $H_2$/kg | [146] |
| 3-ply surgical face masks | Bubbling fluidized bed reactor | Steam | 29.27 g $H_2$/kg | [147] |
| Mixed plastic waste | Hybrid Microwave plasma Enhanced gasification | Steam | 150.9 g $H_2$/kg | [148] |
| Palm kernel shell | Fluidized bed gasifier | Steam | 150 g $H_2$/kg | [149] |
| Urban forest waste | Simulation (stoichiometric thermodynamic equilibrium model) | Steam | 84.25 g $H_2$/Kg | [150] |
| Canola meal hydrochar | Tubular batch reactor | Hydrothermal co-gasification | 11.03 g $H_2$/kg | [151] |

According to a study by Khan et al. [149], steam gasification of palm kernel shells in fluidized-bed reactors produced 150 g $H_2$/kg of $H_2$. A similar $H_2$ production potential (150.9 g $H_2$/kg) was observed by Ganza and Lee [148] in microwave plasma gasification of mixed plastic waste, which is equivalent to 15 wt% of the initial sample. Lower and higher values have also been reported in other studies. In a study by Yao et al. [145], the $H_2$ production potential through steam gasification in a dual-fluidized-bed reactor of wood chips was 39.7 g $H_2$/kg. A higher potential of 199.6 g $H_2$/kg was observed in the gasification of MSW in an allothermal fixed-bed downdraft gasifier [146].

Data on $H_2$ production potential through gasification are divergent and show no patterns. This fact indicates the variability in data between different sources and even the influence of parameters in each process, so comparisons of data and information can lead to inconsistent conclusions. Nevertheless, it is possible to verify that the use of steam as a gasifying agent leads to a higher production of $H_2$. The gasifying agents with the highest potential for $H_2$ production have the following order: steam > mixture of steam and oxygen > oxygen.

### *3.2. Alternative Technologies*

In addition to gasification, different production processes can be found, depending on the original source of hydrogen (e.g., wastewater, waste, and biomass). These production routes include thermochemical, electrolytic, and biological processes. However, some production methods are still under investigation [152,153]. Considering the technologies for converting waste and biomass into $H_2$, the maturity level of the thermochemical pathways (gasification and pyrolysis) is aligned with TRL 7, whereas biological conversion is at TRL 4–5 and electrochemical conversion at TRL 2–4 [154]. Table 13 shows the main considerations for these different processes and Figure 6 represents a schematic of the different processes for producing $H_2$ using renewable resources.

**Table 13.** Considerations of different hydrogen production technologies. Adapted from [154–156].

| Technology | TRL | Process Scale | CAPEX (M€) | Hydrogen Production Cost (€/kg) | Considerations |
|---|---|---|---|---|---|
| Gasification (dry thermal and hydrothermal) | 7 | Mid-scale/Available | 11.0–197.5 | 1.628–1.886 | Dry thermal gasification:<br>Formation of tar and char that deposits on the catalysts (shorter catalyst life) and need for catalyst regeneration;<br>High temperature and complex reaction leading to challenging operation control;<br>High cost for reactor and apparatus;<br>Fluctuating and varying gas composition, $CO_2$ generation |
| | | | | | Hydrothermal gasification:<br>Limited to the material with high moisture content;<br>High energy input for pressure elevation, and high reactor cost;<br>Problems related to corrosion and plugging, difficulty to recover the catalyst, and $CO_2$ generation. |
| Pyrolysis | 7 | Mid-scale/Available | 100.9–263.3 | 1.15–2.024 | Lower production cost of $H_2$;<br>Formation of char and tar, $CO_2$ generation, fluctuating and varying gas composition;<br>Tar and char generation poisons catalysts;<br>Cost of catalyst regeneration;<br>Energy intensive due to feedstock drying, and elevated temperatures and pressures; Lower capital cost than gasification. |
| Dark fermentation | 5 | Pilot-scale | - | 2.364 | Higher productivity than photo-fermentation;<br>Simple design of fermenters;<br>Requirement for pre-treatment;<br>Formation of undesired by-products;<br>Low production rate, low hydrogen yield, low removal of chemical oxygen demand. |
| Photo-fermentation | 4 | Laboratory-scale | 106.0 | 2.604 | More sophisticated design and lower productivity than dark fermentation;<br>Illumination source required;<br>Low production rate, low energy conversion efficiency, requirement of large surface area;<br>Higher production cost of $H_2$;<br>Lower capital costs expected. |
| Microbial electrolysis | 2–4 | Laboratory-scale | 2.8 | - | External voltage source needed;<br>The requirement for external electrical supply, the economic feasibility of scaling up due to expensive construction materials, the long-term stability is questionable;<br>High capital cost of equipment components and higher production cost of $H_2$. |

Note: Original data presented in USD/kg and converted to EUR/kg (USD 1 = EUR 0.92 according to [157].

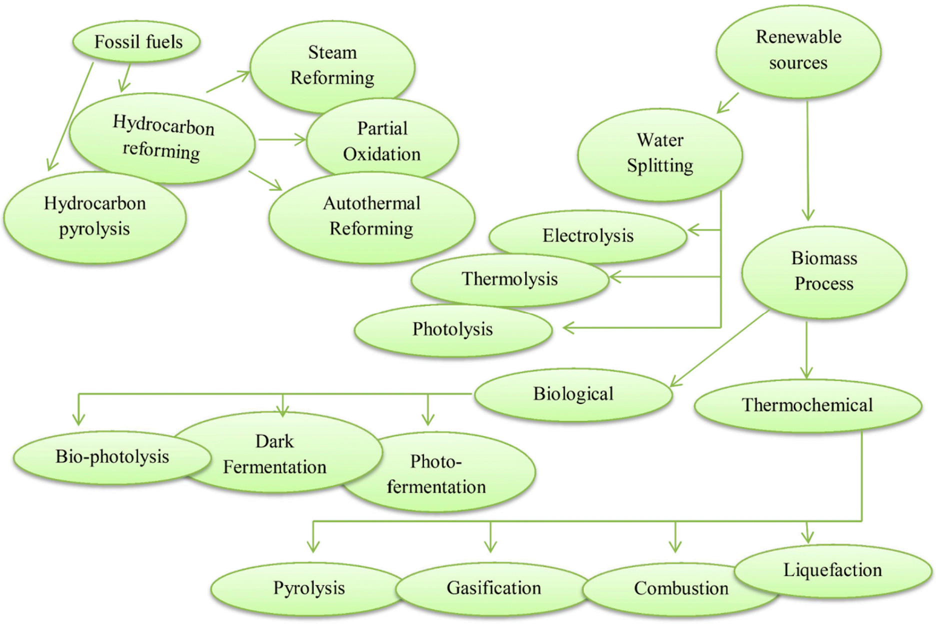

**Figure 6.** Selective hydrogen production methods. Adapted from [138,139,155]. Reproduced with permission from K. Murugesan, Int. J. Environ. Sci. Technol., 2019.

Thermochemical processes, such as gasification, pyrolysis, and steam reforming, are considered the most mature technologies and ready for application in hydrogen production [155]. Despite the low cost of the waste materials used, the high-temperature requirement is still the main limitation for these processes, particularly the steam reforming of methane (T = 1200 °C) [142]. According to Table 13, the CAPEX and hydrogen production costs of the biomass/waste gasification process are approximately 11–197.5 MEUR and 1.628–1.886 EUR/kg $H_2$, respectively. According to Lepage et al. [154], both coal gasification and steam methane reforming of natural gas have a higher CAPEX, of 257.60 MEUR and 170.95–240.20 MEUR, respectively. The opposite effect is seen with the unit costs of hydrogen production are lower than those for biomass/waste gasification. These costs can be twice as low, ranging from 0.846 to 2.604 EUR/kg $H_2$ for coal gasification and 0.71 EUR/kg $H_2$ for steam methane reforming of natural gas [154]. In general, despite the lower CAPEX, $H_2$ production via biomass/waste gasification is more expensive than using fossil resources.

For renewable raw material or waste, the costs of producing hydrogen by thermochemical processes are lower than biological processes according to Table 13. The cost of $H_2$ production by gasification is approximately 22–31% lower than that of dark fermentation and approximately 28–37% lower than that of photo-fermentation.

Biological processes have a lower CAPEX but a high unit cost of $H_2$ production (2364 EUR/kg $H_2$ for dark fermentation and 2604 EUR/kg $H_2$ for photo-fermentation). The possibility of large-scale production of $H_2$ by biological processes is limited because of its low yield and stability [152], requiring pre-treatment processes to improve conversion performance [154]. However, biological processes are carried out by hydrogen-producing microorganisms (such as microalgae and cyanobacteria, which produce the enzymes needed to synthesize $H_2$, including nitrogenases and hydrogenases). These microorganisms can be easily regenerated by replication, decreasing the frequency of renewal compared to chemical catalysts, which are easily deactivated during thermochemical conversions such as gasification [152,154]. In addition, biological conversion routes have the advantages of low temperature (30–60 °C), pressure (1 atm), and energy input (especially dark fermentation and enzyme-free photobiological processes) [154,155]. The main criteria for selecting waste for these biological processes are availability, cost, carbohydrate content, and biodegradability. Simple sugars, such as glucose, sucrose, and lactose, are readily biodegradable substrates and are preferred for hydrogen production [142]. For economical $H_2$ production through biological processes, the substrate should be cheap and renewable. Substrates rich in starch and cellulose, such as plant stems or agricultural waste, or waste from the food industry are reported to support biological processes [158]. The two-stage thermophilic fermentation of three organic wastes (potato, kitchen waste, and okara, which is a bean curd manufacturing waste) was investigated by Chu et al. [159]. The $H_2$ production rate was as follows: potato—2.1 $L_{H2}/L_{feedstock}/d$; garbage—1.7 $L_{H2}/L_{feedstock}/d$; okara—0.4 $L_{H2}/L_{feedstock}/d$ in the continuous processes. The $H_2$ yield was shown to be dependent not only on the proportion of carbohydrates but also on the hydrolysis pH of the organic waste, which was influenced by the nature of the organic materials in the waste [159]. Santos [160] studied the potential production of $H_2$ through biological processes from the organic fraction of MSW. For a total of 25,758 t/year of of MSW, the author estimated the production of 411,233 $m^3$/year of $H_2$, corresponding to 32 vol% of the gas resulting from dark fermentation [160]. The dark fermentation of empty palm fruit clusters was studied by Gonzales et al. [161] and yields lie between 0.015 and 0.026 g $H_2$/g biomass (169.53 and 286.98 mL $H_2$/g biomass).

Biogas, produced from the anaerobic digestion of waste, is considered a good source of hydrogen and is an alternative to natural gas as a feedstock for methane steam reforming processes [162]. The biogas can be converted into 72% $H_2$, resulting in a 10% reduction in costs [163]. Cudjoe et al. [164] studied the potential for $H_2$ production from biogas produced from food waste in China's Guangdong Province from 2004 to 2019. The authors found that 115.96 billion $Nm^3$ of purified biogas produced during a defined period produced 26.60 billion kg of hydrogen [160]. The estimated potential for $H_2$ production in south-western Nigeria from steam reforming of 1789.09 million $Nm^3$/year purified biogas (methane) was 410.50 million kg $H_2$/year, in Lagos alone, which would be 284.93 million kg $H_2$/year [162].

Thermochemical processes generally have a significantly higher hydrogen production rate (up to 190 g $H_2$/kg feed in the case of dry thermal gasification) than the biological process (up to 49 g $H_2$/kg feed for the photo-biological process) [155]. Although dark fermentation has relatively low yields, experimental studies have favored it as a cheap, well-understood, and promising method that requires simple reactor designs, making it attractive among biological conversions [138,155]. Dark fermentation is the main mechanism for $H_2$ production by biological processes [165], and integration with other systems, such as photo-fermentation and/or electrochemical systems as a secondary step, can pave the way for sustainable $H_2$ production in large-scale systems, promoting a higher $H_2$ yield and economic viability [166], being a potential competitor or expansion to the gasification process.

Electrochemical methods, such as electrocoagulation, indirect electrochemical oxidation, anodic oxidation, and electro-Fenton processes, have been effective for industrial wastewater treatment and $H_2$ production [139]. Microbial electrolysis cells also have remarkable potential for wastewater treatment and the production of $H_2$ and other value-added chemicals (e.g., methane ($CH_4$), formic acid (HCOOH), and hydrogen peroxide), but this is still a laboratory-scale process with a low TRL (TRL 2–4). The specific energy consumption is considerably lower than the electricity consumed by the $H_2$ production process through water electrolysis [139]. However, compared to thermochemical and biological technologies, these electrochemical conversion technologies require a huge energy input (approximately 45 kWh/kg $H_2$ for typical electrolysis using water), have very low conversion rates, expensive catalysts, and other technological challenges; therefore, they are not competitive compared with biomass and waste gasification [155].

## 4. Regulations, Mandatory Recycling Quotas

The conversion of waste into hydrogen is considered very promising. However, as all the above technologies are still in research and development, there are many challenges, including technological, economic, and political aspects, that require further attention to be resolved [155]. As for policy issues, the question of mandatory recycling quotas for waste (especially plastics) and landfill reduction targets could contribute to the increased demand for technologies to convert this waste (e.g., gasification) into hydrogen and other energy carriers. However, according to an article published in the Yale School of the Environment (New Haven, Connecticut, USA), this would not be a wise solution, as it is false recycling that takes away from the political will of waste reduction. First, it is necessary to demand that the world's largest plastic polluters reduce the amount of plastic they are pumping into the market [167].

The availability of biomass resources can also be a driving factor for the waste gasification market. It is well known that shrub areas are currently a global forest management problem, as shrubs are the main fuel for frequent forest fires in Europe [168]. Channeling this biomass, together with the use of municipal solid waste, could be a strategic measure for $H_2$ production.

Policies should be strengthened to accelerate the deployment of clean and efficient energy technologies for hydrogen production and application [169]. The success of the market for clean hydrogen produced from wastes depends on the ability to define consistent and transparent norms, standards, and rules to facilitate its deployment. Standard settings can be an arena for geopolitical competition and international cooperation. Divergent standards can slow progress, lead to the fragmentation of the hydrogen market, and erect trade barriers. Standards should be designed to improve market quality, safety, and interoperability [170].

In 2017, only Japan had a national hydrogen strategy. More than 30 countries have now developed or are preparing hydrogen strategies, indicating a growing interest in the development of clean hydrogen value chains. The European Union (EU) published its hydrogen strategy in 2020, identifying hydrogen as a key priority for achieving the European Green Pact [170].

Some countries are implementing concrete policies, with particular emphasis on supporting commercial-scale projects for low-emission hydrogen production and infrastructure, such as the EU's Important Projects of Common European Interest (IPCEI Hy2Tech and IPCEI Hy2Use), REPowerEU (hydrogen vouchers), the US Inflation Reduction Act, and auction systems for hydrogen procurement (German $H_2$Global Initiative)) [5,171].

Hydrogen valleys contribute to REPowerEU's goals by increasing the production and supply of hydrogen, thus meeting the growing demand from industry, transportation, and other sectors. Hydrogen valleys are regional ecosystems that link hydrogen production, transportation, and various end-uses, such as mobility or industrial feedstock. They enable the development of a sustainable hydrogen economy and help to create a virtuous circle between supply and demand, where large-scale production lowers costs and encourages greater demand in the same area. Co-location also reduces the immediate need for a long-haul transportation infrastructure. Even small-scale hydrogen valley projects can shed more light on the viability of a hydrogen economy that encompasses several industries simultaneously. The European Commission has allocated a Clean Hydrogen Partnership of an additional EUR 200 million through REPowerEU to double the number of hydrogen vouchers in Europe by 2025 [172,173].

Another instrument to support hydrogen technologies and drive the market is to provide financial assistance by reducing the high cost of market entry barriers. As the market matures, the nature of financial assistance provided may evolve from direct financial assistance to tax incentives and other types of subsidies [172].

In addition, phasing out fossil fuel subsidies, carbon pricing, and other market reforms can ensure appropriate price signals for hydrogen and foster the market [169].

Nevertheless, countries lack institutionalized mechanisms to monitor and identify the characteristics (origin and life-cycle emissions), production, and consumption of hydrogen. In addition, hydrogen is not accounted for in the official statistics of the total final energy consumption, and the economic value of the contribution of clean hydrogen to emission reductions is not recognized [170].

Therefore, there is not yet sufficient policy activity to create a demand for hydrogen. The lack of demand creation may hinder final investment decisions [5]. Without demand, investments are still too risky for large-scale production, which could reduce costs, but without economies of scale, the technology is still too expensive [170].

## 5. Conclusions

The gasification of waste is a very promising option to produce renewable hydrogen. There is significant literature available for experimental results at the lab and pilot scale. As feedstock, many different types of waste, like MSW, waste tires, or plastic waste, were investigated. Productivities of up to 300 g $H_2$/kg feedstock have been reported, which indicates that technology may have a good basis for attractive economics. One main advantage of the gasification technology is its versatility and suitability for very different input materials, like different types and qualities of waste, and the syngas after treatment always has similar quality, independent of the quality of the feedstock.

Gas treatment is a very challenging step and can be a bottleneck for commercialization. A variety of different process arrangements (e.g., indirect processes such as chemical looping for gases with high inert content, and direct processes) can be applied, impacting the overall process performance and economics.

Overall, hydrogen from waste gasification has a high potential, as the productivity is high and waste is largely available all over the world. Competing technologies include pyrolysis, biological, or electrochemical processes, but most of them are at a lower TRL level than gasification. The main competing technology is combustion, where the energy production has a minor priority, but the main aim is to reduce the volume of the waste. Under the actual frame conditions, combustion is cheaper compared to gasification, as the energetic value is not rated, and the main aim is to remove the waste with as low costs as possible. By giving the energy in the waste a higher value, this situation could be changed, and gasification could become more competitive.

There are not only technical or economic aspects for waste gasification but also political ones. Waste conversion to energy is seen as negative in many countries, as recycling products is preferred. This is especially true for plastic waste. Conversion to hydrogen is a highly promosingoption for agricultural residues and waste streams with high contents of impurities, which are not usable for recycling. If the conversion of waste to hydrogen is accepted as chemical recycling, a much bigger market can be expected which in turn would greatly accelerate the technology development.

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