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Review

Review of Gasification of Thermoplastics and Thermosets

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Abstract: The end-of-life management of plastic represents a significant environmental challenge, largely due to its limited use, low biodegradability, and high volume of disposed material, in the order of 400 million tonnes by 2019. Several types of polymers can be recycled by mechanical means, but some others, like plastics, sometimes require chemical methods for their reuse. In this context, gasification is one of the most promising chemical recycling techniques. Gasification is a thermochemical process performed at moderate temperatures of work (800–1100 °C) that converts carbonaceous materials into rich hydrogen gas, which can be used for energy obtention or the Fisher–Tropsch process. However, this procedure can also produce undesirable by-products like tar and char. The products' composition and relative quantities are highly dependent on the overall process configuration and the input fuel. The current study evaluates the catalytic gasification of the most common plastic waste, seeking to obtain higher gas yields and syngas with high energy. The text focuses on the current state of development and recent advances in various publications over the last fifteen years, with emphasis on thermoplastics and thermosets. The search showed that temperatures, the type of fluidizing gas, and the catalyst have a major influence on the quality of the obtained gas. Optimal gasification conditions, such as temperatures between 600 and 900 °C, depending on the plastic feedstock, steam-to-feedstock ratios > 1, the appropriate selection of a gasifying agent according to gas requirements and energy optimization, and the composition and location of the catalyst in the system (in situ, in the reactor, or ex situ), are identified as critical for maximizing H_2 and CO production and minimizing tar. Finally, we provide summaries of the last advanced patent in the field, where the main focus appears to be feedstock pretreatment intended to ensure handling feasibility due to the variety of plastic wastes.

Keywords: gasification; catalyst; plastic waste; polyethylene; polypropylene; polystyrene; polyvinyl chloride; polyethylene terephthalate; tire; tar removal

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1. Introduction

Plastics are versatile, lightweight, and flexible, making them suitable for a wide range of applications. In the face of climate change, policymakers are seeking to raise awareness of the economic, environmental, and social impacts of plastics, highlighting the need for sustainable production and reducing the negative environmental impacts associated with waste generation. The management of plastic waste has become a major global environmental challenge. The global use of plastics has increased dramatically over the past 50 years, with the annual global production of plastics increasing more than eightfold

since 1976. It has been estimated that in 2019, more than 400 million tonnes of plastic were produced worldwide [1].

Unfortunately, the widespread use of plastics has resulted in a significant increase in plastic waste generation. Moreover, the recycling process presents several challenges depending on the type of polymer. Thermoplastics can be melted for recycling, whereas elastomers and thermosets have more complex structures and need another type of recycling process. Furthermore, polymers can be part of composite materials and separation is impossible, making recycling unfeasible [2]. Of the global plastics volume produced between 1950 and 2015 after an adequate separation process, 55% went directly to landfills, 30% was still in use, 8% was incinerated and 6–7% was recycled, being reused for other functions or employed as raw material for some other manufacturing processes. Of the 5.8 billion tonnes of plastic taken out of use, approximately 9% was recycled [3]. However, recycling methods such as mechanical recycling are not free of CO_2 emissions, even when their emission rate is 50% lower than that of incineration [4]. There is now widespread recognition that a business-as-usual scenario for plastics waste management is no longer an option.

A circular economy for plastics is an alternative economic model that moves from the current 'take, make, dispose' model to 'reuse, recycling, or composting' [5]. There are several plastic recycling methods, each suitable for different types of plastics.

Mechanical recycling is the most common and involves shredding and melting plastics into new products [6,7]. Chemical recycling breaks plastics down into their basic components to make new materials and deals with complex plastics [6,8]. Energy recovery burns non-recyclable plastics for energy [9], while biological recycling uses microorganisms to break down biodegradable plastics, and is still at the research stage [6]. Closed-loop recycling maintains material quality by recycling back the product into the same type of material, while open-loop recycling creates different products which may lower the quality. Combining these methods improves sustainability and supports a circular economy (Figure 1).

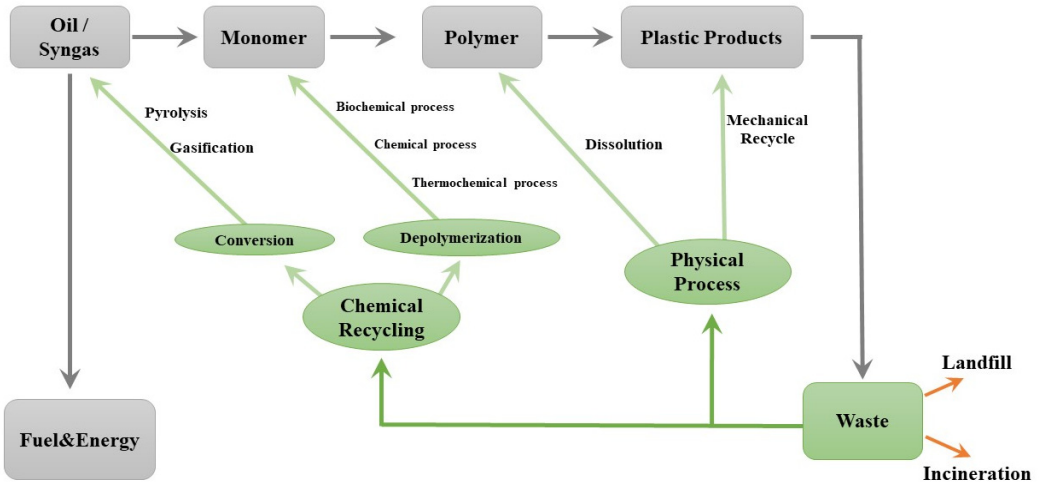


Figure 1. Possible plastic waste management methods are available. Adapted from [10].

The review aims to synthesize existing literature on chemical recycling, with a particular focus on plastic gasification, and to identify key research areas and advancements in the field. It assesses the viability of different types of plastics for the gasification process, and introduces and evaluates recent technological advancements in plastic gasification. Finally, it discusses the main operational parameters and strategies for optimizing gasification

conditions to enhance process efficiency, maximize gas yield, and improve the quality of the final products.

2. Methodology Description

A literature search was carried out using the most widely used database, ScienceDirect. To cover most of the reported literature, the keywords were selected systematically. The selected keywords included "plastics" AND "chemical recycling" AND "mechanical recycling" AND "pyrolysis" AND "gasification" AND "landfill" AND "incineration". Afterward, the abstracts and titles of relevant papers were screened and analyzed according to this review's themes. The numbers of papers obtained over 15 years are shown in Table 1. The ScienceDirect database yielded 1604 records in total. As demonstrated in Table 1, an analysis of the terminology employed in the publications reveals the significance of the keywords and the patterns of co-occurrence within the discipline. The results indicate that the seven most prevalent keywords are pyrolysis (786), gasification (365), incineration (215), landfill (175), anaerobic digestion (164), plastic (129), chemical recycling (115), and mechanical recycling (55).

Table 1. The number of papers identified in the ScienceDirect databases over 15 years.

Technological	Numbers of Papers
Plastic	129
Chemical Recycling	115
Mechanical Recycling	55
Pyrolysis	786
Gasification	365
Landfill	175
Anaerobic digestion	164
Incineration	219

A statistical analysis was performed on keywords using bibliometric analysis and clustering methods. The software VOSviewer was used to analyze the selected bibliographic data. Keywords represent the core and target of an article. The generated mapping shows the keywords as nodes connected by lines, where the proximity between nodes indicates a strong relationship between keywords. Larger nodes represent keywords that appear more frequently, while lines between nodes indicate co-occurrences. This work used VOSviewer 1.6.20 [11] to construct the keyword map of 1604 articles. Of the 219 keywords, 31 with a frequency greater than 50 were selected for visualization and co-occurrence analysis, as shown in Figure 2.

In Figure 2, the size of the circular node indicates the frequency of the keywords' occurrence and thus the extent to which they may be considered to represent research hotspots. The line thickness represents the strength of the association, with thicker lines indicating a higher frequency of appearance in the same article. The colors of the nodes represent the different research themes (clusters) that have been identified.

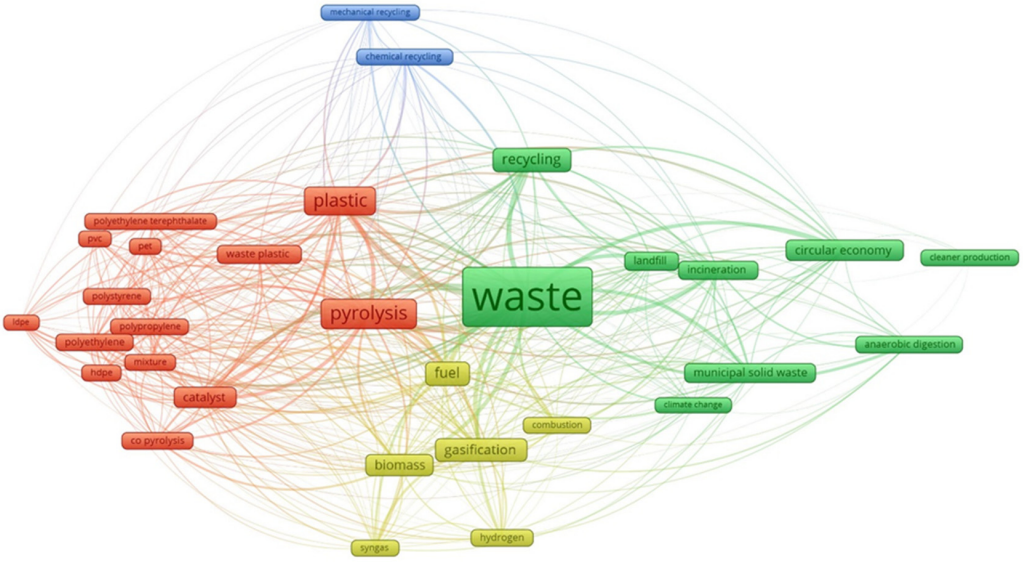


Figure 2. Keywords co-occurrence network.

From the analysis of Figure 2, four clusters have been obtained. The topics are summarized for each cluster, and the keywords in each cluster are listed (see Table 2). Each category is named after its most representative keyword. The four clusters are represented as follows: the green section (cluster #1) represents plastic biological technology, the red section (cluster #2) represents pyrolysis technology, the blue section (cluster #3) represents plastic pyrolysis technology, and the yellow section (cluster #4) depicts gasification technology. The paper will therefore focus primarily on the work of the yellow section, especially those works with high interaction with keywords in the green section. Nearly 365 representative papers on gasification processes using plastic waste (from 2009 to 2024) were reviewed, especially those works with high interaction with keywords from the red section.

Table 2. Keywords of research topics.

Cluster	Topic	Keywords
#1 (green)	Biological technology	Anaerobic digestion, circular economy, cleaner production, climate change, incineration, landfill, municipal solid waste, recycling, waste
#2 (red)	Pyrolysis technology	Co-pyrolysis, catalyst, high-density polyethylene (HDPE), low-density polyethylene (LDPE), mixture, plastic, polyethylene terephthalate (PET), polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), pyrolysis, waste plastic
#3 (blue)	Environmental impact	Chemical recycling, mechanical recycling
#4 (yellow)	Gasification technology	Gasification, hydrogen, syngas, biomass, combustion, fuel

Of the existing literature in the plastic gasification technology cluster, this paper focuses on comparing various operational parameters, including the catalyst, gasifying agent, type of plastic, and product quality.

3. Factors Impacting of Plastic Gasification

It is of critical importance to acknowledge that the configuration parameters have a substantial influence on the quality and yield of the final product. As illustrated in Figure 3, this review aims to provide a comparative analysis of several key factors associated with the catalytic gasification of plastics from different perspectives, including feedstock

composition, operating conditions (temperature and gasifying agent), catalyst, and product quality (syngas).

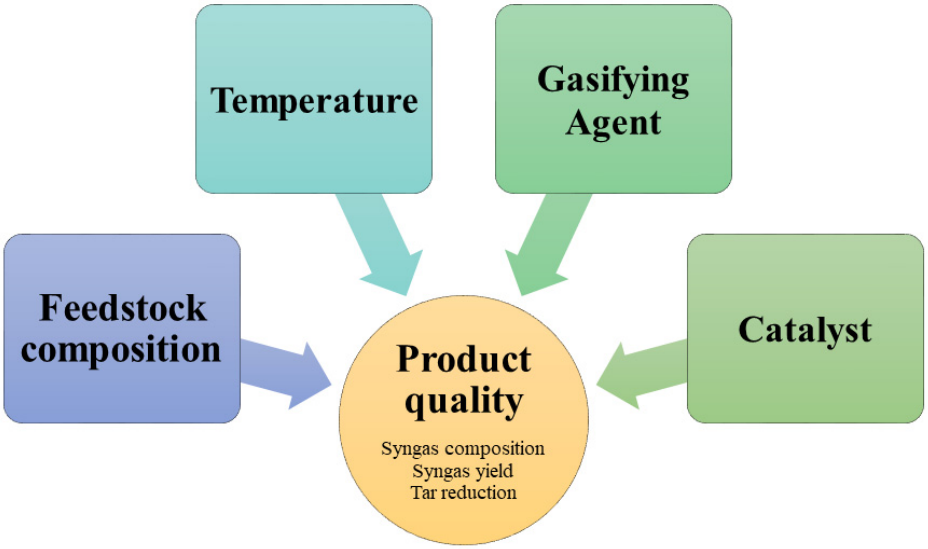


Figure 3. Several important factors of plastic gasification.

The term "syngas" is commonly used to refer to the gas resulting from all types of gasification processes. However, technically, syngas is a gaseous stream consisting only of the hydrogen and carbon monoxide resulting from such a thermochemical process. Although not entirely accurate, syngas is also used in this paper to refer to the gas produced from gasifiers, for the sake of clarity and continuity with the published literature. Numerous studies have been conducted on gasification operational parameters, including temperature, the use of various catalysts, and gasifier agents, assessing the potential of different plastic types for producing gas and liquid products. Particularly, these variables have a significant impact on syngas quality and yield. This review concentrates on the various plastic gasification processes that have been developed, focusing on the key factors that affect these processes, and on those that require attention to maximize the production of gas and improve the quality of the final product (Figure 3 and Table S1).

Table S1 provides an overview of the main feedstocks, process conditions, and catalysts required to achieve a specified quality of gas. It has been developed based on research conducted over the past 15 years on the use of PW for gasification.

3.1. Type of Plastics

Plastics are modified polymers that are classified into thermoplastics, thermosets, and elastomers based on their properties, as is commonly understood [12,13].

Due to the presence of cross-linked chains, a thermoset material cannot be molten or dissolved. Consequently, this type of material is less suitable for recycling in a conventional way. The group in question comprises epoxy resins, phenolic resins, and polyurethane.

On the other hand, thermoplastics can be reshaped and remolded on multiple occasions without undergoing any irreversible chemical alteration. This process can be repeated, allowing for the mechanical recycling of the material. This group comprises PS, PE, PP, HDPE, LDPE, PVC, and PET. Elastomers represent a category of materials situated between thermosets and thermoplastics [14]. Among them, natural rubber (NR) and styrene butadiene rubber (SBR) stand out.

An alternative classification of plastic is based on its biodegradability instead of its physical properties. The term "bioplastic" is also used to describe plastic materials that are bio-based, biodegradable, or both. The biodegradability of a material is not determined

by its resource base, but rather by its chemical structure. Consequently, there are entirely bio-based plastics that are not biodegradable, and conversely, some fossil-based plastics can undergo biodegradation under specific environmental conditions. PE, PP, and PET are non-biodegradable plastics whose source can be fossil or biological. Other non-biodegradable polymers may be fossil-based, such as PVC, PS, and ABS, or bio-based, such as polyamide (PA), polyethylene furanoate (PEF), and polytrimethylene terephthalate (PTT). Polybutylene succinate (PBS), polybutylene adipate terephthalate (PBAT), and polycaprolactone (PCL) are biodegradable fossil-based polymers. On the other hand, polyhydroxyalkanoates (PHA), polyhydroxybutyrate (PHB), and polylactic acid (PLA) stand out among the biodegradable bio-based polymers [15].

The separation and management of non-biodegradable plastic waste remains a complex task due to the limitations of traditional disposal methods, namely, incineration and landfilling. The potential of advanced recycling technologies, such as chemical recycling, lies in their ability to recycle plastics that cannot be recycled mechanically and would otherwise be sent to incineration or landfill [8]. However, there are technological challenges related to the quality of raw materials and their variety of compositions. In addition, due to the costs that these processes can involve, regulatory issues are important. For instance, in regions where a "zero waste" policy is imposed or where there is a high tax on CO_2, the implementation of these methods may be a viable option. Consequently, the characteristics of plastic waste, including moisture content and calorific value, are likely to limit its potential as a raw material. The properties of plastic waste when used as a feedstock in the thermochemical conversion process vary significantly in terms of the type, mineral content, and elemental composition, and the variation of these properties further impacts the properties of the products derived [16]. Municipal solid waste (MSW) is defined as the solid residues generated by the population. It can be categorized into several types, including wood, paper, metal, plastics, rubber, and biodegradable residues [17]. The implementation of an effective separation policy can ensure the availability of plastic MSW for treatment. Even though the composition of MSW varies somewhat in quality in comparison to industrial waste across different regions of the world, and the classifications used to describe the composition are far from uniform, the relative amounts and classes can be identified.

The fundamental characteristics of a fuel, including its volatile matter, ash content, moisture content, fixed carbon, and other properties, provide insight into its combustion behavior [18]. Table 3 shows that HDPE, LDPE, PP, PS, tire and PE are more efficient fuels compared to PET and PVC, because the former have a higher energy content that can be theoretically recovered. However, the extent of energy recovery depends on the amount of energy used in the plastic conversion process. Typically, diesel and gasoline have the highest LHV, 42–46 MJ/kg [19], which is similar to the LHV values of PP and PE. Under certain conditions and in the absence of air, volatile matter is released when a given sample is heated up to 950 °C. It is usually a combination of long- and short-chain hydrocarbons and aromatic hydrocarbons [20,21]. It is easier to ignite at low temperatures due to the higher volatile matter value content. All plastics in the comparison show high volatile matter content, particularly LDPE (99.0%) and PS (99.48%), suggesting they are easier to ignite at lower temperatures due to their significant release of gases during heating. In contrast, tires (63.8%) and PVC (83.4%) have lower volatile matter contents, which may affect their ignitability and combustion efficiency [22,23].

Table 3. Physicochemical properties of different polymers of plastics [17,24–26]. Data relate to a dry basis.

Parameters	LHV (MJ kg^{-1})	Ash (wt. %)	Volatile Matter (wt. %)	Fixed Carbon (wt. %)	Moisture Content (wt. %)	C (wt. %)	H (wt. %)	O (wt. %)	N (wt. %)	S (wt. %)	Cl (wt. %)
HDPE	41.24	0.60	99.40	0.00	0.10	85.5	14.20	0.00	0.00	0.30	0.00
LDPE	41.81	0.3	99.0	0.00	0.00	85.5	14.30	0.00	0.00	0.20	0.00
PP	42.42	0.44	99.54	0.03	0.20	85.02	13.93	0.96	0.08	0.01	0.00
PET	21.28	0.20	92.27	7.53	0.40	62.3	4.43	33.13	0.09	0.05	0.26
PVC	20.85	5.86	83.47	10.67	0.86	39.56	4.85	0.02	0.11	0.28	55.18
PS	39.52	0.19	99.48	0.33	2.51	90.37	8.64	0.90	0.00	0.09	0
PE	44.60	0.12	97.72	2.16	5.60	85.40	15.04	2.77	0.00	0.00	0.00
tire	35.43	6.63	63.78	28.95	0.68	79.55	7.99	2.53	0.15	2.47	

The ash content varies significantly among different plastics, with tire showing the highest at 6.63%, while HDPE and PS have minimal ash (0.60% and 0.19%, respectively). A lower ash content is preferable, as it correlates with higher calorific value and reduced residue after combustion, making HDPE and PS more favorable options. The fixed carbon content is low in most plastics, except for PET (7.53%), PVC (10.67%), and tire (28.95%), indicating that these materials may produce a more carbonaceous solid residue during pyrolysis [22,23].

Due to their inherent properties, such as a calorific value very similar to that of petroleum fuels, plastics can be used as a feedstock to generate heat and steam through various thermochemical processes [27,28].

The most common thermochemical processes used to achieve this are liquefaction, pyrolysis, and gasification [29].

In the liquefaction process, the feedstock is exposed to moderate temperatures (250–400 °C) and high pressures (50–200 bar). This process leads to the recovery of monomers or the production of high-energy liquid fuels [30]. One factor that impacts the transformation of plastics into liquid and gaseous products is the type of solvent employed. Solvents, such as water or organic solvents (methanol, ethanol, and hexane), introduce a further complication into the product recovery process [31].

Pyrolysis is a process that occurs in the absence of oxygen, with the decomposition of materials occurring at moderate–high temperatures ranging from 250 to 800 °C, and at atmospheric pressure. This results in the production of a mixture of gases, liquids, and solids fuels. In the presence of elements other than carbon and hydrogen, it has been demonstrated that significantly divergent yields and compositions can be obtained. The nature of the monomers present has been found to influence the composition of the liquid product. PS, PET, and PVC exhibit a higher proportion of aromatics, while plastics such as polyethylene (PE) have been found to demonstrate a heavier hydrocarbon distribution [32]. However, it should be noted that there are significant limitations to the large-scale utilization of this system [33].

Gasification is a process of heating solids to elevated temperatures (800–1100 °C), which generates a hydrogen-rich gas characterized by an abundance of hydrogen and carbon monoxide [8]. However, the process produces several undesirable by-products, including tar, char, ash, NO_x, and SO_2 [31]. The gas obtained can be utilized in different applications, including methanization, ammonia production, and the Fischer–Tropsch synthesis of synthetic fuels [34]. Furthermore, it can be employed or combusted to generate electricity. The tar produced will condense when the temperature is below its dew point, thereby obstructing and contaminating process equipment such as fuel lines, filters, engines,

and turbines. The specification for a low tar content is typically less than 100 mg/m^3 for internal combustion engines or gas turbine applications, and 0.1 mg/m^3 for methanol synthesis [35].

Therefore, the removal of tars has become one of the most crucial and timely concerns in the context of gasification. As previously discussed, the main purpose of this review is to introduce the currently reported advances in catalytic gasification technology for non-biodegradable plastics.

3.2. Feedstock Composition

The extent to which product distribution is contingent on feed composition is less pronounced in thermochemical conversion technologies, such as gasification. Variations in the gasification of different feedstocks are limited to syngas composition and the generation of minor by-products, including char and tar. The analysis of the co-gasification of plastic mixtures has been encouraged by the adaptability of the gasification process and the more advanced state of development of biomass and coal gasification. Similarities in the chemical structure and composition of the different plastics resulted in the type of plastic marginally influencing product distribution [36].

Elemental analysis based on carbon (C), hydrogen (H), and oxygen (O) contents is a useful tool for determining the properties of solid fuels, mainly their combustion behavior. A useful method of describing any solid fuel's characteristics through elemental concentration is by means of using a van Krevelen diagram. In a typical van Krevelen diagram, the ratio of atomic hydrogen and carbon is plotted against the ratio of atomic oxygen and carbon, representing the transition from biomass to anthracite coal. As illustrated in Figure 4, this transition is presented as a reference point, and the figure also includes other types of solid fuels, such as gas oil, naphtha, and diesel.

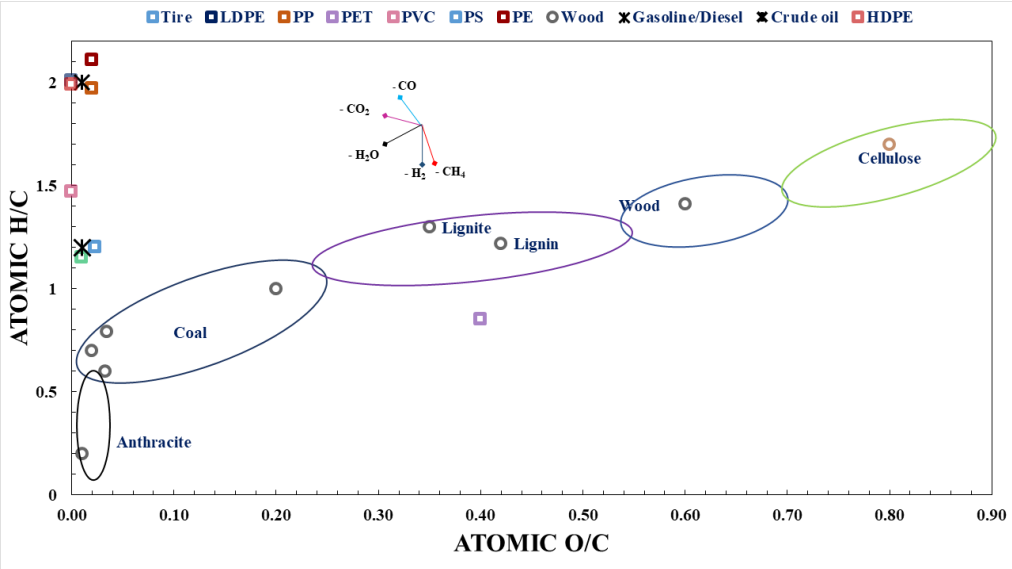


Figure 4. Comparative van Krevelen diagram for plastics.

The raw plastic materials on the van Krevelen diagram [37–39] (Figure 4) fall in the fuel oil region (gasoline, diesel, crude oil), with the exception of PET, which is located close to the lignin region. As the temperature of the thermochemical process increases, the H/C and O/C atomic ratios decrease, resulting in the higher aromaticity, demethylation, and dehydration of the plastic waste (PW), moving towards anthracite [21].

Figure 4 shows the direction of change in the locations of compounds in the van Krevelen diagram when methane (CH_4), hydrogen (H_2), water (H_2O), carbon dioxide

(CO_2), and carbon monoxide (CO) molecules are released. Based on the presented regions, it is possible to estimate the chemical transformations that occur during hydrothermal the treatment of waste. From the figure, it can be observed that the predominant reactions occurring during the thermochemical processing of plastic waste typically result in increased H_2 generation. A similar behavior follows with CH_4, reaching its higher level when the feedstock has lower O/C values. The production of CH_4 during waste gasification is linked to the fundamental components of PW. Long-chain hydrocarbon compounds in plastics undergo cracking and reforming reactions during gasification. These result in the formation of lighter hydrocarbon gases such as CH_4 and C_2H_4 [21]. This process explains why the yield of CH_4 is higher during the gasification of high-H/C feedstocks, such as plastics.

As demonstrated by the study conducted by Wang et al. [39], the yield of CO in the syngas is directly proportional to the O/C content of the feedstock. Higher O/C ratios, like those observed in PET, have been shown to produce more CO. Conversely, the relationship between CO_2 yield and the H/C and O/C ratios is more complex. To reduce the production of CO_2 in the syngas, it is recommended that raw materials with O/C ratios between 0.35 and 0.45 be utilized [39].

In summary, optimizing the H/C and O/C ratios of feedstocks is fundamental to maximizing syngas production and enhancing the efficiency of thermochemical processes. The van Krevelen diagram serves as a valuable tool for evaluating co-processed systems in industrial production, offering deeper insights into the properties of the feedstock. The incorporation of plastic mixtures, either different types of plastics or plastics and other types of solid fuels, has been shown to increase their carbon content and calorific value.

The most commonly studied plastic feedstocks for gasification have been PE [40–43] and PP [42,44–48]. Only a limited number of studies have explored the gasification of PS [42,49,50], tire [51–53], and PET [44,54–57], with even fewer investigating PVC [58]. A comprehensive list of pure plastic types susceptible to gasification in the absence of a catalyst is provided in Table 4.

Table 4. Yields related to different products and the quality of the syngas, when gasifying pure plastics in air and with sand as the bed material.

Feedstock	CO (%)	H_2 (%)	LHV (MJ/Nm^3)	Tar (g/Nm^3)	Gas Yield (Nm^3/kg_{feed})	T (°C)	Reference
PP	5	4.8	2.9	17	4	850	[46]
PE	9.1	9.1	7.9	160	3	845	[40]
PS	5.4	3.2	4.25	10	3.6	804	[49]
PET	15.1	3.2	11.16	13.23	1.99	784	[54]

Understanding the potential for synergistic effects between the producer gas and by-products generated by this feedstock could help to enhance the quality of the producer gas. The formation of carbon fine particles and heavy condensable hydrocarbons is strongly correlated with the feedstock structure and composition. This presents an opportunity to examine the simultaneous combustion of fuels with varying characteristics, including those with differing oxygen contents and contaminant levels [59,60].

Singh et al. [61] studied the co-gasification of sawdust with PE and PP. Plastic co-feeding resulted in an increase in H_2 on the one side, but a decrease in CO concentrations on the other. The calorific value of the producer gas is subject to change when sawdust is co-fed with one plastic or the other. It has been observed that PE produces gas with a higher calorific value than PP. The same results were achieved with mixtures of PE, PP, and PS, which yielded significantly higher concentrations of H_2 and CO compared to the gasification of pure plastics [62].

Furthermore, as the proportion of PE in the mixtures increased, so did the concentrations of CH_4 and ethylene (C_2H_4). This trend indicates that the gas composition can be tailored by adjusting the ratio of PE in the mixture. The blend of PE and PET yields distinct behaviors attributable to the elevated oxygen content of PET. The gas produced from PET-rich feeds contains a significant amount of CO_2. This demonstrates the impact of the chemical composition of the mixture on the gasification outcomes [43].

Benzoic acid is a primary decomposition product generated during the gasification of plastics like PET, often found in the tar produced from such processes. The presence of benzoic acid and terephthalic acid in tar can complicate the gasification process, with methods being necessary for managing or reducing tar formation to ensure efficient gas production [54].

It is noteworthy that PS exhibits a different behavior in char formation compared to other plastics, which may reduce char production. Due to its structural characteristics, PS is a strong precursor of tar in the product gas. The study conducted by Jeong et al. [49] indicated that the generation of aromatic tar compounds is expected to be higher in PS gasification compared to polyolefins, emphasizing the critical importance of the tar management process.

In addition to the diversity of plastic types, the quality of the raw material is also a crucial factor to consider. The term "high-quality raw material" is used to describe a material that is homogeneous in composition, comprising a single type of polymer, and that contains minimal inorganic or organic impurities. In contrast, a material of lower quality is characterized by a heterogeneous composition, comprising a mixture of different polymers and materials, and will often contain high levels of inorganic or organic impurities, as well as contamination with other materials, such as paper, halogens, and metals. This is further highlighted by the chemical recycling of plastic waste. The aforementioned waste materials display a high degree of variability in both contaminant types and concentrations.

It is therefore evident that the chemical recycling of these waste fractions to obtain basic chemicals represents a promising recycling route, as it is expected to be more robust against impure and contaminated plastic waste streams [63]. However, plastics containing heteroatoms, such as PET, PVC, and PA, as well as organic waste, additives, and pigments, represent a significant source of heteroatoms and metals that will ultimately be present in gasification products. Weiland et al. [63] showed the importance of understanding the full system of plastic waste generation, collection, separation, and conversion. They studied the gasification of plastic reject (PR) and automotive shredder residue (ASR). Both PR and ASR require size reduction and drying as essential pretreatment steps, but ASR may need additional metal removal and sorting due to its higher inorganic content. The specific pretreatment processes are more reliable in enhancing the efficiency and effectiveness of the gasification process for each type of feedstock [64].

The application of chemical recycling methods for PVC presents both advantages and disadvantages, and an awareness of these can facilitate the optimal disposal and processing of PVC. The dehydrochlorination of PVC predominantly occurs at low temperatures, between 250 and 320 °C. Dechlorination accelerates the process of biomass pyrolysis [65], and inhibitory and synergistic effects have been observed during the co-gasification of PE, PVC, and sawdust samples. PE has been demonstrated to impede the release of volatile compounds from sawdust, whereas PVC has been found to facilitate this phenomenon. In conclusion, PVC improves the reactivity of sawdust during gasification, while PE enhances the quality of the syngas produced [66].

It is common practice during the production of tires to add a vulcanizing agent, vulcanization accelerator, and other additives, which contribute significantly to the content of nitrogen and sulfur elements. The sulfur content of scrap tires is approximately 1.4% to 2.6%, while the nitrogen content is around 0.2% to 0.8% [53,67,68]. Consequently, these components are transformed into pollutant gases, including H_2S, COS, NH_3, NO, and other organic pollutants, during the thermochemical process [69]. These harmful gases cause secondary pollution and the corrosion of equipment.

Zhang et al. [70] studied the distribution of sulfur species in spent tire pyrolysis char produced during steam gasification. The distribution of sulfur (S) species changed significantly based on the gasification conditions, such as temperature and time. The dominant sulfur species were identified as aliphatic sulfide and zinc sulfide (ZnS). After steam gasification, more than 80% of the sulfur species in the gasified chars were found to be in the form of organic sulfur compounds, thiophene, aliphatic sulfide, sulfoxide, and sulfone. At lower temperatures (850 °C and 950 °C), the retention of sulfur species was higher, while at higher temperatures (1050 °C), there was a notable decrease in sulfur content.

Another point to consider for pretreatment is the particle size of the feed. The particle size affects the transfer of heat within the bed. The use of smaller particles allows for a larger surface area to volume ratio, which can facilitate better heat transfer and improve the overall thermal efficiency of the gasification process. Furthermore, smaller particles may lead to lower tar production due to better mixing and more effective heat transfer, promoting the complete conversion of the feedstock. However, if the particles are too small, they may lead to excessive elutriation (loss of particles from the bed), while too large particles can cause poor fluidization and channeling, both of which can negatively impact the gasification efficiency. To maximize gas yield and heating value, the particle size range of the tire must be modulated; researchers in Ref. [25] worked with a particle size less than 1 mm (0.25 to 0.58), while the optimum range was 0.25 to 0.45 mm under air atmosphere (ER = 0.07) in ref. [71]. Leung and Wang [53] used a 1.5–2.1 mm range in an air/steam atmosphere.

In many scenarios, plastic waste or different plastic mixtures are not regarded as valuable additions in terms of enhancing the yield of syngas or improving its quality. From an economic point of view, the removal of this mixture could be a viable option.

3.3. Reaction Condition

The optimization of gasification conditions is a crucial step in enhancing the efficiency of the gasification process and reducing its environmental impact. By modifying factors such as temperature, gasifying agent, and catalyst, it is possible to enhance the process in terms of energy efficiency. This results in a reduction in emissions and a decrease in the environmental footprint on the whole [51].

3.3.1. Temperature

Temperature is one of the most important parameters in all stages of gasification. The initial stage, drying, converts the moisture in the material into vapor at temperatures between 20 and 100 °C, without resulting in decomposition or chemical reactions. In the second stage, pyrolysis, the plastic materials are highly volatile (more than 60%) and start to devolatilize at low ignition temperatures (250–350 °C) immediately after being introduced into the reactor. At this stage, the dry material is thermally decomposed to release volatiles such as H_2, CO_2, tar, CO, water vapor, and light hydrocarbons. The process leaves a residue of ash and char. In the third stage, oxidation, the volatiles (gases and tar) and char are oxidized, generating chemical reactions that release heat, producing CO_2 and H_2O by the oxidation of H_2. In the third stage, oxidation, the volatiles (gases and tar) and char are

oxidized, generating chemical reactions that release heat, producing CO_2 and H_2O by the oxidation of H_2. Under sub-stoichiometric O_2 conditions, the partial oxidation of carbon produces CO. Finally, the reduction stage takes in the absence of O_2, and produces CH_4, CO, and H_2 (syngas). The gasification process is globally endothermic, and the heat required can be supplied from an external source or internally through exothermic reactions [72].

An increase in the reactor temperature generally increases the gasification reaction rate, producing an increase in the plastic conversion and therefore in the syngas yield. Figures 5 and 6 show the effects of temperature on the H_2 content and tar, respectively. It can be observed in the figures how an increase in the temperature from 600 to 900 °C implies an increase in H_2 content and a decrease in the tar content. This is because, by increasing the temperature, endothermic reactions, like pyrolysis tar cracking, methane steam reforming, water gas/steam carbon, and Boudouard, are made more favorable.

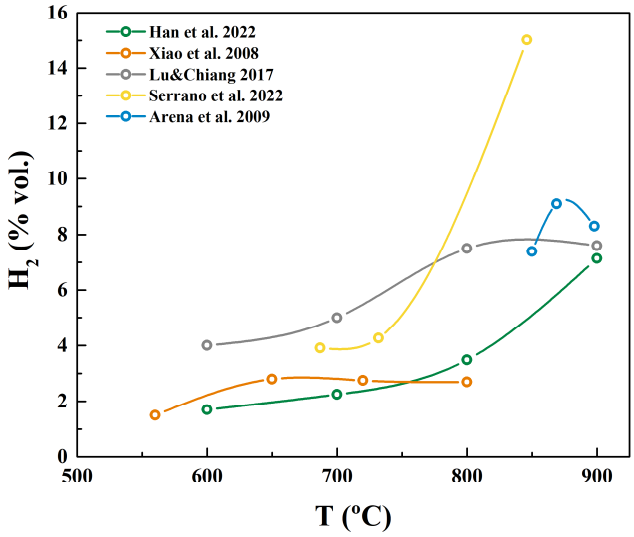


Figure 5. Effect of temperature on H_2 content of the gas produced, reported by different authors [47,73–76].

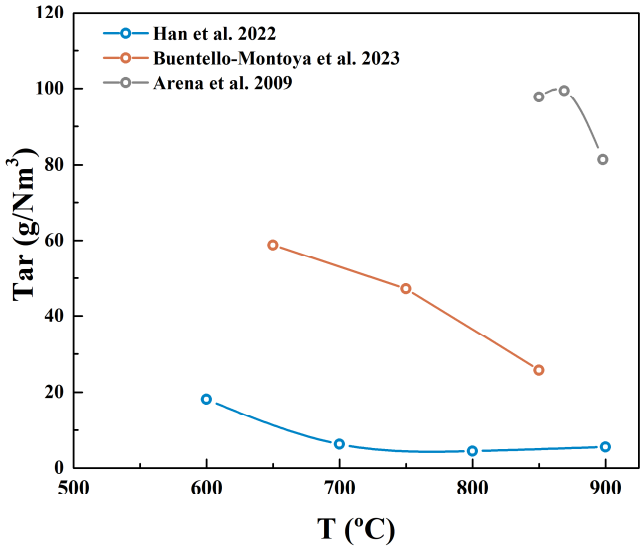


Figure 6. Effect of temperature on tar content of the gas produced, reported by different authors [44,73,76].

Zallaya et al. [43] demonstrated that increasing the gasification temperature during the steam gasification of polyethylene (PE) and polyethylene terephthalate (PET) leads to a reduction in H_2 content and an increased presence of CH_4 in the resulting gas phase. This increase in H_2 production with higher steam/feed ratios can be attributed to the water–gas shift reaction and char gasification reaction. On the other hand, methane formation occurs at lower temperatures, which increases the CH_4 content in the product gas [77]. The effect of temperature on different mixed feedstocks during gasification is also important due to the different hydrogen, carbon, and oxygen (H/C and O/C) ratios of two or more materials being gasified simultaneously in a gasifier [78].

The gasification of solid carbonaceous feedstock is conventionally processed in the temperature range of 700–1000 °C [56,73,79,80].

There is a limitation to how high the temperature for the gasification process can go (tolerable level) due to its effects upon (1) the volatile matter content in fuels; (2) materials of construction used in the gasifier; (3) the production of undesirable gases such as NO_x; and (4) its effect on the ash fusion [81].

Saebea et al. [82] showed the effect of gasifier temperature on the mole fraction of the gas product and LHV obtained from the steam gasification of pure PE. In this study, the gasifier temperature varied from 650 to 1100 °C, whereas the S/F mass ratio was fixed at a value of 1. An increasing gasifier temperature leads to increases in the mole fraction of CO. In contrast, the increment in gasifier temperature causes a reduction in the CO_2 and CH_4 fraction. Increasing the gasifier temperature can promote endothermic reactions such as Boudouard and reforming, increasing the production of H_2 and CO. Thus, the generation of CO_2 and CH_4 will be lower. However, the authors reported that above 900 °C, H_2 and CO mole fractions and LHV values start to decrease.

Lopez et al. [60] studied a non-classical reactor configuration, a conical fluidized bed reactor, exhibiting enhanced heat transfer rates and a turbulent flow pattern with a relatively low pressure drop compared to traditional fluidized beds. They observe that an increase in HDPE gasification temperature up to 850 °C has a significant impact on gas yield, hydrogen content, and tar formation. However, a further increase to 900 °C only results in a slight improvement in process performance.

At lower temperatures, the tar products tend to be more complex and may contain a variety of heavier aromatic compounds. As the temperature increases, the tar composition shifts towards lighter fractions, and the formation of polyaromatic hydrocarbons (PAHs) is reduced. Mastral et al. [83] found that a suitable gas composition could be obtained for electricity generation at relatively low temperatures, the optimum being between 680 and 730 °C. This temperature range also avoids a high level of production of heavy polyaromatic compounds, which can be problematic.

In the temperature range between 600 and 900 °C, the production of CO and H_2 is improved, while the CO_2 and CH_4 concentrations in the syngas are reduced, as evidenced in a study by Singh et al. [61]. Additionally, Han et al. [73] and other authors [44,47,74–76] have indicated that at 800 °C, the process yields the highest values of CCE, heating, and CGE (Figures 7 and 8).

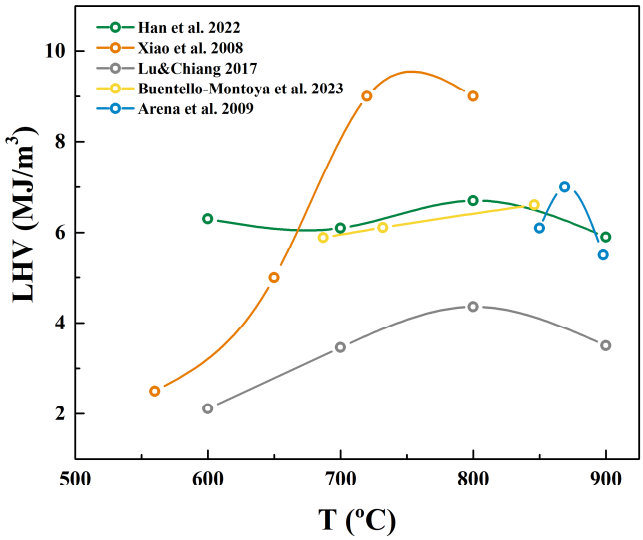


Figure 7. Effect of temperature on the heating value of the gas produced, reported by different authors [44,47,73,74,76].

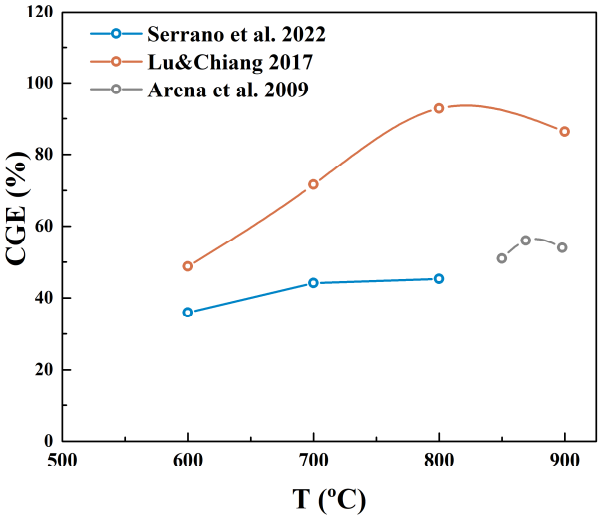


Figure 8. Effect of temperature on the carbon gas efficiency reported by different authors [74–76].

3.3.2. Gasifying Agent

Another important process variable influencing the tar and gas composition is the gasifying atmosphere. Gasification can be performed in air, steam, O_2, CO_2, or a combination of any of these gases. The composition and applications of the syngas strongly depend on the gasifying agent used.

Air is the most popular gas medium used in gasification due to its simplicity and low cost. However, its major disadvantages are the dilution effects of N_2, generating a low calorific value gas that is mainly used for energy production [42,84].

Karatas et al. [71] demonstrated a clear correlation between the lower heating value (LHV) and the equivalence ratio (ER). The study found that the correlation holds across different bed material particle sizes, indicating that the relationship is robust and applicable under various operational conditions.

Using steam as the gasifying agent can facilitate reforming and water gas shift reactions, resulting in gasification products with the highest H_2/CO ratio, fewer impurities (char and tar) [71], and high heating values (Figure 9). However, the generation of steam also has an associated energy cost. Therefore, the efficiency of steam utilization and gen-

eration represents a crucial factor in the overall performance and cost-effectiveness of a gasification system. For example, the study of Han et al. [73] and Singh et al. [61] suggests that an optimal steam-to-feed ratio (S/F), close to 1.5, should be maintained to avoid excessive steam that could lower reactor temperatures and efficiency. The H_2/CO ratio shows an upward trend with increasing S/F ratios, indicating favorable conditions for hydrogen production (Figure 10).

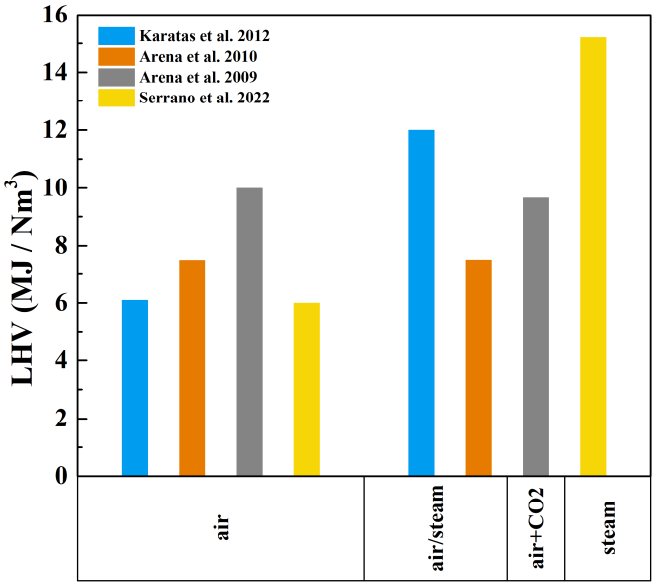


Figure 9. The effect of the gasifying agent on the heating value of the gas produced was reported by different authors [40,71,75,76].

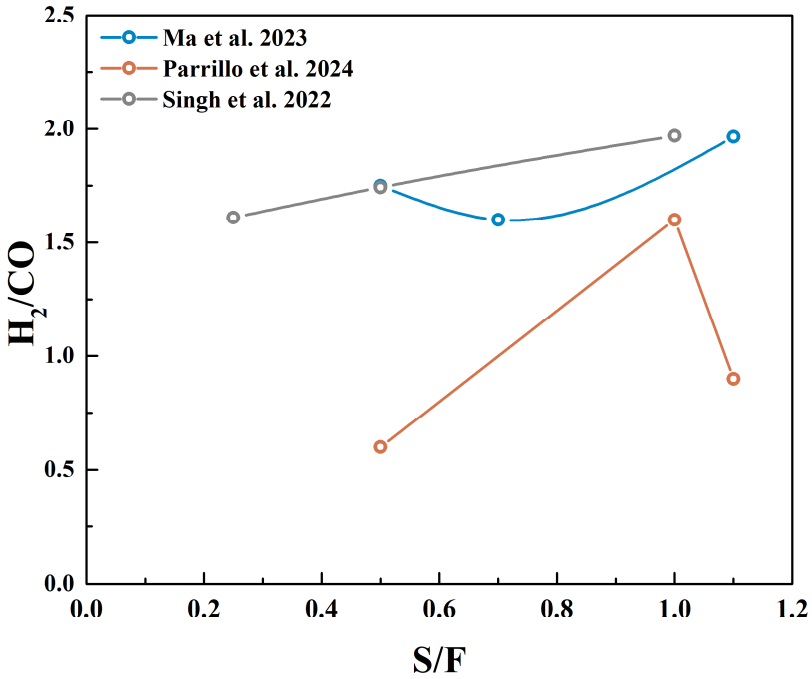


Figure 10. Effect of the steam-to-feedstock ratio over the H_2/CO ratio [61,85,86].

Steam improves gasification efficiency by balancing heat and providing necessary oxidants. With a steam-to-feedstock ratio (S/F) > 1, carbon conversion (99.12%), energy recovery (93.67%), and exergy efficiency (80.04%) are maximized. Oxygen increases energy recovery (42%) and exergy efficiency (28.5%), but pure oxygen slightly reduces these metrics due to energy balance issues and air separation requirements [73].

Supercritical water gasification is a new promising technology that has yet to reach full maturity. Operations performed at supercritical conditions (above 374 °C and 22 MPa) allow the high solubility of organic materials, even with a high moisture content. This enhances the degradation efficiency of complex polymers, and facilitates their conversion into gaseous products (high H_2 yield) and a minimal amount of tar. However, the technology also confronts considerable challenges, including high installation costs [67].

Oxygen plays a significant role in the enhancement of combustion reactions, resulting in the generation of more heat and an elevated bed temperature. Additionally, it reduces the tar content and increases the LVH. Thus, steam and O_2 gasification leads to syngas with high H_2 concentrations (Figure 11) and a suitable H_2/CO ratio for synthesis applications [42,53]. Oxygen-enriched air is beneficial, but the generation of the enriched air requires additional energy. This may be achieved with an air separator or an oxygen supply system. However, the augmented energy consumption can reduce overall cold gas efficiency (CGE), despite the increased energy content of the producer gas [87]. Xiao et al. [47] observed that decreasing the ER favors a higher LHV of the syngas.

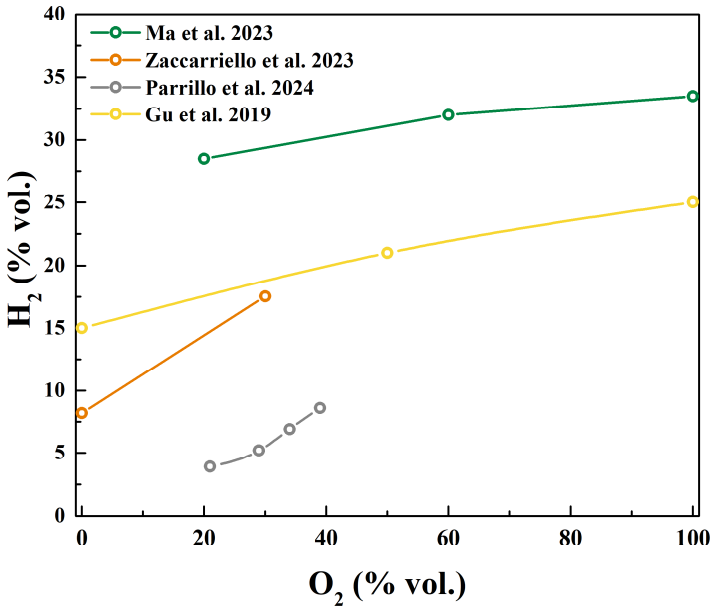


Figure 11. H_2 content as a function of the oxygen content in the enriched air [79,85–87].

It is also worth remarking that when CO_2 is employed as the gasifying medium, there is an increase in CO content. This is of particular significance to syngas production for the manufacturing of liquid fuels through Fischer–Tropsch synthesis.

Gu et al. [79] investigated the impacts of three gasifying agents (air, pure O_2, and O_2-enriched air), gasifier temperature, and ER on gas product composition, LHV, and exergy efficiency. Their results demonstrate that an increase in ER from 0.15 to 0.21 reduced the exergy efficiency from 62.3% to 53.3% when pure O_2 was employed as the gasifying agent. Similarly, using O_2-enriched air and air as gasifying agents, exergy efficiency decreased from 58.1% to 50.7% and 55.1% to 45.8%, respectively.

Parrillo et al. [86] validated a model to predict the reactor behavior under pure oxygen and steam gasification. The model's results indicate the limited influence of the oxygen concentration (in the fluidization/gasification medium) on syngas composition. The steam can play a pivotal role in both the reactions and the thermal stability of the process; however, provided that the steam-to-carbon ration is larger than 1.5, the steam content mainly affects the reactor temperature control rather than the syngas composition.

A lower ER resulted in lower gas production, while a higher ER favored complete combustion, producing CO_2 at the expense of syngas [88]. The optimal ER value is typically in the range of 0.2–0.3 [59].

3.3.3. Catalyst

In the context of gasification processes, catalysts have been demonstrated to play a significant role in enhancing the efficiency and selectivity of the reactions involved. Catalysts enhance carbon conversion processes while reducing tar formation. This is achieved through reactions such as steam or dry reforming, water–gas shift, oxidation, and others.

In consideration of the selected literature, the catalysts utilized can be classified into three principal categories: mineral catalysts, char or activated carbon (AC), alkali and other metal catalysts, and nickel catalysts.

The catalysts employed in the conversion of waste plastics can be classified into two principal categories, according to their position relative to the gasifier (Figure 12). The initial category of catalysts is designated as in-situ catalysts, when catalysts are mixed with the feedstock in the gasifier reactor. The primary objective of these catalysts is to reduce the tar content, with minimal impact on the conversion of methane (CH_4) and C_{2-3} hydrocarbons in the resulting product gas. These catalysts operate under the same conditions as the gasifier, are typically non-renewable, and are composed of inexpensive, disposable materials. The second group is that of the ex situ catalysts, which are placed in a separate reactor (downstream of the gasifier), through which the producer gas is passed. Regardless of the type of gasifier, they can operate under different conditions than the gasification unit. The ex situ catalysts primarily catalyze the reforming of hydrocarbons and methane with steam or CO_2, producing additional CO and H_2 [89].

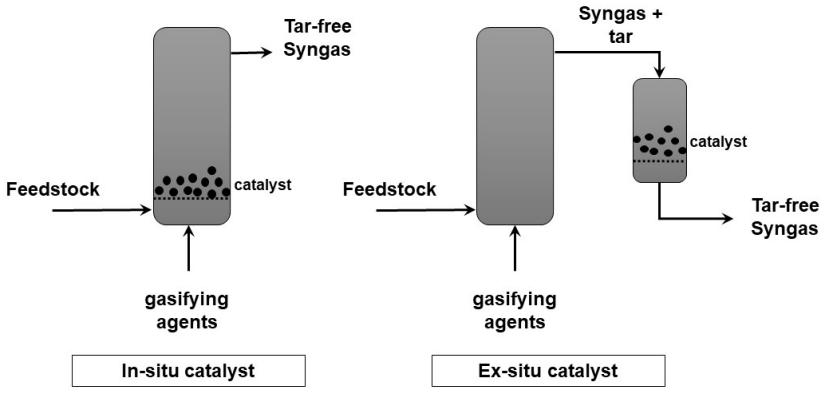


Figure 12. Schematic for tar removal of catalytic gasification.

The utilization of a catalyst to facilitate the reforming of condensable organic compounds and methane has the potential to enhance the overall efficiency of the conversion process (Figure 13). Three main groups of catalysts have been addressed for use in gasifying plastic, and are described in the following sections.

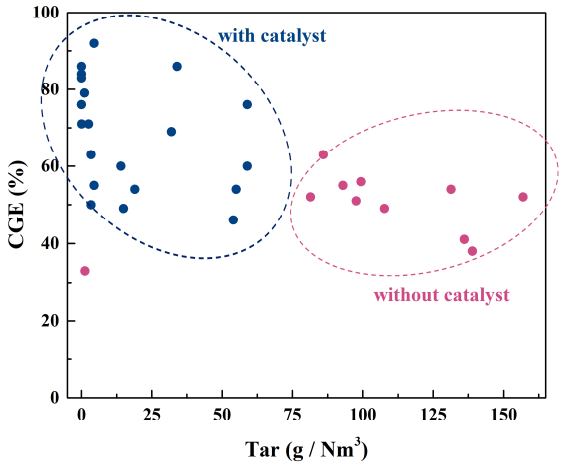


Figure 13. Carbon gasification efficiency vs. tar content affected by presence of catalyst (data obtained from Refs. [40,41,55,59,64,76,86,90,91]).

Mineral Catalysts

Natural catalysts (mainly dolomite and olivine) are one of the most widely used materials for in situ catalysts [76,90,92,93]. The dolomite is a naturally abundant mineral composed of calcium and magnesium, with the general formula of $MgCO_3 \cdot CaCO_3$. Olivine consists mainly of a silicate mineral in which magnesium and iron cations are embedded in the silicate tetrahedral.

In this type of solid, the decomposition mechanism is based on a combination of two actions—the isomerization reactions due to acidic sites like SiO_2 or Al_2O_3, and the catalysis of hydrogenation/dehydrogenation reactions on metallic sites. This combination activates the isomerization of straight-chain paraffins to branched-chain molecules, the dehydrocyclization of paraffins to cycloparaffins, the dehydrogenation of naphthenes to aromatics and the further decomposition of aromatics to pure carbon and hydrogen [91]. The catalytic properties of olivine are ascribed to its active metal sites, which are primarily composed of iron, magnesium, and nickel. These facilitate the breaking of C–H bonds in polyolefin plastics. The formation of metal–carbon complexes at these active metal sites enhances hydrogen production while simultaneously preventing the formation of tar [94].

Although some published works have concluded that, under similar operating conditions, the activity of olivine for tar removal is similar to that of dolomite [40,92,93], the results of other authors show that the activity of dolomite is superior [46].

One aspect to consider is that when the amount of oxygen available is high (high equivalence ratios), CO production within the gasification bed increases. The presence of CO inhibits the catalytic activity of iron present in olivine by forming iron carbonyls, which bind to iron and block the active sites necessary for catalysis. High concentrations of CO can lead to a masking effect, reducing the effectiveness of iron in facilitating some reactions [45]. This inhibition is particularly pronounced at high equivalence ratios, where CO production within the gasification bed increases [91]. On the other hand, dolomite is limited by its poor physical strength, which causes it to elutriate from the gasifier [46].

In a study conducted by Cho et al. [92,93], the effects of dolomite and olivine on the gasification of mixed plastic waste in a fluidized bed reactor were investigated. The study employed a two-stage gasifier, with and without additional additives. The additives in question could be regarded as an external catalyst or a secondary catalyst in the upper stage of the gasifier. The compositions of the producer gas and the tar content were found to be largely similar for both the olivine and the dolomite catalysts. Additives (dolomite and activated carbon) also reduced tar production, with tar removal efficiencies reaching up to 98.2%. Furthermore, olivine and dolomite can also be employed to remove HCl

from the gas, resulting in significantly reduced concentrations of HCl in the producer gas. However, this method is less effective than the one using activated carbon and calcined zeolite. Cho et al. [92] demonstrated that the HCl concentrations in the producer gases and the Cl concentrations of the condensate liquids are higher than those found when dolomite was used as an additive.

Erkiaga et al. [95] tested two different types of catalysts (olivine and γ-Al_2O_3) for the steam gasification of HDPE in a conical spouted bed reactor. Both catalysts exhibited similar results for product yields (gas, tar, and char) and gas composition than sand. This limited behavior differs from the good performance observed for olivine and γ-Al_2O_3 in air gasification. Howver, in general, the higher concentration of steam can compete with the adsorption of tar components, affecting the overall adsorption capacity [31,96]. It can be seen, therefore, that high steam/feedstock ratios (above 1.5) not only affect the conversion of tar but also the concentrations of CO, H_2, and CO_2, due to the reduction in carbon deposition on the olivine catalyst [73].

Activated Carbon

Carbonaceous materials, such as activated carbon (AC), are solids with excellent conductivity, high surface area, low cost, and a high content of oxygen and nitrogen functional groups. This leads to a significant increase in syngas generation. Furthermore, AC exhibits high coke resistance [54], making it an optimal choice as a catalyst. The large surface area of AC makes it an ideal adsorbent for tar removal, facilitating the conversion of tar into lighter gaseous hydrocarbons.

Furthermore, nitrogen and sulfur compounds in plastic waste can be decomposed by adsorption on AC in the initial stage, followed by decomposition in the subsequent stage [97]. It has been established that an AC bed increases H_2 values, attributable to the cracking and reforming of heavier compounds at an elevated temperature of 800 °C [49,84,97]. These authors observed differences in the gas composition, with notable variations in the concentrations of H_2 and CO_2; the hydrogen concentration was found to be higher with AC than with dolomite. However, the use of dolomite resulted in a significant increase in CO_2 production. The coal-derived AC used in the study by Choi et al. [54] contained significant amounts of Fe and Ca, which are reported to be active in tar cracking.

In the long-term steam gasification of PE, Jeong et al. [84] observed a gradual deactivation of AC, which was evident from the low H_2 production and the detection of toluene as the main tar component in syngas. The in situ regeneration of AC with steam resulted in a significant recovery of the textural properties of the AC [55,90].

Others Catalyst

After recycling, MSW is transformed into so-called Solid Recovered Fuel (SRF). This primarily comprises non-recyclable combustible solid waste materials, including a wide range of plastics, degraded textiles, synthetic resins, tires, paper, and woody biomass. The heterogeneous composition of this feedstock, comprising metal oxides such as CaO [98], MgO, TiO_2, Fe_2O_3, SiO_2, and Al_2O_3, exerts a catalytic influence during the gasification and pyrolysis processes [73,99]. The ash component of the bed material catalyst offers certain advantages [55]. The high SiO_2 content can enhance structural stability, while the presence of alkali metals can promote catalytic reactions that improve gas quality. However, high levels of CaO and MgO can lead to undesirable slagging and fouling issues, which can complicate the operation and maintenance of the gasifier [48].

The presence of certain additives has the potential to facilitate the solution of challenges associated with contaminants or reduced yield. Mavukwana et al. [100] focused on the co-gasification of waste tires and gypsum. The addition of gypsum at temperatures ranging from 700 to 1200 °C led to a solid–solid reaction between gypsum and carbon, resulting in the formation of compounds such as CO, CaS, CaO, and SO_2, depending on process temperature and feed composition. The enhancement of the gas yield by 15% was observed, along with a significant increase in CO content. The study by Yu et al. [65] describes the catalytic degradation and dechlorination of PVC. The catalyst, based on a metal oxide such as a zeolite, acted as an adsorbent for the evolved HCl, or as an inhibitor of it. Lerner et al. [101] studied the production of H2 from used car tires via steam–plasma gasification. The process achieved a significant yield of syngas, with approximately 99.5% of the gas being hydrogen and carbon monoxide. CaO is utilized as an absorber in the catalytic conversion process, enhancing the hydrogen yield by reacting with CO_2 to form calcium carbonate ($CaCO_3$). This reaction shifts the equilibrium towards hydrogen production. Ni-loaded activated carbon is significantly more effective in tar removal compared to Ca-based additives, achieving tar-free producer gases with high removal efficiency. While Ca-based additives can catalyze tar cracking and reduce HCl levels, they show limited tar removal efficacy. In contrast, Ni enhances hydrogen production and improves gas composition by increasing CO and decreasing CO_2, but it is susceptible to deactivation by chlorine, which can affect its performance [58].

The use of nickel as a catalyst has been shown to significantly enhance the production of hydrogen [102]. It is a relatively inexpensive option that is sufficiently active to break C–C bonds through reductive elimination and oxidative addition, effectively reducing the dissociation energy of the C–C bond. These reactions generate radicals that interact with various hydrocarbons present in the tar, leading to dehydrogenation and an increase in the hydrogen content of the syngas [103,104] (Table 5). In his study, Farooq et al. [105] investigated the steam gasification of LDPE using an ex situ Ni catalyst. The results indicate that the order of hydrogen production yields from the catalysts was Ni/CeO_2-ZrO_2 > Ni/CeO_2 > Ni/Al_2O_3, highlighting the effectiveness of the Ni/CeO_2-ZrO_2 catalyst for hydrogen generation, corroborating the findings of previous studies that reported a 76% hydrogen selectivity at 800 °C.

Table 5. Literature results for Ni catalytic plastics' gasification.

Reactor Type	Feedstock	Catalyst	Conditions	Gas Composition (Vol. %)	Reference
UOS gasifier	Waste plastic (LDPE, PP, and PVC)	Ni/AC	ER: 0.3; T: 792–796 °C	H_2: 29.7–29.8; CO: 11.7–15.5; CO_2: 3.7–0.7; CH_4: 6.8–7.7;	[58]
Lab-scale fixed-bed	LDPE	Ni/Al_2O_3	S/F: 3; T: 800 °C	H_2: 17.8; CO: 0.62; CO_2: 0.15; $C_{1–4}$: 51.9;	[105]
	LDPE	Ni/CeO_2	S/F: 3; T: 800 °C	H_2: 68.5; CO: 1.15; CO_2: 2.5; C_{1-4}: 28.4;	[105]
	LDPE	Ni/CeO_2-ZrO_2	S/F: 3; T: 800 °C	H_2: 76.8; CO: 1.7; CO_2: 2.8; C_{1-4}: 20.1;	[105]
Fixed-bed reactor	Waste plastic	5 Ni/Ti-Al	Air; T: 750 °C	H_2: 20.4; CO: 18.02; CO_2: 2.98; CH_4: 27.03;	[106]
		10 Ni/Ti-Al	Air; T: 750 °C	H_2: 24.7; CO: 25.04; CO_2: 2.33; CH_4: 21.7;	[106]
		15 Ni/Ti-Al	Air; T: 750 °C	H_2: 21.2; CO: 24.2; CO_2: 2.9; CH_4: 23;	[106]

Summarizing, there are several highlights related to the factors impacting plastic gasification, as follows:

- The feedstock composition can affect the obtained gas composition. According to the chemical structure of plastics, syngas composition can vary, and the generation of tar or char can be affected, as well as the presence of pollutant compounds. Sufficient elemental analysis data could be useful for a better understanding of the system's behavior;
- The system temperature is one of the most critical variables of the process, which influences the development of the gasification, drying, and pyrolysis stages, the thermodynamic balance of the reactions taking place, and the final composition of the syngas obtained. The optimum range is usually between 600 and 900 °C;
- The type and proportion of the gasifying agent directly affects the LHV of the syngas obtained. The three most common gasifying agents are air, steam, and O_2, with air being the most economical but having a diluting effect due to the N_2 content. On the other hand, steam enhances the WGS reaction, which increases the CO_2 and H_2 content, while pure O_2 improves the gasification efficiency and the LHV value of the syngas obtained. The gasifying agent impacts the efficiency, yield, and quality of the resulting syngas;
- Finally, the use of catalysts is a very important factor in the system. Catalysts can be classified according to the type of material to be used (minerals, alkaline metals, and nickel catalysts) and/or according to their position relative to the gasifier (in situ or ex situ). Depending on the type and position of the catalyst, the objective will be to reduce the tar content and/or reform light hydrocarbons to maximize the CO and H_2 contents.

3.4. Future Implications

A review of recent studies on plastic gasification patents reveals a predominant focus on feedstock pre-treatment. The recyclability of certain non-biodegradable waste materials is evident, while others require more complex and expensive processing. When the effort and costs are high, recycling becomes problematic. In gasification processes, thermosets and thermoplastics are subjected to pre-treatment to enhance gas production efficiency and quality. However, thermosets demand more intensive pre-treatment to break down their structure, whereas thermoplastics mainly require size reduction and contaminant removal.

Pre-treatment involves sorting, grinding, cleaning, and sometimes chemical or thermal decomposition. Chemical or thermal methods are applied to thermosets and other challenging plastics to degrade their structure or remove additives. Conversely, process modification entails adjusting the recycling or conversion system to accommodate various plastic types, which may involve altering operational parameters or system configurations. This enhances system flexibility, enabling it to process mixed plastics without compromising product quality or damaging equipment. By augmenting energy recovery and producing higher-quality outputs, process modification contributes to enhanced efficiency and sustainability. While the initial pre-treatment step is used to prepare the material, process modification optimizes the system to handle diverse plastic feedstocks, ensuring more efficient recycling and waste conversion. Researchers have also patented various gasification system configurations to optimize processing.

In 2003, a Japanese patent [107] described the gasification system as a versatile method to convert several feedstocks into syngas, focusing especially on the gasification reactor. Here, a 'down–updraft gasifier' (a combination of a downward feed stream and downward and upward gas stream) is used to prevent the usual batch gasification problems, such as an intermittent gas flow due to the ash and slag generation and a high tar production.

These authors also introduced an additional oxidation zone after the reduction zone to facilitate the oxidation of residual tars.

Specifically, for plastic waste, in 2005, one patent suggested the pre-treatment of the plastic feedstock [108]. The feedstock was first pyrolyzed in a reactor, and then the pyrolysis products were further gasified with steam in another reactor.

In 2007, Shires et al. [109] reported on a gasification process to produce syngas from coal-based feedstocks with the addition of waste polymers, combining one or more materials (plastics such as PE, PP, poly, etc.) with carbon particulates and an oxidant stream in a fluidized bed reactor, and external heating to facilitate the syngas production. The authors suggested the use of alternative reactors for the reforming and conversion processes, such as fixed bed reactors, moving bed reactors, slurry reactors, etc. This invention also uses catalysts for the reforming process, a mixture of zinc and supported copper oxide catalysts. The authors also suggested several recirculation currents and mixtures of oxidants that allow one to control of the reaction temperature.

A patent from 2021 [108] suggested an allothermic system with methods like plasma gasification, in which portions of the produced CO_2 are recirculated to the gasification reactor at high pressure. The authors explain that the reactors for the process could be any of the most widely used types, like fluidized beds, fixed beds, or entrained flow gasifiers. Also, a combination of those types of reactors could be used. Later, some authors [9] compared plasma gasification with other methods for energy production from plastic waste, on a theoretical basis. They concluded that plasma gasification had several economic advantages over the other technologies.

One of the challenges for plastic gasification is the feedstock pre-treatment. Plastics contain impurities that may lead to the formation of undesirable gasification products. To improve the feedstock's performance in gasification, some authors propose operations such as size reduction, the admixing of the plastics with other fuels, solvolysis for plastic liquefaction, or plastic pyrolysis for the oily feedstock obtention for the gasification reactor. Grinding and mixing the obtained material with coal to form the feed is probably the simplest technological solution. Several patents treat the feedstock with this method and focus on other aspects of the process, such as the treatment of gaseous streams, recycling, or combinations of different gasifying agents. The problem with this solution is that for it to be a real improvement, the mixture must contain a higher proportion of fossil fuels, and the plastic waste proportion can only reach 5% of the feed stream [110], which does not suggest a huge advantage for the reduction in plastic waste. However, it could be useful as a complement for those industries that entail the generation of plastic waste and need access to cheap fossil fuel.

Other patents [111] depict fluidized bed gasifiers for producing processed plastics in pellet form with the addition of sand to aid heat transfer, thermal stability, and bed fluidization. No specific information is found on how the problems associated with feed handling are solved.

Solvolysis, on the other hand [112], appears as an option for liquefying a solid material to be subsequently introduced into the gasification process in liquid form. This process allows an extra operation for eliminating halogenated compounds, which results in cleaner gases at the outlet of the gasification reactor. The solvolysis reaction involves the decomposition of the polymeric material in the presence of a solvent. In the case of polymers such as polyester phthalate (PET), the reaction leads to its decomposition into a mainly phthalate product and a mainly glycolic product. The appropriate choice of solvent is necessary to allow the liquefaction of plastic solids. The solvent must have at least one hydroxyl group (-OH). The patent mentions the successful use of solvents such as water, alcohol (more precisely methanol and ethanol), glycols, and even ammonia. However, the

possibility of using other solvents or combinations of different solvents is not ruled out. Once the solvolysis liquors are obtained, they can be used in various processes, either for recycling and reprocessing the glycols and phthalates as new polymers, or in processes such as pyrolysis or gasification. The syngas produced in the gasification process can then produce energy or be used as a reagent for obtaining new chemical products. However, the patent does not specify the design of the gasification reactor, so it is unclear how to overcome the difficulties of dealing with liquid feed.

Lately (2023), some authors have again proposed the use of pyrolysis before gasification [113]. In these cases, the gases obtained from pyrolysis, composed of hydrogen, carbon monoxide, and light hydrocarbons, are sent to the gasifier. Other patents combine processes for the treatment of plastic waste, the liquefaction of plastics with different methods (including solvolysis), and subsequently a combination of pyrolysis and gasification. In this case, the gasifier receives a liquid stream of the treated plastics, so it cannot be considered a traditional gasification process. No specific reactor design was mentioned. Again, the focus of the patent is the combination of operations [114].

As can be seen, the focus of the consulted patents is the combination of operations, intended to overcome the main technological challenge posed by the handling of a feedstock of great heterogeneity. This solution makes the overall process more expensive, since it is necessary to add an extra stage to the entire process.

The use of catalysts to improve syngas quality is mainly explored at the laboratory scale. A detailed study of the feasibility of their use at the pilot scale is essential if the objective is to improve the quality of the syngas obtained [28,104,115,116]. Some publications have shown that cheap catalysts such as dolomite or pyrolysis residues can be used in biomass gasification with good results at pilot scale. The economic viability is, however, not clear.

Nevertheless, the need to drastically reduce the presence of plastics in natural environments (especially the ocean) generates more incentives to consider plastic gasification processes as a viable recycling alternative.

4. Conclusions

The management of non-biodegradable plastic waste is challenging due to the limited number of available disposal methods, such as incineration and landfill. The utilization of advanced recycling technologies, including chemical recycling and gasification, offers considerable potential. However, these technologies are confronted with challenges such as the quality of raw materials and regulatory uncertainties. Gasification has been identified as a potential solution for the large-scale implementation of plastic waste valorization.

The primary challenge associated with this technology pertains to the formation of tar. This is a series of compounds that have the capacity to reduce gas yield and impact overall process productivity.

To address this challenge, researchers have directed their efforts towards an elimination of and reduction in tars through the utilization of catalysts, diverse gasifying agents, and modifications in reactor design.

The quality of the feedstock, its size, and the presence of contaminants such as sulfur have been demonstrated to have a significant impact on the efficiency and the quality of the gas produced. All patented technological advances in recent years have been related to feed pretreatment, making this technology a viable option.

It has been demonstrated that increasing the plastic content enhances both hydrogen production and calorific value. However, this also leads to a rise in tar and impurities.

Air gasification is a cost-effective process; however, it produces a gas with a low calorific value, which is therefore suitable for use in energy production.

The process of steam gasification has been demonstrated to enhance hydrogen production and reduce impurities; however, it necessitates additional energy, which can result in increased operating costs and potentially compromise economic viability, particularly when costly energy sources are employed.

A similar situation is observed in the case of O_2-enriched air, necessitating an energetic analysis of the process to evaluate the applicability of the conditions.

In the context of an effective catalytic investigation of the gasification of waste containing plastic, it is essential to consider not only the analysis of the gas yield and composition, but also the effects that impurities, which are characteristic of complex feeds, have upon the process.

To achieve a greener and more sustainable future, it is essential that the catalysts utilized become more sustainable, efficient, economical, and reusable, in addition to contributing to processes that are less energy intensive.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/pr13030647/s1, Table S1: Experimental results of gasification of plastic waste by different authors.

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References

1. Global Plastics Outlook. Available online: https://www.oecd.org/en/publications/global-plastics-outlook_aa1edf33-en.html (accessed on 30 November 2024).
2. Singh, N.; Hui, D.; Singh, R.; Ahuja, I.P.S.; Feo, L.; Fraternali, F. Recycling of Plastic Solid Waste: A State of Art Review and Future Applications. *Compos. Part B Eng.* **2017**, *115*, 409–422. [CrossRef]
3. Ritchie, H.; Samborska, V.; Roser, M. Plastic Pollution. In *Our World in Data*; Global Change Data Lab: Oxford, UK, 2023.
4. Jeswani, H.; Krüger, C.; Russ, M.; Horlacher, M.; Antony, F.; Hann, S.; Azapagic, A. Life Cycle Environmental Impacts of Chemical Recycling via Pyrolysis of Mixed Plastic Waste in Comparison with Mechanical Recycling and Energy Recovery. *Sci. Total Environ.* **2021**, *769*, 144483. [CrossRef] [PubMed]
5. World Economic Forum. The New Plastics Economy: Rethinking the Future of Plastics. Available online: https://www.ellenmacarthurfoundation.org/the-new-plastics-economy-rethinking-the-future-of-plastics (accessed on 13 November 2024).
6. Kumar, R.; Sadeghi, K.; Jang, J.; Seo, J. Mechanical, Chemical, and Bio-Recycling of Biodegradable Plastics: A Review. *Sci. Total Environ.* **2023**, *882*, 163446. [CrossRef] [PubMed]
7. Muzata, T.S.; Matuana, L.M.; Rabnawaz, M. Challenges in the Mechanical Recycling and Upcycling of Mixed Postconsumer Recovered Plastics (PCR): A Review. *Curr. Res. Green Sustain. Chem.* **2024**, *8*, 100407. [CrossRef]
8. Davidson, M.G.; Furlong, R.A.; McManus, M.C. Developments in the Life Cycle Assessment of Chemical Recycling of Plastic Waste—A Review. *J. Clean. Prod.* **2021**, *293*, 126163. [CrossRef]

9. Cudjoe, D.; Wang, H. Plasma Gasification Versus Incineration of Plastic Waste: Energy, Economic and Environmental Analysis. *Fuel Process. Technol.* **2022**, *237*, 107470. [CrossRef]
10. Pan, D.; Su, F.; Liu, C.; Guo, Z. Research Progress for Plastic Waste Management and Manufacture of Value-Added Products. *Adv. Compos. Hybrid Mater.* **2020**, *3*, 443–461. [CrossRef]
11. VOSviewer. Available online: https://www.vosviewer.com/ (accessed on 3 December 2024).
12. Voet, V.; Jager, J.; Folkersma, R. *Plastics in the Circular Economy*; De Gruyter: Berlin, Germany, 2021; ISBN 978-3-11-066676-2.
13. Kutz, M. *Mechanical Engineers' Handbook, Volume 1: Materials and Engineering Mechanics*, 4th ed.; Wiley: Hoboken, NJ, USA, 2015. Available online: https://www.wiley.com/en-us/Mechanical+Engineers%E2%80%99+Handbook,+Volume+1:+Materials+and+Engineering+Mechanics,+4th+Edition-p-9781118112823 (accessed on 13 November 2024).
14. Jansen, J. Comparing Thermoplastic Elastomers and Thermoset Rubber. Available online: https://read.nxtbook.com/wiley/plasticsengineering/april2016/consultantscorner.html (accessed on 3 December 2024).
15. Shah, M.; Rajhans, S.; Pandya, H.A.; Mankad, A.U. Bioplastic for future: A review then and now. *World J. Adv. Res. Rev.* **2021**, *9*, 56–67. [CrossRef]
16. Islam, M.K.; Khatun, M.S.; Arefin, M.A.; Islam, M.R.; Hassan, M. Waste to Energy: An Experimental Study of Utilizing the Agricultural Residue, MSW, and e-Waste Available in Bangladesh for Pyrolysis Conversion. *Heliyon* **2021**, *7*, e08530. [CrossRef]
17. Zhou, H.; Meng, A.; Long, Y.; Li, Q.; Zhang, Y. Classification and Comparison of Municipal Solid Waste Based on Thermochemical Characteristics. *J. Air Waste Manag. Assoc.* **2014**, *64*, 597–616. [CrossRef]
18. Che, C.A.; Heynderickx, P.M. Hydrothermal Carbonization of Plastic Waste: A Review of Its Potential in Alternative Energy Applications. *Fuel Commun.* **2024**, *18*, 100103. [CrossRef]
19. NIST Standard Reference Data. Available online: https://webbook.nist.gov/chemistry/ (accessed on 13 November 2024).
20. Vitale, A.; Papa, A.A.; Iannello, S.; Ciro, E.; Hatunoglu, A.; Corradetti, V.; Rovelli, N.; Foscolo, P.U.; Di Carlo, A. Devolatilization of Polypropylene Particles in Fluidized Bed. *Energies* **2023**, *16*, 6324. [CrossRef]
21. Vitale, A.; Papa, A.A.; Di Carlo, A.; Rapagnà, S. Three-Dimensional Computational Fluid-Dynamic Simulation of Polypropylene Steam Gasification. *Int. J. Hydrogen Energy* **2024**, *95*, 1328–1341. [CrossRef]
22. Jia, Y.; Li, Z.; Wuang, X.; Lou, C.; Xiao, B.; Lim, M.L.M. Visualization of Combustion Phases of Biomass Particles: Effects of Fuel Properties. *ACS Omega* **2021**, *6*, 27702–27710. [CrossRef]
23. Ye, L.; Zhang, J.; Wang, G.; Wang, C.; Mao, X.; Ning, X.; Zhang, N.; Teng, H.; Li, J.; Wang, C. Feasibility Analysis of Plastic and Biomass Hydrochar for Blast Furnace Injection. *Energy* **2023**, *263*, 125903. [CrossRef]
24. Götze, R.; Pivnenko, K.; Boldrin, A.; Scheutz, C.; Astrup, T.F. Physico-Chemical Characterisation of Material Fractions in Residual and Source-Segregated Household Waste in Denmark. *Waste Manag.* **2016**, *54*, 13–26. [CrossRef]
25. Karatas, H.; Olgun, H.; Engin, B.; Akgun, F. Experimental Results of Gasification of Waste Tire with Air in a Bubbling Fluidized Bed Gasifier. *Fuel* **2013**, *105*, 566–571. [CrossRef]
26. Vuppaladadiyam, S.S.V.; Vuppaladadiyam, A.K.; Sahoo, A.; Urgunde, A.; Murugavelh, S.; Šrámek, V.; Pohořelý, M.; Trakal, L.; Bhattacharya, S.; Sarmah, A.K.; et al. Waste to Energy: Trending Key Challenges and Current Technologies in Waste Plastic Management. *Sci. Total Environ.* **2024**, *913*, 169436. [CrossRef]
27. Munir, M.T.; Mansouri, S.S.; Udugama, I.A.; Baroutian, S.; Gernaey, K.V.; Young, B.R. Resource Recovery from Organic Solid Waste Using Hydrothermal Processing: Opportunities and Challenges. *Renew. Sustain. Energy Rev.* **2018**, *96*, 64–75. [CrossRef]
28. Wu, Y.; Wang, H.; Li, H.; Han, X.; Zhang, M.; Sun, Y.; Fan, X.; Tu, R.; Zeng, Y.; Xu, C.C.; et al. Applications of Catalysts in Thermochemical Conversion of Biomass (Pyrolysis, Hydrothermal Liquefaction and Gasification): A Critical Review. *Renew. Energy* **2022**, *196*, 462–481. [CrossRef]
29. Solis, M.; Silveira, S. Technologies for Chemical Recycling of Household Plastics—A Technical Review and TRL Assessment. *Waste Manag.* **2020**, *105*, 128–138. [CrossRef] [PubMed]
30. Boel, M.J.; Wang, H.; Farra, A.A.; Megido, L.; González-LaFuente, J.M.; Shiju, N.R. Hydrothermal Liquefaction of Plastics: A Survey of the Effect of Reaction Conditions on the Reaction Efficiency. *React. Chem. Eng.* **2024**, *9*, 1014–1031. [CrossRef]
31. Meng, S.; Li, W.; Li, Z.; Song, H. Recent Progress of the Transition Metal-Based Catalysts in the Catalytic Biomass Gasification: A Mini-Review. *Fuel* **2023**, *353*, 129169. [CrossRef]
32. Calero, M.; Solís, R.R.; Muñoz-Batista, M.J.; Pérez, A.; Blázquez, G.; Ángeles Martín-Lara, M. Oil and Gas Production from the Pyrolytic Transformation of Recycled Plastic Waste: An Integral Study by Polymer Families. *Chem. Eng. Sci.* **2023**, *271*, 118569. [CrossRef]
33. Quesada, L.; Calero, M.; Martín-Lara, M.A.; Pérez, A.; Blázquez, G. Characterization of Fuel Produced by Pyrolysis of Plastic Film Obtained of Municipal Solid Waste. *Energy* **2019**, *186*, 115874. [CrossRef]
34. Spath, P.L.; Dayton, D.C. *Preliminary Screening—Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas*; National Renewable Energy Lab. (NREL): Golden, CO, USA, 2003.
35. Woolcock, P.J.; Brown, R.C. A Review of Cleaning Technologies for Biomass-Derived Syngas. *Biomass Bioenergy* **2013**, *52*, 54–84. [CrossRef]

36. Ajorloo, M.; Ghodrat, M.; Scott, J.; Strezov, V. Experimental Analysis of the Effects of Feedstock Composition on the Plastic and Biomass Co-Gasification Process. *Renew. Energy* **2024**, *231*, 120960. [CrossRef]
37. Peters, K.E.; Xia, X.; Pomerantz, A.E.; Mullins, O.C. Chapter 3—Geochemistry Applied to Evaluation of Unconventional Resources. In *Unconventional Oil and Gas Resources Handbook*; Ma, Y.Z., Holditch, S.A., Eds.; Gulf Professional Publishing: Boston, MA, USA, 2016; pp. 71–126. ISBN 978-0-12-802238-2.
38. Shen, Y. A Review on Hydrothermal Carbonization of Biomass and Plastic Wastes to Energy Products. *Biomass Bioenergy* **2020**, *134*, 105479. [CrossRef]
39. Wang, S.; Wang, Y.; Shi, Z.; Sun, K.; Wen, Y.; Niedzwiecki, L.; Pan, R.; Xu, Y.; Zaini, I.N.; Jagodzińska, K.; et al. Van Krevelen Diagrams Based on Machine Learning Visualize Feedstock-Product Relationships in Thermal Conversion Processes. *Commun. Chem.* **2023**, *6*, 273. [CrossRef]
40. Arena, U.; Zaccariello, L.; Mastellone, M.L. Fluidized Bed Gasification of Waste-Derived Fuels. *Waste Manag.* **2010**, *30*, 1212–1219. [CrossRef]
41. Martínez-Lera, S.; Torrico, J.; Pallarés, J.; Gil, A. Thermal Valorization of Post-Consumer Film Waste in a Bubbling Bed Gasifier. *Waste Manag.* **2013**, *33*, 1640–1647. [CrossRef] [PubMed]
42. Jeong, Y.-S.; Kim, J.-W.; Ra, H.W.; Seo, M.W.; Mun, T.-Y.; Kim, J.-S. Characteristics of Air Gasification of 10 Different Types of Plastic in a Two-Stage Gasification Process. *ACS Sustain. Chem. Eng.* **2022**, *10*, 4705–4716. [CrossRef]
43. Zallaya, S.; El Achkar, J.H.; Chacra, A.A.; Shatila, S.; El Akhdar, J.; Daher, Y. Steam Gasification Modeling of Polyethylene (PE) and Polyethylene Terephthalate (PET) Wastes: A Case Study. *Chem. Eng. Sci.* **2023**, *267*, 118340. [CrossRef]
44. Buentello-Montoya, D.A.; Duarte-Ruiz, C.A.; Maldonado-Escalante, J.F. Co-Gasification of Waste PET, PP and Biomass for Energy Recovery: A Thermodynamic Model to Assess the Produced Syngas Quality. *Energy* **2023**, *266*, 126510. [CrossRef]
45. Toledo, J.M.; Aznar, M.P.; Sancho, J.A. Catalytic Air Gasification of Plastic Waste (Polypropylene) in a Fluidized Bed. Part II: Effects of Some Operating Variables on the Quality of the Raw Gas Produced Using Olivine as the In-Bed Material. *Ind. Eng. Chem. Res.* **2011**, *50*, 11815–11821. [CrossRef]
46. Sancho, J.A.; Aznar, M.P.; Toledo, J.M. Catalytic Air Gasification of Plastic Waste (Polypropylene) in Fluidized Bed. Part I: Use of in-Gasifier Bed Additives. *Ind. Eng. Chem. Res.* **2008**, *47*, 1005–1010. [CrossRef]
47. Xiao, G.; Ni, M.-J.; Chi, Y.; Cen, K.-F. Low-Temperature Gasification of Waste Tire in a Fluidized Bed. *Energy Convers. Manag.* **2008**, *49*, 2078–2082. [CrossRef]
48. Xiao, R.; Jin, B.; Zhou, H.; Zhong, Z.; Zhang, M. Air Gasification of Polypropylene Plastic Waste in Fluidized Bed Gasifier. *Energy Convers. Manag.* **2007**, *48*, 778–786. [CrossRef]
49. Jeong, Y.-S.; Kim, J.-W.; Seo, M.-W.; Mun, T.-Y.; Kim, J.-S. Characteristics of Two-Stage Air Gasification of Polystyrene with Active Carbon as a Tar Removal Agent. *Energy* **2021**, *219*, 119681. [CrossRef]
50. Zhang, S.; Bie, X.; Qian, Z.; Wu, M.; Li, K.; Li, Q.; Zhang, Y.; Zhou, H. Synergistic Interactions between Cellulose and Plastics (PET, HDPE, and PS) during CO_2 Gasification-Catalytic Reforming on Ni/CeO_2 Nanorod Catalyst. *Appl. Energy* **2024**, *361*, 122975. [CrossRef]
51. Batuecas, E.; Serrano, D.; Horvat, A.; Abelha, P. Sustainable Conditions for Waste Tires Recycling through Gasification in a Bubbling Fluidized Bed. *J. Clean. Prod.* **2023**, *415*, 137839. [CrossRef]
52. Oboirien, B.O.; North, B.C. A Review of Waste Tyre Gasification. *J. Environ. Chem. Eng.* **2017**, *5*, 5169–5178. [CrossRef]
53. Leung, D.Y.C.; Wang, C.L. Fluidized-Bed Gasification of Waste Tire Powders. *Fuel Process. Technol.* **2003**, *84*, 175–196. [CrossRef]
54. Choi, M.-J.; Jeong, Y.-S.; Kim, J.-S. Air Gasification of Polyethylene Terephthalate Using a Two-Stage Gasifier with Active Carbon for the Production of H2 and CO. *Energy* **2021**, *223*, 120122. [CrossRef]
55. Kim, J.-K.; Jeong, Y.-S.; Kim, J.-W.; Kim, J.-S. Two-Stage Thermochemical Conversion of Polyethylene Terephthalate Using Steam to Produce a Clean and H2- and CO-Rich Syngas. *Energy* **2023**, *276*, 127651. [CrossRef]
56. Bai, B.; Liu, Y.; Zhang, H.; Zhou, F.; Han, X.; Wang, Q.; Jin, H. Experimental Investigation on Gasification Characteristics of Polyethylene Terephthalate (PET) Microplastics in Supercritical Water. *Fuel* **2020**, *262*, 116630. [CrossRef]
57. Türker Üzden, Ş.; Seçer, A.; Fakı, E.; Hasanoğlu, A. Utilization of PET (Waste) via Hydrothermal Co–Gasification with Sorghum for Hydrogen Rich Gas Production. *J. Energy Inst.* **2023**, *107*, 101193. [CrossRef]
58. Cho, M.-H.; Choi, Y.-K.; Kim, J.-S. Air Gasification of PVC (Polyvinyl Chloride)-Containing Plastic Waste in a Two-Stage Gasifier Using Ca-Based Additives and Ni-Loaded Activated Carbon for the Production of Clean and Hydrogen-Rich Producer Gas. *Energy* **2015**, *87*, 586–593. [CrossRef]
59. Arena, U.; Di Gregorio, F. Energy Generation by Air Gasification of Two Industrial Plastic Wastes in a Pilot Scale Fluidized Bed Reactor. *Energy* **2014**, *68*, 735–743. [CrossRef]
60. Lopez, G.; Erkiaga, A.; Amutio, M.; Alvarez, J.; Barbarias, I.; Bilbao, J.; Olazar, M. Steam Gasification of Waste Plastics in a Conical Spouted Bed Reactor. In *ECI Digital Archives*; ECI: New York, NY, USA, 2013.
61. Singh, M.; Salaudeen, S.A.; Gilroyed, B.H.; Dutta, A. Simulation of Biomass-Plastic Co-Gasification in a Fluidized Bed Reactor Using Aspen Plus. *Fuel* **2022**, *319*, 123708. [CrossRef]

62. Wilk, V.; Hofbauer, H. Conversion of Mixed Plastic Wastes in a Dual Fluidized Bed Steam Gasifier. *Fuel* **2013**, *107*, 787–799. [CrossRef]
63. Weiland, F.; Lundin, L.; Celebi, M.; van der Vlist, K.; Moradian, F. Aspects of Chemical Recycling of Complex Plastic Waste via the Gasification Route. *Waste Manag.* **2021**, *126*, 65–77. [CrossRef] [PubMed]
64. Arena, U.; Di Gregorio, F.; Amorese, C.; Mastellone, M.L. A Techno-Economic Comparison of Fluidized Bed Gasification of Two Mixed Plastic Wastes. *Waste Manag.* **2011**, *31*, 1494–1504. [CrossRef] [PubMed]
65. Yu, J.; Sun, L.; Ma, C.; Qiao, Y.; Yao, H. Thermal Degradation of PVC: A Review. *Waste Manag.* **2016**, *48*, 300–314. [CrossRef] [PubMed]
66. Liu, Q.; Sun, J.; Gu, Y.; Zhong, W.; Gao, K. Experimental Study on CO_2 Co-Gasification Characteristics of Biomass and Waste Plastics: Insight into Interaction and Targeted Regulation Method. *Energy* **2024**, *292*, 130509. [CrossRef]
67. Nie, S.Q.; Chen, M.Q.; Li, Q.H. Evaluation on Hydrothermal Gasification of Waste Tires Based on Chemical Equilibrium Analysis. *Int. J. Hydrogen Energy* **2022**, *47*, 1435–1448. [CrossRef]
68. Portofino, S.; Donatelli, A.; Iovane, P.; Innella, C.; Civita, R.; Martino, M.; Matera, D.A.; Russo, A.; Cornacchia, G.; Galvagno, S. Steam Gasification of Waste Tyre: Influence of Process Temperature on Yield and Product Composition. *Waste Manag.* **2013**, *33*, 672–678. [CrossRef]
69. Cheng, S.; Ding, X.; Dong, X.; Zhang, M.; Tian, X.; Liu, Y.; Huang, Y.; Jin, B. Immigration, Transformation, and Emission Control of Sulfur and Nitrogen during Gasification of MSW: Fundamental and Engineering Review. *Carbon Resour. Convers.* **2023**, *6*, 184–204. [CrossRef]
70. Zhang, J.; Zhu, M.; Jones, I.; Onyeka Okoye, C.; Zhang, Z.; Gao, J.; Zhang, D. Transformation and Fate of Sulphur during Steam Gasification of a Spent Tyre Pyrolysis Char. *Fuel* **2022**, *321*, 124091. [CrossRef]
71. Karatas, H.; Olgun, H.; Akgun, F. Experimental Results of Gasification of Waste Tire with air&CO_2, Air&steam and Steam in a Bubbling Fluidized Bed Gasifier. *Fuel Process. Technol.* **2012**, *102*, 166–174. [CrossRef]
72. Materazzi, M.; Lettieri, P.; Mazzei, L.; Taylor, R.; Chapman, C. Thermodynamic Modelling and Evaluation of a Two-Stage Thermal Process for Waste Gasification. *Fuel* **2013**, *108*, 356–369. [CrossRef]
73. Han, S.W.; Lee, J.J.; Tokmurzin, D.; Lee, S.H.; Nam, J.Y.; Park, S.J.; Ra, H.W.; Mun, T.-Y.; Yoon, S.J.; Yoon, S.M.; et al. Gasification Characteristics of Waste Plastics (SRF) in a Bubbling Fluidized Bed: Effects of Temperature and Equivalence Ratio. *Energy* **2022**, *238*, 121944. [CrossRef]
74. Lu, C.-H.; Chiang, K.-Y. Gasification of Non-Recycled Plastic Packaging Material Containing Aluminum: Hydrogen Energy Production and Aluminum Recovery. *Int. J. Hydrogen Energy* **2017**, *42*, 27532–27542. [CrossRef]
75. Serrano, D.; Horvat, A.; Batuecas, E.; Abelha, P. Waste Tyres Valorisation through Gasification in a Bubbling Fluidised Bed: An Exhaustive Gas Composition Analysis. *Renew. Energy* **2022**, *200*, 1438–1446. [CrossRef]
76. Arena, U.; Zaccariello, L.; Mastellone, M.L. Tar Removal during the Fluidized Bed Gasification of Plastic Waste. *Waste Manag.* **2009**, *29*, 783–791. [CrossRef]
77. Arregi, A.; Amutio, M.; Lopez, G.; Bilbao, J.; Olazar, M. Evaluation of Thermochemical Routes for Hydrogen Production from Biomass: A Review. *Energy Convers. Manag.* **2018**, *165*, 696–719. [CrossRef]
78. Shahbaz, M.; Al-Ansari, T.; Inayat, M.; Sulaiman, S.A.; Parthasarathy, P.; McKay, G. A Critical Review on the Influence of Process Parameters in Catalytic Co-Gasification: Current Performance and Challenges for a Future Prospectus. *Renew. Sustain. Energy Rev.* **2020**, *134*, 110382. [CrossRef]
79. Gu, H.; Tang, Y.; Yao, J.; Chen, F. Study on Biomass Gasification under Various Operating Conditions. *J. Energy Inst.* **2019**, *92*, 1329–1336. [CrossRef]
80. Inayat, M.; Sulaiman, S.A.; Kurnia, J.C.; Shahbaz, M. Effect of Various Blended Fuels on Syngas Quality and Performance in Catalytic Co-Gasification: A Review. *Renew. Sustain. Energy Rev.* **2019**, *105*, 252–267. [CrossRef]
81. Emami Taba, L.; Irfan, M.F.; Wan Daud, W.A.M.; Chakrabarti, M.H. The Effect of Temperature on Various Parameters in Coal, Biomass and CO-Gasification: A Review. *Renew. Sustain. Energy Rev.* **2012**, *16*, 5584–5596. [CrossRef]
82. Saebea, D.; Ruengrit, P.; Arpornwichanop, A.; Patcharavorachot, Y. Gasification of Plastic Waste for Synthesis Gas Production. *Energy Rep.* **2020**, *6*, 202–207. [CrossRef]
83. Mastral, F.J.; Esperanza, E.; Berrueco, C.; Juste, M.; Ceamanos, J. Fluidized Bed Thermal Degradation Products of HDPE in an Inert Atmosphere and in Air–Nitrogen Mixtures. *J. Anal. Appl. Pyrolysis* **2003**, *70*, 1–17. [CrossRef]
84. Jeong, Y.-S.; Park, K.-B.; Kim, J.-S. Hydrogen Production from Steam Gasification of Polyethylene Using a Two-Stage Gasifier and Active Carbon. *Appl. Energy* **2020**, *262*, 114495. [CrossRef]
85. Ma, Y.; Qi, H.; Zhang, J.; Cui, P.; Zhu, Z.; Wang, Y. Thermodynamic Analysis of a Carbon Capture Hydrogen Production Process for End-of-Life Tires Using Plasma Gasification. *J. Clean. Prod.* **2023**, *384*, 135662. [CrossRef]
86. Parrillo, F.; Ardolino, F.; Calì, G.; Pettinau, A.; Materazzi, M.; Sebastiani, A.; Arena, U. Plastic Waste Gasification Using Oxygen-Enriched Air and Steam: Experimental and Model Results from a Large Pilot-Scale Reactor. *Waste Manag.* **2024**, *183*, 53–62. [CrossRef]

87. Zaccariello, L.; Battaglia, D.; Mastellone, M.L. Gasification of Recycled Plastic Waste in a Fluidized Bed Reactor: Effect of Operating Conditions. *Chem. Eng. Trans.* **2023**, *101*, 253–258. [CrossRef]
88. Gao, N.; Kamran, K.; Quan, C.; Williams, P.T. Thermochemical Conversion of Sewage Sludge: A Critical Review. *Prog. Energy Combust. Sci.* **2020**, *79*, 100843. [CrossRef]
89. Sutton, D.; Kelleher, B.; Ross, J.R.H. Review of Literature on Catalysts for Biomass Gasification. *Fuel Process. Technol.* **2001**, *73*, 155–173. [CrossRef]
90. Jeong, Y.-S.; Choi, Y.-K.; Kim, J.-S. Three-Stage Air Gasification of Waste Polyethylene: In-Situ Regeneration of Active Carbon Used as a Tar Removal Additive. *Energy* **2019**, *166*, 335–342. [CrossRef]
91. Mastellone, M.L.; Arena, U. Olivine as a Tar Removal Catalyst during Fluidized Bed Gasification of Plastic Waste. *AIChE J.* **2008**, *54*, 1656–1667. [CrossRef]
92. Cho, M.-H.; Mun, T.-Y.; Choi, Y.-K.; Kim, J.-S. Two-Stage Air Gasification of Mixed Plastic Waste: Olivine as the Bed Material and Effects of Various Additives and a Nickel-Plated Distributor on the Tar Removal. *Energy* **2014**, *70*, 128–134. [CrossRef]
93. Cho, M.-H.; Mun, T.-Y.; Kim, J.-S. Air Gasification of Mixed Plastic Wastes Using Calcined Dolomite and Activated Carbon in a Two-Stage Gasifier to Reduce Tar. *Energy* **2013**, *53*, 299–305. [CrossRef]
94. Mastellone, M.L.; Zaccariello, L. Metals Flow Analysis Applied to the Hydrogen Production by Catalytic Gasification of Plastics. *Int. J. Hydrogen Energy* **2013**, *38*, 3621–3629. [CrossRef]
95. Erkiaga, A.; Lopez, G.; Amutio, M.; Bilbao, J.; Olazar, M. Syngas from Steam Gasification of Polyethylene in a Conical Spouted Bed Reactor. *Fuel* **2013**, *109*, 461–469. [CrossRef]
96. Ravenni, G.; Sárossy, Z.; Ahrenfeldt, J.; Henriksen, U.B. Activity of Chars and Activated Carbons for Removal and Decomposition of Tar Model Compounds—A Review. *Renew. Sustain. Energy Rev.* **2018**, *94*, 1044–1056. [CrossRef]
97. Kim, J.-W.; Mun, T.-Y.; Kim, J.-O.; Kim, J.-S. Air Gasification of Mixed Plastic Wastes Using a Two-Stage Gasifier for the Production of Producer Gas with Low Tar and a High Caloric Value. *Fuel* **2011**, *90*, 2266–2272. [CrossRef]
98. Lazzarotto, I.P.; Ferreira, S.D.; Junges, J.; Bassanesi, G.R.; Manera, C.; Perondi, D.; Godinho, M. The Role of CaO in the Steam Gasification of Plastic Wastes Recovered from the Municipal Solid Waste in a Fluidized Bed Reactor. *Process Saf. Environ. Prot.* **2020**, *140*, 60–67. [CrossRef]
99. Li, S.; Cañete Vela, I.; Järvinen, M.; Seemann, M. Polyethylene Terephthalate (PET) Recycling via Steam Gasification—The Effect of Operating Conditions on Gas and Tar Composition. *Waste Manag.* **2021**, *130*, 117–126. [CrossRef]
100. Mavukwana, A.; Burra, K.G.; Sempuga, C.; Castaldi, M.; Gupta, A.K. Effect of Gypsum Waste Inclusion on Syngas Production during CO_2-Assisted Gasification of Waste Tires. *Waste Manag.* **2023**, *171*, 375–381. [CrossRef]
101. Lerner, A.S.; Bratsev, A.N.; Popov, V.E.; Kuznetsov, V.A.; Ufimtsev, A.A.; Shengel', S.V.; Subbotin, D.I. Production of Hydrogen-Containing Gas Using the Process of Steam-Plasma Gasification of Used Tires. *Glass Phys. Chem.* **2012**, *38*, 511–516. [CrossRef]
102. Lopez, G.; Erkiaga, A.; Artetxe, M.; Amutio, M.; Bilbao, J.; Olazar, M. Hydrogen Production by High Density Polyethylene Steam Gasification and In-Line Volatile Reforming. *Ind. Eng. Chem. Res.* **2015**, *54*, 9536–9544. [CrossRef]
103. Raizada, A.; Shukla, A.; Yadav, S.; Katiyar, P.; Kumar, R. Enhancement of H2 Production via Catalytic Steam Gasification of Food Waste as Feedstock and Its Ash as a Support and Promoter for Ni Catalyst. *Int. J. Hydrogen Energy* **2024**, *60*, 272–281. [CrossRef]
104. Wu, S.-L.; Wey, M.-Y. Synthesis of Ni@Al_2O_3 Nanocomposite with Superior Activity and Stability for Hydrogen Production from Plastic-Derived Syngas by CO_2-Sorption-Enhanced Reforming. *Int. J. Hydrogen Energy* **2021**, *46*, 39728–39735. [CrossRef]
105. Farooq, A.; Moogi, S.; Jang, S.-H.; Kannapu, H.P.R.; Valizadeh, S.; Ahmed, A.; Lam, S.S.; Park, Y.-K. Linear Low-Density Polyethylene Gasification over Highly Active Ni/CeO_2-ZrO_2 Catalyst for Enhanced Hydrogen Generation. *J. Ind. Eng. Chem.* **2021**, *94*, 336–342. [CrossRef]
106. Khani, Y.; Valizadeh, S.; Yim, H.; Chen, W.-H.; Ko, C.H.; Lee, S.H.; Jung, S.-C.; Park, Y.-K. Upgrading of Plastic Waste-Derived Wax Through Air Gasification Using Promoted Ni/Al_2O_3 Catalysts for H2 Generation. *Chem. Eng. J.* **2023**, *477*, 147053. [CrossRef]
107. Dogru, M.; Akay, G. Gasification. U.S. Patent US8252072B2, 28 August 2012.
108. Dreiser, C.; Wachsen, O.; Brand, S.; Hungsberg, M.; Drochner, A.; Etzold, B. Process for the Production of Synthesis Gas via Allothermic Gasification with Controlled Carbon Dioxide Reduction. EP Patent EP20162983A1, 15 September 2021.
109. Shires, P.; Salazar, N.; Ariyapadi, S. Methods for Producing Synthesis Gas. U.S. Patent US20080081844A1, 25 May 2010.
110. Trapp, W.L.; Murphy, J.W.; West, N.M. Gasification of Plastics and Solid Fossil Fuels to Produce Organic Compounds. U.S. Patent 11939546, 7 July 2022.
111. Seo, S.-W.; Ra, H.-W. A Waste Plastic Gasification System Removing Tar and Driving Method Thereof. K.R. Patent KR102458037B1, 26 October 2022.
112. DeBruin, B.R.; Lange, D.M.; Trapp, W.L.; Ekart, M.P. Gasification of Liquefied Waste Plastics. EP Patent 20230407198, 21 December 2023.
113. Bitting, D.; Slivensky, D.E.; Wu, X.; DeBruin, B.R.; Billodeaux, D.R. Chemical Recycling of Plastic-Derived Streams to a Cracker Separation Zone with Enhanced Separation Efficiency. U.S. Patent US20230081980A1, 16 March 2023.
114. DeBruin, B.R.; Trapp, W.L. Partial Oxidation Gasification of Wet Waste Plastic. U.S. Patent US20230212469A1, 7 November 2023.

115. Garcia, L.; Cordoba, M.; Dosso, L.; Vera, C.; Busto, M.; Badano, J. Catalytic Steam Reforming of Biomass Tar Model Compounds with Low Cost Catalysts: Effect of Operation Conditions. *Top. Catal.* **2022**, *65*, 1382–1393. [CrossRef]
116. Garcia, L.; Cordoba, M.; Dosso, L.; Nardi, F.; Vera, C.; Quiroga, M.; Busto, M.; Badano, J. Catalytic Gasification and Reforming of Residual Biomass in a Bench Scale System with Low Cost Catalysts. *ChemPlusChem* **2023**, *88*, e202300376. [CrossRef]

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