

"Un Paese di paesi": riflessioni per la cura di borghi e paesaggi abbandonati del Molise

Original

"Un Paese di paesi": riflessioni per la cura di borghi e paesaggi abbandonati del Molise / Testa, M.P.. - STAMPA. - 1:(2023), pp. 202-210. (Restauro dell'architettura. Per un progetto di qualità Napoli (ITA) 15-16 giugno 2023).

Availability:

This version is available at: 11583/2986164 since: 2024-02-20T15:21:41Z

Publisher:

Edizioni Quasar

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Review

A Critical Review of SCWG in the Context of Available Gasification Technologies for Plastic Waste

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Received: 20 July 2020; Accepted: 5 September 2020; Published: 10 September 2020



Abstract: End of life packaging is nowadays one of the major environmental problems due to its short usage time, the low biodegradability, and the big volume occupied. In this context, gasification is one of the most promising chemical recycling techniques. Some non-recyclable or non-compostable waste gasification plants are already operating such as Enerkem Alberta Biofuels in Canada or the Sierra’s FastOx Pathfinder in California. In this review, we have examined works about plastic gasification from the last fifteen years with a specific focus on polyolefin (PP, PE), plastics mix, and co-gasification of plastic with biomass. For each of these, the best operating conditions were investigated. A very in-depth section was dedicated to supercritical water gasification (SCWG). The most used reactors in gasification processes are fluidized bed reactors together with air or steam as gasifying agents. Tar removal is commonly performed using olivine, dolomite, or nickel based catalysts. SCWG has numerous advantages including the inhibition of tar and coke formation and can be used to remove microplastics from the marine environment. In co-gasification of plastic material with coal or biomass, synergistic effects are observed between the raw materials, which improve the performance of the process, allowing to obtain higher gas yields and a syngas with a high energy content.

Keywords: gasification; waste plastics; packaging; recycling; polyolefins; plastic mix; supercritical water gasification; co-gasification; syngas; review

1. Introduction

Plastics are very versatile material which, due to their properties, have replaced many of the traditional materials in the last century [1]. Compared to wood, they are more resistant to attack by microorganisms, molds, and atmospheric agents and so more durable in time. Some plastics such as plexiglass or polycarbonate are used in place of glass, thanks to their high transparency, lightness, and greater impact resistance. They are widely used also in the construction sector as excellent thermal and acoustic insulators, to replace traditional materials such as glass wool or cork. Finally, thanks to their low cost, they are used for disposable containers and products. For this set of characteristics, plastic is considered an indispensable material in our daily life and it covers various important sectors such as health and food, transport, safety and protection, sport, industry innovations [2,3]. Especially in the medical field, plastic has some characteristics that make it irreplaceable, such as the possibility of making sterile, hypoallergenic instruments, devices, prostheses. Global plastic production is continuously growing and has reached an annual production of 360 million tons (Mt) worldwide in

2018 [4]. Despite the Directive 2008/98/EC of the European Parliament and Council, which should help the European Union to approach a “recycling society” by trying to avoid waste production and use waste as resources [3], in Europe, plastics production almost reached 62 million tons and the greatest demand for plastic material is related to packaging (39.9%), as shown in Figure 1 [4].

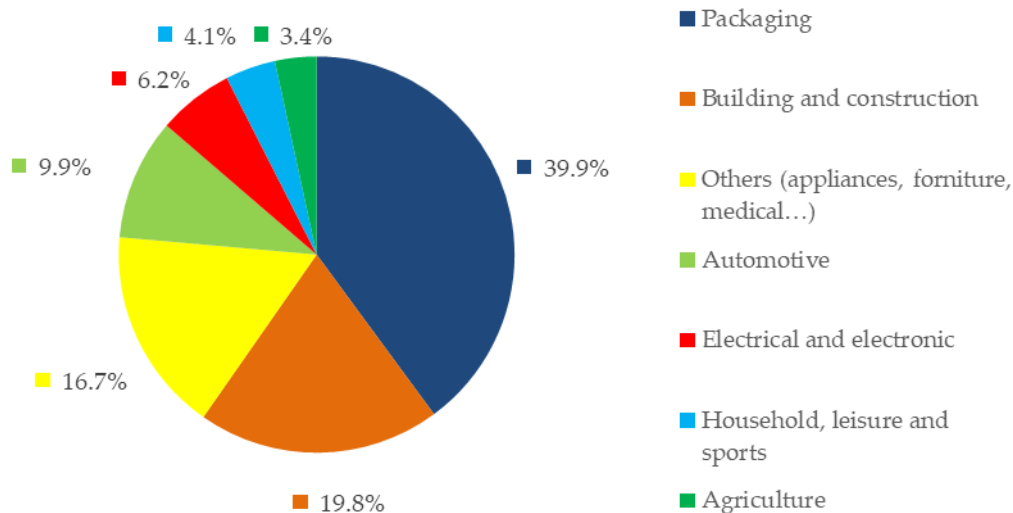


Figure 1. Distribution of the European (EU28+NO/CH) use sectors of plastic material in 2018 [4].

Typical polymers used for packaging are PP (polypropylene), PE-LD (low density polyethylene), PE-LLD (low linear density polyethylene), HDPE (high density polyethylene), PS (polystyrene), EPS (expanded polystyrene), PVC (polyvinyl chloride), and PET (polyethylene terephthalate) [5,6]. Packaging has many applications not only for the storage and transport of products but also in guaranteeing their integrity and protection from humidity, breakage, dust, and microorganisms [7]. Massive uses of packaging are typical of the food, beverage, cosmetics, and pharmaceutical industries [8].

Waste plastic material from packaging is nowadays one of the major environmental problems due to its short usage time, low biodegradability, high resistance to ageing, and the big volume occupied (caused by its low bulk density) [9]. The environmental impacts of packaging are very serious and concern air and water pollution [10]. An example is the recent discovery of 238 tons of plastic waste on the Cocos (Keeling) Island group, in the Indian Ocean [11]. Plastic debris are accumulating in increasing quantities in the marine environment, originating huge plastic islands. When polymers are exposed to UVB radiation, to the oxidative properties of the atmosphere, and to the hydrolytic properties of seawater, they become more and more fragile over time, breaking into smaller and smaller pieces originating thus into microplastics (MPs), known to cause a bio magnification problem [9,12]. The packaging sector is constantly growing and this represents a huge risk to the environment [8]. For this reason, the European Commission in 2018, developed “a strategy for plastic material in circular economy” (COM(2018) 28 final, Brussels, 16.1.2018), establishing that by 2030, all plastic packaging placed on the European market must be reusable or can be cost-effectively recycled [13].

In recent years, there has been a greater sensitivity towards waste management and its disposal in landfills. Different approaches were then examined, such as reuse to date, recycling, and energy recovery. According to statistics from Plastic-the Facts 2019 [4], in Europe the 32.5% of plastic materials is recycled, the 42.6% is sent to energy recovery, and the rest (24.9%) is landfilled. Recycling is an important road, as it provides a solution to the environmental and ecological problems associated with the use of fossil energy sources, the CO₂ emissions, and the quantities of waste that require disposal [14].

We can distinguish four different types of recycling:

- **Primary Recycling:** Primary recycling, also called re-extrusion, consists of recycling a single type of polymer, with properties close to the virgin material and free of contaminations. This process uses processing wastes, which are regenerated as they are or added to virgin polymer. This process is characterized by simplicity and low cost [15,16].
- **Secondary Recycling (Mechanical Recycling/Waste to materials):** Secondary recycling consists in the mechanical transformation of plastic waste, with the aim of obtaining raw materials for the creation of new objects [17]. Secondary recycling can only be done on thermoplastic polymers as they can be remelted and reprocessed. This process consists of a physical method, in which the plastic waste is shredded, washed, and then melted to make the new product by extrusion. The disadvantages of this method are related to the heterogeneity of plastic waste and the deterioration of products' properties occurring cycle after cycle, due to the decrease in the molecular weight of the recycled polymers in comparison with originals. To partially obviate this last problem, the material can be blended with virgin polymer or specific additives [18].
- **Tertiary recycling (Waste to energy/Waste to chemicals):** This recycling consists of obtaining, by chemical or physical methods, monomers, oligomers, or other compounds from plastic waste. [15]. In chemical recycling, polymers are chemically depolymerized through chemical reactions. The resulting monomers can be used for new polymerization reactions, to reproduce the original polymer or other products [17,18]. Physical methods, refer to processes that consist of thermal degradation of polymers, that can be carried out in the complete absence of oxygen (pyrolysis) [19] or in the presence of sub-stoichiometric oxygen (gasification) [20]. Pyrolysis products are a gas, an oil, and a char, instead syngas (syngas is an abbreviation for synthesis gas) is the main product from gasification.
- **Quaternary recycling (Energy recovery):** In quaternary recycling, the waste material is treated to recover energy through incineration [15]. With this method a considerable energy is obtained from the polymers (the calorific value of different plastic polymers is comparable to oil and petroleum), but it is not considered a good solution at an ecological level because it leads to the formation of toxic substances for humans and the environment, such as dioxins [18]. Furthermore, with incineration all the energy used to form the object itself is lost. Recycling plastic waste by the energy recovery method is only logical when the recycling of waste is not possible due to other constraints [21].

In recent years, numerous authors have dealt with the recycling of plastic waste. For example, Ragaert et al. in 2017 [22] reported a detailed description of the current routes for recycling of polymers, via both mechanical and chemical recycling. In the section of chemical recycling they described not only gasification but also other techniques such as pyrolysis, chemolysis, and fluid catalytic cracking. Lopez et al. in a 2018 review [20] analyzed the state of art of the main waste plastic conversion technologies for syngas production. Moreover, the review assessed the influence of operating conditions such as temperature, excess ratio (ER), composition of the power supply, on the conversion efficiency. In a more recent work, Okolie et al. [23] examined the chemistry of subcritical and supercritical water and the possibility of generating syngas through the hydrothermal decomposition of different raw materials, not only polymeric wastes but also biogenic and organic wastes.

The goal of this review is to describe the state of art of gasification of plastic waste, examining different types of feedstock: Polyolefin for packaging (PP, PE), plastic mixes containing other polymers such as PVC, PET, PMMA, and plastic waste with biomass (co-gasification). Operating conditions such as the gasification temperature, the gasifying agent, the bed material, and the use of catalysts have been carefully reviewed. Tar formation and the operational techniques for its elimination were also examined. Finally, an in-depth section was dedicated to supercritical water gasification (SCWG), a thermochemical conversion route well known for biomass but nowadays little used for plastic waste. The present work reviews the literature of the past fifteen years (2005–2020). To the best of the Authors

knowledge, it was not possible to find review focusing on supercritical water gasification as chemical recycling technologies for plastic.

2. Gasification Process

2.1. Fundamentals of Gasification

Gasification is a well-known process since the mid-1800s. In this period, a gas was produced from coal to illuminate the streets of important cities such as London. During the second world war gasification played an important role as it was used to produce syngas, which, by the Fischer–Tropsch process, was converted into synthetic gasolines [24]. It was due to lower fossil fuel prices that wood gasification has been discharged. However, coal gasification is well known and is still used around the world.

In recent years, gasification has received particular attention as a thermochemical recycling technique. It is possible to gasify a considerable variety of biomass and waste-derived feedstock, such as wood, plastic, municipal solid waste (MSW), sewage sludge, crop residues, agricultural, and industrial waste [24]. Regarding plastic waste, one of the greatest advantages is linked to the possibility of being able to treat heterogeneous and contaminated polymers with limited use of pre-treatment [25–27].

The gasification of plastic waste has numerous environmental advantages over incineration and other technologies. In the incineration process dangerous substances can be released in the environment such as heavy metals (Hg or Cd), dioxins, furans, HCl, SO₂, NO_x, HF [28–30]. For example, polyvinyl chloride and halogenated additives, such as flame retardants, are typically found in mixed plastic waste. This can lead to the risky release of dioxins, other polychlorinated biphenyls and furans [31]. On the contrary, gasification plants, using a sub-stoichiometric amount of oxidant and operating at a lower temperature than combustion produce a smaller quantity of the pollutants mentioned above, i.e., NO_x [32]. A comparison between the combustion and gasification products is shown in Table 1 [32]. Gasification of waste is also preferred over incineration because it provides a syngas product that can be used for different purposes as opposed to combustion gases [33]. Syngas is defined as a gas mixture of mainly H₂ and CO, produced from gasification of carbonaceous feedstock in oxygen and steam, followed by gas separation to remove CO₂. Instead, the term “producer gas” refers to a gas mixture with a low heating value, composed of H₂, CO, CO₂, CH₄, other hydrocarbons with a low molecular weight, and N₂. In this case the gasifying agent used is air [34]. Commonly, the term syngas is used to describe the gaseous product from any type of gasification process, even if this is not perfectly correct. This convention will be herein retained.

Table 1. Comparison between the combustion and gasification products [32].

	Carbon	Hydrogen	Nitrogen	Sulfur
Combustion	CO ₂	H ₂ O	NO, NO ₂	SO ₂ or SO ₃
Gasification	CO	H ₂	HCN, NH ₃ or N ₂	H ₂ S or COS

As described by El-Nagar et al. [35], about 6 EJ of syngas are produced per year. As in the past, the main source of syngas production is coal. This is attributed to the high availability of coal reserves in countries such as China, United States, and Russia. Markets such as China and India are mainly engaged in the production of syngas and coal based derivatives [36]. However, there are already some commercial companies such as Enerkem and Sierra Energy that use waste for syngas production. The end uses of syngas are shown in Figure 2.

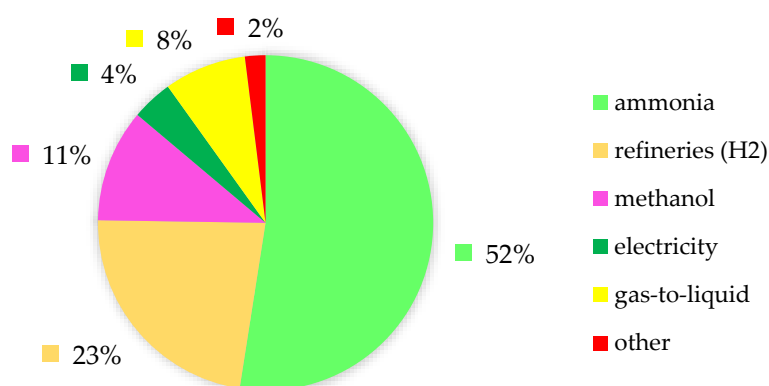


Figure 2. End uses of syngas, totally ~6 EJ/y [35].

Syngas can be used for the generation of thermal energy by direct combustion of H₂ and CO in heat generation equipment, such as steam boilers, cement kilns, dryers, etc., and for the electricity production. Syngas is used also for fuel production, in particular, one of the commercially accessible methods of manufacturing clean synthetic liquid fuels from syngas is the Fischer-Tropsch process. Fischer-Tropsch synthesis is a surface polymerization reaction, in which hydrogen and carbon monoxide react on the surface of a catalyst in situ. The catalysts are based on iron or cobalt [37–39]. Syngas can also be used for chemicals production such as ammonia, ethylene glycol, DME, and methanol. One example is the Waste-to-Biofuels-and-Chemicals (WTFC) process developed by Enerkem, designed to gasify post-recycled residual from MSW into methanol and eventually ethanol. Enerkem operates a commercial-scale facility in Edmonton, Alberta, Canada, as well as an innovation center in Westbury, Quebec, Canada [40]. The company is developing another commercial facility in Canada (Varenes). The plant will use various types of municipal waste from the industrial, commercial, and institutional sectors as raw materials, as well as construction and demolition debris. As reported by the detailed Enerkem website [41], another facility planned by Enerkem in consortium with other entities is a waste-to-chemicals plant in the Botlek area of the Port of Rotterdam. The aim of this project is to provide a valid alternative to incineration for non-recyclable waste (coming from different sectors including industrial and municipal) by converting them into chemicals or biofuels.

Making a comparison between gasification and pyrolysis, it is important to observe how the yields and compositions of the pyrolysis products (gas, oil, char) are strongly influenced by the nature of the feedstock used. Instead, in the gasification process, different types of raw materials influence only the composition of the syngas and modify the yields of the products considered of least interest: Tar and char [20]. Therefore, the gasification process is characterized by greater versatility.

2.2. Gasification Mechanism

As defined by Kumar et al. [42], gasification is a thermochemical process in which a solid or liquid carbon-based feedstock is converted into a syngas, working at high temperatures (600–1000 °C) and in the presence of a sub-stoichiometric amount of oxidizing agent (also called gasifying agent). Heat can be supplied both directly and indirectly to the gasifier. As previously said, syngas is suitable for use in electricity production or for the manufacture of chemicals, hydrogen, or transportation fuels [43].

The syngas is mainly composed of H₂, CO, CO₂, N₂, and some low molecular weight hydrocarbons (CH₄, C₂H₄, C₂H₆, etc.). Very small amounts of H₂S, NH₃, tar, and char may also be produced [44]. Tar and char are unwanted products [45,46]. Gasification occurs in several stages, involving numerous chemical reactions but it can be explained by summarizing it in four steps: Drying of feedstock, pyrolysis, oxidation, and reduction reactions [47].

These steps are summarized below:

- Drying: Feedstock with variable moisture content are dried in a drying process in a range of temperatures between 100–150 °C. In this step no chemical reactions take place and the heat

supplied is spent in the phase change between liquid water and water steam [33]. Unlike biomass or coal, plastics have a very low moisture content. Since it is external humidity, drying is a very rapid process, not being subject to diffusion processes [20].

- **Pyrolysis:** During this process complex chemical reactions of endothermic nature take place. Volatile substances and a solid or carbonized residue are formed. The proportions of these products are influenced by the process conditions such as the heating rate ($^{\circ}\text{C}/\text{s}$) and the temperature. Furthermore, products distribution is affected by feedstock composition and size [33]. Pyrolysis is a “delicate” step, as the melted plastic particles tend to stick together. This causes the formation of agglomerates and defluidization in fluidized bed reactors [48]. An interesting aspect, is that some polymers such as PP, PE, and PS can be almost totally converted into volatile substances when fast pyrolysis is conducted [19,49]. This usually occurs in common gasification technologies.
- **Oxidation:** At elevated temperatures and in the presence of sub-stoichiometric oxygen, heterogeneous reactions occur between oxidant and raw material, forming carbon monoxide and water steam as shown in Table 2. Oxidation depends on the chemical composition of the feedstock, the nature of oxidant used, and the operating conditions. This step is mainly exothermic and the thermal energy released provides the heat needed for the process [47].
- **Reduction:** It is an endothermic step in which high-temperature chemical reactions take place in the absence of oxygen [47]. These reactions are shown in Table 2. Steam promotes two reactions: The steam reforming of char and tar (endothermic) and the water-gas shift reaction (exothermic) [50]. Both reactions lead to the formation of H_2 . In particular, the reduction of water in steam gasification is the most effective way of increasing H_2 production [51]. CO_2 reacts with char to produce CO . This reaction is known as the Boudouard reaction and it is endothermic in nature [52]. CO_2 may also be recirculated with O_2 within oxy-fuel combustion/gasification [53].

Table 2. Reactions occurring in the gasification process [20,42,47].

Oxidation Reaction		Reduction Reaction	
$\text{C} + \text{O}_2 \rightleftharpoons \text{CO}_2$	$\Delta\text{H} = -393.5 \text{ kJ/mol}$	$\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO}$	$\Delta\text{H}_{\text{R1}} = 172.5 \text{ kJ/mol}$ (Boudouard reaction)
$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{H}_2\text{O}$	$\Delta\text{H} = -285.9 \text{ kJ/mol}$	$\text{C} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}$	$\Delta\text{H}_{\text{R2}} = 131.3 \text{ kJ/mol}$ (Char steam reforming)
		$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2$	$\Delta\text{H}_{\text{R3}} = -41.2 \text{ kJ/mol}$ (Water-gas shift reaction)
		$\text{C} + 2 \text{H}_2 \rightarrow \text{CH}_4$	$\Delta\text{H}_{\text{R4}} = -74.5 \text{ kJ/mol}$ (Carbon hydrogenation reaction)
		$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons 3 \text{H}_2 + \text{CO}$	$\Delta\text{H}_{\text{R5}} = 205.8 \text{ kJ/mol}$ (Methane reforming)

In the case of plastics, it is important to remember that each polymer follows a different degradation path, which determines the composition of the volatile substances that are formed [20,54]. As explained by Lopez et al. [20], for polyolefin the main thermal degradation mechanism is random scission. Random degradation occurs at any random point along the polymer chain [15,55] and leads to a wide product distribution [56]. For example, PE undergoes random degradation through migration of a hydrogen atom from one carbon to another thus generating two fragments [57], but at high temperatures (above $800 \text{ }^{\circ}\text{C}$) other degradation mechanisms such as the chain-end scission are also established [58]. Moreover, vinyl polymers such as PS are degraded through this process. The obtained fragments have dimensions greater than those of the corresponding monomeric unit [15]. In the case of PS, oligomers can give rise to styrene or other monoaromatic and polyaromatic species in the gas phase depending on the temperature and the residence time. Furthermore, PET undergoes a random scission,

that produces vinyl and carboxyl groups [15]. In this case, the gaseous phase contains numerous oxygenated compounds, such as benzoic acid, terephthalic acid, aldehydes, and acetophenone [59].

2.3. The Role of Gasifying Agent

Depending on the gasifying agent different processes can be distinguished [44]: Air gasification [60], oxygen gasification [61], steam gasification [62], carbon dioxide gasification [63], supercritical water gasification [64], etc. Generally, oxygen gasification, steam gasification, carbon dioxide gasification, and supercritical water gasification result in higher heating values (HHVs) of syngas than air gasification, but the latter technique is the most studied and used experimentally, as it has some advantages: Air is an inexpensive gasifying agent, the structure of the reactor is simple, and the reaction process is easy [44]. A further advantage in the use of air as a gasifying agent is linked to a lower tar content in the gaseous product compared to steam gasification. Moreover, in gasification with air (or oxygen) there are no external energy requirements, while in the other kind of gasification external heating is required because the overall gasification reaction is generally endothermic. The use of air leads to a syngas with a low heating value due to dilution with N_2 [43,65]. Air gasification of plastic waste is commonly performed in fluidized bed reactors [20]. In regards to other gasifying agents, the addition of steam has been reported as a strategy to manipulate the H_2/CO ratio from dry reforming of simulated mixed waste plastics [66]. The syngas obtained from steam gasification, being rich in H_2 , can be used for chemical synthesis applications [67] and may allow matching the specific H_2/CO ratio requested by the end-use process [68,69]. The disadvantage in the use of this gasifying agent is related to the need to supply heat from the outside. An alternative to air or steam is pure oxygen. This gasifying agent allows obtaining a hydrogen-rich syngas, but its use is too complex and expensive for small- and medium-scale plants. Gasification with supercritical water (SCWG) is currently receiving considerable interest. This promising technique will be explored in detail in the next chapter.

2.4. Variables Affecting the Gasification Process

Kirubakaran et al. [70] studied biomass gasification and identified some variables that influence the gasification rate. Some of these parameters are of fundamental importance also in the gasification of plastic material such as:

- **Size:** The smaller the feedstock size, the better would be the heat transfer. The temperature would be uniform resulting in a reaction taking place throughout the particle. In the case of plastic waste due to the great variety of shapes and sizes, shredding is necessary to create a feed material of less than 5 cm in diameter. Some forms of waste plastics such as thin films may require a simple agglomeration step to produce particles of higher bulk density to facilitate feeding [71].
- **Temperature:** Temperature influences the yield and composition of the syngas [72,73] and the production of tar and ash. The increase in gasification temperature gives rise to an increase in gas formation and a subsequent decrease in tar and char yields [74]. The greater amount of gas produced at higher temperatures is explained by the larger release of gases during the initial devolatilization stage, and the secondary reactions undergone by the char and tar (char gasification and tar cracking/reforming) [74]. Many studies have shown that the H_2 content in syngas increases as the gasification temperature increases. This phenomenon is due to the chemical breakdown (thermal cracking) of heavy hydrocarbons which favors molar fraction of the permanent gases such as H_2 and CO at high temperature [75]. Qin et al. [76] examined the effects of reaction temperature on biomass gasification in a laboratory scale atmospheric pressure entrained flow reactor. They observed that by increasing the temperature from 1000 to 1350 °C, the yield of producer gas (defined as the sum of H_2 , CO , CO_2 , and hydrocarbons up to C_3 species) increased dramatically by 72%. Moreover, a higher temperature was beneficial to decrease the amount of tar. In general, operating temperatures higher than 800 °C are recommended to minimize tar formation [74]. However, these high temperatures favor the formation of slag from ash

agglomeration. Furthermore, higher temperatures are due to a greater oxidation of the feedstock that causes a decrease of the chemical energy of the syngas.

- **Heating rate:** Heating rate is one of the main parameters that affect the decomposition of waste [77]. In particular, it determines the yield and composition of the derived products of pyrolysis step. Pyrolysis involves a process of cracking polymeric structures to convert the feedstock into charcoal and volatile matter [78]. In general, the char yield is expected to increase at lower heating rates. Hence, the slow pyrolysis processes are always preferred for producing charcoal. Higher pyrolysis temperatures, high heating rates, and long residence times lead to the formation of gas products.
- **Environment and reactor design:** Generally, it is observed that the reactive environment (air/oxygen) results in complete gasification of feedstock while inert environment (nitrogen/argon) aids devolatilization (pyrolysis) yielding more char [70]. The equivalence ratio is commonly used to indicate quantitatively whether a fuel oxidizer mixture is rich, lean, or stoichiometric. Therefore, for fuel rich mixtures, the $ER > 1$, for fuel lean, $ER < 1$, and for stoichiometric mixture, $ER = 1$ [79,80]. Commercial gasifiers employ air at a sub stoichiometric quantity to generate producer gas. Plastic material has some particular characteristics given by the low thermal conductivity, the sticky nature when heated, the high volatile content, and the remarkable tar formation. Therefore, a suitable gasifier design for plastic handling must take these aspects into account [20]. Fluidized beds reactors are widely used in the gasification of plastics waste. Plastic gasification studies are often carried out in bubbling reactors [48,81–87]. In this gasifier, gas flows upward through a bed of free-flowing granular material at a gas velocity sufficient to agitate the material into a churning emulsion of levitated particles and gas bubbles. The fluidized bed itself resembles a boiling liquid and has many of the same physical properties as a fluid. Typical bed materials used in this kind of gasifier are sand, olivine, limestone, dolomite, or alumina. Beds can be fluidized with the gasification agent, typically air, oxygen, and/or steam [34].
- **Other types of reactors** are used in the gasification of plastic material, such as fixed beds ([88–90]) and spouted beds reactors ([67,91]). Fixed bed reactors represent the oldest and most proven technology for gasification. They are chosen for their simple design and low cost, but they are characterized by a poor heat transfer rate and a limited gas-solid contact. Fixed bed reactors are commonly used on small scale units and have many different designs. Spouted beds are gas-solid contactors in which the gas is introduced through a single orifice from the center of a flat [92]. They are characterized by their high heat and mass transfer rates, good solid mixing, and suitable gas-solid contact. A disadvantage for their application deals with the short residence of the volatiles, which hinders tar cracking reactions [93].

3. Supercritical Water Gasification (SCWG)

3.1. Properties of Supercritical Water

Supercritical water is water above its critical temperature, 374.1 °C, and critical pressure, 22.1 MPa [94]. Subcritical water (SbCW) occurs at temperatures below or near the critical temperature and at a pressure above the saturation pressure [95]. These concepts are clarified in Figure 3.

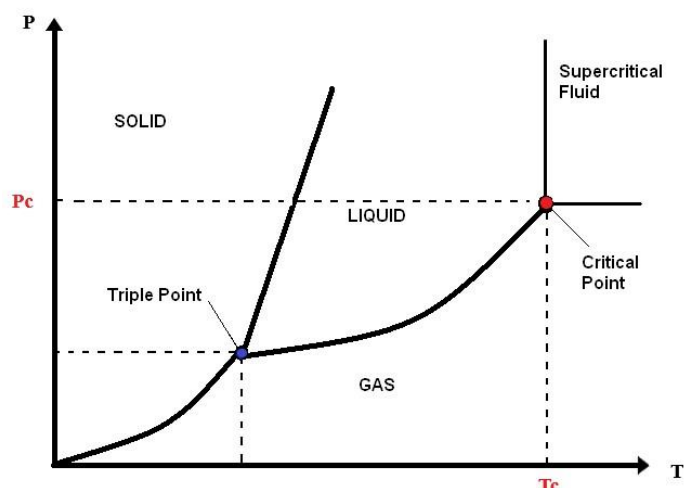


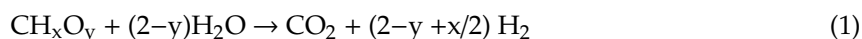
Figure 3. Schematic diagram phase of water.

The supercritical water (SCW) is a single phase that possesses the characteristics of both gas and liquid without surface tension and liquid/gas phase boundary. Supercritical water has sufficient density to give appreciable dissolving power, diffusivity higher than that in liquids, and lower viscosity to enhance mass transport [64]. The dielectric constant of water changes near the critical point, for example it decreases from $78.5 \text{ F}\cdot\text{m}^{-1}$ at $25 \text{ }^\circ\text{C}$ and 0.1 MPa , to $5.9 \text{ F}\cdot\text{m}^{-1}$ at $400 \text{ }^\circ\text{C}$ and 25 MPa [96]. Therefore, water is a highly polar solvent at room temperature and a non-polar solvent in supercritical conditions. SCW is, therefore, an excellent solvent for non-polar organic compounds [96,97] such as lignin. Thanks to these properties SCW provides a homogeneous and rapid reaction environment for gasification.

3.2. Biomass SCWG Process

Gasification with supercritical water, as well as other types of gasification, has been studied extensively for biomass [98]. These studies allowed laying the foundations for the understanding of the SCWG of plastic material.

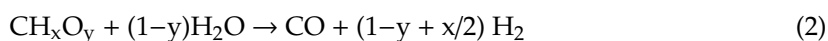
Supercritical water gasification of biomass is typically performed at temperatures between 600 and $650 \text{ }^\circ\text{C}$ and at a pressure of about 30 MPa . Above $600 \text{ }^\circ\text{C}$, water acts as a strong oxidant. Carbon atoms are oxidized and CO_2 is preferably formed. Moreover, the use of water results in a high hydrogen yield, in fact hydrogen atoms not only from biomass but also from water are released to form hydrogen [99]. We can write an overall chemical reaction that describes the biomass SCWG process [96]:



where x and y are the elemental molar ratios of H/C and O/C of the biomass, respectively. The product of the reaction is the synthesis gas, whose quality depends on x and y .

During the process, however, three other competitive reactions can occur:

1. Steam reformation



2. Methanation for CO



3. Methanation for CO_2



4. Water–gas shift reaction



As described by Okolie et al. [23], the effects of pressure on the SCWG process are still not very clear. With an increase in pressure, the methanation reactions are shifted to the right (towards a smaller number of molecules) with an increase in the formation of methane at the expense of CO, CO₂, and H₂. Moreover, the increase in pressure causes a change in the density of the water. In particular, ionic reactions are favored at high pressure due to the ion stabilization effect given by the high density water. On the contrary, the radical reactions are disadvantaged.

A typical SCWG plant is described in detail by Basu et al. [96]. Below, we summarize the main features of the plant:

1. Water and feedstock must be pressurized to the supercritical pressure required for the process. The biomass is then ground and mixed with water using an emulsifying agent, in order to obtain a pumpable liquid.
2. The resulting slurry is pumped into the reactor. The pressurized water is preheated by passing it through a heat exchanger, which exploits the heat of the product leaving the reactor. The pressurized water also passes through an externally heated preheater before entering the reactor.
3. The syngas obtained in the process is cooled and passed through a gas-liquid separator. The gas mixture passes through further purification equipment such as the scrubber or pressure-swing adsorption unit.

3.3. Advantages and Disadvantages in The Use of SCW

Supercritical water gasification has numerous advantages over conventional gasification:

- Supercritical water is an active reactant which results in a high hydrogen yield [99].
- In the SCWG, the drying step of feedstock is not required. This leads to greater energy efficiency especially for biomass with a high moisture content. Therefore, there is a considerable economic saving, since drying and pre-treatment of biomass add extra cost to the process economics [100].
- High pressure of the gaseous product enables the transportation, usage, carbon capture, and further purification of the product gas through steam reforming or PSA (pressure swing adsorption).
- The reaction temperature is much lower than that used in conventional gasification and pyrolysis processes.
- Tar and coke formation is inhibited by a fast solution of the formed gas components in the supercritical water [99].
- The gaseous product is very clean, as NO_x and SO_x are generated in very small quantities and the CO concentration is very low, especially in the presence of a catalyst to improve the water-gas shift reaction [101].

At the same time, this technique has some disadvantages that must be taken into consideration. First of all, the reactor must be made of materials resistant not only to corrosion but also to high temperatures and pressures. Furthermore, there is a considerable energy expenditure to heat up the water to the reaction temperature. This entails high investment costs.

3.4. SCWG of Plastic

As said previously, in supercritical conditions, water acts as a non-polar solvent which can solve the problems of poor heat transfer and high viscosity of plastic material by dissolving the plastic fragments [102]. Moreover, water also acts as a hydrogen donor which helps plastic cracking and gasification. For these reasons, this technology can be used for various types of plastic material, for example cross-linked polyethylene, plastic with flame retardants or contaminants. Figure 4 shows a graphic scheme of the SCWG of waste plastics.

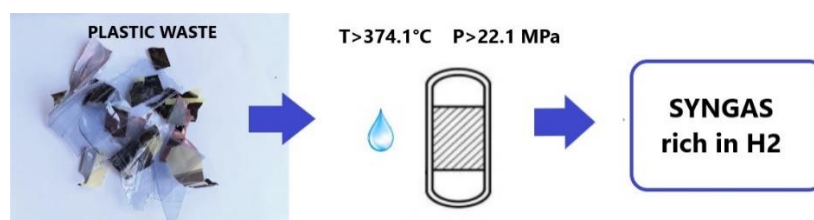


Figure 4. Graphical scheme of the supercritical water gasification (SCWG) of waste plastics.

An interesting application is that related to the removal of microplastics from the marine environment. Other types of processes such as pyrolysis and gasification are not a suitable choice because, the high water content of plastics recovered from the ocean would require a drying step, which would significantly increase the cost of recycling [103]. At present, there are few studies on the characteristics of plastic supercritical water gasification and how plastics react with supercritical water. A very active research group on this technology is that of Bai Bin, at Xi'an Jiaotong University (China). This group between 2018 and 2020 had published five articles on this topic. These and other articles will be described in Section 6.

4. Co-Gasification

Co-gasification involves the concurrent conversion of two or three carbonaceous fuels (one of them of fossil origin, such as coal, fuel-oil, or plastic wastes) into a gas with an useable heating value [104]. This technology looks very promising as it is able to reduce GHG (greenhouse gas) emissions by offsetting some of the fossil carbon with bio-based carbon [105].

In recent years, the co-gasification of biomass and coal has been much studied [106,107] because it represents an opportunity to manage large quantities of agricultural and woody fuel waste typical of agricultural or forestry waste. In addition, the cost of adapting an existing coal power plant to co-fire biomass is significantly lower than the cost of building new systems dedicated only to biomass power [105]. The partial replacement of coal with waste and biomass materials can be introducing renewable energy and thus resulting in environmental benefits. On the other hand, coal/lignite can be regarded as being beneficial because the security of supply of biomass and waste materials is uncertain, and the quality of the delivered fuel is subject to only limited control [108].

The co-gasification of coal with other types of fuels allows reducing CO₂, SO₂, and NO_x emissions, this happens because during the process the volatiles decompose forming free radicals. The latter react with the organic substances present on the coal, so the conversion rate increases while the emissions of these gases are reduced [105]. Co-gasification of mixtures of biomass and plastic wastes, for instance, has been suggested as a useful strategy to prevent problems normally occurring during the gasification of plastics alone such as feeding difficulties and the formation of contaminants [109]. Furthermore, synergistic effects deriving from the use of mixtures of raw materials are exploited in the co-gasification process [110]. As explained by Block et al., when synergistic effects occur the experimental values, such as product yield or gas composition, differ from those calculated by linear interpolation based on the results for the pure components in the feedstock [111].

These effects are also observed in co-pyrolysis processes of plastic and biomass. Biomass devolatilize in a temperature range between 200–400 °C instead plastics (PS, PE, PP, PET, PVC) in a higher temperature range (300–500 °C). The different devolatilization of the materials makes possible interactions between the volatiles of the plastic and the char of the biomass. Char acts as a donor of radicals in the initiation of the polymer chain scission (this means that there is a transfer of H from the polymer to the biomass). At the same time, coal is also capable of adsorbing volatiles from polymers [111]. One of the first studies on this topic is that of Jakab et al., in 2000, in which they studied the thermal decomposition of polypropylene (PP) in the presence of wood flour, lignin, cellulose, and charcoal [112].

5. The Problem of Tar: Formation and Removal

One of the major problems in gasification is the formation of tar during the process. Tar is a complex mixture of condensable hydrocarbons, which includes aromatic, polyaromatic, and linear organic compounds some of which contain oxygen [46,84]. The formation of tar gives rise to some important problems related to the formation of carcinogenic substances, the interruption of the process operations, and the deactivation of the catalyst [113]. Tar condensates in a wide temperature range from ca. 180 to 300 °C and in temperatures below zero, polymerizing in equipment such as engines and turbines [46]. As the tar condensates, it creates an adhesive liquid coating on cool surfaces which, together with dust, forms deposits that are very difficult to remove [114].

As explained in detail by Lopez et al. [20], in the case of plastic waste, tar formation depends on the nature of the polymers, as shown in Figure 5. The formation of primary aromatic tar occurs only in the degradation of polymers such as PS and PET, which contain aromatic rings in their structure. In the case of polyolefin such as PP and PE, the volatiles and the primary tar are made up of alkanes and alkenes of varying chain length. The components of the primary tar generally have an unstable nature and evolve into more stable structures which give rise to the so-called secondary and tertiary tar [115].

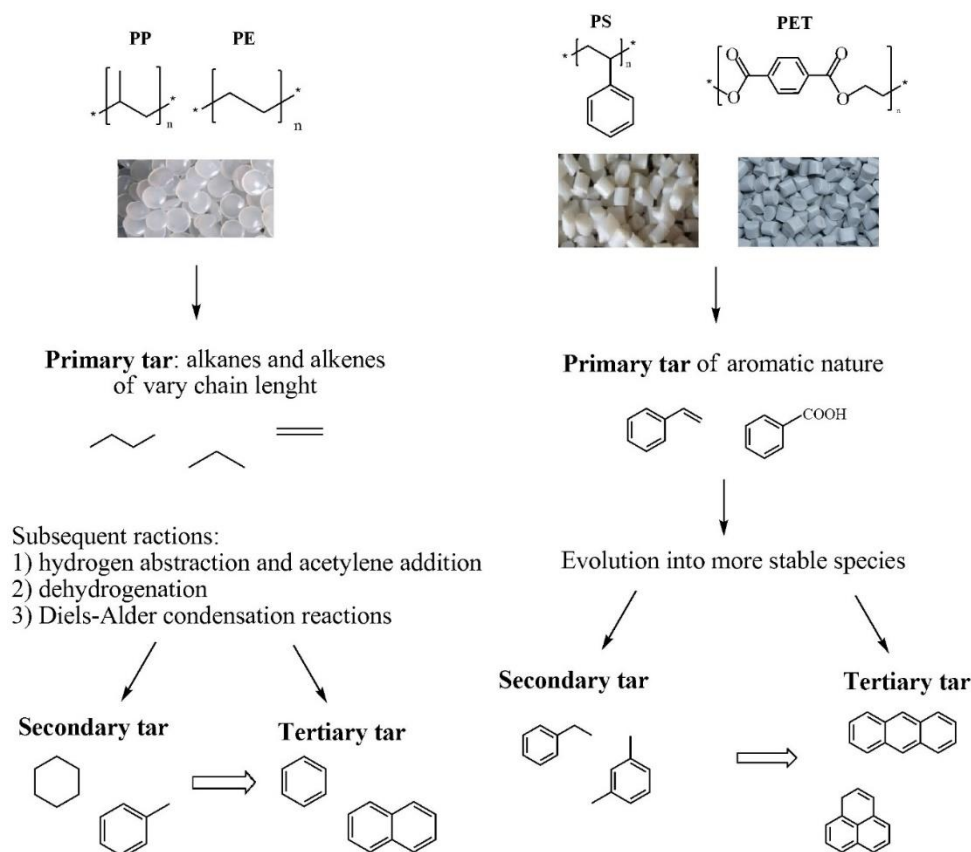


Figure 5. Tar formation from plastics of different nature (polyolefin, polystyrene (PS), polyethylene terephthalate (PET)) [20]. For each polymer we have represented only a small portion. With the symbol "*" we indicate that the chain continues.

The removal of the tar can take place in two different ways: Primary methods, which consist of an internal treatment in the gasifier [116,117] and secondary methods, which consist of the purification of the heated gas after gasification [118]. As described by Arena et al. [84], secondary methods, including thermal or catalytic cracking of tar and mechanical methods such as cyclones or filters, are very effective but at the same time extremely expensive. Furthermore, with these methods it is difficult to obtain a syngas with a very low tar content [42,119,120]. Treatments inside the gasifier are gaining

much attention for solid waste gasification since they may eliminate or strongly reduce the need for downstream clean up [84].

In a primary treatment, gasification is optimized to produce a gas with the minimum concentration of tar as possible [46]. For this purpose, several factors must be taken into account such as:

- A selection of specific operational parameters (temperature, gasifying agent, equivalence ratio, and residence time) [50,121,122].
- Modification of the gasifier.
- The use of catalysts in the bed.

Regarding the use of catalysts, Mohammed et al. [123] identified three main groups. They are:

- Naturally occurring catalysts such as dolomite and olivine.
- Alkali metals such as KOH, K_2CO_3 , $KHCO_3$, Na_2CO_3 , $CaCO_3$, $CsCO_3$, KCl, $ZnCl_2$, and NaCl.
- Nickel-based catalysts, which have been evaluated for tar reduction in syngas.

The dolomitic material is a double calcium and magnesium carbonate ($MgCO_3 \cdot CaCO_3$) and is the most common catalyst as it is readily available, inexpensive, disposable, and significantly reduces the tar content [124,125]. However, dolomite undergoes rapid deactivation due to calcination inside the gasifier. When it calcined it decomposes into CaO and MgO that are highly basic [126]. Moreover, dolomite is a soft and fragile material that erodes easily, generating a raw gas with a high particulate content [127]. Olivine, natural mineral containing magnesium, iron, and silicon in the form of either $(Mg,Fe)_2SiO_4$ [122,128] and it is known for its effectiveness in the decomposition of tar. The catalytic activity of olivine for tar elimination can be related to the magnesite (MgO) and iron oxide (Fe_2O_3) contents, where the latter is much higher in olivine than in dolomite [129]. Moreover, olivine is mechanically stronger than dolomite and for this reason generates fewer particulates in the gasification gas than dolomite.

Alkali metals, such as lithium, sodium, potassium, and rubidium, have been widely used as catalysts in biomass gasification [130]. Despite the fact that these catalysts provide a considerable increase in initial reaction activity, they are susceptible to loss of activity at high temperature due to particle agglomeration [131].

Alternatively, transition metal-based catalysts, particularly nickel, are excellent for gasification due to their high activities in tar elimination and ability to improve producer gas quality. These types of catalysts can be used as the primary catalyst in the gasifiers but also in secondary methods in post gasification or post pyrolysis reactor [129].

6. Gasification of Plastic Waste: An Overview

6.1. Polyolefin

Polyolefin are polymers produced from an olefin (or alkene) as a monomer. This category includes polyethylene (low-density, high-density, and linear low-density) and polypropylene [132]. Their versatility has made them one of the most popular plastics in use today for packaging production. In the scientific literature, several publications can be found about gasification experiments on these polymers.

6.1.1. Polypropylene

Xiao et al. [43] in 2006 conducted an experimental study on the gasification of spherical PP particles in a fluidized bed gasifier using air as the gasifying agent. They obtained a syngas with calorific value in the range of 5.2–11.4 MJ/Nm³ and with a low tar content (the lowest tar content determined in the product gas was 250 mg/Nm³). Among the various operating parameters tested, the equivalence ratio is the one that most influences the reactor temperature, the distribution of the product yield, the gas

composition, the calorific value of the gas, and the gas yield. The choice of the ER, strictly depends on the final use of the gas.

Ishii et al. in 2007 [133] investigated the gasification of plastic compounds containing flame retardants. For this purpose, they prepared PP pellets with non-halogenated flame retardants ($\text{Al}(\text{OH})_3$ and $(\text{NH}_4\text{PO}_3)_n$). The samples were decomposed in an image furnace at 1500 K, with a flow of gas (air or nitrogen) introduced from the bottom. Mass reduction during thermal decomposition was measured by an electric micro-balance. The presence of the flame retardant had a small effect on the thermal decomposition temperature of the polymer. However, the flame retardant ratio to the polymer influenced the gas composition and the mass of remains.

Sancho et al. [127] in 2008 studied air gasification of PP waste supplied by a recycling company. The study compared the effectiveness of dolomite and olivine as additives in the gasifier bed for the elimination of tar. Working with the same amount of additive in the gasifier bed (30%), they found that dolomite is more active in the removal of tar than olivine. However, dolomite, unlike olivine, generated a high amount of particulate by obstructing the gas purification devices. Therefore, olivine is preferentially used as a gasifier bed material, leading to excellent results: A tar content of $2 \text{ g}/\text{Nm}^3$ at the exit, with an LHV (low heating value) of $6 \text{ MJ}/\text{Nm}^3$ and a gas yield of $6 \text{ Nm}^3/\text{kg}_{\text{daf}}$.

In 2009, Wu and Williams [134] investigated the suitability of different nickel-based catalysts for the production of hydrogen from the two-stage pyrolysis/steam gasification of virgin polymer pellets of PP. Pyrolysis was carried out working at a temperature of $500 \text{ }^\circ\text{C}$. The pyrolysis gases were sent to the second reactor heated to $800 \text{ }^\circ\text{C}$, where the gasification took place in the presence of the catalyst and steam. The catalyst/polypropylene ratio was 0.5. Among all the catalysts tested in the study Ni-Al (1:2) and Ni-Mg-Al (1:1:2) have showed good catalytic abilities in terms of both H_2 production and prevention of coke formation. The ZSM-5 zeolite with a higher surface area was also shown to be a good support for the nickel-based catalyst, since, the Ni/ZSM-5 catalyst showed a high rate of hydrogen production (the 44.3 wt% of the theoretical, where the maximum theoretical amount of H_2 produced from steam gasification of polypropylene was estimated to be 42.9 g per 100 g PP).

The next year, Wu and Williams [88] tested a novel Ni-Mg-Al-CaO catalyst/sorbent, for hydrogen production from the pyrolysis-gasification of polypropylene by using always a two stage fixed-bed reaction system. Moreover, in this case they used virgin PP pellets. They observed that an increase in the amount of catalyst promoted the production of hydrogen from the pyrolysis-gasification of polypropylene. In particular, 70 wt% of the potential H_2 production was obtained, when the Ni-Mg-Al-CaO catalyst/polypropylene ratio was 5 and the steam gasification temperature was $800 \text{ }^\circ\text{C}$.

Toledo et al. [82] in 2011 continued the work of Sancho et al. [127] and studied air gasification of recycled PP in a fluidized-bed gasifier. In particular, they investigated several operating variables such as the amount of catalyst in the bed of the gasifier, the ER, and the temperature in the freeboard of the gasifier. Regarding olivine, using 100 wt% of this mineral in the gasifier bed they obtained: $\sim 2 \text{ g}$ of tar/ mNm^3 ; net calorific value (LHV), $\sim 6 \text{ MJ}/\text{Nm}^3$; and gas yield, $\sim 5.5 \text{ Nm}^3_{\text{dry basis}}/\text{kg}_{\text{daf}}$. Instead, by varying the ER and the freeboard temperature they obtained a tar content of about 2 g of tar/ Nm^3 , an LHV of about $9 \text{ MJ}/\text{Nm}^3$, and a gas yield of about $3.5 \text{ Nm}^3_{\text{dry basis}}/\text{kg}_{\text{daf}}$.

Martínez-Lera et al. [83] in 2013 studied the air gasification of post-consumer film waste and two reference polymers, PE and PP, in a bubbling fluidized bed. The experiments were conducted at a temperature of $750 \text{ }^\circ\text{C}$ and with different ER values (0.25–0.30–0.35). The experiments prove that film waste and analogue polymer derived wastes can be successfully gasified in a fluidized bed reactor, yielding net cold gas efficiency up to 61%, associated to gas heating values up to $5.7 \text{ MJ}/\text{m}^3$ and gas yields around $3.6 \text{ m}^3/\text{kg}$.

Wu and Williams [135] in 2014 investigated a screw kiln continuous reaction system for hydrogen production from the pyrolysis/steam gasification of virgin PP pellets. The pyrolysis was carried out at $500 \text{ }^\circ\text{C}$, while the gasification temperature was varied in the tests (600, 700, 800, and $900 \text{ }^\circ\text{C}$). The water injection rate was controlled at 14.23 g/h. Two catalysts (a laboratory-prepared Ni-Mg-Al catalyst and a

commercial nickel catalyst) were used. The results show that an increase in the gasification temperature or in the water injection rate together with the presence of catalysts, favored the production of hydrogen.

Yin et al. [136] in 2018 investigated the use of plastic waste from PP snack packaging as a carbon resource for steel carburization. By heating together some plastic waste from snack packaging and a steel sample to the carburizing temperature (1200 °C), carbon-rich reducing gases, such as CO and CH₄, could be released from the plastic waste and absorbed by the steel sample such as carbon precursor for carburization. The resulting carburization effect on steel was investigated by optical microscopy, scanning electron microscopy, electron probe micro analyzer, and X-ray photoelectron spectrometer techniques. The results obtained showed that plastic waste from snack packaging could function effectively as a valuable carbon resource for carburizing steel, as it leads to an increase in the surface carbon content and in a corresponding evolution of the microstructure in steel.

A summary view of the operating conditions used in the various works is shown in Table 3. As can be seen from the table, most of the experiments were carried out on a virgin polymer and not on a real waste polymer, using both fluidized and fixed bed reactors and air or steam as gasifying agents. Olivine or nickel-based catalysts are preferred over dolomite to reduce tar production.

Table 3. Polypropylene gasification summary table.

Reactor	Feedstock	Bed Material	Gasification Temperature	Tar Content	Gasifying Agent	Heating Value	Reference	Year
Fluidized bed	Virgin PP	ash	690–950 °C	250 mg/Nm ³	air	LHV: 5.2–11.4 MJ/Nm ³	Xiao et al. [43]	2006
Image furnace	PP + Al(OH) ₃ and PP + (NH ₄ PO ₃) _n	-	1227 °C	-	air	-	Ishii et al. [133]	2007
bubbling fluidized bed	Recycled PP	bed of silica sand with dolomite or olivine	~850 °C	(1) 30 wt% dolomite: 1.5 g/Nm ³ (2) 30 wt% olivine: 10 g tar/Nm ³ (3) 100 wt% olivine: 2 g tar/Nm ³	air	LHV: (1) 30% dolomite: 7.4 MJ/Nm ³ (2) 30 wt % olivine: 5 MJ/Nm ³ (3) 100 wt % olivine: 6 MJ/Nm ³	Sancho et al. [127]	2008
two-stage fixed bed	Virgin PP.	PP in pyrolysis reactor nickel-catalyst supported on quartz wool in gasification reactor.	800 °C	-	steam	LHV: from 10.9 to 13.1 MJ/Nm ³ depending on the nature of the catalyst	Wu and Williams [134]	2009
Two-stage fixed bed	Virgin PP	PP in pyrolysis reactor nickel-catalyst in gasification reactor	700–800 °C	-	steam	-	Wu and Williams [88]	2010
bubbling fluidized bed	Recycled PP	Silica sand-mixtures silica sand/olivine-olivine	850 °C;	2 g of tar/m ³	air	LHV: 9 MJ/Nm ³	Toledo et al. [82]	2011
bubbling fluidized bed	Pure PP Pure PE Film waste	Silica sand	750 °C	Waste: 102 g/m ³ Pure PE: 128 g/m ³	air	HHV: 3.6 to 5.6 MJ/Nm ³	Martinez–Lera [83]	2013
screw kiln reaction system (fixed bed)	Virgin PP	Ni/SiO ₂ /Al ₂ O ₃ catalyst	850 °C	-	steam	-	Wu and Williams [135]	2014

6.1.2. Polyethylene

Arena et al. [84] in 2008 investigated the gasification of recycled polyethylene pellets in a pilot plant bubbling fluidized bed gasifier. The experiments were conducted in various operating conditions: The bed temperature was kept fixed at 850 °C while the ER was varied. Both sand and olivine were used as the bed material. Air and steam were used as fluidizing agents. The results confirmed that primary methods for tar removal can eliminate or greatly reduce the need for further cleaning downstream of the syngas. The use of olivine leads to a reduction in tar and significantly improves the quality of the gas produced.

Erkiaga et al. in 2013 [67] carried out a steam gasification of HDPE chippings in a continuous bench-scale plant in a conical spouted bed reactor. This type of reactor is considered an interesting technology for the continuous steam gasification of plastic waste due to the high level of the heat transfer rates provided by these beds. The effect of temperature and the vapor/plastic mass ratio on the distribution of products (gas and tar) and on their composition, were examined in the study. To reduce the formation of tar, two in situ catalysts were used (olivine and γ -Al₂O₃). The study showed that at 900 °C and with a steam/plastic mass ratio = 2, a syngas rich in hydrogen was obtained together with a low concentration of CO₂, hydrocarbons and polyaromatic tar. This syngas was particularly suitable for the synthesis of hydrocarbons (Fischer-Tropsch) or DME.

Mastellone and Zacariello in a work of 2013 [85] studied air gasification of PE (obtained by the recycling chain of domestic waste) in a bubbling fluidized bed gasifier, injecting air in three different modes:

- (a) At bed bottom without any splitting of the flow rate;
- (b) At bed bottom and in the splashing zone, that is the volume just above the primary zone, by
- (c) splitting into two streams the necessary air flow rate;
- (d) at bed bottom, in the splashing zone and in the freeboard region, by splitting into three
- (e) streams the air flow rate.

The results indicate that airflow staging may be a valid method to prevent or reduce the formation of condensable compounds.

In 2015, Lopez et al. [91] studied the steam gasification of virgin HDPE in a conical spouted bed reactor followed by steam reforming in a fixed bed reactor in the presence of a Ni commercial catalyst. Gasification was carried out at a temperature of 900 °C instead steam reforming was carried out in the range of 600–700 °C. The reforming leads to a full transformation of C²⁺ hydrocarbons and tar. Reforming temperature has an important effect on the product yields ob. The better reforming temperature was 700 °C because:

- A high H₂ yield was obtained.
- The CH₄ conversion was almost full.
- A high H₂/CO ratio was obtained in the product stream.
- A low coke yield was obtained.

A recent article is that of Cagnetta et al. [137] that in 2018 proposed “a high energy milling pre-treatment to boost H₂ generation” during virgin PE gasification. The polymer was co-milled with calcium and nickel hydroxides and then it was subjected to thermal treatment in a glass tube connected to the argon gas source and inserted in a furnace. The experiments were conducted in the range of temperature between 350–700 °C. Ca(OH)₂ favored the production of hydrogen. It removes the CO₂ generated by cracking PE by trapping it in a solid form (calcium carbonate). The equilibrium of all reactions is therefore shifted towards the formation of H₂. Moreover, high amounts of the hydroxide prevent excessive CH₄ formation, so the gas product is almost pure H₂ (~95%).

A summary view of the operating conditions used in the various works is shown in Table 4. As can be seen, the gasification of the PE is carried out mainly using steam as a gasifying agent and both fluidized and fixed bed reactors. The conical spouted bed reactor is used by Erkiaga and Lopez and consist of a reactor with conical section. Despite the endothermic nature of the steam gasification process, in this reactor bed, isothermicity is ensured by the vigorous solid circulation of the sand, which also promotes high heat transfer rates. Commonly, it is used to reduce tar production.

Table 4. Polyethylene gasification summary table.

Reactor	Feedstock	Bed Material	Gasification Temperature	Tar Content	Gasifying Agent	Heating Value	Reference	Year
bubbling fluidized bed	Recycled PE	quartz sand or olivine	783–898 °C	14.6–6.2 kg/h	Air, steam	LHV 5500–9200 kJ/Nm ³	Arena et al. [84]	2008
Conical spouted bed	Virgin HDPE	Sand or olivine or γ -Al ₂ O ₃	800–900 °C	sand: 16.7g/Nm ³ olivine: 15.0 g/Nm ³ γ -Al ₂ O ₃ : 16.1 g/Nm ³	steam	LHV 15.5 MJ/kg at 900 °C	Erkiaga et al. [67]	2013
bubbling fluidized bed	Recycled PE	silica sand	-	11–68 g/Nm ³	Air, steam	LHV 7737–10,349 kJ/Nm ³	Mastellone and Zacariello [85]	2013
conical spouted bed	Virgin HDPE	Olivine + Ni catalyst	900 °C	-	steam	-	Lopez et al. [91]	2015
glass tube	Virgin PE + Ca(OH) ₂ + Ni(OH) ₂	-	350 °C	-	-	-	Cagnetta et al. [137]	2019

6.2. Plastics Mix

Very often the gasification of plastic material does not concern a single type of feedstock but a mix of different plastic materials, for example, those coming from municipal solid waste (MSW). Among these materials we find not only PP and PE but also PS, PVC, polymethylmethacrylate (PMMA), and PET. In particular, PS is used for protective packaging containers, lids, bottles, trays, tumblers, and disposable cutlery. PVC is used for tamper-resistant over-the-counter medications and shrink wrap for consumer products. The PVC rigid vinyl film is used in blister and clamshell packaging to protect medicines, personal care products, and other household goods. PET is widely used for packaging foods and beverages, especially convenience-sized soft drinks, juices, and water. Finally, PMMA is known for its applications in various markets such as car, windows, smartphone, screens and aquariums.

A research group that has been interested in the problem of gasification of plastic mixes is that of Cho et al. (Department of Energy and Environmental System Engineering, University of Seoul). In 2013, this research group has published two papers about this topic.

In the first one [89], they studied air gasification of a mix of recycled polymers (PP, PE, PS, PVC, PMMA, and PET) in a two-stage gasifier, using olivine as a bed material and activated carbon (AC) as a tar-cracking additive. In all experiments, the reaction temperatures of the lower and upper reactors were maintained at 800 °C. With 1500 g of AC, a 30% by volume of H₂ was obtained and the tar removal efficiency reached 98% using steam as a gasifying agent. With the combined use of olivine and activated carbon and an ER of about 0.31, LHV_s in the range of 5.3–6.2 MJ/Nm³ were obtained.

In the second one [138], they investigated again air gasification of a mix of recycled polymers (PP, PE, PS, PVC, PMMA, and PET) using a two-stage gasifier. Instead of olivine, calcined dolomite was used as a bed material together with activated carbon as a tar-cracking additive. Moreover, in this case, various operational parameters were examined. When the amount of activated carbon increased from 0 to 900 g using calcined dolomite as the bed material, the concentrations of H₂ and CO in the producer gas increased considerably (H₂: From 14.9 to 26.1 vol%; CO: From 9.4 to 16.8 vol%). Using 900 g of AC, the total amount of tar was reduced by 96%. The maximum LHV of the producing gas was approximately 13.4 MJ/Nm³.

In 2013, Wilk and Hofbauer [115] studied steam gasification of plastic wastes in a dual fluidized bed gasification pilot plant (DFB) using olivine as a bed material. Several types of common plastics (both recycled and virgin) were studied: PE, PP and blends of PE + PS, PE + PET, and PE + PP. This experimental work demonstrates that the tested polymers are suitable feedstock for the DFB gasifier. The study showed how polymer mixes behave differently than pure polymers. In particular, the polymer mixtures PE + PP and PE + PS generated more H₂ and CO than pure polymers. The mixture of PE + PET gave rise to a high amount of CO₂ due to the high oxygen content of PET.

The most recent study on plastic mix gasification is that of Friengfung et al. [139] in 2020. They evaluated the catalytic steam gasification of different polymers and their mixtures (LDPE, HDPE, PP, and PS) with a dolomite supported Ni catalyst in a drop-tube fixed-bed reactor. "A 5 wt% NiO/dolomite catalyst gave the highest degree of carbon conversion for all evaluated plastics and mixtures". The study revealed synergistic interactions between different plastics mixed together. These interactions can lead to an increase or decrease in the amount of gas produced. For example, mixtures containing PE show a reduced production of gas, while those containing polystyrene give rise to a very high production of H₂, CO, and CO₂.

A summary view of the operating conditions and of the obtained results in the various works is shown in Table 5. As can be seen, the gasification of the plastic mix is carried out using mainly air or steam and temperature of 800–850 °C. Moreover, in this process olivine or dolomite are used as a catalyst to reduce tar content.

Table 5. Plastics mix gasification summary table.

Reactor	Feedstock	Bed Material	Gasification Temperature	Tar Content	Gasifying Agent	Heating Value	Reference	Year
Two-stage gasifier	PP, PE, PS, PVC, PMMA, PET	Olivine and activated carbon	800 °C	2–2170 mg/Nm ³	air	LHV: From 3.9 to 8.2 MJ/Nm ³ .	Cho et al. [89]	2013
Two-stage gasifier	PP, PE, PS, PVC, PMMA, PET	Calcined dolomite and activated carbon	800 °C	20–3490 mg/Nm ³	air	LHV: 13.4 MJ/Nm ³	Cho et al. [138]	2013
Dual fluidized bed	PE, PP, and mixtures of PE + PS, PE + PET and PE + PP	olivine	850 °C	100 g/Nm ³	steam	LHV: From 27.2 to 41.2 MJ/Nm ³	Wilk and Hofbauer [115]	2013
drop-tube fixed bed	LDPE, HDPE, PP, and PS	Dolomite supported Ni catalyst, alumina balls over a quartz wool filter	850 °C	-	steam and oxygen	-	Friengfung et al. [139]	2020

6.3. Supercritical Water Gasification (SCWG)

The first work related to the gasification of plastic material in supercritical water is that of Okajima et al. [140]. In 2004, they studied the production of H₂ from cross-linked polyethylene (XLPE), using high pressure superheated steam and supercritical water (500–700 °C and 30 MPa). The optimal operating conditions identified in the study were: 700 °C, 30 min, 20 molar ratio of water to carbon in XLPE, and 20% by weight of nickel catalyst. Gas production is improved by increasing the temperature and molar ratio of water to carbon in XLPE.

In 2016, Onwudili and Williams [141] studied SCWG of virgin polyolefin plastics (LDPE, HDPE, PP, PS) in a batch reactor at 450 °C, with a reaction time of 60 min and in a range of pressures between 10 and 38 MPa. This process involves the use of RuO₂ as a catalyst and it aims to identify a possible strategy to eliminate pollutants from ocean waters. The key reactions in the process are steam reforming (which implies the reduction of RuO₂ to Ru metal) and water gas shift reaction. The resulting CO₂ and H₂ reaction was catalyzed by metallic Ru to produce CH₄. This work shows how SCWG in the presence of a catalyst is an effective technique for solving the hydrocarbon pollution of water.

Bai Bin and his research group published the first paper about SCWG in 2018 [142]. In this paper, they studied SCWG of high impact polystyrene (HIPS) at a reaction temperature in the range of 500–800 °C, a reaction time of 1–60 min, a feed concentration of 2–10 wt%, and a reaction pressure of 22–25 MPa. The increase of some parameters such as temperature and reaction time and the reduction of others such as the concentration of feedstock, increase the gasification efficiency of the plastic. The optimal conditions identified in the study are: A temperature of 800 °C, a reaction time of 60 min, a reaction pressure of 23 MPa, and a feedstock concentration of 3% by weight. In these conditions, the carbon conversion rate of the plastic reaches 94.48% by weight.

In 2018, Liu et al. [143] reported about SCWG of Acrylonitrile Butadiene Styrene (ABS) plastics for fuel gas production. The experiments were firstly conducted from 450 to 700 °C, at 23 MPa. They showed that an increase of reaction time, temperature, and material ratio (water/ABS) could significantly promote the gasification reaction, and the whole reaction process was obviously divided into three stages: The gasification efficiency rapidly increased firstly, maintaining nearly unchanged then, and restarted to grow. Finally, they investigated the subcritical water hydrolysis for oil products recovery from 375 to 450 °C at 21 MPa and the results showed that most of the monomers were converted into more stable substances at a long residence time. The optimal reaction condition for monomer recovery was determined to be 400 °C and 3 min through the experimental results.

Bai, Wanga and Jina [144] in 2019 investigated gasification of virgin PP in supercritical water using a quartz tube reactor. The results showed that the optimal conditions for gasification were 750 °C and 60 min, and the effect of temperature on gasification was more important than time. Moreover, they tried to use artificial seawater for gasification instead of ultrapure water and they saw that metal salts had a positive impact on the gasification of PP plastics, so this process was an effective way to solve marine microplastics pollution.

In order to solve the ecological and environmental problems caused by microplastics, Bai B. has conducted further researches on this problem, which culminated in two articles published in 2019 and 2020. The first one was in regards to ABS microplastics [145], the second PET microplastics [146]. In the first one, he studied SCWG on ABS microplastics using a quartz tube reactor at 1000 °C and 35 MPa. Moreover, he used a novel in situ hydrogenation induction gasification of organic acid (formic acid) and inorganic acid (hydrochloric acid) to achieve optimal gasification. The acids act as an H donor by promoting the cracking of unsaturated hydrocarbons and polycyclic aromatic hydrocarbons. The optimal working conditions to achieve 97% of carbon conversion are: A temperature of 800 °C, a reaction pressure of 23 MPa, a reaction time of 60 min, a feedstock concentration of 3 wt%, and a solution of 1 wt% formic acid.

In the second one [146], he carried out experiments on PET microplastics using a quartz tube reactor. The effects of operational parameters on SCWG were investigated. Again, artificial seawater was used instead of ultrapure water. The results showed that the increase in gasification temperature

and time improved gasification efficiency, but an increase in the reaction pressure had little. By working at a temperature of 800 °C, at a pressure of 23 MPa, and with a reaction time of 10 min, it was possible to obtain a carbon conversion of 98%. As seen from previous studies, the metal salts contained in seawater favor the gasification of plastics, therefore, SCWG can be used successfully for the removal of microplastics from the oceans.

Another highly environmental problem is that related to the incorrect sorting of waste. For example, in some cities in China there is no waste sorting and plastic is thrown away with food waste. For this reason, Su et al. [147] in 2020 studied SCWG of a mixture of model food waste (cabbage, rice, chicken, and banana peel in equal quantities) and LDPE in a 4:1 mixing ratio. In this study, they also tested the effect of three food additives: NaCl, NaHCO₃, and Na₂CO₃. The experiments were conducted in a batch reactor in a temperature range of 420–480 °C, with a residence time of 30–75 min, with a pressure of 35 MPa, and a raw material concentration of 5–15 wt%. Again, the results indicated that an increase in the reaction temperature, a longer residence time, and a lower feedstock concentration led to a syngas rich in H₂. Moreover, the addition of food additives which release Na⁺ ions had a positive effect on SCWG of unsorted food waste with plastic.

A summary view of the examined works is shown in Table 6. Almost all the experiments were conducted in a quartz tube reactor or in a batch reactor and the optimal operating conditions concern pressures of 23 MPa and temperatures in the range between 450–800 °C. The reaction time is often around 60 min.

Table 6. Supercritical water gasification summary table.

Reactor	Feedstock	Optimal Reaction Conditions	Catalyst	Reference	Year
Batch reactor	XPLE	700 °C, 30 MPa, 30 min, 20 of molar ratio of water to carbon in XPLE	Nickel	Okajima et al. [140]	2004
batch reactor	LDPE, HDPE, PP, PS	450 °C, 10–38 MPa, 60 min	RuO ₂	Onwudili and Williams [141]	2016
quartz tube reactor	HIPS	800 °C, 60 min, 23 MPa, feedstock concentration of 3 wt%	-	Bai et al. [142]	2018
quartz tube reactor	ABS	450 °C, 60 min, 23 MPa, water/ABS (15:1)	-	Liu et al. [143]	2018
quartz tube reactor	PP	750 °C, 60 min, 23 MPa, feedstock concentration was 5–25 wt%	inorganic salts in seawater	Bai, Wanga and Jina [144]	2019
quartz tube reactor	ABS	800 °C, 60 min, 23 MPa, a feedstock concentration of 3 wt% and a solution of 1 wt% formic acid	formic acid, hydrochloric acid	Bai et al. [145]	2019
quartz tube reactor	PET	800 °C, 10 min, 23 MPa	inorganic salts in seawater	Bai et al. [146]	2020
batch reactor	food waste and LDPE	420–480 °C, 35 MPa, 30–75 min	food additives (NaCl, Na ₂ CO ₃ , and NaHCO ₃)	Su et al. [147]	2020

6.4. Co-Gasification

Co-gasification is a relatively new process where the industrial know-how is far from exhaustive, even if the scientific literature is full of interesting research studies on the co-feeding effect of different fuels mainly into fluidized bed gasifiers.

Ponzio et al. [148] in 2006 studied the high temperature air/steam gasification technique (HTAG) for a particular feedstock named Rofire©. This name indicates a fuel consisting of paper fibers mixed with other substances such as fabric fiber, wood chips, and plastics. Small amounts of PVC are also present. The feedstock was gasified in a fixed bed updraft reactor using a mixture of air and steam at a temperature of 1400 °C. The process resulted in syngas with an LHV of 9.5 MJ/Nm³ and yields as high as 3.4 Nm³/kg. The high calorific value of the gas is due to the high content of synthetic polymers in the raw material and favorable conditions for cracking.

In the same year, Aznar et al. [48] investigated the co-gasification of ternary mixtures: Coal, biomass (pine sawdust), and automotive plastic waste. The studies were conducted using a fluidized bed reactor and air as a gasifying agent. The gasifier bed consisted of silica sand mixed with dolomite. Operating variables studied were the gasifier bed temperature (750–880 °C), equivalence ratio (0.30–0.46), feedstock composition, and the influence of secondary air insertion in freeboard. The optimal operating conditions identified experimentally were a bed temperature of 850 °C and an ER of 0.36. In these conditions, a syngas with LHV: 4–8 MJ/Nm³ dry basis, was obtained. The injection of secondary air into the freeboard reduces the tar content to less than 0.5 g/m³_n.

Mastellone et al. in 2010 [86] studied co-gasification of coals, plastics, and wood into a pre-pilot scale fluidized bed gasifier. During the study, they observed that each component can change the overall behavior of the process, for example, there was the possibility of reducing the level of tar by adding wood. Wood favors the formation of a solid phase of pure carbon, thus reducing the presence of hydrocarbons in the syngas and making it cleaner.

Always, Mastellone et al. [149] in 2011 investigated co-gasification in a fluidized bed of a mixture of coal, plastic (PE and PP), and wood, using oxygen enriched air. Quartz sand was used as a bed material. The main advantage of using O₂ enriched air is the ability to increase the bed temperature. Or, working at low temperatures, to reduce the size of the cross section and the total cost of the preheating.

Meng et al. [150] in 2012 studied co-gasification with air of a mixture of PP and sawdust at a fixed feed gas flow rate in a packed-bed reactor. The reactor temperature was varied from 400 to 800 °C. The increase in temperature led to “a decrease in the solid fraction and a convex shape curve for the gas yield”. Moreover, it increased the liquid fraction, favoring the cracking of the latter. In particular, the liquid phase is rich in hydrocarbons containing oxygen.

In the same year, Ruoppolo et al. [151] studied the co-gasification of wood pellets, biomass/plastic, and olive husks using a catalytic fluidized bed gasifier in which inert quartzite sand or nickel-based catalyst supported on γ -alumina, were used as a bed material. Gasification experiments were conducted both in the presence and absence of steam. Pelletization, which consists of reducing the size of the material, is an effective strategy to make the feedstock more homogeneous and facilitate the feeding of the device. Independently of the fuel used, the presence of steam favors the production of H₂. The presence of the catalyst greatly increases H₂ production and reduces the tar content, more effectively than steam.

In 2013, Wilk and Hofbauer [110] investigated co-gasification of biomass and plastics in a fluidized bed pilot plant using four types of plastic material of different origins (plastics from MSW, plastics from automotive shredder residues, PE regrind, and virgin PE) and soft wood pellets. During the experiments, the quantity of wood was kept constant while the mixing ratios between the plastics were varied. Gasification was carried out at 850 °C. The composition of syngas as well as the tar content were influenced by the simultaneous presence of biomass with plastics. More CO and CO₂ were measured than expected for pure substances, while the amount of H₂ was underestimated or overestimated depending on the plastic material. It has been observed that the presence of wood charcoal with plastics favors polymers decomposition and significantly reduces tar formation.

In 2015, Parparita et al. [152] studied steam gasification of PP/biomass mixtures and of their constituents using a two-stage process, in a dual-bed microreactor. The mixes consist of 70% plastic and 30% biomass. The experiments were carried out at 700 °C in the absence or presence of Fe₂O₃/CeO₂ catalyst. The presence of the catalyst favors the formation of gaseous products. Furthermore, confirming previous studies, also in this case a synergistic effect is observed by combining biomass with plastic, as the production of H₂ is greater compared to the added contribution of production of H₂ from the individual components.

In 2016, Pinto et al. [87] studied co-gasification in a fluidized bed as a strategy for energetic valorization of rice processing wastes (rice husk, straw, and plastics, mainly PE from bags for rice packaging). During the process, different types of gasifying agents were tested. Good results were obtained with steam and oxygen, because the gas was not diluted in N₂ and it had a higher heating value. Moreover, CO₂ proved to be a good gasifying agent as it leads to a decrease in tar content and an increase in the yield of gas.

In the same year, Baloch et al. [153] studied co-gasification in a bench scale plant of ternary blends of rice straw (RS), PE, and PVC using steam as a gasifying agent. Different operating parameters such as temperature, the type of plastics, and their mixtures were examined. It has been shown that the increasing temperature, increases the gas yield, its H₂ content, and its LHV. Similar results are also obtained by increasing the PE and PVC content. This work confirmed that the synergistic interactive effect takes place during the co-gasification of ternary blends of PE, PVC, and RS due to volatile-char interaction and mineral catalytic effects.

In 2018, Burra and Gupta [154] studied steam gasification of biomass and plastics in a semi-batch reactor at 1173 K. The waste plastics used in the process were recycled black polycarbonate (BPC) pellets, PP pellets, and PET. Mixtures with different biomass/plastic ratios were examined. Moreover, in this case there were synergistic effects that led to obtaining greater quantities of syngas than the weighted sum of single components gasification for all the plastics examined.

Fan et al. [155] in 2019 investigated co-pyrolysis and co-gasification of some types of biomass (eucalyptus wood (EW) and rice straw (RS)) with PE. The studies were conducted through a complex instrumentation consisting of a thermogravimetric analyzer coupled with a Fourier transform infrared spectrometer and a scanning electron microscope coupled with energy dispersion spectroscopy. They observed that the process can be divided into three stages: Two during pyrolysis (decomposition of biomass material; degradation of PE) and one during gasification (reaction of pyrolysis products with CO₂). The experimental results showed that the addition of PE promotes the decomposition of EW and RS.

Cao et al. [156] in 2020 studied co-gasification of soda lignin produced from black liquor and various plastics (PE, PC, PP, and ABS) in SCW. Once again, synergistic effects were observed between the feedstock. Plastic decomposition generated many alkane gases (CH₄ and C₂H₆). The alkaline salts present in the biomass favored their reforming reaction, which led to the production of H₂. The gasification efficiencies of the plastics examined in the study were classified as follows: PE > PC > PP > ABS.

Chai et al. [90] in 2020 developed a new Ni-based catalyst (Ni-CaO-C) and examined its performance in pyrolysis/gasification of plastics (LDPE) and biomass (pine sawdust). They used a two-stage fixed bed reactor with quartz wool as a bed material. The experimental results indicate that the new catalyst leads to a syngas rich in H₂ and poor in CO₂. This result is related to the synergy between Ni (active core), CaO (CO₂ adsorption), and activated carbon (active in reforming reactions, massive pore structure, and good reduction ability).

A summary view of all works is reported in Table 7. In co-gasification, both fluidized and fixed bed reactors are used. Quartz sand is often used as a bed material. The gasifiers agents commonly used are air (in some cases enriched with oxygen) and steam. The temperature range depends on the type of feedstock and is generally between 700 and 1000 °C.

Table 7. Co-gasification summary table.

Reactor	Feedstock	Bed Material	Gasification Temperature	Tar Content	Gasifying Agent	Heating Value	Reference	Year
bubbling fluidized bed	Coal + biomass + plastic waste	silica sand mixed with dolomite	850 °C	lower than 0.5 g/Nm ³	air	LHV: 4–8 MJ/Nm ³	Aznar et al. [48]	2006
fixed bed (KTH/Energy and Furnace Technology)	Rofire (paper fiber mixed with other substances such as fabric fiber, wood chips, and plastics)	Solid feedstock	1400 °C	1118–2164 µg	air-steam	LHV: 7.5–9.5 MJ/Nm ³	Ponzio et al. [148]	2006
pre-pilot scale fluidized bed gasifier	Coals + plastics + wood	Quartz sand	850 °C	25–45 g/Nm ³	air, oxygen, steam	LHV: 11100–45500 KJ/Nm ³	Mastellone et al. [86]	2010
bubbling fluidized bed	Coal + plastics + wood	Quartz sand	850 °C	13,500–21,800 mg/Nm ³	oxygen-enriched air	LHV: 5150–8950 kJ/Nm ³	Mastellone et al. [149]	2011
packed-bed	PP + poplar sawdust	150 g sawdust and 250 g PP	400–800 °C	-	air	LHV: 4334–9805 kJ/Nm ³	Meng et al. [150]	2012
catalytic fluidized bed gasifier	Wood + biomass + plastic + olive husks	inert quartzite sand or 5.5wt% Ni-based catalyst supported on γ-alumina	780 °C	60 g/Ncm ³	steam	LHV: 21.9 MJ/Kg	Ruoppolo et al. [151]	2012
dual fluidized bed	plastics + soft wood pellets	olivine	850 °C	-	steam	-	Wilk and Hofbauer [110]	2013
dual-bed quartz reactor	isotactic PP and different types of lignocellulosic biomass waste	quartz wool bed + Fe ₂ O ₃ /CeO ₂ catalyst	700 °C	-	steam	LHV: 14,599–32,594 kJ/kg	Parparita et al. [152]	2015
bubbling fluidized bed gasifier	rice husk + straw PE	Silica sand	850 °C	5–15 g/m ³	Mixtures of air, oxygen, steam and CO ₂	HHV/10: 11–22 KJ/Ndm ³	Pinto et al. [87]	2016
glass tube	rice straw + PE+ PVC	-	700–900 °C	-	electrically heated	LHV: 15.3 MJ/Nm ³	Baloch et al. [153]	2016
laboratory scale semi-batch	pine wood + PP+PET+PBC	-	900 °C	-	steam	-	Burra and Gupta [154]	2018

Table 7. *Cont.*

Thermogravimetric analyzer	eucalyptus wood or rice straw + PE	-	1000 °C	-	-	-	Fan et al. [155]	2019
autoclave	soda lignin (from black liquor) + PE, PC, PP and ABS	-	750 °C, 23–26 MPa	-	SCW	-	Cao et al. [156]	2020
two-stage fixed bed	LDPE+ pine sawdust	quartz wool + Ni-CaO-C	800 °C	-	steam	-	Chai et al. [90]	2020

7. Conclusions and Final Remarks

The gasification of plastic material as a technology has achieved the technical maturity to disrupt the plastic recycling sector, with demo processes and plant (Enerkem, Sierra Energy) currently in operation at the industrial scale. However, it is currently underexploited compared to other forms of recycling such as mechanical recycling or pyrolysis. This technology draws its foundations from the well-known gasification of coal or biomass. As observed from the analysis of literature, gasification is a very versatile process, because starting from different types of feedstock (pure plastic, plastic mixtures, plastic with biomass) are possible to obtain a gaseous product rich in hydrogen. Regarding the gasification of polyolefin, virgin polymers are commonly used as a model feedstock in many of the analyzed papers. According to our experience in the sector, this leads to results that are not representative of reality, as real recycled polymers generally show important forms of cross-contamination, for example, with PET or PVC. Cross-contamination can lead to the formation of unwanted products. Therefore, it would be interesting to conduct studies not on virgin polymers but on polymers coming from recycling companies. Gasification reactions are also conducted on plastic mixes commonly found in waste streams: PP, PE, PS, PVC, PMMA, PET. Synergistic effects can occur between different polymers increasing the gas yield. Gasification in supercritical water is a poorly studied technology, which has generated great interest in recent years thanks to its numerous advantages, for example, the inhibition of tar and coke formation and the fact that the gaseous product is very clean (no NO_x and SO_x are generated in SCWG) and the CO concentration is very low, especially with the catalyst to enhance the water-gas shift reaction. This technology can be used for microplastic removal as described by the recent works of Bai B., but also for the recycling of particular types of plastics (strongly cross-linked polymers). The high costs and complexity of the process made it difficult to implement gasification plants with supercritical water on a large scale. Therefore, it will be important to understand which operating parameters can be optimized for greater energy savings.

Finally, the last type of technology considered in this review is co-gasification of plastic material with coal or biomass. The latter technology represents a promising form of recycling for those industries (for example in the food sector) that have processing waste both in the form of biomass and plastic packaging. Co-gasification exploits the synergistic effects between the different components of the raw material, allowing to obtain higher gas yields, with a composition rich in H₂. The synergistic effects also lead to an increase in the energy content of the syngas.

Author Contributions: Conceptualization, L.R.; writing—original draft preparation, B.C.; writing—review and editing, L.R., D.C., M.F., A.M.R.; supervision and correction, L.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research was partially funded by Fondazione Cassa di Risparmio di Firenze (project no. 2018-0930 “PIRACY”)

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

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