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*Review*

# From Waste to Energy: Enhancing Fuel and Hydrogen Production through Pyrolysis and In-Line Reforming of Plastic Wastes

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**Abstract:** Plastics have become integral to modern life, playing crucial roles in diverse industries such as agriculture, electronics, automotive, packaging, and construction. However, their excessive use and inadequate management have had adverse environmental impacts, posing threats to terrestrial and marine ecosystems. Consequently, researchers are increasingly searching for more sustainable ways of managing plastic wastes. Pyrolysis, a chemical recycling method, holds promise for producing valuable fuel sustainably. This study explores the process of the pyrolysis of plastic and incorporates recent advancements. Additionally, the study investigates the integration of reforming into the pyrolysis process to improve hydrogen production. Hydrogen, a clean and eco-friendly fuel, holds significance in transport engines, power generation, fuel cells, and as a major commodity chemical. Key process parameters influencing the final products for pyrolysis and in-line reforming are evaluated. In light of fossil fuel depletion and climate change, the pyrolysis and in-line reforming strategy for hydrogen production is anticipated to gain prominence in the future. Amongst the various strategies studied, the pyrolysis and in-line steam reforming process is identified as the most effective method for optimising hydrogen production from plastic wastes.

**Keywords:** plastic waste; pyrolysis; pyrolysis and in-line reforming; fuel; hydrogen; review

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## 1. Introduction

Over the last decades, the global manufacturing of plastics has experienced a significant surge. For instance, among many other fields of use, plastics have made significant contributions to the development of computers, light weight automobile parts, cell phones, kitchen utensils, roofing and ceiling materials, textiles, as well as the majority of the life-saving innovations in modern medicine. Even the personal protective equipment used in large quantities during the early outbreak of the COVID pandemic were largely plastics [1]. This broad use of plastics can be ascribed to their beneficial qualities, which include being lightweight, versatile, durable, flexible, and its low production cost and pressure resistance [2]. As a result, plastic production has experienced significant growth, increasing from 1.5 million tons in 1950 to 400.3 million tons in 2022 [3] (see Figure 1). The packaging industry accounts for the majority of this volume, approximately 44% as of 2021 (see Figure 2). The ever-growing demand for plastics leads to an annual increase in production rates, contributing to a substantial accumulation of plastic waste. This poses a severe environmental burden, particularly since the majority of plastics used are non-biodegradable, persisting in the environment for hundreds of years. The irresponsible disposal of these plastic wastes is a growing concern due to their detrimental impact on the ecosystem, human health, and marine life, with an estimated considerable quantity of 4–12 Mt/y ending up in the oceans [4,5].

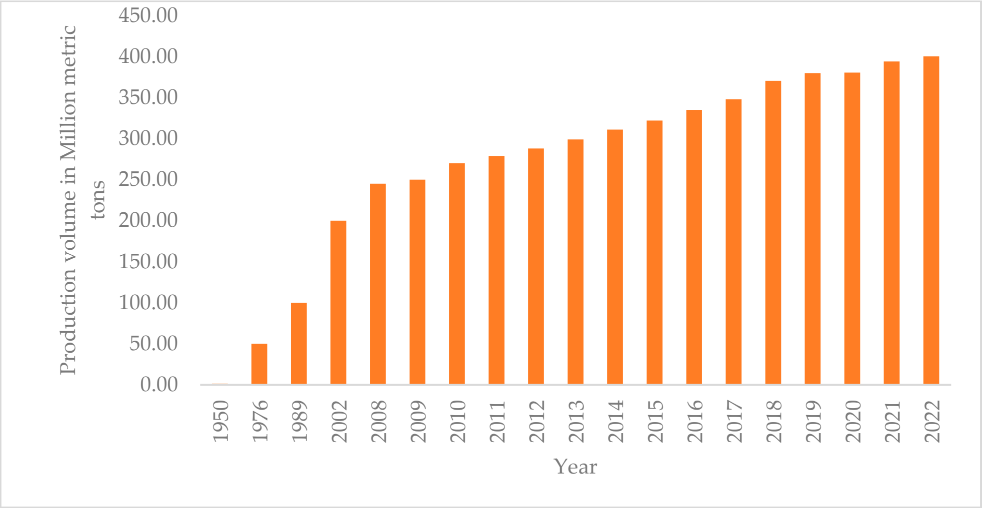


**Figure 1.** Production volume of plastics worldwide [3].

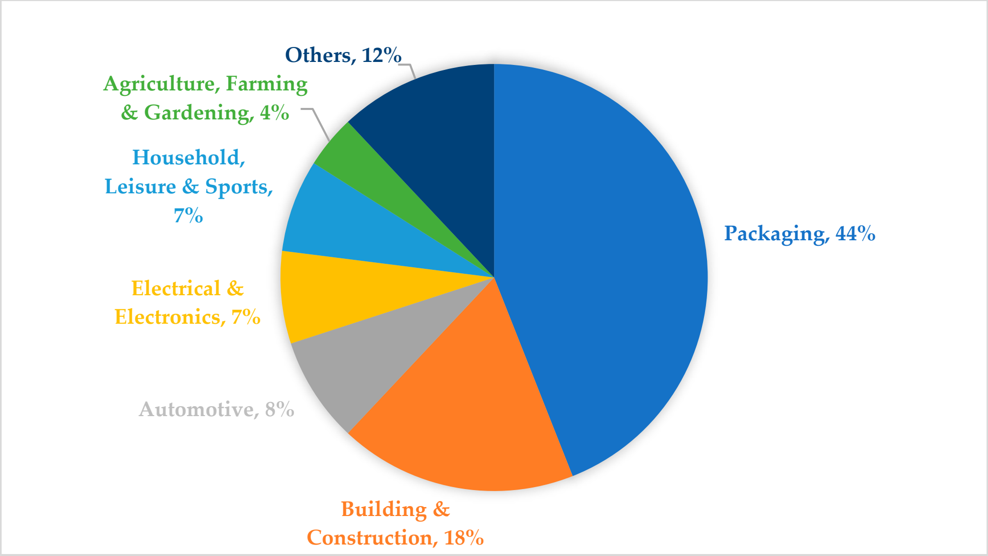


**Figure 2.** Global industry demand for plastics, 2021 [6].

The two most common end-of-life management practices for plastics are landfilling [5] and incineration [7–9]. Landfilling entails the utilisation of valuable land space for waste storage, resulting in the waste of energy inherent in plastics. Moreover, the degradation of plastic waste in landfills can release toxins and hazardous substances, contaminating soil and groundwater [8,10,11]. Due to unregulated landfill sites, degraded plastic waste may eventually reach water bodies, posing risks to marine life [12]. Annually, 8 million tonnes of plastic are dumped into the oceans, and by 2050, this figure is estimated to double, potentially resulting in oceans containing more plastic than fish [13,14]. These plastics can disintegrate into numerous smaller bits that may be ingested by marine animals due to ocean currents [10]. Incineration involves the combustion of plastics in the presence of complete oxygen to recover heat energy. While this process produces ash and flue gases as by-products, which are typically treated before release into the environment, it also generates significant amounts of greenhouse gases, such as carbon dioxide and nitrous oxide emissions [11,15–17]. With the recent Paris Agreement focused on reducing greenhouse gas emissions, incineration is no longer considered a viable waste management method [18]. The concept of a circular economy offers an attractive approach to reduce plastic accumulation in a sustainable manner by implementing the 4R concept of reduce, reuse, recycle, and recover. There has been an increased emphasis on the third R—recycle, depicted in Figure 3, as a key driver of sustainability. This increased attention has spurred a concentrated effort on employing chemical recycling techniques, such as pyrolysis, to retrieve valuable products from waste plastics such as useful chemicals, liquid fuel, or hydrogen [18].

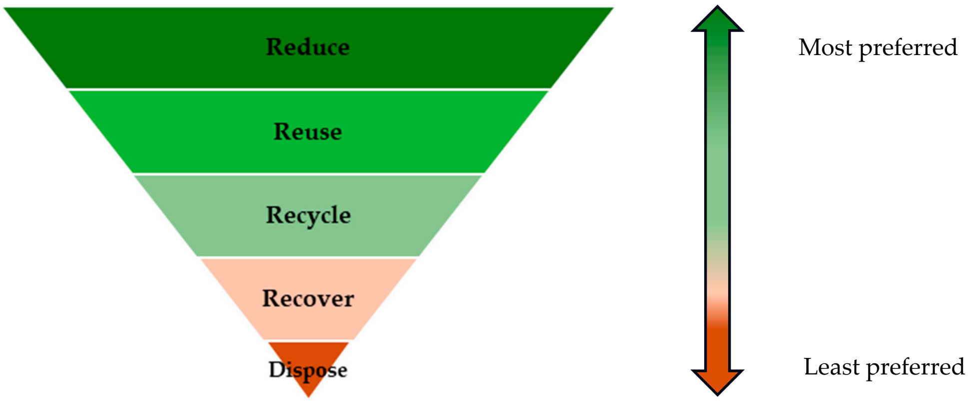


**Figure 3.** Waste management hierarchy (revised by the European Union Waste Framework Directive) [19].

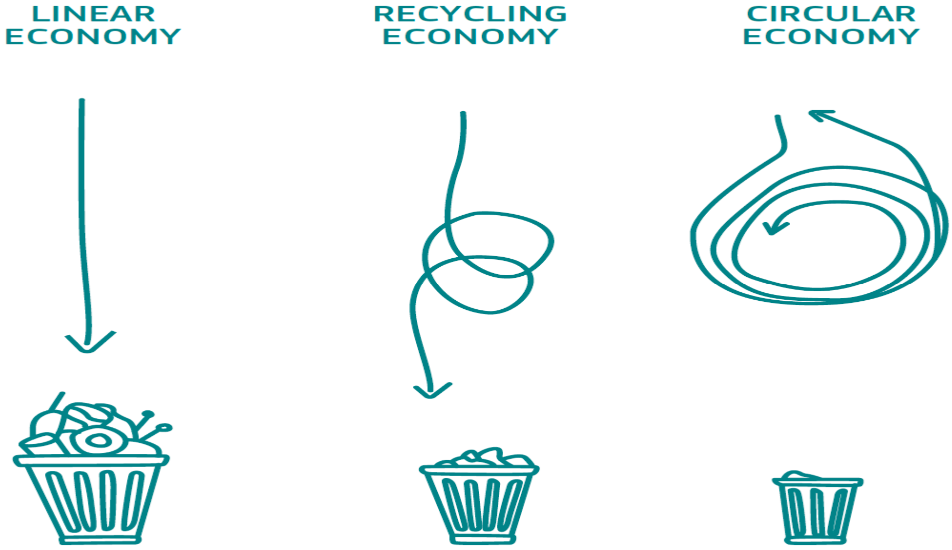
As the world increasingly emphasises the shift towards sustainable energy, pyrolysis, a chemical recycling technique, is gaining prominence. Previous review articles [20–22] have established the potential of plastic waste pyrolysis to yield valuable products in solid, liquid, and gaseous forms. Expanding upon this knowledge, this review article aims to explore the potential of pyrolysis and in-line reforming as an effective method for managing plastic wastes sustainably. The objectives of this study include investigating the mechanism of pyrolysis, the pyrolysis of various types of plastics as a single-type and as a mixture, analysing the influence of the process parameters on both the quantity and quality of resulting products, assessing the environmental impact of the pyrolysis process including energy consumption and greenhouse gas emissions, examining the emerging reactor technologies aimed at improving the efficiency of the pyrolysis process, exploring the integration of in-line reforming with pyrolysis to enhance the hydrogen yields, and discussing the catalysts employed in reforming to optimise hydrogen distribution and mitigate coke formation.

While this review extensively explores plastic waste pyrolysis and in-line reforming strategies, it is essential to acknowledge specific limitations within this study. Firstly, although the review discusses the influential process parameters of pyrolysis, it may not delve deeply into the kinetic modelling of pyrolyzing single or mixed plastics due to the constraints in the scope of this paper. A more thorough examination of pyrolysis kinetics could yield valuable insights into reaction pathways, rates, and temperature dependencies, thereby enriching our comprehension of the fundamental mechanisms propelling pyrolysis reactions and guiding optimisation strategies. Additionally, while the review predominantly focuses on conversion efficiency, product yields, the technical feasibility of pyrolysis technologies, and the sustainability of the pyrolysis process, it might not entirely encompass the downstream environmental impacts associated with the usage of pyrolysis-derived fuels, such as emissions from vehicle combustion. A comprehensive life cycle assessment is warranted to evaluate the overall environmental footprint and potential risks of employing these fuels in real-world scenarios. Therefore, future research endeavours should strive to address these knowledge gaps.

By synthesising a wide range of studies, this review paper provides a comprehensive understanding of the current state of knowledge in the field of pyrolysis and in-line reforming to produce liquid fuel and hydrogen. This synthesis of studies enables researchers, policymakers, and industry stakeholders to access and understand the collective findings and advancements in the field, and to identify research gaps and knowledge deficiencies in the current understanding of pyrolysis technologies. Moreover, by highlighting emerging innovations, this paper can inspire further research and innovation. Furthermore, the recommendations presented in this paper can guide researchers and policymakers in formulating effective strategies for sustainable waste management.

### *Sustainability of Pyrolysis Process*

The conventional linear model approach of producing, using, and disposing plastic as depicted in Figure 4a is no longer sustainable as various concerns regarding the protection of the environment and natural resources have risen [14,23]. Therefore, an alternative, more sustainable approach gaining recognition is the circular economy framework [24], shown in Figure 4c. This framework aims to keep resources in use for longer periods, extract the maximum value from them, and recover and regenerate products at the end of their life cycle [24]. This approach promotes responsible and cyclical resource utilisation, minimising material input and waste generation, thereby reducing the reliance on natural resources for economic growth [25].



(**a**) (**b**) (**c**)

**Figure 4.** Illustration of different economies by the European Commission [26]. (**a**) Linear economy: make, use and dispose model (**b**) Recycling economy: make, use, recycle and dispose model (**c**) Circular economy: make, use and regenerate model.

Although incineration reduces the volume of waste by 90% [10], from the perspective of circular economy, it results in the loss of material from the value chain. This lost resource then needs to be replaced through the production of virgin plastic [7]. Landfilling, on the other hand, avoids the rapid release of carbon into the atmosphere unlike incineration, but traps the plastic on land, hindering further utilisation within the value chain, which contradicts the principles of a circular economy [7,13]. Additionally, the increasing demand for plastic requires the replacement of trapped plastic with virgin plastic, further depleting finite resources and contributing to environmental emissions associated with fossil fuel extraction and virgin plastic production [7]. Mechanical recycling, initially appearing as a promising solution, ultimately falls short of addressing the plastic waste problem. As depicted in Figure 4b, this process essentially delays the inevitable disposal of plastics into landfills and oceans. The mechanical process gradually deteriorates the quality of plastics, rendering them unsuitable for their original purpose after undergoing a few cycles. This degradation is attributed to the heating and reshaping involved, resulting in a decrease in molecular weight and the loss of key properties like clarity and strength [1,7]. To effectively manage plastic usage and promote sustainable economic growth, a holistic close-loop approach is necessary. In contrast to mechanical recycling, chemical recycling methods such as pyrolysis emerges as a viable method for recovering materials and energy from plastic waste [1].

## 2. Plastic Pyrolysis

### *2.1. Plastic*

Plastics are organic polymers formed through linking monomers together in repeated units to form a long chain through a process known as polymerisation. The Resin Identification Code system, developed by the Society of Plastic Industry (SPI) (Washington, DC, USA), classifies plastics into seven various groups (see Figure 5) based on their application and chemical structure [27].

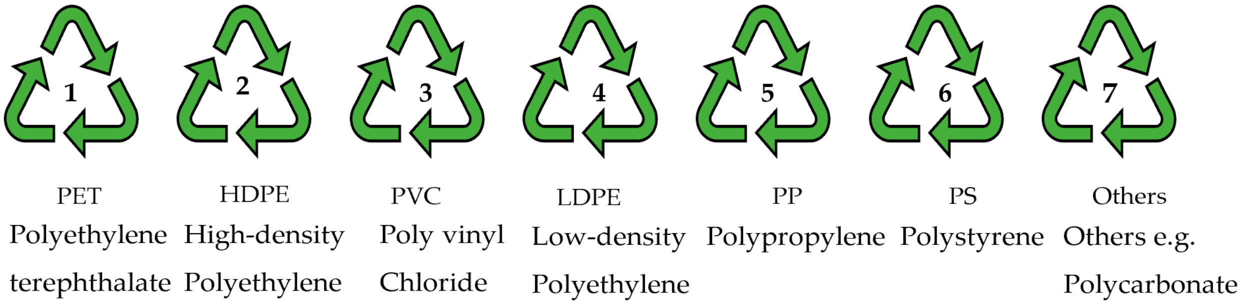


**Figure 5.** Resin Identification codes developed by the Society of Plastic Industry (SPI).

The different compositions for plastics are typically stated in terms of their proximate and ultimate analysis. Table 1 shows the proximate and ultimate analysis of the various plastic types. Proximate analysis is a technique employed to evaluate the chemical composition of a plastic material using four distinct parameters: volatile matter, ash content, moisture content, and fixed carbon [5]. Research indicates that the volatile matter and ash content are primary factors influencing the yield of liquid oil in the pyrolysis process. A high volatile matter tends to enhance liquid oil generation, whereas an elevated ash content tends to inhibit it, leading to increased gaseous yield and char formation [28]. The ash content measures non-volatile substances, most frequently metals and inorganic substances. A higher ash content implies a lower proportion of plastic in a given sample available for processing [29]. Most plastics, upon proximate analysis, are composed of a high level of volatile matter and a low ash content (see Table 1). These characteristics suggest that plastics possess significant potential for producing substantial amounts of liquid oil when subjected to pyrolysis [30]. Ultimate analysis, also referred to as elemental analysis, is a method to determine the proportion of CHONSCl elements (carbon, hydrogen, oxygen, nitrogen, sulphur, and chlorine) present in plastic. Plastics with a high volatile matter content, alongside an elevated amount of carbon and hydrogen, exhibit favourable attributes for the pyrolysis process, leading to a high conversion of the plastic materials into liquid and gaseous products [31].

**Table 1.** Proximate and ultimate analysis of various plastic types.

| **Proximate Analysis** | **PET [32]** | **HDPE [33]** | **PVC [34]** | **LDPE [35]** | **PP [31]** | **PS [33]** |
|---|---|---|---|---|---|---|
| Moisture content (%) | 0.27 | 0.15 | 0.01 | 0.76 | 0.20 | 0.79 |
| Fixed carbon (%) | 17.89 | 4.08 | 3.47 | 2.82 | 1.20 | 0.80 |
| Volatile matter (%) | 79.92 | 92.04 | 96.52 | 95.59 | 97.80 | 98.31 |
| Ash (%) | 1.92 | 3.73 | 0.00 | 0.83 | 1.90 | 0.10 |
| **Ultimate analysis** | [36] | [33] | [34] | [35] | [34] | [33] |
| Carbon (%) | 62.51 | 81.69 | 37.78 | 85.68 | 85.71 | 93.32 |
| Hydrogen (%) | 4.19 | 13.72 | 4.83 | 14.20 | 14.18 | 6.14 |
| Oxygen (%) | 33.30 | 0.26 | 0.36 | 0.02 | 0.04 | 0.50 |
| Nitrogen (%) | 0.00 | 3.75 | 0.14 | 0.05 | 0.03 | 0.04 |
| Sulphur (%) | 0.00 | 0.58 | 0.16 | 0.00 | 0.04 | 0.00 |
| Chlorine (%) | 0.00 | 0.00 | 56.73 | 0.05 | 0.00 | 0.00 |

### 2.2. Pyrolysis

Pyrolysis is the thermal decomposition of organic materials in the absence of oxygen, typically occurring at moderate temperatures ranging from 350 to 700 °C, influenced by various parameters to yield gas, liquid, and solid products. The solid product, known as char, remains as residue after decomposition, while the gas and liquid products are the obtained volatiles [37]. Pyrolysis is an endothermic process; hence, a supply of energy is required for the process to be initiated. Depending on the type of plastic being processed, pyrolysis results in the breakdown of plastics into components such as hydrogen, methane, light hydrocarbons ($C_2$-$C_4$), liquid/wax hydrocarbons ($C_5$-$C_{35}{}^+$), and a solid residue [38]. The composition and energy content of the pyrolysis products are significantly influenced by the waste input, which can vary considerably.

### 2.3. Mechanism of Plastic Pyrolysis

When the plastic is heated in an inert environment, heat is initially directed into the interior of the plastic molecule, raising its temperature and modifying the physical properties of the plastic [39]. The plastics undergo the following three main thermal transitions as the temperature increases: glass transition, melting phase, and decomposition phase. The glass transition and melting temperatures are influenced by the composition and structure of the polymer and is primarily attributed to the various side chains [40]. At room temperature, the plastics (specifically thermoplastics) typically exist in a solid, glassy state [41]; however, as the temperature rises above the glass transition temperature $T_g$, the Van der Waal forces responsible for molecular attraction weaken due to the increased vibration of the molecules. Consequently, the polymer chains gain sufficient kinetic energy to transition into a rubberlike state, allowing them to move freely. As the temperature continues to rise and reaches the melting point $T_m$, the rubberlike polymers further transform into liquid-like substances. This transition process from the glassy state to liquid is depicted in Figure 6.

With further temperature increase, the kinetic energy becomes sufficient to overcome the bond dissociation energy of the C-C bonds, leading to the decomposition of the plastic. Chemical changes take place within the polymer as the temperature exceeds the decomposition temperature. Initially, the reaction yields wax as a product, composed of shorter hydrocarbon chains when compared to the polymer, but still relatively long. As the wax undergoes further cracking, they eventually become short enough to be volatised, producing volatiles (gas and liquid). These volatiles are emitted at high temperatures, with some of the heat being transferred back into the feedstock. After a specific duration, the entire feedstock is converted into volatiles, leaving behind the non-volatile fraction as solid residue. The further cracking of the volatiles results in the formation of non-condensable gases due to secondary reactions. As heat dissipates, the condensable volatile fraction results in the formation of liquid products [38]. A visual representation of this mechanism can be found in Figure 7.

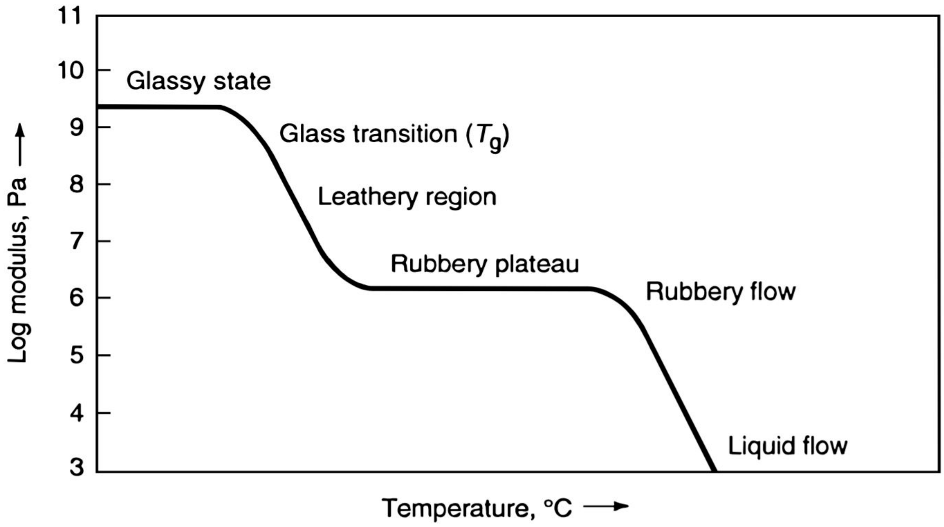


**Figure 6.** Elastic modulus of plastics vs. temperature [39,42].

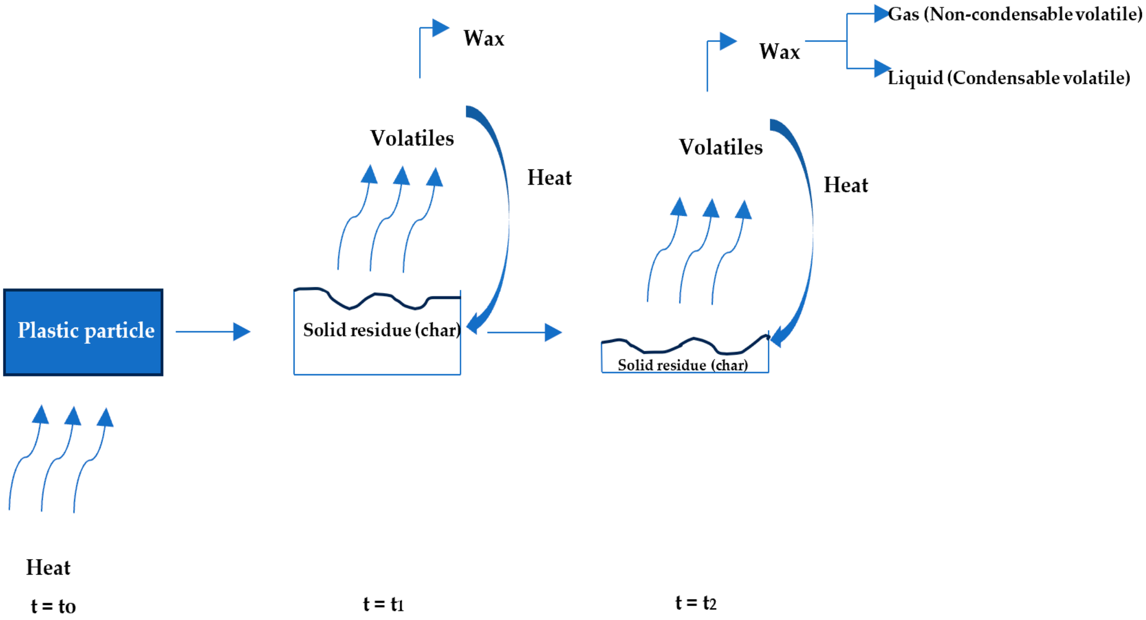


**Figure 7.** Mechanism of plastic waste pyrolysis [38,43].

### 2.4. Factors Affecting Plastic Pyrolysis

The operating parameters, which influence the rate of degradation reactions, have a significant impact on the selectivity and quality of pyrolytic products. Optimising pyrolysis conditions and increasing the efficiency of transforming plastic wastes into valuable products both require an understanding of these factors.

#### 2.4.1. Temperature

Temperature plays a crucial role in pyrolysis as it directly impacts the cracking process of the plastics. As the pyrolysis temperature rises, the liquid product diminishes while the generation of gaseous products increase [44,45]. This is attributed to the increased frequency of C-C bond cracking at higher temperatures, resulting in the generation of lighter hydrocarbons with shorter carbon chains (gaseous product, $C_1$-$C_4$) [46]. Moreover, under mild temperature conditions, the polymer can be broken into medium-sized chains (liquid product, $C_5$-$C_{40}$). For instance, HDPE pyrolysis was conducted by Marcilla et al. [47] in a batch reactor at 550 °C, obtaining 84.7 wt% liquid oil and 16.3 wt% gas. Additionally, Singh et al. [48] observed a shift in the distribution of PP pyrolysis products when the temperature was raised from 500 to 600 °C, increasing the gas yield from 8.5% to 13.5%. This indicates that an increase in temperature decreases the oil yield while increasing the gas yield. The concentration of aromatic hydrocarbons in liquid products is also affected by the pyrolysis temperature. With the occurrence of secondary reactions, the concentration of aromatic and poly-aromatic compounds in the liquid products increases as the temperature rises [49–51]. For instance, Williams and Williams [52] examined the fast pyrolysis of plastic waste within a temperature range of 500–700 °C, noting a rise in the number of aromatic compounds in the oil with increasing temperature. In another study investigating the impact of temperature on HDPE pyrolysis by Gracida-Alvarez [53], higher temperatures were found to promote the synthesis of aromatics and light aliphatics, facilitating degradation into wax and diesel range aliphatics [28]. Due to the presence of aromatic and poly-aromatic hydrocarbons, the generated oil may exhibit increased viscosity at higher pyrolysis temperatures. Conversely, the production of viscous oil could also occur at lower temperatures due to the increased number of long hydrocarbon chains which are not properly broken-down being present in the oil [46]. The temperature range for thermal degradation for most plastics is between 420–500 °C; nevertheless, a higher temperature (up to 550 °C) is recommended for HDPE [21,48]. On the other hand, if the temperature is below this range, the plastics may not be sufficiently decomposed, leading to the presence of solid feedstocks in the reactor.

### 2.4.2. Heating Rate and Residence Time

Generally, residence time is the average duration that the particles spend in the reactor, and this can influence the yield and distribution of pyrolysis products [54]. The residence time of the plastic feedstock is directly influenced by the heating rate [5,8]. While slow pyrolysis ($\Delta T < 10$ °C/min) prolongs the plastic residence time, fast pyrolysis ($\Delta T > 10$ °C/min) shortens it. To achieve the optimum liquid yield, it can be inferred that the residence time depends majorly on the heating rate [8]. The definition of residence time varies according to the type of pyrolysis. Fast pyrolysis operates primarily as a continuous system; hence, the residence time is defined as the contact time of the feedstock on the heated reactor surface until the reaction is complete. In contrast, slow pyrolysis operates in a batch configuration, so the residence time is defined as the time from the commencement of the feedstock heating to the removal of the products from the reactor [5,55]. A prolonged residence time usually increases the possibility of secondary reactions such as additional cracking, alkylation, isomerisation, and hydrogenation/dehydrogenation [28,56], resulting in a higher yield of thermally stable products, including light molecular weight hydrocarbons and non-condensable gas, while reducing the liquid yield [5,21,54]. However, Mastral et al. [57] found that the residence time has a minimal effect on the yield of liquid and gas when the temperature rises above 685 °C. Hence, the impact of the residence time on the yield of pyrolysis products is more evident at lower temperatures than higher temperatures [54]. For a slow heating rate, the slower conversion of plastic allows the volatiles to stay in the heating zone for a longer duration, resulting in the formation of low-carbon range hydrocarbons or more char due to repolymerisation, while more long-range hydrocarbons such as wax are formed at higher heating rates [5]. For instance, as observed by Encinar and Gonzalez [58], the pyrolysis of PS at 5 K/min yielded 1.96% char, 95.77% oil/wax, and 2.28% gas; at 10 K/min, yielded 1.81% char, 95.79% oil/wax, and 3.40% gas; at 15 K/min, yielded 1.60% char, 92.75% oil/wax, and 5.65% gas; and at 20 K/min, yielded 1.04% char, 92.65% oil/wax, and 6.31% gas. In addition, for commercial applications, the heating rate would also be a significant parameter as it would be dependent on the reactor being utilised [58]. Therefore, a short residence time and precise temperature control, considering the maximum degradation temperature of the plastic type, are required to optimise the liquid yield.

### 2.4.3. Pressure

Plastic wastes may be pyrolyzed at pressures ranging from a vacuum environment (<0.1 atm) to atmospheric pressure (1 atm) [59] and even elevated pressures (above atmospheric pressure). However, most plastic pyrolysis investigations have been conducted under atmospheric pressure [30], primarily due to the significant operating cost advantages, with only a limited number of studies being conducted at vacuum pressures or elevated pressures [15,60]. As a result, the influence of pressure is not fully presented in the literature, representing a research gap. Lopez et al. [61] investigated the continuous pyrolysis of used tyres under vacuum (25 and 50 kPa) and atmospheric pressures in a pilot plant conical sprouted bed reactor. It was observed that the major effect vacuum pyrolysis had over pyrolysis at atmospheric pressure was the increase in the diesel fraction yield of the liquid product [30]. Vacuum pyrolysis enhances wax generation. However, some limitations include poor heat transfer, high maintenance, and investment costs [5]. A high rate of monomer recovery and a lesser rate of Benzene, Toluene, Ethyl benzene, and Xylene (BTEX) production was observed by Zayoud et al. [62] under vacuum pyrolysis, which could be attributed to the quick removal of pyrolytic vapours from the reactor through vacuum suction, preventing the formation of BTEX and other secondary products that could be formed from secondary reactions. Moreover, Parku et al. [63] also reported that the quick extraction of pyrolytic vapours inhibited the reduction of heavy hydrocarbons (wax) to light oil and gases.

Like the residence time, the effect of pressure was also found to diminish at higher temperatures [21,30]. For instance, Murata et al. [64] studied the impact of pressure on the HDPE pyrolysis in a continuous flow reactor operating at 0.1–0.8 MPa. According to the studies, the gaseous product increased greatly from 6 wt% to 13 wt% at 410 °C, but only slightly from 4 wt% to 6 wt% at 440 °C, as the pressure increased from 0.1 to 0.8 MPa. Similarly, Chang [15] observed a steady decline in plastic oil production from 95 to 89 wt% as the pressure increased from 6 to 51 bar with more produced gas at 380 °C. This indicates that pressure is a temperature-dependent factor, having a considerable impact at lower temperatures and a diminishing effect at higher temperatures in pyrolysis [15,30]. However, according to another study conducted by Newalkar et al. [65], the pyrolysis products obtained at 600 °C and 15 bar were comparable to those obtained at 800 °C and 5 bar. Thus, more investigations are required to determine how pressure affects plastic pyrolysis.

### 2.4.4. Catalyst

In the presence of a catalyst, pyrolysis is categorised as catalytic pyrolysis, and in the absence of a catalyst, it is known as thermal pyrolysis. Given that pyrolysis is an endothermic process, it is considered energy-intensive [10,21,30]. Hence, catalysts can be employed to lower the temperature and reaction time required for pyrolyzing the plastics [21,30]. Due to the enhanced degradation of carbon bonds, catalytic pyrolysis tends to generate more gas and less liquid yield than thermal pyrolysis. For instance, according to Rehan et al. [66], the thermal pyrolysis of LDPE yielded a higher liquid yield (80.8%) than the catalytic process (54%). However, a higher aromatic liquid yield than the thermal process was achieved due to the greater selectivity towards aromatics generation [67]. In general, catalysts can be homogeneous or heterogeneous, depending on their phase and the reaction phase. While the heterogeneous catalysts have different phases from the reaction phase (solid), homogeneous catalysts occupy the same phase as the reaction mixture (usually a liquid solution). The most common type utilised in plastic pyrolysis are the heterogeneous catalysts because they are solid materials that can be isolated from the final products and they can withstand severe conditions (up to 1300 °C and 35 MPa). Some common types of heterogeneous catalysts are mesostructured catalyst, conventional acid solid, metal supported on carbon, basic oxides, and nanocrystalline zeolites (such as HUSY, Y, HY, HZSM-5). Heterogeneous catalysts receiving more attention in research are Silica-Alumina (SA), FCC, and Zeolite catalysts [21].

#### 2.4.5. Feedstock Composition

The composition of the feed has an impact on the pyrolysis products and their yield [54]. The main products of pyrolysis are directly related to the chemical structure and degradation of the resin [68]. For example, PET is not a desirable feedstock component for pyrolysis because of the presence of oxygen and the aromatic benzene ring. This results in the formation of terephthalic acid and benzoic acid, lowering the calorific value of the fuel to 28.2 MJ/kg and restricting its potential applications. Furthermore, the presence of oxygen leads to corrosion in the experimental unit, contributing to the instability of the liquid oil. PVC is another unfavourable feedstock component as its large concentration of chlorine content (57%) decreases the calorific value of the liquid oil to 21.1 MJ/kg and produces HCl in the gas stream. On the other hand, PE (HDPE, LDPE), PS, and PP are suitable for pyrolysis as they do not contain heteroatoms like PET and PVC [10]. The degradation of PS yields a liquid product with an increased aromatic content, approximately 97 wt%, serving as a source of value-added aromatics [10]. This can be attributed to the polycyclic nature of polystyrenes and the difficulty associated with converting cyclic compounds into aliphatic chains or alkene compounds due to thermodynamics. Furthermore, PS produces the highest liquid yield when compared to other plastics owing to its higher percentage of volatile matter [5]. PE has a long carbon chain, leading to its initial transformation into wax at 350 °C and subsequently into waxy oil at 425 °C, resulting in 89.5% liquid fraction. Moreover, PE degradation predominantly yields alkanes. Both polyethylene and polypropylene break down into a range of paraffins and olefins, with the ratio of paraffin to olefin decreasing as the temperature and time increase [68].

#### 2.4.6. Type of Reactors

The reactor design has a significant impact on the efficiency of the reaction, residence time, mixing of plastics and catalysts, and heat transfer to produce the desired product [21]. Due to the sticky nature and low thermal conductivity of the plastics, the transport effects and temperature distribution within the reactor must be considered [10]. Reactors used for pyrolysis are either in batch/semi batch or continuous flow configuration [21].

##### Batch/Semi-Batch Reactors

Batch reactors operate as closed systems where neither reactants nor products are introduced or removed during the reaction. Conversely, semi-batch reactors permit the simultaneous addition of reactants and removal of products, offering advantages in the reaction selectivity and flexibility [21]. Batch/semi-batch reactors are frequently utilised in lab-scale plastic pyrolysis because of their simplicity in the design and ease of control of operational parameters [5,10,21]. However, they are not suitable for large-scale operations due to their labour intensiveness and non-uniformity across batches [5]. Moreover, they may not be ideal for catalytic pyrolysis because of the possibility of coke formation on the catalyst's outer surface, potentially reducing the overall product yield [54]. Some other operational drawbacks associated with batch/semi-batch reactors include a prolonged residence time, difficulties in char removal, and inconsistencies in the product yield and quality across batches. The prolonged residence time can be due to its poor heat transfer rate, which is typical with batch reactors [5,10,21]. Additionally, temperature gradients affect batch and semi-batch reactors because of the low thermal conductivity and high viscosity of plastics. The yield and quality of the liquid product can be improved through utilising a stirrer with an appropriate design and speed to regulate the temperature uniformity and enhance the mixing of the reactants [5].

Continuous Flow Reactors

These types of reactors allow for the continuous inflow of reactants and the removal of products during the process. As a result, they are more adaptable for large scale operations than batch reactors. Some of these types of reactors include a fixed bed, fluidised bed, conical spouted bed reactor, and rotary kiln [15]. They are commonly used in plastic pyrolysis. In addition to them being effective at the pilot scale, they have also shown positive feasibility.

a. Fixed bed reactor: This type of reactor can be used for catalytic pyrolysis and is predominantly used for laboratory-scale studies due to its ease of design. However, it has certain limitations including a restricted available surface area for the catalyst and challenges relating to the irregular shape and particle size of the plastics used as feedstock, which can pose difficulties during feeding [18]. The feedstock is introduced into the reactor, usually made of stainless steel and heated externally with an electric furnace. Typically, the heating rate of a fixed bed reactor is usually low [17]. Moreover, since there is no movement of feedstock during the process, achieving the uniform heating of a significant amount of municipal solid waste (MSW) on an industrial scale can be challenging, unless technologies such as heat pipes are employed to improve the heat transfer [17,69]. Consequently, this type of reactor is mostly employed for gathering experimental data on the pyrolysis parameters and its products [21] or utilised as secondary reactors [54].
b. Fluidised bed reactor (FBR): Unlike the fixed bed reactor, the fluidised bed reactor has better heat and mass transfer efficiencies [10]. This reactor is usually employed to examine the behaviour of fast pyrolysis due to its ability to effectively blend feedstock and achieve high heating rates. Fluidised bed reactors offer a significant advantage in their ability to control operational parameters like temperature, providing direct flexibility to achieve the desired product distribution. Furthermore, fluidised bed reactors are renowned for their excellent heat and mass transfer capabilities, facilitated by a heated fluidising medium within the reactor [21]. The heat transfer characteristics are improved due to the remarkable mixing within the bed induced by the motion of fluidised particles. When compared to fixed bed reactors, fluidised bed reactors reduce the time needed for degradation. The favourable heat transfer rate of this reactor is notable, especially considering the low thermal conductivity of plastics and their melt [10]. Additionally, this reactor type is well-suited for catalytic pyrolysis. Unlike in fixed bed reactors where the catalyst is packed into a static bed, in fluidised bed reactors, the catalyst rests on a distributor plate through which the fluidising gas passes [21]. The industrial application of this reactor presents challenges when handling non-uniform particle sizes, as it necessitates different velocities for fluidising particles of varying shapes and sizes [10].
c. Conical spouted bed reactor (CSBR): This reactor is a type of fluidising bed reactor that utilises spouting characteristic behaviours. It has a small inlet connected to a fixed-diameter column containing static spouting media via a conical section. In contrast to a fluidised bed reactor, this reactor can effectively handle particles with a wide size distribution, sticky solids, irregular textures, and varying densities. Sand is employed in this reactor as a heat transfer medium due to its crystalline structure, which improves heat transfer to plastic melts surrounding the particle, thereby decreasing de-fluidisation problems [10]. This reactor offers attractive conditions for the pyrolysis of plastic wastes due to lower attrition, low bed segregation, and drops in pressure in comparison to the fluidised bed reactors, as observed by Elordi et al. [70]. Waste plastic melt, as they are fed into this type of reactor, and because of their cyclic movement, coat the sand particles uniformly. It provides a high heat transfer between phases and minimal de-fluidisation issues when handling sticky solids. The action of the spout and the solid flow pattern contribute to a decrease in the formation of agglomerates. Additionally, it is very versatile in terms of gas flow, enabling operations with short gas residence times. This reactor is appropriate for

flash pyrolysis because of its excellent solid movement, resulting in rapid heat transfer rates between phases. Notably, the CSBR is capable of continuous operation, a crucial feature for implementing pyrolysis on a larger scale [17,21]. The spouted bed design proved effective in wax generation for pyrolysis at low temperatures. However, some of the technical limitations during the reactor's operation include catalyst feeding, catalyst entrainment, and the collection of products (solid and liquid) [18,71]. Also, the high running costs associated with its complex design, which necessitates the use of numerous pumps in the system to provide sufficient pressure for spouting behaviours, makes it less favourable [5,21].

d. Rotary/screw kiln reactor: A rotary kiln reactor is recommended for the industrial pyrolysis of plastics, given its capability in handling irregular particles with a wide range of heat capacity. It is beneficial in terms of the heat input to the feedstock material. By varying the screw speed which influences the product distribution, the heat input and residence time can be regulated. To optimise the product distribution, rotary kiln reactors set at an angle can help control the degree of mixing [10]. Rotary kilns are less complicated to operate than fluidised bed reactors and offer better heat transfer to the feedstock than fixed bed reactors. A crucial parameter in the pyrolysis process of rotary kilns is the residence time of the feedstock in the reactor since it affects how much energy the charge receives at a specific heating rate. As reported by Fantozzi et al. [72], the residence time in rotary kilns is often a function of the mean volumetric flow and kiln rotation speed [17]. Good mixing is enabled by the slow rotation of the inclined kiln in order to yield more homogenous pyrolytic products [17,73]. The heating is uniform; however, because only the reactor wall transports heat, the heating is relatively slow. These reactors are widely used for conventional pyrolysis (slow pyrolysis), usually carried out at 500 °C for a residence time of 1 h [73]. Similar to the CSBR, these reactors are highly flexible for treating mixed waste plastic with a wide variety of shape and size distributions, but with a simpler design and mode of operation [5]. More benefits of using this reactor type over other reactors are low capital costs, the flexible modification of residence times and temperature control, good mixing, and an ease of maintenance [73].

In addition to the above reactors, some other technologies including microwave-assisted and plasma reactors are in the early stages of development. These technologies and their potential are discussed below:

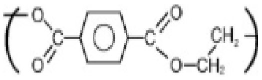
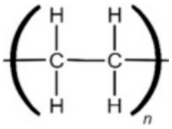
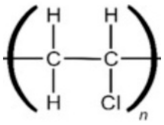
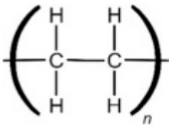
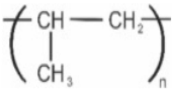
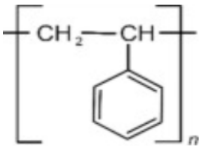
e. Microwave-assisted technology: This technology has not received as much research attention as other reactor setups. It is an attractive technique in providing volumetric heating at improved heating efficiencies [73]. In this type of reactor, the plastic feedstock is mixed with a microwave absorbent material, such as particulate carbon [74]. This material provides the required heating for feedstock conversion into the desired product through transforming microwave radiation energy into thermal energy [8,21]. In the electromagnetic spectrum, microwave frequencies fall between infrared and radio frequencies [17]. Microwaves have wavelengths between 1 mm and 1 m, and their corresponding frequencies range from 300 GHz to 300 MHz, respectively. The most popular microwave frequencies are 2.45 GHz and 916 MHz [17,75]. Suitable materials for converting microwave radiation into heat at a frequency of 2.45 or 0.972 GHz are metals or carbon. Moreover, the reducing nature of carbon prevents undesired oxygenated compounds from forming if the plastic waste contains oxygen-bearing contaminants. Unlike conventional reactors, microwave energy is supplied directly to the material via molecular interactions with the electromagnetic field. This leads to a shorter time being required for heating the surrounding area, resulting in a reduced heating time and lower operational costs. Plastics have low dielectric constants [8]; therefore, a microwave absorbent with a high dielectric constant is required to be mixed with the plastics in order to absorb the microwave energy and attain the required temperature [30]. The efficiency of microwave heating is significantly dependent on the dielectric properties of the material [76]. A pyrolytic temperature of 1000 °C can be attained quickly using microwave heating because of the strength and amount of microwave absorbent materials used [8]. Therefore, this technique offers many benefits over conventional heating methods, including rapid and uniform internal heating rates, operational flexibility (prompt response for quick start-up and shutdown), economical and high-product selectivity, and consistent volumetric heating. Unfortunately, research on microwave-assisted reactors is still in its early stages, and there are still many challenges to its usage [8,21]. For instance, Lam and Chase [74] employed microwave pyrolysis in waste-to-energy processes, accurately characterising the process, but concluded that the development of industrial microwave heating applications was constrained by an apparent lack of technical knowledge in terms of designing commercial equipment for this pyrolysis and a lack of understanding of microwave systems [17]. Using microwave absorbents on an industrial scale may be very challenging given that the heating efficiency may vary greatly for different absorbents [8]. The varying composition of plastic wastes and the lack of knowledge regarding the dielectric characteristics of various materials further compound this limitation. In addition to the universal parameters for all reactors, other factors influencing the efficiency of microwave pyrolysis include the microwave output power, microwave type (single-mode or multimode), reactor design/type, and microwave receptor properties (size, type, and amount/concentration) [5]. The microwave heating in the pyrolysis of polyolefin wastes (PP and HDPE) was investigated by Undri et al. [77] using two types of microwave absorbers, namely carbon and tyres. According to the results, HDPE had the highest liquid yield at 83.9 wt%, whereas PP had a yield of 74.7 wt%. Microwave powers ranging from 3 to 6 kW were employed. The results indicated that, due to the reduction in the residence time caused by the high power, more polymers were converted into liquid rather than gases. Additionally, utilising tyre as the microwave absorber increased the solid residue (33 wt%) due to the other tyre components that could not be pyrolyzed. However, when carbon was used as the microwave absorber, the solid residue was far less (0.4 wt%) [21,77]. Therefore, carbon material was a better microwave absorbent with a high capacity to absorb and transform microwave energy into heat [77]. In addition, to maximise the liquid yield, the microwave power and absorber type must be prioritised [21]. A pyrowave is a recently developed microwave pyrolysis unit with the aim to recover styrene from polystyrene waste [78].

f. Plasma reactors: This is also a relatively new pyrolysis technology. It has been gaining increased attention because of its manageability, rapid heating, and ability to function effectively at a relatively low power consumption [17,79]. Plasma, characterised as an ionised gas, is often considered as the fourth state of matter following solid, liquid, and gas. Typically, it is considered as a gaseous mixture of positively charged ions and negatively charged electrons, produced either through the intense heating of a gas or the exposure of the gas to a strong electromagnetic field. The three categories of plasmas are high-temperature plasma (also known as Equilibrium plasma), thermal plasmas (quasi-equilibrium plasma), and non-equilibrium plasma (also cold plasma) [80]. Thermal plasma can be generated by employing direct current, alternating current, microwave discharge, or radio frequency induction. Plasma can also be produced using a 2.45 GHz magnetron from a commercial microwave oven [17]. When waste-derived carbonaceous particles are introduced into plasma, the rapid heating by the plasma induces the release and cracking of volatile materials. This process generates hydrogen and light hydrocarbons such as acetylene and methane [17,81]. Huang and Tang [81] conducted a review on the thermal plasma pyrolysis of organic waste, noting the production of the following two main streams: a solid residue and a combustible gas. The gas yield, composed of $H_2$, $CH_4$, CO, $C_2H_2$, and $C_2H_4$, ranged from 50 to 98 wt%, with the heating value varying from 4 to 9 MJ/Nm$^3$. Therefore, it can be utilised directly as fuel in many energy applications, including direct firing in boilers, gas engines, and gas turbines [17].

### 2.5. Pyrolysis of Single-Type Plastics

Several researchers have investigated the pyrolysis of single plastics utilising various reactor designs and reaction conditions. The chemical structure and applications of the various plastic types are shown in Table 2. This section is a review of the literature on the pyrolysis of single-type plastics as reported by various researchers.

**Table 2.** Chemical structure and applications of various plastic types.

| Plastic Resin Code | Chemical Structure [8] | Applications [5,8,82,83] |
|---|---|---|
| 1<br>PETE<br>Polyethylene terephthalate |  | Soft drink and mineral water plastic bottles, food trays, textiles, and fibres |
| 2<br>HDPE<br>High-density Polyethylene |  | Detergent and bleach containers and milk and shampoo bottles |
| 03<br>PVC<br>Polyvinyl Chloride |  | Plumbing pipes, wall and floor coverings, and wiring and cable insulation |
| 4<br>LDPE<br>Low-density Polyethylene |  | Cling wraps, Ziploc, and grocery and trash bags |
| 5<br>PP<br>Polypropylene |  | Microwave-safe containers, bottle caps, and reusable food containers |
| 6<br>PS<br>Polystyrene |  | Plastic utensils, Styrofoam, and disposable cups |
| 7<br>OTHER | | Baby bottle, 5-gallon water bottle, fibreglass, and acrylic nylon |

#### 2.5.1. Polyethylene (PE)

PE is a polyolefin polymer, considered among the most widely used plastic, with an annual production of about 80 million tonnes globally [84]. It can be categorised majorly into two groups based on density namely: low-density polyethylene (LDPE) and high-density polyethylene (HDPE). While LDPE is used for plastic bags, wrapping foil, and trash bags, HDPE is utilised in making toys, bottles, and oil containers [85]. The primary components of oil from PE pyrolysis are typically aliphatic substances, such as paraffins and olefins. Depending on the operating conditions, the specific alkene and alkane composition can vary significantly [8].

##### High-Density Polyethylene (HDPE)

HDPE is a polyethylene polymer, characterised by little branching, a higher density, and a high degree of crystallinity, resulting in its high strength characteristics. The compact alignment (linear arrangement with less branching) of the molecules in HDPE leads to a higher density, rendering it stronger, stiffer, and less translucent when compared to LDPE [10,86]. Regarding the thermal degradation mechanism of polyethylene, it has been found that HDPE initiates degradation within a temperature range of 651–677 K (378–404 °C) and undergoes complete degradation within a temperature range of 790–854 K (517–581 °C) [82]. At temperatures above 600 °C, a significant decrease in liquid yield and an increase in gaseous products are observed. In a study conducted by Geyer et al. [87], the pyrolysis of HDPE produced 70% of oil, predominantly composed of 96% aliphatic hydrocarbons ($C_8$–$C_{12}$ range) and trace amounts of longer chain hydrocarbons (>$C_{12}$) [88]. Al-Salem et al. [89] pyrolyzed HDPE between 500 and 800 °C and obtained maximum liquid and gaseous yields at 550 and 700 °C, respectively. Kumar and Singh [90] investigated the thermal pyrolysis of HDPE in a semi-batch reactor at a temperature range of 400–550 °C. At 550 °C, the study observed a maximum liquid yield and gaseous product of 79.08 wt% and 24.75 wt%, respectively, along with the generation of a dark brownish oil. Furthermore, Marcilla et al. [47] pyrolyzed HDPE plastics at 550 °C, resulting in an 84.7 wt% liquid yield and a 16.3 wt% gaseous yield. These results suggest that higher temperatures enhance the production of liquid oil from HDPE. However, excessively high temperatures may reduce the liquid oil yield and increase gaseous product yields as the process surpasses the maximum thermal degradation point of HDPE. This is evidenced in the experiment on HDPE pyrolysis in a fluidised bed reactor at 650 °C conducted by Mastral et al. [91], which yielded 31.5 wt% gas and 68.5 wt% liquid oil. In conclusion, temperatures exceeding 550 °C induce the cracking of liquid oil into gaseous states [21].

#### Low-Density Polyethylene (LDPE)

LDPE is a polyethylene polymer characterised by increased branching, a lesser density, and a lower crystallinity, allowing for easy moulding [92]. Bagri and Williams [93] conducted LDPE pyrolysis in a fixed bed reactor with a heating rate of 10 °C/min at 500 °C. They achieved a substantial liquid yield of 95%, accompanied by a low gas yield and negligible char. A similar experiment conducted by Marcilla et al. [47] in a batch reactor at a temperature of 550 °C resulted in a liquid oil yield of 93.1 wt%. This highlights the ability of LDPE pyrolysis to generate a significant liquid yield. Numerous studies [93–95] have reported high liquid yields in the range of 80–95 wt% when pyrolyzing LDPE at an elevated temperature of 500 °C. However, LDPE pyrolysis at temperatures exceeding 550 °C results in an increase in the gas yield at the expense of the liquid yield [8,96].

### 2.5.2. Polypropylene (PP)

PP is a polyolefin polymer characterised by a methyl group attached to every alternate carbon along the molecular backbone. The presence of the methyl group in the polymer chain is primarily responsible for its higher modulus, flexural, tensile and compressive strength [10]. It possesses favourable attributes such as good processability, low density, attractive mechanical properties, and high resistance to heat and chemicals [82]. The thermal degradation of PP has been investigated by some researchers [97,98], and it was found that its degradation initiates at 327 °C and is nearly complete at 587 °C. In an experiment conducted by Ahmad et al. [99] at temperatures ranging from 250 to 400 °C, a liquid yield of 69.82 wt% was achieved at 300 °C. Similarly, Sakata et al. [100] performed the pyrolysis of PP at 380 °C, obtaining a liquid yield of 80.1 wt%, gas yield of 6.6 wt%, and solid residue of 13.3 wt%. Fakhrhoseini and Dastanian [94] carried out PP pyrolysis at 500 °C, and an 82.12 wt% liquid yield was obtained; however, as the temperature was raised above 500 °C, the liquid yield decreased. Demirbas [101] conducted PP pyrolysis at 740 °C in a batch reactor; the product yields were 48.8 wt% liquid, 49.6 wt% gas, and 1.6 wt% char. This indicates that at temperatures below 300 °C, PP may not undergo sufficient decomposition, but as the temperature is raised above 500 °C, it yields more liquid. However, at temperatures exceeding 700 °C, the gas yield is enhanced [21,92].

### 2.5.3. Polystyrene (PS)

PS is characterised by a benzene ring connected to every alternate carbon in its polymer chain. Due to its aromatic skeleton, the thermal degradation of PS usually results in the large generation of aromatic hydrocarbons. Numerous investigations indicate the feasibility of producing styrene from PS pyrolysis, with a recovery rate ranging from 40 to 79 wt%. Additionally, valuable petrochemicals such as benzene, toluene, ethylbenzene, and xylene (BTEX) can be obtained through the pyrolysis of PS waste [8]. This was shown in a study conducted by Park et al. [102], where the highest BTEX and oil yields of 26.3% and 86% were achieved at 780 °C. The presence of stable aromatic rings in PS limits the gas production during thermal decomposition, resulting in relatively low gas yields. The degradation of PS usually initiates at about 314–360 °C, reaching complete decomposition at 428–533 °C [21]. In a study by Liu et al. [103] utilising a fluidised bed reactor, PS pyrolysis was conducted between the temperature range of 450 and 700 °C, resulting in a substantial 98.7 wt% liquid oil yield at 600 °C. Even at lesser temperatures of about 450 °C, a considerable amount of liquid oil was still produced [92]. In comparison with PP and PE, the thermal degradation of PS occurs at lower temperatures during the pyrolysis process, and the produced liquid is typically less viscous. The highest liquid yield is obtained from PS amongst other plastics due to its higher percentage of volatile matter [5]. The pyrolytic oil derived from PS pyrolysis generally possesses a lower heating value when compared to that of PE and PP due to its predominant composition of aromatic compounds. Styrene constitutes the major component in the oil fraction of PS pyrolysis (48%), followed by ethyl benzene and toluene [10].

### 2.5.4. Polyethylene Terephthalate (PET)

PET is the most prevalent plastic in everyday modern life. However, due to the presence of terephthalic acid and oxygen in its structure, pyrolysis is not an ideal treatment method for PET. The oxygen within the polymeric chain of PET leads to the formation of water and other undesirable oxygenated compounds during pyrolysis, diminishing the calorific value of the produced fuel [8]. Encinar and González [58] conducted the pyrolysis of various plastic types including LDPE, PS, PP, and PET. The results of the product yields at a heating rate of 10 K/min for these plastics were as follows: LDPE—0.10% char, 81.33% liquid, 18.57% gas; PS—1.81% char, 95.79% liquid, 3.40% gas; PP—0.13% char, 82.67% liquid, 17.20% gas; and PET—8.28% char, 35.40% liquid, 56.32% gas. These findings indicate that PET produced the highest char and gas yields while yielding the least amount of oil. This high gas yield can be attributed to the presence of oxygen in its structure, leading to the generation of CO and $CO_2$. Furthermore, the pyrolysis of PET gives rise to benzoic and terephthalic acid, a general sublimate that can potentially clog pipes and diminish the quality of the liquid product as fuel [8,21]. Various reports [104–106] have indicated that the thermal breakdown of PET initiates between 360 and 400 °C, with the PET losing 79.78% of its initial weight after reaching its degradation peak at 427.7 °C. For instance, the oil obtained from PET pyrolysis contained nearly half of it as benzoic acid (49.93%), as revealed by gas chromatography–mass spectroscopy (GC-MS) analysis, adversely affecting the fuel quality due to its corrosiveness [5]. Given the well-established infrastructure for gathering clean and well-sorted PET waste and its low calorific value, mechanical recycling [8] and depolymerisation [107] are the predominant methods of managing PET waste, i.e., PET is either recycled to manufacture new plastic bottles, downcycled to produce textiles, or depolymerised to generate new monomers for the production of PET [108].

### 2.5.5. Polyvinyl Chloride (PVC)

PVC is characterised by a chloride group linked to every alternate carbon in its polymer chain. Consequently, 46–56.7 wt% of PVC mass is composed of chlorine, leading to a reduction in its chlorine value. The reported calorific value of PVC is 21.1 MJ/kg, which is lesser than that of PET [8]. The chlorine atoms bonded to the carbon backbone makes PVC flame-resistant and hard, making it suitable for applications like electrical insulation [21,82].

However, the pyrolysis of PVC results in the generation and release of HCl due to its high chlorine content, causing potential damage to the process equipment. This issue played a significant role in the shutdown of the pyrolysis plant in Ebenhausen, Germany [21]. Direct pyrolysis without chlorine removal can lead to the synthesis of hazardous chlorinated hydrocarbons, including polychlorinated dibenzodioxins (PCDD), polychlorobiphenyls (PCB), and polychlorinated dibenzofurans (PCDF). Unlike other polymers such as PE, PP, and PS which degrade in one step, PVC degrades in two steps [8]. The initial step is the dehydrochlorination step, where 99 wt% of the chlorine is released as HCl within a temperature range of 200–360 °C, lesser than the typical decomposition temperature of PE, PP, and PS [109]. PVC is usually avoided in the plastic feedstock for pyrolysis, as only a negligible amount of PVC (0.1–1%) may be tolerated during plastic pyrolysis. Numerous techniques such as stepwise pyrolysis, hydrothermal treatment, metal sorbents, chemical removers, and catalytic pyrolysis have been proposed to eliminate chlorine from PVC feedstocks. However, these methods often incur additional costs, which can be a disadvantage to the industry [21]. The most commonly used method is stepwise pyrolysis, initiated by heating the PVC feedstock to a moderate temperature (~330 °C), providing sufficient energy to break the carbon–chlorine bond but not carbon–carbon bonds [8]. After the chlorine has been volatised, the primary polymeric chain can be pyrolyzed in a secondary reactor conventionally. According to a review by Kusenberg et al. [110], dechlorinating PVC-containing waste (i.e., mixed waste containing PVC) is more challenging than dechlorinating pure PVC. This is based on the findings of Yuan et al. [111], who observed that the dechlorination of pure PVC resulted in 99.5 wt% chlorine elimination, while the dechlorination of a mixture of PVC and PP and/or linear low-density polyethylene (LLDPE) resulted in 34–74% chlorine elimination [8].

The pyrolysis of PVC was conducted by Miranda et al. [112] in a batch reactor at a heating rate of 10 °C/min and a temperature range of 225–520 °C. The experiment was carried out under vacuum with a total pressure of 2 KPa. The main product obtained was HCl, with a yield ranging from 44.35 to 58.2 wt% and liquid oil ranging from 0.45 to 12.79 wt%, while the solid residue decreased from 54.77 to 8.53 wt%. Another study by Cepeliogullar and Putun [113] on PVC pyrolysis in a fixed bed reactor reported a production of 12.3 wt% liquid oil and 87.7 wt% gas at 500 °C [5]. The high gaseous yield can be attributed to the significant presence of chlorine compounds in its structure which undergo conversion into HCl, consequently reducing the liquid yield.

### 2.6. Pyrolysis of Mixed Plastics

When distinct plastics are co-pyrolyzed, their respective temperature intervals for pyrolysis may overlap, resulting in synergistic interactions and a reorganisation of their pyrolysis products. Such synergistic interactions have the potential to accelerate the breakage of molecular chains, thereby decreasing the activation energy required for the plastic pyrolysis [114].

Briceno et al. [115] examined different ratios of HDPE and PP using thermogravimetric analysis. They found that HDPE, PP, and mixtures followed a one-step degradation process. The apparent activation energy for the pyrolysis of the mixture was lower than that of single plastics, suggesting a synergistic effect between the two plastics. Tuffi et al. [116] explored the pyrolysis behaviour and kinetics of single plastics (PE, PP, PET, PS) and binary mixtures of various proportions (PP/PE, PET/PP, PS/PP, and PET/PE) commonly found in packaging plastics. Pyrolysis for single plastics and mixed plastics with a high proportion of PP occurred in a single phase, whereas other binary mixtures exhibited two consecutive and partially overlapping pyrolysis processes [114].

Hujuri et al. [117] examined the pyrolysis of PET/PE, PP/PET, and PE/PP binary plastic mixtures. In the case of PET/PE degradation, the maximum degradation temperature decreased with an increasing percentage of PET, suggesting synergistic interaction. This was explained by the intermolecular transfer of a hydrogen atom from the less stable plastic (PET) to a free radical chain of the other component (PE) during the decomposition process. A similar qualitative description can be extended to the experimental results of the PET/PP mixture. Unlike the PET/PE and PET/PP mixtures, which exhibited multiple peaks in the derivative thermogravimetry curve (DTG) that is instrumental in determining the maximum degradation temperature of the plastics, the peaks in the PE/PP binary mixtures were less distinct due to the close melting points and maximum degradation temperature of the two plastics. The study revealed that an increase in the amount of PE led to a higher peak height, and the curve became less dispersed. Moreover, the overall degradation rate of the mixture was accelerated by the less stable polymer (PP), partially destabilising the more stable polymer (PE). Therefore, the experimental findings for the three binary mixtures underscore the significant impact of the mixture's composition on the interaction between the plastics present [117].

Anene et al. [118] explored the thermal degradation of a blend comprising LDPE and PP at various compositions. The pyrolysis of the LDPE/PP mixture was observed to initiate at lower temperatures than that of pure LDPE, indicating interactions between the combined polymers. Nevertheless, pure PP initiated pyrolysis before pure LDPE. Kruse et al. [119] investigated the binary degradation of PS and PP, noting a 25% increase in the PP degradation rate in comparison to no pre-mixing [117,119]. Marongiu et al. [120] studied the mixing scale effect of pyrolyzing a binary mixture of PE and PP, finding that each polymer decomposes independently if the mixing scale of the polymers is poor. Conversely, co-pyrolysis with partial interactions occurs when the mixture reaches the molecular scale. Quadri and Dohare [76] conducted individual pyrolysis and mixed pyrolysis of PP, PS, and PE. Their findings revealed that single plastic pyrolysis generated more liquid oil than mixed plastics pyrolysis, consistent with the results of Ziad et al. [121], Liu et al. [103], and Grause et al. [122]. Ziad et al. [121] performed the pyrolysis of mixtures of PE/PP, PE/PS, and PP/PS, with a 50% ratio for each. Among the blended plastics, PE/PS produced the most liquid oil (51%), followed by PE/PP (49%), while PS/PP yielded the least oil (47%). The gas product was maximum in the PE/PS mixture (40%), followed by PE/PP (33%), and was the least in PS/PP (40%). Furthermore, the thermal degradation of PP, PS, and PE as single-type plastics was reviewed by Peng et al. [56], who found that the composition of PP pyrolytic oil was more complex than that produced from PE and PS. Similar findings were reported by Ciliz et al. [123] who also noted that PP has a more complex structure than PE and PS. Regardless of lesser or higher temperatures, the thermal pyrolysis of PS exhibited the highest conversion into liquid oil (80.8%) with less gas (13%) and char (6.2%).

### 2.7. Hydrogen Production from Pyrolysis

To produce hydrogen from the waste plastics, a two-step process is essential. In the initial step, the waste plastics undergo pyrolysis to produce gas, liquid, and char. Subsequently, the produced volatiles (gas and liquid) are reformed for further cracking in the second step to generate hydrogen-rich gas [124] and by-products such as carbon nanotubes [18]. This two-step is known as the pyrolysis and in-line reforming process [125] or a pyrolysis–gasification process [126]. Figure 8 depicts some various plastic waste valorisation routes and their various products.

The pyrolysis and in-line reforming process presents significant advantages over conventional single-step waste plastic gasification. These advantages include operating at lower temperatures, which enables the selection of distinct temperatures for the pyrolysis and in-line reforming stages [125]. In addition, the two-step process enables 100% conversion, yielding a gaseous stream with a high concentration of $H_2$, devoid of tar or liquid hydrocarbons [18]. Furthermore, the direct contact of plastic impurities with the reforming catalyst is minimised [125]. Consequently, various authors have reported hydrogen production values exceeding 30 wt% [18]. The reforming process is implemented by means of an endothermic or exothermic reaction to produce hydrogen and carbon monoxide [127]. Various reforming strategies of hydrocarbons include steam reforming [128–130], partial oxidation [131], and dry reforming [126,132]. The block flow for producing hydrogen from the pyrolysis and in-line reforming process is illustrated in Figure 9.

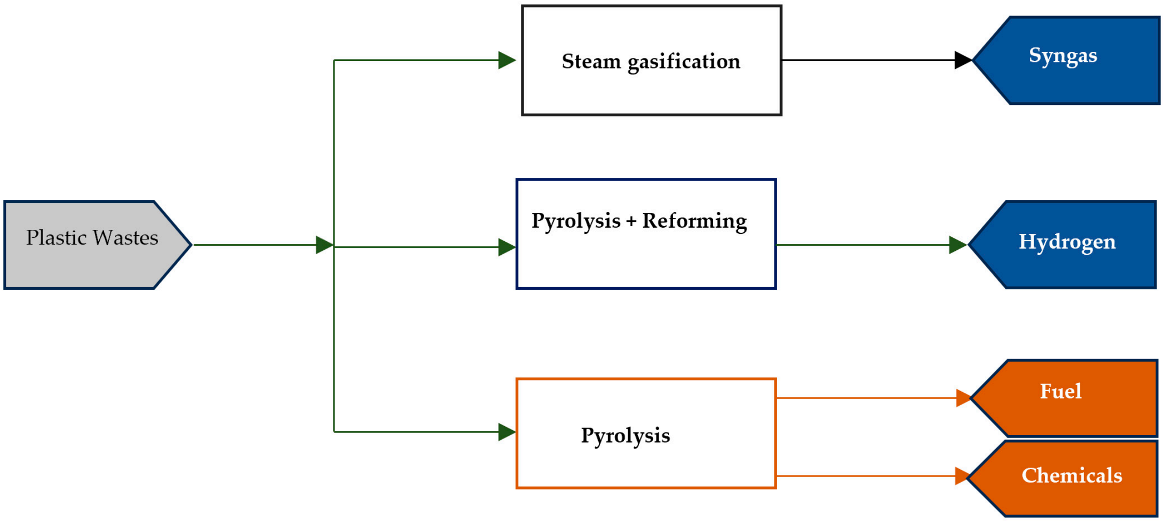


**Figure 8.** Some plastic waste valorisation routes and their products [18].

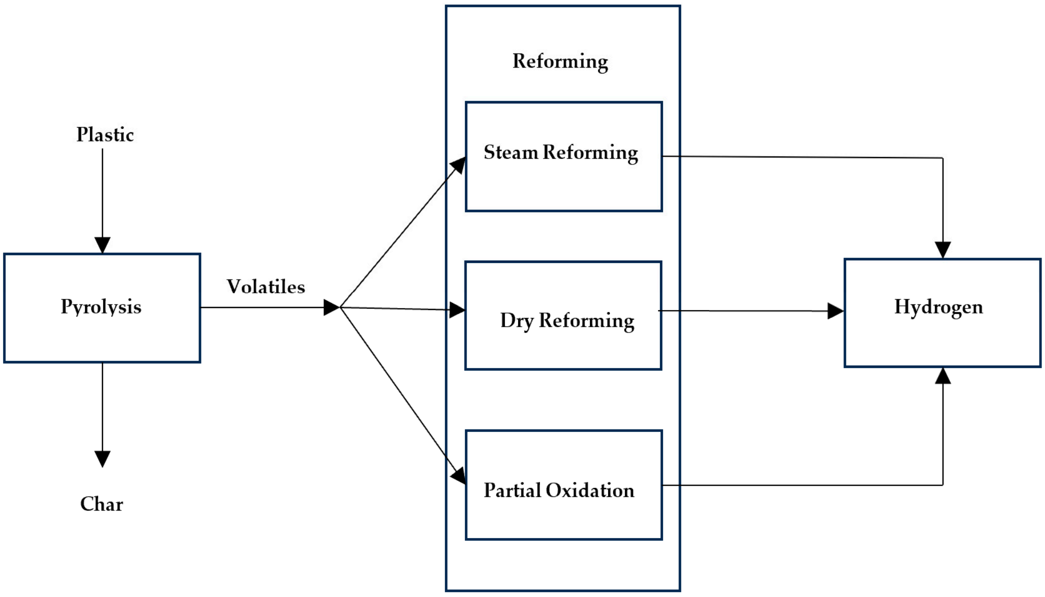


**Figure 9.** Hydrogen production via pyrolysis and in-line reforming.

### 2.7.1. Steam Reforming

Steam reforming is the process by which steam reacts catalytically and endothermically with hydrocarbons [127]. The steam reforming process is usually conducted at high temperatures (700–1000 °C) under 3–25 bar pressure in the presence of a catalyst to produce $H_2$, CO, and a relatively small amount of $CO_2$ [133]. The reaction produces a mixed gas of $H_2$ and CO in a 3:1 ratio, denoted by Equation (1) [128,134]. Additional hydrogen is produced from the water–gas shift reaction by the further reaction of the produced CO with steam to generate $CO_2$ and $H_2$ [133]. Pressure swing adsorption or scrubbing is used to eliminate $CO_2$ and other impurities from the gas stream, leaving high purity $H_2$ [133]. Steam reforming is commonly employed in industries for hydrogen production due to its high thermal efficiency, reaching up to 85% [128]. The exothermic nature of the water–gas shift reaction [130] helps offset some of the energy requirements for the overall process, contributing to its thermal efficiency. In addition, the water–gas shift (WGS) shown in Equation (2) minimises the formation of carbon, which is crucial for maintaining catalyst activity and overall process efficiency. Steam reforming is a proven technology which is preferred for syngas requirements with high $H_2/CO$ ratios (3:1) [135] and industrial production [136].

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H_{298K} = 206\ kJ/mol \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_{298K} = -41\ kJ/mol \tag{2}$$

Methane serves as a basis for the reforming process due to the prevalent commercial natural gas reforming process widely employed for hydrogen production. However, the pyrolysis of plastic wastes not only include methane but an extensive array of hydrocarbon gases as well, ranging from $C_1$ to $C_{60}$ for linear and branched hydrocarbon plastics like polypropylene and polyethylene [130]. The general steam reforming equation for the pyrolysis hydrocarbon volatiles from polystyrene and polyolefins (PE and PP) with steam is denoted by Equation (3), while that for PET volatiles is represented by Equation (4).

$$C_nH_m + nH_2O \rightarrow nCO + \left(n + \frac{m}{2}\right)H_2 \tag{3}$$

$$C_nH_mO_k + (2n - k)H_2O \rightarrow nCO_2 + \left(2n + \frac{m}{2} - k\right)H_2 \tag{4}$$

### 2.7.2. Dry Reforming (DR)

Dry reforming, also known as carbon dioxide reforming [127], is an endothermic catalytic reaction between carbon dioxide and hydrocarbons, producing an equimolar syngas consisting of a mixture of $H_2$ and CO [137]. This method gained popularity because it utilises the two most abundant greenhouse gases, $CH_4$ and $CO_2$, and produces syngas with a ratio ($H_2/CO$) of ~1, depicted in Equation (5) [127,134,137,138]. The dry reforming process is slightly more endothermic than the steam reforming process and tends to exhibit severe coke formation due to the carbon-rich feed [135].

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \Delta H_{298K} = +247\,kJ/mol \tag{5}$$

Like steam reforming, the dry reforming of hydrocarbons requires temperatures ranging from 700–1000 °C and can be operated at atmospheric pressures. Side reactions, most notably the reverse water–gas shift (RWGS) reaction (see Equation (6)), occur simultaneously with the dry reforming of hydrocarbons, which impacts the production of syngas [128].

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad \Delta H_{298K} = 41\ kJ/mol \tag{6}$$

The RWGS reaction consumes the produced hydrogen to generate $H_2O$, consequently reducing the $H_2/CO$ ratio in the resulting syngas. In addition, this process enhances a higher conversion of $CO_2$ into carbon oxides.

$$2CO \rightarrow CO_2 + C \quad \Delta H_{298K} = -171\ kJ/mol \tag{7}$$

The carbon monoxide generated by the DR and RWGS will undergo disproportion, leading to the formation of carbon deposits (see Equation (7)) [134]. This leads to a notable technical challenge in the dry reforming (DR) reaction, the deactivation of the catalyst [128,134]. Therefore, precious metals like Rh and Ru, which have strong anti-coking property and high catalytic activities, are employed in most dry reforming applications [134]. This reforming strategy is suitable for producing CO-rich syngas [135,139]. Processes that require low hydrogen to carbon monoxide ratios are the direct conversion of syngas to olefins and the direct synthesis of dimethyl ether (DME). Some disadvantages of dry reforming, including high energy requirements, a low quality $H_2/CO$ ratio, and carbon deposition, decreases its successful implementation at an industrial scale, demanding more research as an alternative to syngas production for the generation of hydrogen [138].

### 2.7.3. Partial Oxidation

Partial oxidation is an exothermic process [131,140] where methane and other hydrocarbons present in natural gas undergo a reaction with a limited amount of oxygen to produce syngas with a ratio of 2 (see Equation (8) [131]). This amount is insufficient for complete oxidation, resulting in the production of hydrogen and carbon monoxide (and nitrogen if the reaction is carried out with air instead of pure oxygen), along with a relatively small amount of carbon dioxide and other compounds [141]. Subsequently, in a water–gas shift reaction, carbon monoxide reacts with water to form carbon dioxide and additional hydrogen, as depicted in Equation (2).

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad \Delta H_{298\ K} = -36\ \text{kJ/mol} \tag{8}$$

The process is generally faster than steam reforming and requires a smaller reactor vessel. However, as seen in the chemical reactions of partial oxidation, this process initially yields less hydrogen per unit of the input fuel when compared to the steam reforming of the same fuel [141]. An advantage of this method is that external heating is not required due to the natural exothermic nature of oxygen [136], thereby increasing the compactness of the reaction system [142]. However, a notable drawback is the essential requirement for pure oxygen in partial oxidation to sustain an adequately high reaction temperature in the reformer and to guarantee the full conversion of plastic pyrolysate into a gaseous product. The use of pure oxygen in a partial oxidation process leads to a preference for the consumption of hydrogen, leading to a decrease in the overall hydrogen yield in the product gas [143]. Nitrogen and carbon dioxide take a significant volume in the product, acting as a form of heat sink, thereby diminishing the thermal efficiency of the process [142]. The syngas ratio of 2 obtained by partial oxidation, as depicted in (8), is most suitable for downstream processes such as direct methanol synthesis or Fischer–Tropsch synthesis for alkane production [131,135].

Amongst the three reforming strategies, steam reforming is considered more energy-efficient and preferable for large-scale hydrogen production. This is because partial oxidation and dry reforming result in a lower $H_2/CO$ ratio in comparison to steam reforming [135]. The advantages and disadvantages of the reforming processes are outlined in Table 3.

**Table 3.** Advantages and disadvantages of the various reforming processes.

| Process | Advantages [127,135,144] | Disadvantages [140,144] |
|---|---|---|
| Dry reforming (DR) | Reforms two of the most abundant greenhouse gases ($CO_2$ and $CH_4$)<br>Less $CO_2$ product compared to steam reforming | High energy requirements (more endothermic than steam reforming)<br>Requires constant supply of pure $CO_2$<br>Formation and deposition of coke occurs more rapidly in contrast to steam reforming |
| Partial oxidation | Commercially viable<br>External heat not required<br>Low overall cost<br>Compactness | Less efficient than steam reforming<br>Pure $O_2$ required which incurs extra costs |
| Steam reforming (SR) | Commercially viable<br>High efficiency<br>High $H_2/CO$ ratio | High energy requirements<br>Large reformer required |

Catalysts play a crucial role in facilitating the transformation of volatiles derived from pyrolysis to gas. Some of the catalysts commonly used in the pyrolysis–catalytic steam reforming of waste plastics include metals like ruthenium, rhodium, platinum, iron, and nickel [129,136]. Precious metals, including ruthenium, rhodium, and platinum, have demonstrated superior catalytic activity due to their high activation and resistance to carbon deposition, but their high cost and limited availability make them impractical for commercial use [128,129,131]. Instead, cost-effective catalysts like nickel and other transition metal-based catalysts such as Co or Fe, which exhibit similar activation to precious metal catalysts, are used. Nickel is preferred due to its abundance in nature, low cost, and good catalytic activity. The industrial scale commercialisation of Ni catalysts in reforming reactions is well established. The major drawbacks associated with Ni-based catalysts include rapid deactivation and low stability due to carbon deposition and the sintering of Ni components [128]. The primary approaches for preventing carbon deposition on nickel-based catalysts include (i) incorporating additives to boost the surface basicity of nickel-based catalysts, thereby enhancing the adsorption and dissociation of $CO_2$ and reducing carbon deposition; (ii) achieving smaller nickel particles and enhancing their dispersion; and (iii) employing nickel-based composite catalysts with a high oxygen storage capacity. Numerous studies indicate that nickel-based composite catalysts with oxygen defects demonstrate commendable resistance to coke formation [134].

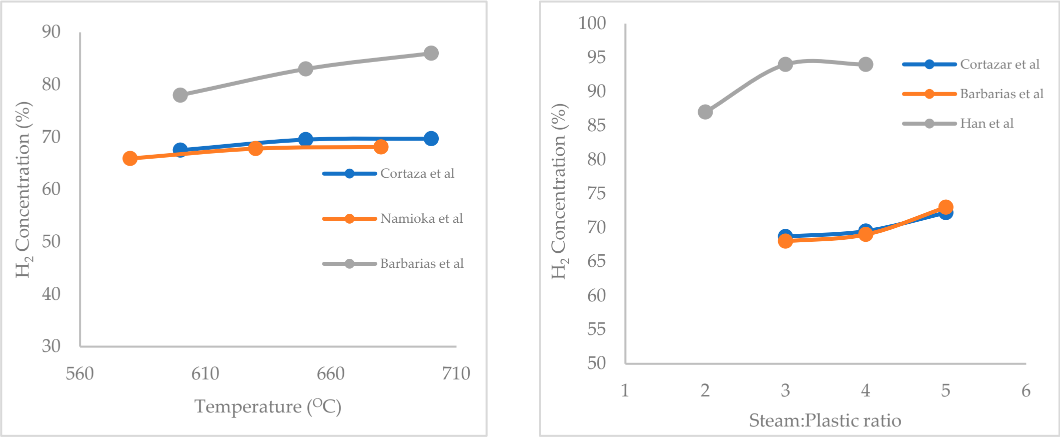
Catalyst activation can be aided by the dispersion of a small quantity of catalyst material to provide support. Typically, Ni-based catalyst supports include $Al_2O_3$, $SiO_2$, $ZrO_2$, $CeO_2$, $La_2O_3$, and $TiO_2$. $Al_2O_3$ is an inexpensive, porous support material that has a high specific surface area [128]. Physicochemical properties of catalyst support can strongly impact the size of Ni crystals and the surface characteristics, reducing the ability of the catalyst [128]. The stability and dispersion of the active phase of the catalytic system are influenced by the metal–support interaction, which makes the choice of support a critical factor in the characteristics of the catalytic system. Furthermore, because of its acidic/basic characteristics, the support can influence the carbon deposition and the reaction mechanism [145]. It has been observed that carbon forms on surfaces with acidic carriers; therefore, using basic promoters (MgO and CaO) may improve the resistivity to carbon formation, thereby exhibiting good catalytic performance. Bimetallic catalysts have been discovered to perform better than monometallic catalysts due to their stability, activity, and coke resistivity [128]. Ni has a great capacity to form bimetallic systems with other metals. Thus, precious metals like Pt could be applied to improve the catalytic performance. Bimetallic catalysts containing Ni–precious metal have been experimentally investigated in methane dry reforming. Reports suggest that the inclusion of specific quantities of precious metals, such as Pt, enhances the reducibility of Ni and reduces the metal crystal size when compared to monometallic Pt and Ni catalysts. Pt-Ni bimetallic catalysts effectively mitigate coke formation in the DRM process, but typically exhibit lower activity when compared to Ni catalysts. Conversely, there are reports of higher activity in the case of Pt-Ni/$Al_2O_3$ bimetallic catalysts [146].

In a study conducted by Cho et al. [147], the pyrolysis and in-line reforming processes were carried out using dual fixed bed reactors operating in batches. The pyrolysis reactor produced volatiles at a temperature range of 40 °C to 500 °C/min, and these volatiles were subsequently processed in the reforming fixed bed reactor at 800 °C. The hydrogen production from PP feedstock was 26.6 wt%, while PS resulted in a lower $H_2$ production of 18.5 wt%. The Ni-Mg-Al catalyst was employed in both cases. In a separate investigation by Wu and Williams [148,149], $CO_2$ was used instead of steam to explore the dry reforming of pyrolysis volatiles from plastics using the Ni-Mg-Al catalyst. PET, PS, PP, and PE were used as feedstock, being subjected to temperatures of 500 °C and 800 °C, resulting in $H_2$ production values of 2.5%, 7.6%, 13.6%, and 15%, respectively. These results were notably inferior when compared to those obtained in pyrolysis and in-line steam reforming processes [18].

Furthermore, Erkiaga et al. [150] explored plastic pyrolysis and in-line reforming, employing a novel experimental setup comprising a CSBR reactor and a fixed bed reactor for the pyrolysis and steam catalytic reforming steps. HDPE underwent pyrolysis at 500 °C, followed by reforming at 700 °C using a commercial Ni catalyst. The reforming catalysts exhibited notable efficiency, completely converting waste plastics into gaseous products, yielding 34.5 wt% of $H_2$, equivalent to 81.6% of the stoichiometric maximum allowable.

However, the primary challenge in this process was the formation of coke (4.4 wt% of the feed), hindering the reactant flow in the reforming fixed bed reactor. To address these challenges, Barbarias et al. [151] substituted the fixed bed reactor with an FBR reactor for the reforming step. This modification resulted in a higher $H_2$ yield (38.1 wt%) when compared to Erkiaga et al. [150], reaching 92.6% of the allowable stoichiometry. This underscores the advantages of employing an FBR for the reforming process. Subsequent research using PS validated the efficiency of this CSBR and FBR setup for the pyrolysis and reforming process [152].

In the pyrolysis and in-line reforming process, crucial factors influencing the end products are the steam/carbon ratio and the reforming phase temperature [18,125,128]. Figure 10 illustrates the impact of these factors on $H_2$ production. As depicted in Figure 10a, $H_2$ production increases with the elevation of the reforming temperature. The rise in temperature boosts both endothermic reforming reactions and cracking [153]. The production of hydrogen is also improved by increasing the steam/plastic ratio, as shown in Figure 10b, due to a rise in the partial steam pressure [125] and steam available [128], thereby promoting both the water–gas shift reaction and reforming processes [125]. However, a moderate adjustment in the steam/plastic ratio is advised as high steam/plastic ratio necessitates high energy requirements for steam generation, potential sintering at the activation site [154], and the costs associated with gas–liquid separation processes [128]. As observed in Figure 10b, Han et al. [128] observed an increase in the hydrogen yield when the steam/plastic ratio was increased from 2 to 3, but a slight decrease from 3 to 4. This was attributed to the reduced catalyst activity.



(**a**) (**b**)

**Figure 10.** (**a**) Effect of temperature [18,125,143,155] and (**b**) steam–plastic ratio on hydrogen concentration [18,125,128,155].

Polyolefins (PE and PP) have greater potential of producing hydrogen owing to their higher carbon and hydrogen contents [125]. This was further corroborated by Barbarias et al. [155] who investigated the hydrogen production from various plastic wastes, including polyethylene, polypropylene, polyethylene terephthalate, and polystyrene. They found that the pyrolysis-reforming of polyolefins resulted in the highest $H_2$ production, with yields of 37.3 wt% for HDPE and 34.8 wt% for PP, whereas yields of 29.1 wt% and 18.2 wt% were obtained for PS and PET, respectively. The lower hydrogen content in the PS composition and the formation of more carbonaceous residue in the PET pyrolysis step contributed to their lesser hydrogen production. Czernik and French [156] also investigated the pyrolysis and in-line reforming of PP using a Ni-based catalyst at 650 and 800 °C in two FBRs and achieved a 34 wt% $H_2$ production. Similarly, Namioka et al. [143] conducted pyrolysis and in-line reforming using PS and obtained a 29.1 wt% $H_2$ yield. Hence, polyolefins are deemed suitable for hydrogen production due to their chemical composition.

The pyrolysis and in-line reforming approach generates a significant quantity of hydrogen when compared to the single-stage steam gasification process. Typically, the single stage steam gasification process yields hydrogen below 20 wt%, whereas the pyrolysis and in-reforming approach yields hydrogen exceeding 30 wt% [18,157–159].

### 2.8. Environmental Impact and Energy Efficiency of Pyrolysis

A life cycle environmental impact assessment was conducted by Jeswani et al. [12], comparing the pyrolysis of mixed plastic waste with incineration (energy recovery) and mechanical recycling. Their findings revealed that pyrolysis exhibited a 50% lower climate change impact and life cycle energy use when compared to incineration, while showing similar impacts to mechanical recycling when considering the quality of the recyclate. Moreover, the pyrolysis of plastic wastes generates lesser emissions of carbon monoxide and carbon dioxide when compared to gasification and incineration, thereby reducing the carbon footprint of plastic products [30]. Pyrolysis offers environmental benefits through potentially advancing the circular economy and addressing plastic pollution [160] through the processing of a broader range of plastic types, including mixed plastics and composites that pose challenges for mechanical recycling [78]. This capability enhances the recycling rates and aids in mitigating plastic pollution.

While pyrolysis indeed yields energy in the form of solid, liquid, and gaseous products, it is considered energy-intensive due to the requirement for high temperatures to efficiently decompose plastic waste materials into hydrocarbons [161]. However, strategies such as employing catalysts [30,162], optimising process parameters [21], utilising the produced gas for process [10,17], and leveraging innovative technologies like stepwise pyrolysis [163] offer opportunities to mitigate energy requirements and enhance the overall efficiency and sustainability of the process.

## 3. Conclusions

In conclusion, this paper has provided a thorough examination of the pyrolysis and in-line reforming processes as applied to various plastic types, emphasising its potential for generating fuel and hydrogen. The adoption of a circular economy framework presents a promising avenue towards sustainable resource management, particularly in addressing the challenges posed by plastic pollution. Within this framework, pyrolysis emerges as a promising method for effectively managing plastic waste, offering environmental benefits over conventional methods like incineration, thereby moving towards a more sustainable future. Its capability to process diverse plastic types, including mixed plastics, enhances the recycling rates and aids in reducing plastic pollution. While pyrolysis technologies such as microwave-assisted and plasma reactors are still in their early stages of development, their potential to enhance the efficiency of pyrolysis processes signifies a pathway towards further innovations in waste management. Additionally, integrating pyrolysis with in-line reforming processes facilitates the production of hydrogen-rich gas. Although pyrolysis demands significant energy due to its endothermic nature, employing catalysts, optimising process parameters, and utilising generated gas can reduce the energy requirements and improve the overall efficiency and sustainability. Therefore, adopting chemical recycling methods like pyrolysis is fundamental for effectively managing plastic waste, fostering sustainable economic development, and advancing towards a circular economy.

## 4. Future Recommendation

Combining mechanical and chemical recycling methods offers a promising avenue to enhance recycling rates and promote a circular economy. Conducting a study on the quality of fuel or chemicals derived from mechanically recycled plastic waste utilised as feedstock for pyrolysis could provide valuable insights into the effectiveness of this approach. In addition, employing renewable sources to supply heat energy for the pyrolysis of plastic wastes presents a promising avenue for improving the sustainability and environmental impact of this process. Further exploration into the economic feasibility of this approach is warranted.

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