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Waste Plastics Valorization by Fast Pyrolysis and in Line Catalytic Steam Reforming for Hydrogen Production

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Abstract

This chapter summarizes the most recent results obtained in the plastic waste pyrolysis-reforming strategy for hydrogen production. An original two-reactor configuration consisting of a conical spouted bed reactor for the pyrolysis step and a fluidized bed reactor for the pyrolysis volatile reforming is proposed. The fundamental aspects and challenges of this joint process are discussed in detail, and the prospects for the full-scale implementation of this valorization route are assessed. Thus, the influence the main reforming parameters (temperature, space time and steam/plastic ratio) have in the pyrolysis-reforming of HDPE on product yields and catalyst stability are reported. Moreover, the role played by plastic composition on process performance is also described by studying the influence of following polymers: high density polyethylene (HDPE), polypropylene (PP), polyethylene terephthalate (PET) and polystyrene (PS). The operating conditions used for the valorization of different plastics have been as follows: pyrolysis temperature of 500°C, reforming temperature of 700°C, space time of $16.7 \text{ g}_{\text{catalyst}} \text{ min g}_{\text{plastic}}^{-1}$ and steam/plastic ratio of 4.

Keywords: hydrogen, pyrolysis, reforming, waste plastics, spouted bed

1. Introduction

The current overall hydrogen production has reached a value of 7.7 EJ/year, and an increase to 10 EJ/year is expected by the year 2050 [1]. Hydrogen demand is mainly related to ammonia production (51%), oil refining (31%), methanol production (10%), and other uses (8%). Moreover, new fossil sources of lower quality than conventional oil are increasingly been used, but they require severe hydroprocessing for their upgrading. This is the case of oil sands, which surely will contribute to meeting the increasing requirements of hydrogen.

Approximately 96% of the world hydrogen produced is of fossil origin. Thus, 48% is produced from natural gas reforming, 30% from oil fractions and the remaining 18% by means of coal gasification [2]. Accordingly, only 4% is produced from renewable sources, such as water electrolysis.

The future of the hydrogen market is conditioned by the need to reduce CO₂ emissions, which requires obtaining it from raw materials and renewable energy sources. The so-called hydrogen economy contemplates a future scenario in which this gas produced in a clean and economical way from a wide range of renewable sources would contribute to meeting the society's energy needs through combustion engines or preferably, by means of fuel cells, to a more efficient energy generation. This proposal would help to decentralize and diversify the energy system and reduce the current dependence on fossil fuels and air pollution [3].

In this scenario, the processes aimed at hydrogen production from biomass and waste are gaining growing attention [1, 4–6], with the thermochemical routes being those with best perspectives for their full scale implementation. Thus, hydrogen production from waste plastics has been mainly approached by means of steam gasification and pyrolysis-reforming processes [6].

Gasification allows for the conversion of waste plastics into a gaseous stream with varying contents of H₂, CO, CO₂, CH₄ and N₂ depending on process conditions and the gasifying agent used. The main advantage of gasification in relation to other thermochemical processes lies in its flexibility to valorize plastics of different composition or mixtures or plastics with other feedstocks. The main technologies for waste plastics gasification are those previously developed for biomass and coal gasification. It is to note that fluidized bed reactors have been widely used in the gasification of plastics [7–13]. However, these studies were mainly performed using air as fluidizing agent, so that the resulting gas has low hydrogen content and its main interest is restricted to energy production. The dual fluidized bed technology has been successfully applied to the steam gasification of plastics [13] and plastics mixtures with coal and biomass [14, 15]. The relevance of this technology is related with the fact that it allows overcoming the problems associated by the endothermic nature of the process. In spite of the promising results reported by Wilk et al. [13] in the gasification of different waste plastics, the high tar content in the syngas (above 100 g m⁻³) is a great challenge. However, waste plastic gasification has been scarcely studied in fixed bed reactors. Moreover, the results obtained are of preliminary nature as the reactors used are of laboratory scale and operate in batch regime [16–19]. Erkiaga et al. [20, 21] used the conical spouted bed reactor in the steam gasification of HDPE, and a hydrogen rich syngas was obtained with moderate tar contents. Moreover, this reactor design was also used subsequently in the co-gasification of HDPE and biomass (pine sawdust) with promising results [22]. The high temperatures attained in plasma reactors are also suitable for tar elimination, and this technology has therefore been proposed for the gasification of waste plastics [23, 24].

The hydrogen production from plastics via pyrolysis-reforming strategy has been recently proposed as an alternative to conventional gasification. The interest of this strategy lies in the fact that a tar free syngas is produced due to the high activity of the reforming catalyst. Moreover, the mild conditions in the reforming step and the physical separation of waste plastic impurities and the catalysts improve catalyst stability. Nevertheless, this strategy has been scarcely studied and the results reported were mainly obtained in lab scale units [6]. The studies by the team of Professor Williams [25–28] were carried out in a system in which pyrolysis is carried out in discontinuous regime in a fixed bed reactor and the volatiles are reformed in a second fixed bed. The reaction equipment used by the team of Professor Yoshikawa [29, 30] is a step forward, as it operates in continuous regime, although the use of fixed beds for pyrolysis and reforming can involve serious limitations for the process scale up. Czernik and French [31] made a step forward in this technology by studying the continuous pyrolysis and in-line reforming of polypropylene in a system of two in-line fluidized beds, with a commercial naphtha reforming catalyst. Erkiaga et al. [32] originally proposed a two-step reactor unit operating in continuous regime by

combining a spouted bed reactor for the plastic fast pyrolysis and a fixed bed for the catalytic steam reforming. However, the fixed bed reactor led to an excessive coke formation and severe operational problems subsequent to some minutes operation. Accordingly, the fixed bed reactor was replaced by a fluidized bed reactor in subsequent studies to overcome the mentioned problems [33–36].

This chapter describes the main results obtained in the pyrolysis and in-line reforming of plastics in a system composed of a spouted bed for the pyrolysis step and a fluidized bed for the reforming one. Section 2 provides background information on the application of conical spouted beds to plastics pyrolysis. In addition, the results obtained in the pyrolysis of different plastics are also reported in this section, as long as the pyrolysis step product distribution is critical for the evaluation of the subsequent reforming step. Finally, Section 3 deals with the effect operating conditions (temperature, space time and S/P ratio) have on the reforming step performance. Moreover, the influence the polymer type in the feed to the pyrolysis step has on reforming step yields has also been evaluated. Thus, the interest of this chapter is centered on the maximization of hydrogen production under different conditions by treating plastics of different composition. Furthermore, one of the main challenges of this process, as is catalyst stability, has also been approached in detail.

2. Waste plastics pyrolysis in conical spouted beds

Pyrolysis (or thermal cracking) for the valorization of waste plastic is currently receiving great attention, especially for addition polymers, which accounts for most plastics in the municipal solid waste stream. One of the main advantages of pyrolysis lies in its efficiency for the recovery of monomers and for the production of automotive and hydrogen fuels, with reduced emission of pollutants [37–40].

The pyrolysis process is flexible and may treat plastic mixtures in the municipal solid waste, and those from automobile recycling, electronics and computers or construction, as well as mixtures of these materials with others (such as biomass) [41]. The requirements for scaling up and operation in continuous regime have led to the proposal of a significant number of technologies provided with very different reactors, such as fluidized beds, screw kilns, stirred or microwave reactors [37, 38]. Amongst these technologies, the fluidized bed reactor has been widely used because it ensures good heat and mass transfer, and therefore isothermal operation [42]. The main international reference in the development of this technology is known as the Hamburg process [43–45].

One of the main challenges in the pyrolysis of plastics is the sticky behavior of fused plastic particles, which causes agglomeration and subsequent defluidization in fluidized bed reactors [46]. The high heat transfer rates and vigorous cyclic movement of the particles in the conical spouted bed reactor, as well as the role of the spout to break up the agglomerates, are suitable features for continuous pyrolysis of plastics. Therefore, this technology allows operating below 500°C without defluidization problems [47]. Accordingly, the conical spouted bed has been successfully applied to the continuous pyrolysis of different polymeric materials [48–52]. Moreover, this technology has also been applied to the pyrolysis of biomass and, in fact, a 25 kg h⁻¹ pilot plant has been developed for this process [53, 54].

The main interest in analyzing the results obtained in the pyrolysis of the plastics lies in the fact that it constitutes the first step of the integrated pyrolysis-reforming strategy, and therefore the volatile products of the pyrolysis process are the reactants of the catalytic reforming step. Consequently, it is essential to know the composition of the volatile stream leaving the pyrolysis step. Accordingly, the composition of the volatile stream for the pyrolysis of polyolefins (HDPE and PP), PET and PS, are analyzed in this section.

The different nature of the plastics studied led to volatile streams of different composition in their pyrolysis. It is to note that HDPE and PP are made up of saturated hydrocarbon chains, the thermal degradation of these chains mainly occurs by random radical scission mechanism, which gives way to a wide product distribution ranging from light gases to waxes. The fast pyrolysis conditions of the conical spouted bed reactor and especially the short residence time attained favor the selective formation of primary products, i.e., waxes and hydrocarbons in the diesel range, with the yield of gases, gasoline and aromatics being very low. However, in the PS chains aromatic rings are included, thus, the depolymerisation of this plastic leads to the formation of monomers (styrene), oligomers and other secondary products of aromatic nature. Due to the low temperature and the suitable features of the reactor used in this study, the product stream obtained in PS pyrolysis is mainly made up of styrene. Finally, PET is produced by polymerization of terephthalic acid and ethylene Glycerol. Accordingly, a wide product distribution with oxygenates and aromatics are formed in PET pyrolysis. The different nature of the pyrolysis product stream has a remarkable influence on its behavior in the reforming step, and the following section deals with this aspect.

According to the results obtained in previous studies, pyrolysis temperature was fixed at 500°C [47, 49, 52]. This temperature ensures a stable process without operational problems and minimizes secondary reactions of pyrolysis products and energy requirements. Moreover, below this temperature the plastic pyrolysis kinetic is very slow. Although the polymer degradation in the pyrolysis-reforming process occurs under steam atmosphere, the results obtained in previous studies using steam are very similar to those obtained using nitrogen as fluidizing agent, and therefore steam has hardly any effect at this temperature [33, 35]. This result is associated with the mild pyrolysis conditions used, 500°C, which hinders steam reactivity. The experiments were performed with continuous plastic feed and using a bed of inert sand in the pyrolysis of all the polymers studied.

The results obtained in the continuous pyrolysis of different plastics, HDPE, PP, PS and PET at 500°C are summarized in **Figure 1**. Due to the similar nature of HDPE and PP, similar product yields are obtained in their pyrolysis. As observed in **Figure 1**, the pyrolysis of polyolefins (HDPE and PP) leads to high yields of waxes (C_{21+}) and liquid hydrocarbons in the diesel range ($C_{12}-C_{20}$), with the yield of the gasoline fraction being low and that of gases below 1.5 wt%. It is to note that the solid residue formed in the pyrolysis of polyolefins is negligible, and therefore the whole product stream is fed into the fluidized bed for its reforming. Waxes are made up of long chain hydrocarbons and are solid at room temperature. However, these products do not cause any operational problem in the pyrolysis-reforming process as long as they are fully converted into gaseous products in the reforming step.

On the other hand, PET showed a wider product distribution than those observed in the case of polyolefins. A remarkable solid residue yield (7 wt%) was obtained in the pyrolysis of PET, with this residue being obtained coating the sand particles. The main product fraction in PET pyrolysis is the gaseous stream, whose yield is of 42.8 wt%. This gas is mainly made up of carbon monoxide and dioxide. In addition, a remarkable yield of a solid fraction (benzoic and benzoylformic acids) is obtained at room temperature, which accounts for 37.4 wt%. However, the yield of oil is the lowest (12.8 wt%) in the polymers studied.

The pyrolysis of PS leads to a high monomer recovery, with the yield of styrene being 70.6 wt%. The gaseous product yield is very low, 1.5 wt%, and that of the solid residue negligible. Thus, the product distribution obtained in PS pyrolysis is made up of styrene and other secondary products of aromatic nature.

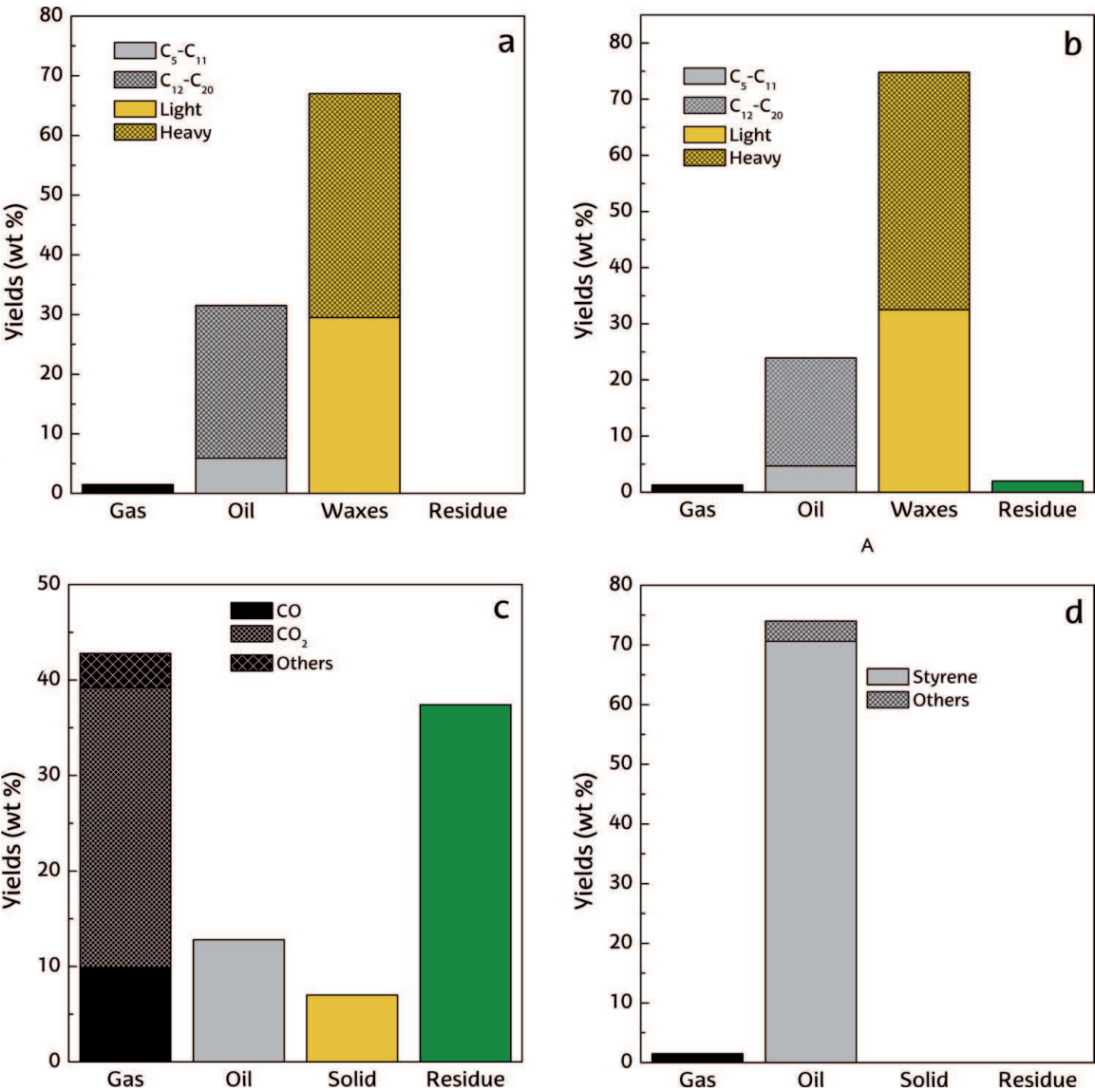


Figure 1.
Product distributions obtained in the continuous pyrolysis of HDPE (a), PP (b), PET (c) and PS (d) in a conical spouted bed reactor at 500°C.

3. Pyrolysis and in-line reforming of plastics

The fast pyrolysis of waste plastics has been extensively studied in the literature [38, 55, 56], due to its interest for producing fuels and chemicals. Recently, the pyrolysis and in-line reforming route for hydrogen production has gained attention, with several studies published over the last years [30, 31, 57]. In this scenario, the optimization of the process operating conditions is essential for its industrial implementation.

Thus, the following section shows the results obtained in the reforming of HDPE derived pyrolysis volatiles carried out using the configuration described above, i.e., the conical spouted bed reactor for the pyrolysis step and the fluidized bed reactor for the catalytic steam reforming step. The aim of this research was to study how different operating conditions affect the reforming of HDPE pyrolysis volatiles. The parametric study includes the effect of temperature, space time and steam/plastic (S/P) ratio on the conversion, hydrogen production and the yields of the products both at zero time on stream and over time, taking into account the evolution of these results as a consequence of the catalyst deactivation.

3.1 Parametric study of HDPE pyrolysis and in-line reforming

The results obtained in the parametric study carried out at zero time on stream are described below.

3.1.1 Effect of temperature

This section deals with the effect the reforming temperature in the 600–700°C range has on conversion, hydrogen production and gaseous products yields at zero time on stream. The operating conditions selected to carry out this study have been the following: (i) temperature in the pyrolysis step has been 500°C; (ii) a high space time of $16.7 \text{ g}_{\text{catalyst}} \text{ min g}_{\text{HDPE}}^{-1}$ (corresponding to 12.5 g of catalyst); (iii) steam/plastic (S/P) ratio of 4. These conditions have been established in order to avoid operational problems. The space time value has been given as the amount of catalyst used by mass unit of the plastic fed into the pyrolysis reactor. High value of space time ($16.7 \text{ g}_{\text{catalyst}} \text{ min g}_{\text{HDPE}}^{-1}$) has been used in order to ensure high initial conversion of the volatiles coming from pyrolysis step and ensure a slow deactivation of the catalyst. Moreover, using a S/P ratio of 4 catalyst stability is guaranteed, given that coke gasification is favored and at the same time hydrogen production is increased.

The gaseous products quantified are as follows: H_2 , CO_2 , CO , CH_4 and light hydrocarbon fraction ($\text{C}_2\text{—C}_4$), composed mainly of ethylene, ethane, propylene and propane. The unreformed liquid fraction in the volatile stream coming from pyrolysis step has been called C_{5+} fraction. This fraction is conventionally called tar and should be removed in order for the product gas to be used as synthesis gas or conduct a further separation to isolate hydrogen.

The evolution of the conversion and hydrogen production with temperature is shown in **Figure 2a** and **b** shows the evolution of gaseous products yields with temperature. In order to quantify the results obtained in the reforming step, some reaction indices have been defined. The conversion is defined as the carbon conversion efficiency, i.e., the percentage of carbon moles contained in the plastic feed that are recovered in the gaseous products. **Figure 2a** shows that the conversion is greater than 94% in the temperature range studied. In addition, an increase in temperature enhances the reforming reaction, achieving a conversion of 98% at 700°C. Therefore, at this temperature only 2% of the carbon fed, which is in the C_{5+} fraction of the product stream, remains without transforming into gas. It should be noted that, at the temperature range studied, the conversion of hydrocarbons entering the reforming reactor (mostly waxes as aforementioned in the previous section) is almost full. This trend is characteristic of steam reforming reactions [29, 58], which is because the endothermic hydrocarbon reforming reactions and cracking reactions are enhanced as temperature is increased.

Another interesting index for quantify the results obtained is hydrogen production. This index is calculated as the mass of hydrogen produced per plastic mass unit fed into the pyrolysis step. **Figure 2a** shows the evolution of hydrogen production with temperature. The production of hydrogen increases with temperature, reaching a value of 37.3 wt% at 700°C. In fact, as temperature is increased the endothermic reaction of reforming is favored, enhancing hydrogen production. Based on the mass balance of hydrogen, approximately 63% of this hydrogen is formed from steam and the remaining 37% from the plastic. This hydrogen production is slightly higher than that obtained by Czernik and French [31], 34 wt%, in their study of pyrolysis-reforming of PP.

The increase in conversion and hydrogen production with temperature in the catalytic steam reforming of municipal solid wastes [59] is explained because all the endothermic steps involved are favored: (i) initial pyrolysis of waste; (ii) char

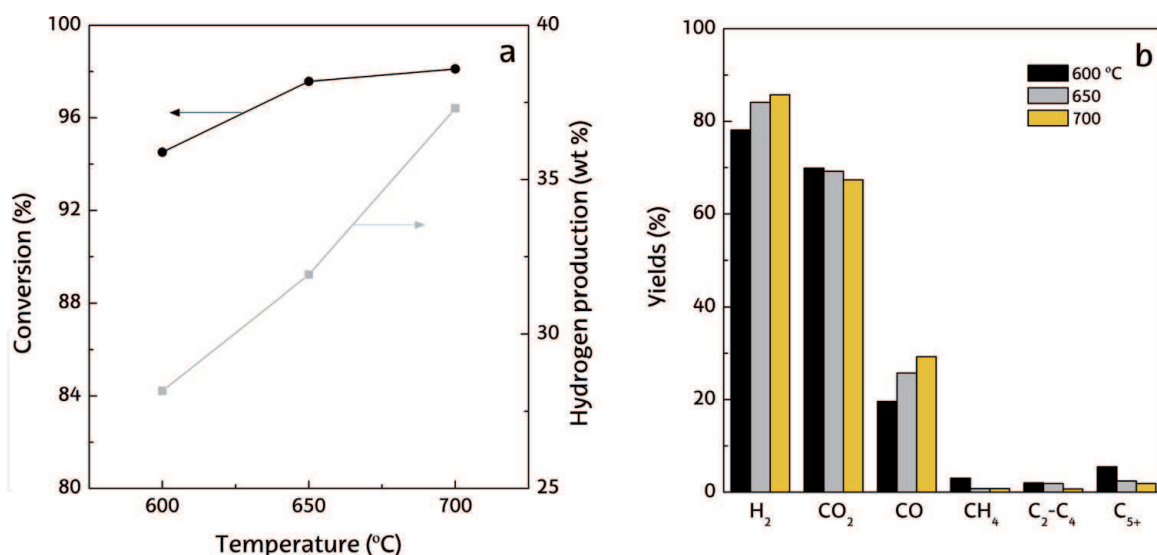


Figure 2. (a) Evolution of HDPE conversion and hydrogen production with temperature; (b) effect of reforming temperature on product yields. Reaction conditions: $T_{\text{pyrolysis}}$ 500°C; space time, $16.7 \text{ g}_{\text{catalyst}} \text{ min g}_{\text{HDPE}}^{-1}$ and S/P ratio: 4.

gasification reactions; (iii) cracking and steam reforming of the tar. In the latter case, the increase in temperature enhances the endothermic reactions of reforming, as well as cracking.

Figure 2b shows the effect reforming temperature in the 600–700°C range has on products yields. Product yields are the reaction indices defined for the assessment of the reforming step performance. The yield of C containing individual compounds is defined by mass unit of plastic in the feed, and the hydrogen yield is a percentage of the maximum allowed by stoichiometry, which accounts for the hydrogen coming from the polymer and the steam. **Figure 2b** reveals that an increase in the reforming temperature leads to an increase in the yields of hydrogen, from 78.1% at 600°C to 85.7% at 700°C. Simultaneously, it is observed that temperature increase favors the formation of CO, obtaining a yield of 29.2% at 700°C. The effect of temperature on the CO₂ yield is lower, since it remains constant due to the shift in the equilibrium of the water-gas shift (WGS) exothermic reaction.

The increase in the yield of hydrogen and CO is because an increase in the reforming temperature favors the reforming of waxes, light hydrocarbons and CH₄. Thus, although CH₄, C₂–C₄ and C₅+, yields are very low in the whole temperature range studied, a slight decrease is observed as temperature is increased, obtaining yields of 0.8, 0.7 and 1.9% at 700°C, respectively. This result indicates the reforming of these compounds is enhanced selectively over their formation by cracking. On the other hand, it must be taken into account that the WGS reaction is exothermic, and therefore its thermodynamic equilibrium shift towards CO formation by increasing temperature.

3.1.2 Effect of space time

The effect the space time has on the reforming step has been studied in the $2.8\text{--}20.8 \text{ g}_{\text{catalyst}} \text{ min g}_{\text{HDPE}}^{-1}$ range, by varying the amount of the catalyst, with the plastic feed rate being 0.75 g min^{-1} . The remaining conditions are as follows: (i) temperature in the pyrolysis step, 500°C; (ii) temperature in the reforming step, 700°C; (iii) S/P ratio, 4. As in the previous section, the effect of space time on the conversion, hydrogen production and gaseous products yields has been studied.

Figure 3 shows the evolution with space time of conversion and hydrogen production (**Figure 3a**) and of the products yields (**Figure 3b**). As observed in **Figure 3a**,

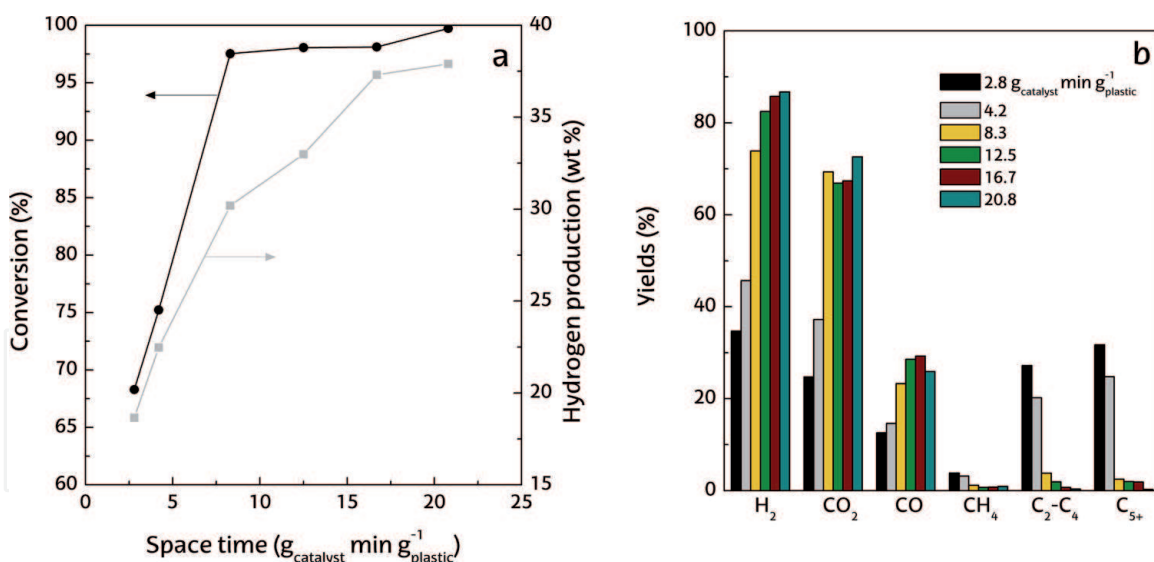


Figure 3.

(a) Evolution of HDPE conversion and hydrogen production with space time; (b) effect of space time on product yields. Reaction conditions: $T_{\text{pyrolysis}}$ 500°C; $T_{\text{reforming}}$ 700°C; and S/P ratio, 4.

there is a sharp increase in conversion when space time is increased from 2.8 (68.3%) to 8.3 $\text{g}_{\text{catalyst}} \text{min g}_{\text{HDPE}}^{-1}$ (97.5%). An increase in space time above the latter value only contributes to slightly increasing conversion, which is almost full (99.7%) for a space time of 20.8 $\text{g}_{\text{catalyst}} \text{min g}_{\text{HDPE}}^{-1}$. Regarding hydrogen production, it increases from 18.6 wt% at 2.8 to 38 wt% at 20.8 $\text{g}_{\text{catalyst}} \text{min g}_{\text{HDPE}}^{-1}$. The production of hydrogen increases more significantly in the space time range from 2.8 to 8.3 $\text{g}_{\text{catalyst}} \text{min g}_{\text{HDPE}}^{-1}$, whereas in the 8.3–20.8 $\text{g}_{\text{catalyst}} \text{min g}_{\text{HDPE}}^{-1}$ range the increase is milder.

Figure 3b shows the effect space time in the 2.8–20.8 $\text{g}_{\text{catalyst}} \text{min g}_{\text{HDPE}}^{-1}$ range has on product yields. By enhancing the extent of reforming reactions and WGS reactions, the increase in space time increases the yields of hydrogen, CO_2 and CO , whereas it decreases the yields of CH_4 , $\text{C}_2\text{--C}_4$ and C_{5+} . An increase in space time (**Figure 3a**) from 2.8 to 8.3 $\text{g}_{\text{catalyst}} \text{min g}_{\text{HDPE}}^{-1}$ leads to a pronounced increase in the yield of hydrogen and CO_2 to 73.8 and 69.3%, respectively. In the mentioned range of space time, the increase in CO yield is less significant, reaching a value of 23.2% for 8.3 $\text{g}_{\text{catalyst}} \text{min g}_{\text{HDPE}}^{-1}$. Therefore, it seems that increasing space time in this range the WGS reaction is selectively favored. It is also important to highlight the decrease in the yields of CH_4 , $\text{C}_2\text{--C}_4$ and C_{5+} , especially in the case of $\text{C}_2\text{--C}_4$ and C_{5+} , whose yields decrease from 27.2 to 3.8%, and from 31.7 to 2.4%, respectively, in the 2.8–8.3 $\text{g}_{\text{catalyst}} \text{min g}_{\text{HDPE}}^{-1}$ range.

For space times higher than 8.3 $\text{g}_{\text{catalyst}} \text{min g}_{\text{HDPE}}^{-1}$ there is hardly any change in the yields. However, in the case of hydrogen, its yield continues increasing, reaching 86.7% for a space time of 20.8 $\text{g}_{\text{catalyst}} \text{min g}_{\text{HDPE}}^{-1}$. On the other hand, an increase in space time from 8.3 to 16.7 $\text{g}_{\text{catalyst}} \text{min g}_{\text{HDPE}}^{-1}$ hardly affects CO_2 yield, whereas it leads to a slight decrease in CO , which reaches a maximum value of 29.3%.

The remarkable effect of space time on conversion and gaseous product yields is well established in the literature in both the pyrolysis and reforming of plastics [60] and the gasification and reforming of municipal solid waste [59, 61, 62], which is explained by the enhancement of the reforming and WGS reactions.

3.1.3 Effect of steam/plastic (S/P) ratio

In this section, the effect S/P ratio in the 3–5 range has on conversion, hydrogen production and products yields at zero time on stream is shown. The operating conditions selected to carry out this study have been the following: (i) temperature

of the pyrolysis step, 500°C; (ii) temperature of the reforming step, 700°C; (iii) space time, 16.7 g_{catalyst} min g_{HDPE}⁻¹. The effect of S/P ratio is directly related to the steam partial pressure, thus the steam partial pressure in the reaction medium is more significant when this ratio is increased.

Figure 4 shows the evolution of conversion and hydrogen production with the steam/plastic (S/P) ratio (**Figure 4a**), as well as the evolution of products yields with S/P ratio (**Figure 4b**). **Figure 4a** shows that in the S/P range studied conversion is over 98%, reaching almost 99.6% with a ratio of 5. By increasing the S/P ratio from 3 to 4, the effect of the ratio is not very relevant and, as mentioned above, by increasing to 5 conversion is almost full. The reaction rate of the reforming and WGS reactions are enhanced by increasing the steam partial pressure in the reaction environment, which explains the high conversions obtained. Consequently, hydrogen production significantly increases in the S/P range studied, from 31.0 wt% for a S/P ratio of 3 to 38.1 wt% for a S/P ratio of 5.

Figure 4b displays the effect S/P ratio in the 3–5 range has on product yields. It is observed that an increase in this ratio leads to a progressive increase in the hydrogen and CO₂ yields and a decrease in those of CO, CH₄, C₂–C₄ and C₅₊. This effect is due to the higher concentration of steam in the reaction environment, which favors the displacement of both hydrocarbons reforming reactions and the WGS reaction. By favoring all the reactions involved in the reforming, an increase in the S/P ratio enhances the yield of hydrogen and CO₂, up to 92.5 and 80.9% for a ratio of 5. Consequently, the yield of CO decreases to 18.1%. The yields of CH₄, C₂–C₄ and C₅₊, which are small for a S/P ratio of 4, decrease until becoming insignificant.

As observed, an increase in S/P ratio causes a positive effect on conversion and hydrogen production; however, an excessive increase affects significantly on the energy efficiency of the process.

Qualitatively similar effects of S/P ratio were observed in the pyrolysis-reforming of PP [63, 64], LDPE and PS [63] and municipal plastic wastes [65], which is a widely proven fact in the gasification of different polymeric materials [58, 66].

3.1.4 Catalyst deactivation

Knowledge of catalyst deactivation is essential for its choice, design of the reactor and establishment of the optimal strategy for the operation of industrial

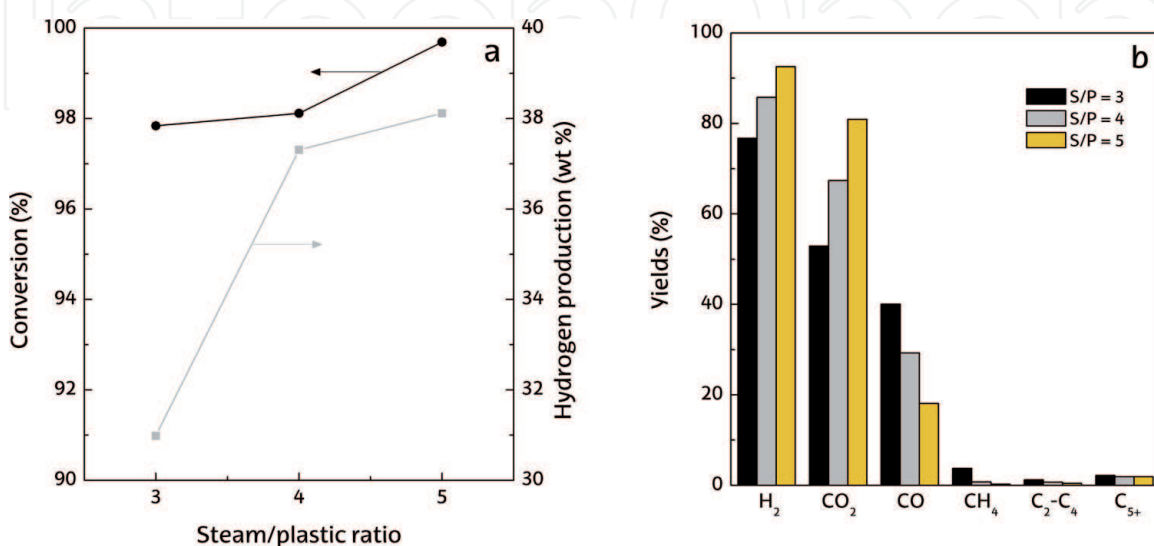


Figure 4. (a) Evolution of HDPE conversion and hydrogen production with S/P ratio; (b) effect of the S/P ratio on product yields. Reaction conditions: $T_{\text{pyrolysis}}$ 500°C; $T_{\text{reforming}}$ 700°C; and space time, 16.7 g_{catalyst} min g_{HDPE}⁻¹.

catalytic processes. It is well documented that coke deposition is the main cause of catalyst deactivation in the pyrolysis-reforming of plastics [63, 67], as well as in the reforming of hydrocarbons and oxygenates (methanol, DME, ethanol, bio-oil) [68, 69]. This deposition is especially important for Ni based catalysts.

The commercial catalyst used in this study does not undergo a significant Ni sintering because it is designed to use in CH₄ reforming, which is a reaction carried out at a temperature of around 850°C, i.e., higher than the highest used in this study (700°C). The plastics used do not contain S, and therefore the deactivation cause is the deposition of coke. Three different types of coke have been identified in the reforming of CH₄ on Ni catalyst: pyrolytic, encapsulating and filamentous [70]. Numerous studies support this classification of the coke deposited in the reforming of CH₄, hydrocarbons and biomass derivatives.

Wu and Williams [26] have verified by transmission electron microscopy (TEM) that the coke deposited on Ni catalyst used in the production of hydrogen by pyrolysis-reforming of PP is composed of two types of coke, amorphous and filamentous, with the latter having similar characteristics as carbon nanotubes and graphene (according to their graphitization degree). Considering the commercial interest of filamentous coke for these applications, Acomb et al. [63] have studied the simultaneous production of carbon nanotubes and hydrogen through pyrolysis-reforming of PP, which improves the economy of the process and provides an additional incentive for the viability of plastic recycling.

In this section, a study is carried out of the effect catalyst deactivation has on conversion and product yields with time on stream. The reaction conditions used are as follows: (i) temperature in the pyrolysis step, 500°C; (ii) temperature in the reforming step, 700°C; (iii) space time, 16.7 g_{catalyst} min g_{HDPE}⁻¹ and (iv) S/P ratio, 4. The study has been carried out under conditions in which a slow deactivation of the catalyst is observed, evaluating the effect of the incipient deposition of coke and the evolution of this deposition up to 123 min of reaction.

Figure 5 shows the effect catalyst deactivation has on plastics conversion (**Figure 5a**) and product yields (**Figure 5b**). As observed, whilst the reforming reaction progresses with time on stream the conversion of plastics decreases due to the deactivation undergone by the catalyst, decreasing linearly from 98.1% at zero time on stream to 90.3% in 123 min. Besides, comparing the evolution of conversion (**Figure 5a**) and the evolution of product yields (**Figure 5b**), the decrease in H₂ and CO₂ yields decrease in a similar trend to that of conversion, as catalyst deactivation hinders the reforming reaction, as well as the WGS reaction. Consequently, CH₄, C₂—C₄ and C₅₊ hydrocarbon yields increase. As observed in **Figure 5**, the conversion and the yields of H₂ and CO₂ decrease linearly and those of CH₄, C₂—C₄ and C₅₊ hydrocarbons increase linearly. The lineal catalyst deactivation rate observed should be attributed to: (i) high temperature favoring the kinetics of reforming reactions due to their endothermic nature, which leads to a low concentration of hydrocarbons in the reaction medium, and therefore low coke deposition rate (low catalyst deactivation); (ii) high temperature enhances the gasification of the deposited coke and so minimize catalyst deactivation [68].

As a result of reforming activity decrease, CH₄, C₂—C₄ and C₅₊ fraction yields increase over time, which is more noticeable as the molecular weight of the hydrocarbons increases. This trend is explained by the reforming of C₅₊ hydrocarbons in parallel with the thermal cracking of these compounds towards CH₄ and C₂—C₄. Consequently, as reforming rate decreases due to catalyst deactivation the thermal cracking reactions are favored. This cracking phenomenon is well known in deactivated catalysts and is more important as the molecular weight of aliphatic compounds is higher [71].

It is established in the literature that paraffin capacity for coke formation is greater as their molecular weight is higher [72]. Similarly, the capacity for coke

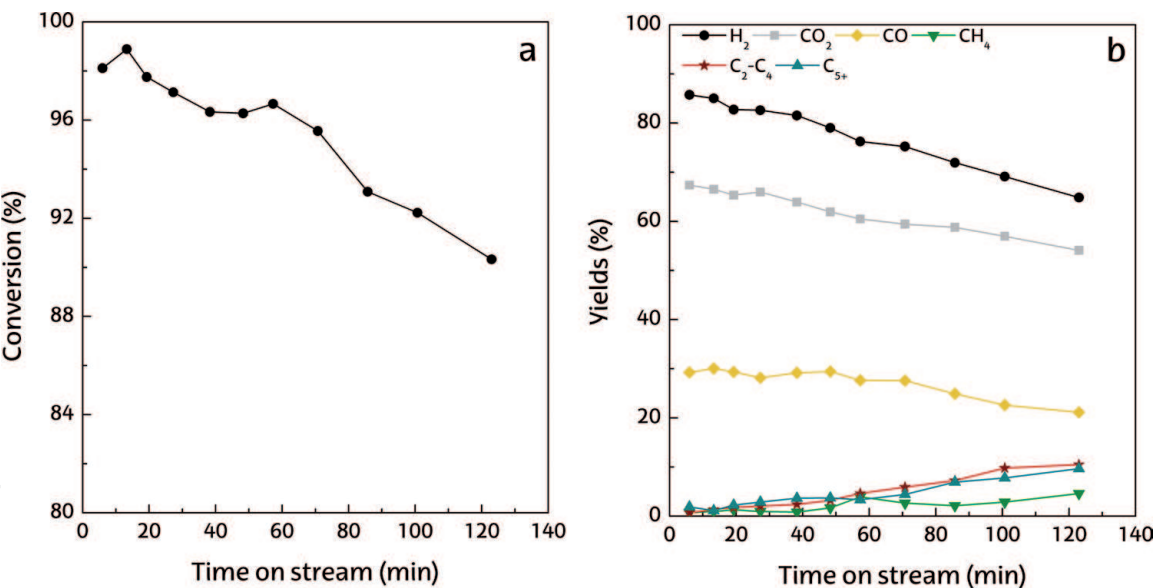


Figure 5.
(a) Evolution of HDPE conversion with time on stream; (b) evolution of product yields with time on stream.
Reaction conditions: $T_{\text{pyrolysis}}$ 500°C; $T_{\text{reforming}}$ 700°C; space time, 16.7 g_{catalyst} min g_{HDPE}⁻¹; S/P = 4.

formation of ethylene and benzene, is higher than that of paraffin compounds [71]. It is also well recognized that the coke formed on a Ni catalyst at high temperature is more filamentous and with less capacity for blocking Ni sites [68, 71].

Figure 6 displays a temperature programmed oxidation (TPO) profile of the coke deposited on the catalyst after 123 min reaction. Moreover, an average coke deposition rate has been quantified in order to calculate the extent of coke deposition. According to the TPO profile obtained, it has been determined that the average coke deposition rate is 0.7 mg_{coke} g_{catalyst}⁻¹ g_{HDPE}⁻¹. Furthermore, two different peaks may be observed in **Figure 6**, which are evidence of two cokes of different

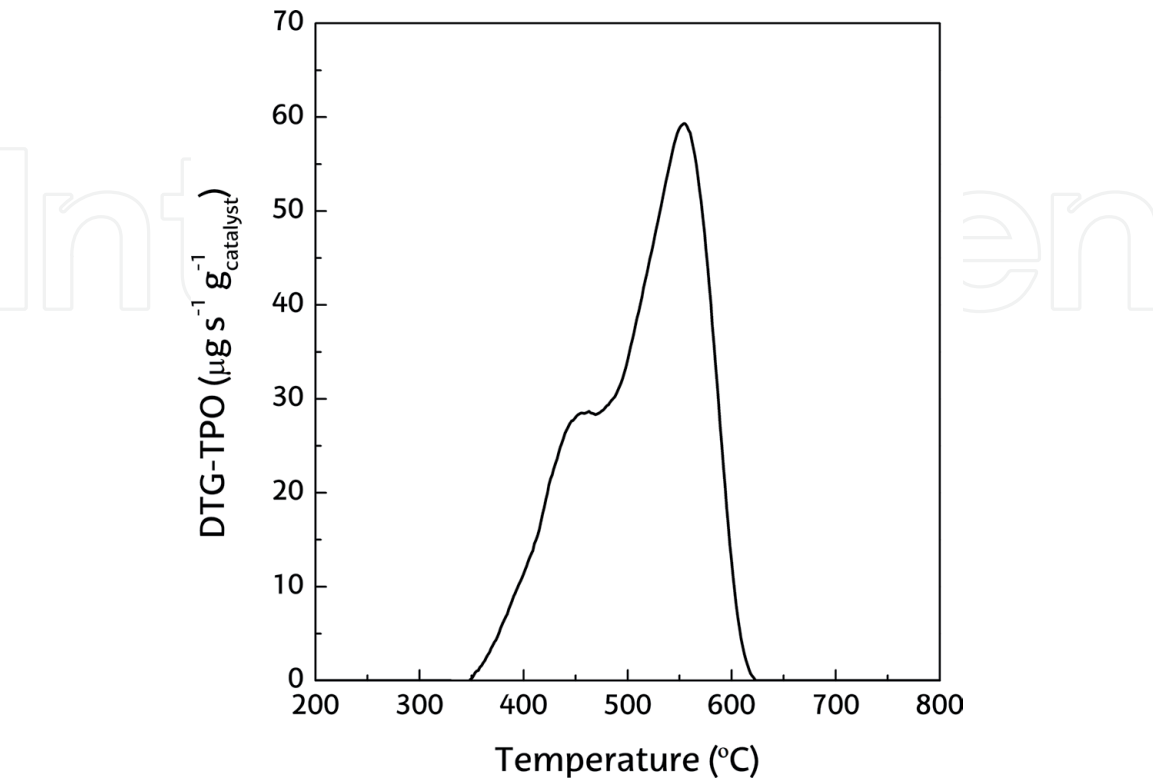


Figure 6.
TPO profile of the coke deposited on the catalyst.

nature and location on the catalyst. The main peak appears at 550°C and accounts for a partially structured coke, whereas the second peak at 430°C corresponds to an encapsulating coke, which is deposited on the Ni metal.

The encapsulating coke is deposited close to the active sites, which promote coke combustion. Furthermore, this amorphous structure hinders the adsorption of reactants, which increases the concentration of non-converted hydrocarbons in the reaction environment, and consequently deactivates the catalyst. On the other hand, the combustion of the partially structured coke occurs at higher temperature due to the further location of the coke from the metallic sites, thereby hindering its combustion [63, 73]. This type of deposited coke corresponds to the filamentous coke, which generally does not affect directly to catalyst deactivation, as it does not block the active sites [69]. However, when its content is severe, it blocks the active sites, hindering the adsorption of reactants, and consequently increasing the concentration of non-converted hydrocarbons in the reaction medium.

The aforementioned identification of two types of coke has been corroborated based on the scanning electron microscopy (SEM) image of the deactivated catalyst displayed in **Figure 7**. It should be noted that the nature of the coke deposited on the deactivated catalyst at 123 min reaction is amorphous and fibrillary. Ochoa et al. [74] demonstrated that coke content evolves with time on stream. In this evolution, both types of cokes growth throughout time on stream with different rates, with the one for filamentous coke being higher. However, it can be concluded that coke deposition is more influenced by the growth of encapsulating coke, as has also been established in the literature [75, 76].

3.2 Pyrolysis and in-line reforming of different plastics

Approximately 40% of the post-consumption wastes come from agriculture, construction, automotive and distribution sectors, and the remaining 60% from municipal solid wastes (MSW). Although the plastics only account for 7 wt% in the MSW, its contribution is 20 vol% of the total MSW volume. Therefore, the

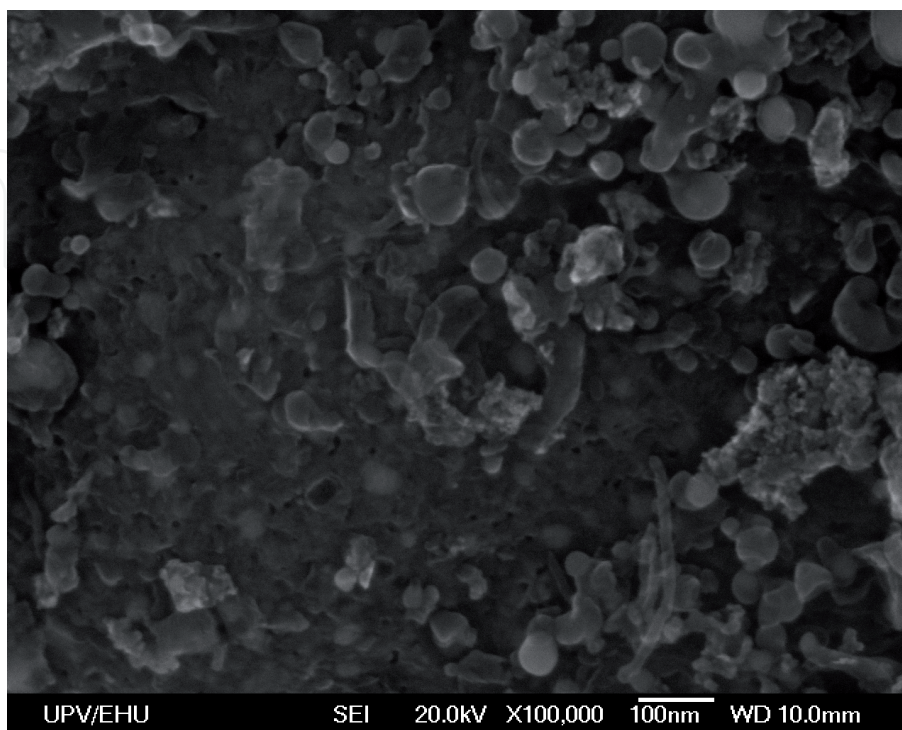


Figure 7.
SEM image of the deactivated catalyst.

thermochemical routes are of especial relevance for plastic valorization for obtaining fuels or for the production of chemical products, such as hydrogen. Moreover, the large scale viability of these processes will presumably require the joint valorization of different plastics from MSW. Accordingly, this section deals with the valorization of plastics of different nature by means of pyrolysis and in-line reforming strategy in order to evaluate its feasibility. Based on their production scale, the following plastics were selected: high density polyethylene (HDPE), polypropylene (PP), polyethylene terephthalate (PET) and polystyrene (PS). The operating conditions selected to carry out this study have been as follows: (i) temperature of the pyrolysis step, 500°C; (ii) temperature of the reforming step, 700°C; (iii) space time, 16.7 g_{catalyst} min g_{HDPE}⁻¹; (iv) S/P ratio of 4.

The hydrogen produced in the pyrolysis and in-line catalytic reforming of different plastics is shown in **Figure 8a**. As observed, the highest hydrogen production is obtained when HDPE and PP are used as feed, 37.3 and 34.8 wt%, respectively, followed by PS (29.1 wt%), which has a lower hydrogen content in its composition. However, the oxygenated nature of the PET and the residue formed in its pyrolysis step leads to a lower hydrogen production in the reforming step (18.2 wt%). Wu and Williams [26] also observed lower conversion of PS pyrolysis volatiles compared to HDPE in the pyrolysis and in-line reforming of different plastics. A hydrogen production of 34 wt% was obtained by Czernik and French [31] in the pyrolysis and in-line reforming of PP using two fluidized bed reactors. Namioka et al. [29] performed the pyrolysis-reforming of PP and PS, with hydrogen production being 36 and 33 wt%, respectively. Recently, Saad and Williams [28] studied the pyrolysis and in-line dry reforming of different plastics, obtaining hydrogen productions of 15, 7.6 and 2.5 wt% for PE, PS and PET, respectively.

It should be highlighted that the Ni catalyst used for the pyrolysis-reforming process allows achieving a high conversion of pyrolysis products to gases (>98%), with a space time of 16.7 g_{catalyst} min g_{plastic}⁻¹. This result is comparable to those obtained in the literature on Ru catalysts. Park et al. [30] obtained a similar conversion in the pyrolysis-reforming of PP, in a continuous regime system consisting of fixed bed reactors at 400 and 630°C, respectively, and using a space time of 9.8 g_{catalyst} min g_{plastic}⁻¹. Based on this result, these authors note that the advantage of using Ru catalysts instead of Ni is the reduction of the reforming temperature by 70°C. Namioka et al. [29] extended the study using Ru catalysts to the pyrolysis-reforming of PS, verifying that under the indicated conditions the differences

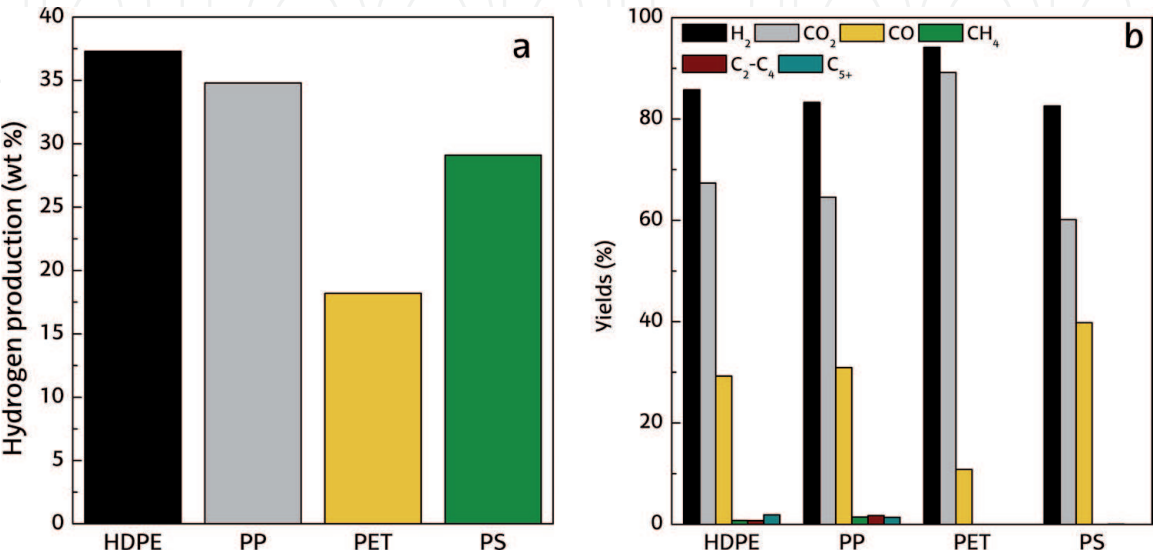


Figure 8.
Hydrogen production (a) and product yields (b) in the pyrolysis and in-line reforming of different plastics.

between the results for PP and PS are small. However, the most used catalysts in reforming processes are those based on Ni and Co, due mainly to its low cost in relation to noble metals.

Figure 8b shows the product yields obtained in the reforming of plastic pyrolysis volatiles. It should be noted that the hydrogen yield is based on the maximum allowable by stoichiometry, but those of the other compounds are given by C mole unit fed into the reforming step. As observed, there is a considerable effect on H₂, CO₂ and CO yields. On the one hand, the product yields are similar for HDPE and PP, as a consequence of the similar composition of the pyrolysis volatiles to be reformed, with hydrogen yields being 85.7 for HDPE and 83.3% for PP, respectively, and CO₂ yields of 67.4 and 64.6% and CO yields of 29.3 and 30.9%, respectively.

However, the distribution of the reforming products is different in the case of PET due to the differences in the pyrolysis volatile stream, with CO₂ and CO yields being of 29.3 and 9.9%, respectively. Thus, the product distribution in the reforming step is as follows: hydrogen yield 94.1%, CO₂ yield 89.2% and CO yield 10.8%. The high hydrogen yield and low CO yield obtained allow discarding the hypothesis that the origin of the CO₂ is the thermal decomposition of the oxygenate compounds. It is in fact produced by the WGS reaction, which is enhanced by the higher value of the effective space time (by carbon atom unit) for this plastic. In addition, it should be noted that yields of CH₄, C₂—C₄ hydrocarbons and non-converted C₅₊ are lower than in the case of HDPE and PP, which is a consequence of the higher effective space time used with this plastic.

On the other hand, the hydrogen yield obtained when PS is fed is similar to that obtained in the cases of HDPE and PP, whereas the CO₂ yield is slightly lower (60.2%) and that of CO slightly higher (39.8%). This result may also be associated with the lower extent of the WGS reaction due to the lower effective space time used in the case of this plastic.

It should also be pointed out that the results obtained for the PP and HDPE are similar to those obtained in the literature using Ru catalysts [29, 30], although they are obtained at lower temperatures (630 vs. 700°C) and using lower space time values (9.8 vs. 16.7 g_{catalyst} min g_{plastic}⁻¹).

4. Conclusions

The hydrogen production from plastic has been studied in a two-step process. The first is the polymer fast pyrolysis and the second the catalytic steam reforming of pyrolysis volatiles. The process has been developed in a bench scale unit operating in continuous regime. The conical spouted bed reactor has been selected for the pyrolysis step because its features avoid operational problems and allow operating at low pyrolysis temperatures (500°C), minimizing the energy requirement. It has been observed that the yields and the composition of pyrolysis volatiles obtained at 500°C feeding steam are similar to those corresponding to the pyrolysis under N₂ atmosphere.

The temperature, space time and steam/plastic ratio in the reforming step have a great influence on the product yields and distributions obtained. An increase in the three variables favors the reforming of the pyrolysis volatiles, obtaining a hydrogen yield of 92.5% of that allowable by stoichiometry for a space time of 16.7 g_{catalyst} min g_{HDPE}⁻¹ at 700°C when a steam/plastic ratio of 5 is used. An increase in temperature in the 600–700°C range increases the conversion from 94.5 to 98.1% and the hydrogen yield from 78.1 to 85.7%. However, the WGS reaction is hindered, which increases the CO yield. An increase in space time causes a considerable increase in the conversion and yields of H₂, CO₂ and CO, and a decrease in the yields of CH₄, C₂—C₄ and C₅₊ hydrocarbons.

Moreover, an increase in the steam/plastic ratio increases the hydrogen yield, by displacing the reforming and the WGS reactions. The conversion obtained with a steam/plastic ratio of 5 at 700°C and with a space time of $16.7 \text{ g}_{\text{catalyst}} \text{ min g}_{\text{HDPE}}^{-1}$ is almost full (99.7%), with a hydrogen yield of 92.5%.

The use of a fluidized bed reactor in the reforming step allows the operation without problems. However, reaction rate decreases due to the deposition of coke on the catalyst. As a result of this deposition, the specific surface and pore volume of the catalyst decrease and the yields of non-reformed hydrocarbons (CH_4 , light hydrocarbons ($\text{C}_2\text{—C}_4$) and C_{5+} fraction) increase with time on stream.

The individual valorization of the different plastics leads to conversion values above 98% in all cases. The reforming behavior is similar for HDPE and PP. PET leads to higher yields of H_2 (94.1%) and CO_2 (89.2%). In the case of PS, H_2 yield is similar to those obtained when HDPE and PP (82.5%) are fed, whereas the CO_2 yield is slightly lower (60.2%).

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Conflict of interest


The authors of this chapter declare no conflict of interest.

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