

Research article

Analysis of hydrogen production potential from waste plastics by pyrolysis and in line oxidative steam reforming

Maria Cortazar^a, Ningbo Gao^c, Cui Quan^c, Mayra Alejandra Suarez^a, Gartzzen Lopez^{a,b,*}, Santiago Orozco^a, Laura Santamaria^a, Maider Amutio^a, Martin Olazar^a

^a Department of Chemical Engineering, University of the Basque Country UPV/EHU, P.O. Box 644, E48080 Bilbao, Spain

^b IKERBASQUE, Basque Foundation for Science, Bilbao, Spain

^c School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, China



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ABSTRACT

A study was carried out on the valorization of different waste plastics (HDPE, PP, PS and PE), their mixtures and biomass/HDPE mixtures by means of pyrolysis and in line oxidative steam reforming. A thermodynamic equilibrium simulation was used for determining steam reforming data, whereas previous experimental results were considered for setting the pyrolysis volatile stream composition. The adequacy of this simulation tool was validated using experimental results obtained in the pyrolysis and in line steam reforming of different plastics. The effect the most relevant process conditions, i.e., temperature, steam/plastic ratio and equivalence ratio, have on H₂ production and reaction enthalpy was evaluated. Moreover, the most suitable conditions for the oxidative steam reforming of plastics of different nature and their mixtures were determined. The results obtained are evidence of the potential interest of this novel valorization route, as H₂ productions of up to 25 wt% were obtained operating under autothermal conditions.

1. Introduction

Plastic are playing a critical role in the modern consumer society due to their excellent features and numerous applications, such as building, packaging, healthcare, electronics, automotive or agriculture. Thus, plastics global production has continuously grown in recent years, with a global annual production of 360 million tons (Mt) in 2018 [1].

The environmental concern associated with waste plastics is growing due to the persistent impact of plastics on the oceans, freshwater and terrestrial environments [2]. Within this scenario, the development of feasible processes for waste plastic management is an urgent matter to which increasing attention has been paid in recent years.

In spite of the high calorific value of waste plastics, their incineration involves high emission levels of environmentally noxious contaminants [3,4]. Furthermore, the high CO₂ amounts released by plastics incineration, as well as the increasing priority towards tertiary recycling methods, have pushed this process into the background [5]. This situation has promoted the development of alternative environmentally friendly waste plastics management routes. Over the last decades, several thermochemical approaches have been proposed for the

valorization of waste plastics [6–9]. The interest of these valorization routes lies in their possibility to produce fuels and chemicals from plastics of different nature and their mixtures, as well as from mixtures of plastics with other solid residues. The pyrolysis or thermal degradation is performed under inert atmosphere, and a wide variety of reactor designs have been proposed [9–11]. Thermal pyrolysis is usually performed at mild temperatures. However, this is not a selective process and wide product distributions are usually obtained [12–15], which limits the commercial interest of this process. The use of in situ or in line catalysts is a common strategy for the improvement of process selectivity towards specific fuels and chemicals [16–18]. More recently, the joint valorization of waste plastics with other feedstocks, especially biomass, has gained increasing attention. Thus, this strategy contributes to the reduction of oxygen content in the biomass pyrolysis oil (bio-oil) [19,20], apart from interesting synergistic interactions involving radicals during the co-pyrolysis process, which lead to stable pyrolysis oil, and so avoid phase separation [19]. Moreover, positive effects have also been observed in the oil yield and composition when biomass and waste plastics are jointly pyrolysed [21].

Gasification is performed at higher temperatures, usually above

* Corresponding author at: Department of Chemical Engineering, University of the Basque Country UPV/EHU, P.O. Box 644, E48080 Bilbao, Spain.

E-mail address: gartzzen.lopez@ehu.es (G. Lopez).

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Table 1
Product distributions obtained in the fast pyrolysis of different plastics and biomass.

HDPE		PP		PET		PS		Biomass	
Compound	Yield (wt %)	Compound	Yield (wt %)	Compound	Yield (wt %)	Compound	Yield (wt %)	Compound	Yield (wt %)
<i>Gases</i>	1.5	<i>Gases</i>	1.28	<i>Gases</i>	42.78	<i>Gases</i>	1.49	<i>Gases</i>	7.3
Methane	0.03	Methane	0.02	Carbon monoxide	9.88	Methane	0.09	Carbon monoxide	3.38
Alkanes	0.32	Alkanes	0.3	Carbon dioxide	29.28	Alkanes	0.17	Carbon dioxide	3.27
Alkenes	1.15	Alkenes	0.96	Alkenes	1.28	Alkenes	1.23	C ₁ -C ₄ hydrocarbons	0.68
C ₅ -C ₁₁	5.87	C ₅ -C ₁₁	3.79	<i>Liquid</i>	12.82	<i>Liquid</i>	98.51	Hydrogen	0.05
Paraffins	0.34	Paraffins	0.22	Acetaldehyde	11.11	Single ring aromatics	10.25	<i>Bio-oil</i>	75.3
Isoparaffins	2.5	Isoparaffins	1.6	n-Butyl acetate	0.25	Styrene	70.57	Acids	2.73
Aromatics	0.28	Aromatics	0.16	Benzene	1.04	α-Methylstyrene	3.86	Aldehydes	1.93
Naphthenes	0.19	Naphthenes	0.11	Acetone	0.14	Toluene	3.54	Alcohols	2.00
Olefins	2.56	Olefins	1.7	<i>Solid volatiles</i>	35.45	Ethylbenzene	1.28	Ketones	6.37
C ₁₂ -C ₂₀	25.64	C ₁₂ -C ₂₀	19.93	Benzoic acid	26.98	Polyaromatics	1.7	Phenols	16.49
Diolefins	6.22	Diolefins	2.5	4-		/1,1-		Furans	3.32
Olefins	13.07	Olefins	10.16	Carboxybenzaldehyde	2.55	Diphenylethylene	1.2	Saccharides	4.46
Paraffins	6.35	Paraffins	7.27	2-Methylbenzofuran	1.09	1,1-Diphenylethane	2.05	Water	25.36
Waxes	67	Waxes	75	Biphenyl	0.41	Fluorene	1.12	<i>Char</i>	17.3
				<i>Solid residue</i>	7.02	1,3-Diphenyl propane	0.79		

700 °C, using gasifying agents, such as steam, air, CO₂ or their mixtures [22–24]. The composition and applications of the syngas strongly depend on the gasifying agent used. Thus, steam and O₂ gasification leads to a syngas with high H₂ concentrations and a H₂/CO ratio suitable for synthesis application [25–27]. However, the gas product obtained in the air gasification is diluted in N₂, and is therefore mainly used for energy production [28,29]. Recently, the combination of pyrolysis and in line steam reforming was proposed as a new strategy for the selective H₂ production [22,30]. In this strategy, pyrolysis is performed at low temperatures in a first step, and the plastic derived volatiles are transferred to a second reactor for the catalytic steam reforming process. It is to note that this process has been mainly studied in lab scale units made up of two fixed bed reactors operating in batch regime [31–39]. However, the attempts for the development of a continuous process in bench scale units are scarce. Thus, Czernik and Frech [40] proposed a process based on two fluidized bed reactors for fast pyrolysis at 650 °C and catalytic steam reforming over a commercial Ni based catalysts at 850 °C. The process developed by Namioka et al. [41,42] used two fixed bed reactors and a Ru based catalysts in a wide temperature range, and the effect of plastic composition was also analyzed. More recently, a combination of a conical spouted bed reactor (CSBR) operating at 500 °C and a fluidized bed reactor (FBR) at 700 °C was proposed by the research group headed by Prof. Olazar for the fast pyrolysis and in line steam reforming of plastics [43–45].

The pyrolysis and in line reforming strategy has some important advantages in relation to the conventional single-step waste plastic gasification. Thus, the process is carried out at lower temperatures and, furthermore, different temperatures may be selected for the pyrolysis and in line reforming processes. In addition, the two-step strategy avoids the direct contact of plastic impurities with the reforming catalyst [22,46]. The pyrolysis-reforming process has proven to have a remarkable capacity for H₂ production from different waste plastics, biomasses and other feedstocks [35,44,47–50]. Interestingly, this process is a sustainable route for H₂ production from alternative resources and wastes, whereas the current global production of H₂ is mainly based on the reforming of fossil fuels, such as natural gas, oil streams and coal [51–53].

The full-scale implementation of the pyrolysis-reforming process is conditioned by certain serious limitations. On the one hand, the development of reaction units and specific catalysts for biomass and waste reforming and, on the other hand, the process faces operational challenges, as are the high endothermicity of steam reforming reactions. Moreover, the complex nature of biomass and waste plastics pyrolysis volatiles leads to high deactivation rates of the catalyst associated with

severe coke formation [53–55]. Although further research is required for the fine-tuning of the pyrolysis-reforming technology, oxygen co-feeding may potentially contribute to overcoming some of the mentioned operational constraints. Thus, operation under oxidative conditions may reduce or even avoid energy requirements in the reforming step. Moreover, the presence of oxygen in the reforming reactor may also contribute to the in situ combustion of the coke deposited on the catalyst, and therefore improve its stability [56–58].

The aim of this study is to explore the potential of pyrolysis and in line oxidative steam reforming for H₂ production from different waste plastics and plastic/biomass mixtures. The use of the thermodynamic equilibrium approach is proposed for the reforming step simulation in a wide range of operating conditions, as previous studies reported accurate predictions of this simulation tool [59–61]. Moreover, an independent optimization of the main process conditions, i.e., temperature, steam/plastic (S/P) ratio and equivalence ratio (ER), was carried out for each feed studied. In order to evaluate the adequacy of the used simulation approach, the results obtained were compared with those obtained under steam reforming conditions by feeding different plastics and their mixtures into a continuous pyrolysis-reforming unit made up of a CSBR and a FBR [43,45,62,63]. Accordingly, this novel simulation tool was originally proposed to determine both the optimum reforming conditions of plastics pyrolysis volatiles and the H₂ production potential of this process.

2. Methodology

2.1. Equilibrium data calculation in the reforming of plastic derived volatiles

The product distribution in the reforming of fast pyrolysis volatiles was obtained based on the Gibbs free energy minimization method. This procedure is based on the resolution of material and energy balances by minimizing Gibbs free energy, i.e., those corresponding to the equilibrium condition. This tool is able to predict the experimental results for different process conditions when full conversion of pyrolysis volatiles is attained [60]. In this case, the oxidative reforming reactions were simulated by feeding the products obtained in the fast pyrolysis step. Interestingly, this thermodynamic calculation procedure allows solving complex reaction environments without the need of equilibrium constants for the reactions involved. Moreover, this approach also avoids the need to simulate reactor operation limitations (bypasses and so on) and the considerations regarding the catalyst. Therefore, the maximum H₂ yields given by thermodynamics can be determined. The commercial

Pro II 10.1 software was used for calculations, with the state equation used being the one by Soave-Redlich-Kwong. A non-stoichiometric method was used due to the low computational time required and easy convergence. The reactor was considered isothermal and operated at constant pressure.

The basis considered in the simulation was 100 kg h^{-1} of plastics or plastics/biomass mixtures fed into the pyrolysis and in line reforming process. The aim is to simulate the continuous pyrolysis-reforming process performed in an original unit made up of a CSBR and FBR. Thus, detailed pyrolysis product yields and compositions determined in previous experimental studies conducted in a CSBR were used to accurately define the stream entering the reforming unit and perform a rigorous simulation of the overall process.

In order to simulate the reforming of plastics pyrolysis volatiles, the following inlet streams to the Gibbs free reactor were considered: i) pyrolysis oil, which is the liquid product obtained in the polymer degradation and made up of hydrocarbons and oxygenates. The composition of this stream was based on previous experimental results obtained in the fast pyrolysis performed in CSBR for each individual feedstock [13,64–66]; ii) pyrolysis gases, whose composition was also defined based on previous experimental results of plastics and biomass fast pyrolysis; iii) steam, whose mass flow rate is conditioned by the S/P ratio; iv) oxygen, which was only used in the oxidative reforming reactions, with its flow rate being determined by the ER used.

In the simulation of the pyrolysis and in line reforming of HDPE/biomass mixtures, the results obtained in the pyrolysis of the single materials were used [13,67]. It should be noted that the pyrolysis of waste plastics and biomass leads to a wide product distribution, from light gases to heavy molecular weight compounds and solid products. The product yields obtained in the fast pyrolysis of polyolefins (HDPE and PP), PS, PET and biomass are summarized in Table 1.

The pyrolysis of polyolefins under fast pyrolysis conditions ensures their full conversion to volatile products without the formation of a measurable solid residue. Under these conditions, the random radical scission pyrolysis mechanism leads to a wide product distribution, with waxes and heavy hydrocarbons being the main products [66,68,69]. However, the degradation of PS is highly selective towards the formation of styrene and other single-ring aromatics [65,70,71]. The pyrolysis of PET is probably the most complex of the polymers considered in this study. In fact, a remarkable amount of carbonaceous residue is formed, apart from highly oxygenated volatile products in the gaseous, liquid and solid (at room temperature) streams [64]. In the same line, biomass pyrolysis also produces three product fractions, i.e., gases, bio-oil and char. Bio-oil is the main fraction obtained under fast pyrolysis at low temperatures, with this liquid being composed of several oxygenate families [72]. It should be noted that only volatile products are considered in the simulation, as the solid products, such as biomass char or the PET derived solid residue, remain in the pyrolysis reactor and are not fed into the subsequent reforming step.

The simulation of the reforming step was carried out in a wide range of operating conditions: temperature, 500–800 °C; S/P ratio, 0–6 (corresponding to steam/carbon molar ratios from 0 to 9.6 based on the volatiles fed into the reforming step), and ER, 0–0.25.

2.2. Experimental runs

The adequacy of the Gibbs free energy minimization method was assessed for determining the product yields in the reforming process by comparing simulation results with the experimental ones. Thus, the experimental results obtained in the pyrolysis and in line reforming of different waste plastics and biomass/plastic mixtures were used for the validation.

The experiments were carried out in a bench scale unit operating in continuous regime by feeding 0.75 g min^{-1} of plastics or biomass/plastic mixtures. A CSBR was used for the pyrolysis step, whereas a FBR was the reforming one. The design and operation details of the reaction unit can

be found elsewhere [43,62]. A commercial Ni/Al₂O₃ catalyst doped with Ca (Süd Chemie-G90LDP) was used in all the experimental runs in the reforming reactor. This catalyst was selected because of its well-proven activity and stability in the reforming of plastics and biomass pyrolysis volatiles [43,73]. The features of this catalyst were reported in previous studies [74].

Based on previous results, a pyrolysis temperature of 500 °C was selected as the optimum one for the pyrolysis step. In the pyrolysis reactor, steam is the fluidizing agent used rather than an inert gas like nitrogen. Nevertheless, the low temperature used in this pyrolysis reactor hinders any relevant impact on the product distribution. The pyrolysis volatile stream containing steam was fed into the FBR, with the operating conditions in this reactor (temperature and space time) being changed depending on the experimental run. Thus, the steam reforming temperature was varied between 600 and 700 °C and S/P ratio in the 3–5 range [43]. The space time in the steam reforming step was $16.7 \text{ g}_{\text{cat}} \text{ min g}_{\text{p}}^{-1}$, as this value ensures an almost full conversion of pyrolysis volatiles, which allows a suitable comparison with the results obtained by the equilibrium simulation. These experiments, in which the effect of S/P ratio and temperature were analyzed, were performed by feeding HDPE into the pyrolysis step. In addition, the reforming of different plastics and biomass/plastic mixtures was studied by operating at 700 °C with a S/P ratio of 4 and a space time of $16.7 \text{ g}_{\text{cat}} \text{ min g}_{\text{p}}^{-1}$. The plastics considered were HDPE, PP, PS, PET and their mixture with a composition representative of the municipal solid waste (MSW), i.e., HDPE, 48 wt%; PP, 35 wt%; PS, 9 wt% and PET, 8 wt%. Moreover, HDPE/biomass mixtures in the ratios of 25/75, 50/50 and 75/25 wt% were studied. Pure polymers were used to avoid the impact of waste plastics impurities on the reforming catalyst. Thus, HDPE, PP and PS were supplied by Dow Chemical, whereas PET was supplied by Artenius. All the polymers were fed in the form of chippings. Pine wood sawdust was used as biomass feedstock, as it is abundant and representative of lignocellulosic biomass; its detailed characterization can be found elsewhere [67]. The analysis of the reforming products was conducted by combining in line gas chromatography (Agilent 6890 GC) and gas micro chromatography (Varian 4900 micro GC) [43].

3. Results

3.1. Validation of the equilibrium simulation approach

In order to evaluate the adequacy of the proposed simulation procedure, the results obtained theoretically were compared with those obtained experimentally under steam reforming conditions. The effect of the operating conditions was ascertained by varying the temperature between 600 and 700 °C and the S/P ratio in the 3 to 5 range in the steam reforming of HDPE pyrolysis volatiles. Moreover, the performance of this simulation approach was also assessed by reforming pyrolysis volatiles of different composition. Thus, the products obtained in the pyrolysis of different plastics, plastic mixtures and biomass-plastic mixtures were considered.

H₂ concentration in the gas product and conversion in the reforming step were the parameters selected for the comparison of experimental and calculated results. The former is the key point to assess the quality of the produced gas, whereas the latter provides valuable information about the closeness to equilibrium conditions. The conversion is the ratio between the moles of C obtained in the gaseous product and those fed into the reforming step:

$$X = \frac{C_{\text{gas}}}{C_{\text{volatiles}}} \cdot 100 \quad (1)$$

In this definition, the solid products formed in the pyrolysis step are not considered, as they were not fed into the reforming step.

Moreover, the main reactions considered for the interpretation of the results obtained in the reforming of plastic pyrolysis volatiles are as follows:

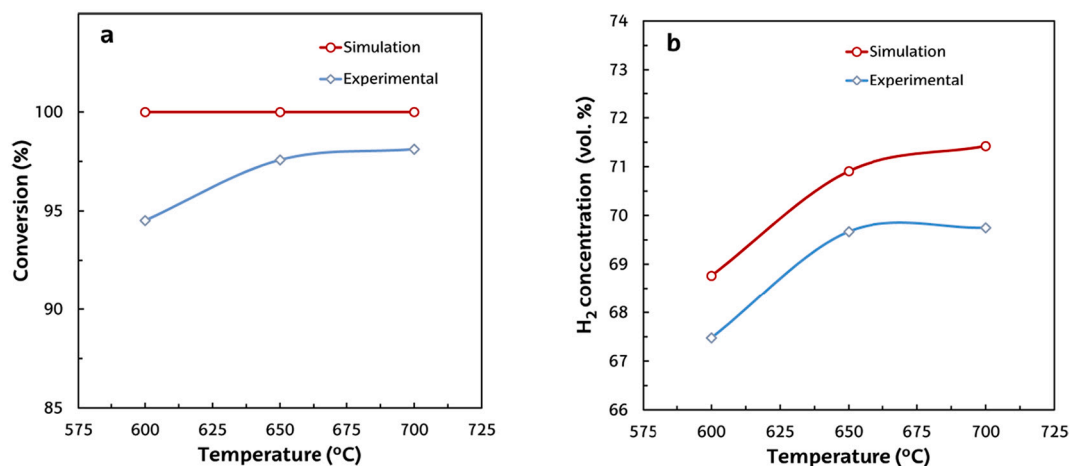


Fig. 1. Comparison of calculated and experimental results of HDPE volatile conversion (a) and H_2 concentration (b) in the steam reforming process at different temperatures.

Methane steam reforming:



Water gas shift (WGS):



Methane dry reforming:



Hydrogen oxidation:



Methane oxidation:



Carbon monoxide oxidation:



It should be noted that the reactions involving hydrocarbons heavier than CH_4 are not considered. Although CH_4 concentrations in the pyrolysis gases fed into the reforming reactor are relatively low, this compound is the most stable based on thermodynamics. Accordingly, it is the prevailing hydrocarbon in the reaction environment under equilibrium conditions, with the concentration of other hydrocarbons

(ethylene, propylene, butanes and so on) being negligible. Therefore, the steam reforming of the other hydrocarbons was not considered.

Fig. 1 shows the comparison of experimental and calculated results obtained in the steam reforming of HDPE pyrolysis volatiles (S/P of 4 and a space time of $16.7 \text{ g}_{\text{cat}} \text{ min g}_p^{-1}$). As observed, equilibrium simulation predicts full conversion of the polymer derived hydrocarbons, mainly the waxes and the diesel fraction oil, into gaseous products. However, full conversion was not attained in the experimental runs. At low temperatures, the low reforming reaction rates hindered full conversion of the pyrolysis volatiles, but conversion values were close to those of equilibrium conditions at higher temperatures. However, the gas by-pass in fluidized beds led to a small non-converted fraction, which prevents reaching full conversion. It is to note that this effect can be attenuated using fixed bed reactors in the reforming step [75]. In the same line, an increase in temperature produced an increase in the H_2 content in the gas product due to the higher reaction rate and extent of reforming reactions. Obviously, the lower conversions obtained experimentally also involved lower H_2 concentrations than those obtained in the simulation. However, experimental and calculated values show a similar trend.

The results obtained operating with different S/P ratios by simulation and experiments ($700 \text{ }^\circ\text{C}$ and a space time of $16.7 \text{ g}_{\text{cat}} \text{ min g}_p^{-1}$) are shown in Fig. 2. The equilibrium simulation predicts full conversion of pyrolysis products, and the experimental conversion values increase as S/P ratio is increased, reaching a value close to full conversion for a S/P

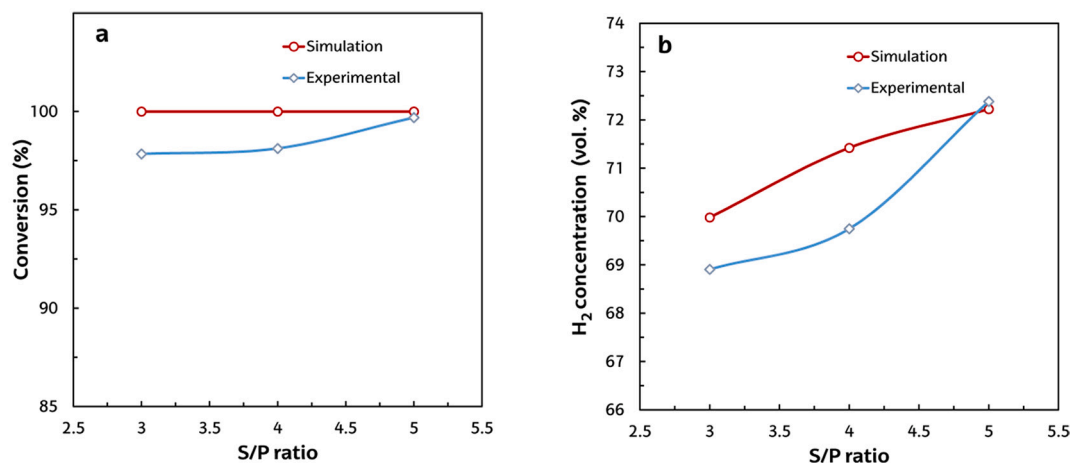


Fig. 2. Comparison of calculated and experimental results of HDPE volatile conversion (a) and H_2 concentration (b) in the steam reforming process at different S/P ratios.

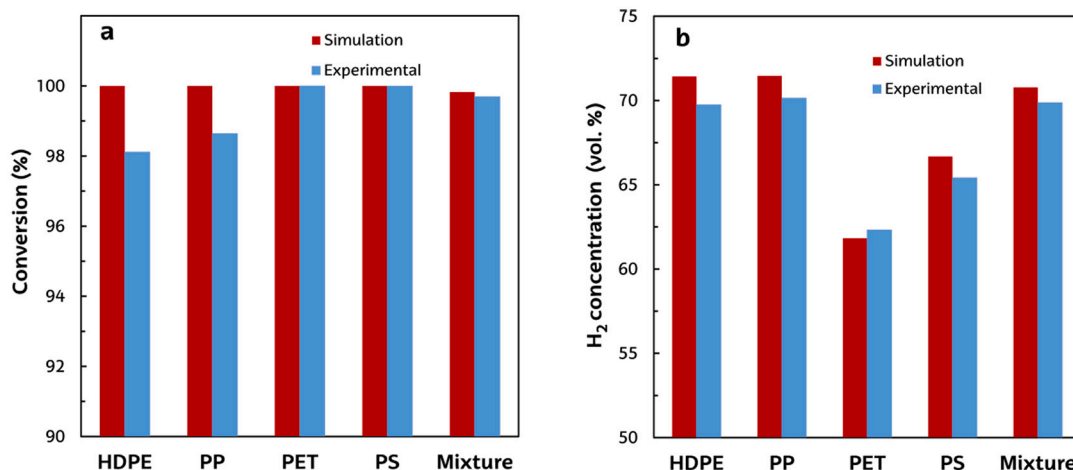


Fig. 3. Comparison of calculated results with the experimental ones in the steam reforming of individual plastics and their mixture. Conversion (a) and H₂ concentration (b).

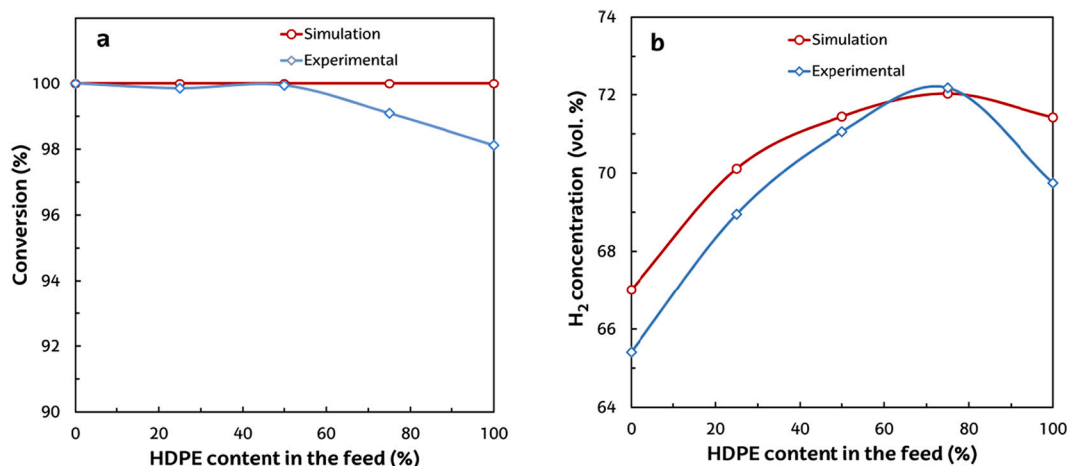


Fig. 4. Comparison of the calculated results with the experimental ones in the co-pyrolysis of HDPE/biomass mixtures. Conversion (a) and H₂ concentration (b) in the steam reforming process for different HDPE contents in the feed.

of 5. This fact is related to the increase in the steam partial pressure in the reaction environment, which increases the reforming reaction rate. This effect, together with the displacement of the WGS reaction (Eq. (3)), leads to an increase in the H₂ content observed both experimentally and theoretically. This effect was observed either in the reforming of plastic pyrolysis volatiles or in their direct steam gasification [25,76–78]. The slightly higher H₂ concentration obtained in the run carried with an S/P ratio of 5 is within the experimental error.

The validation of the theoretical procedure has been carried out based on the results obtained in the reforming of different plastics (HDPE, PP, PS and PET) and a plastic mixture with a composition representative of that typically observed in MSW. Fig. 3 compares the conversion and H₂ concentrations obtained experimentally and by simulation in the steam reforming at 700 °C with an S/P ratio of 4. It is to note that the lowest experimental conversion values were obtained for polyolefins. However, the experimental values for the other plastics were close to the full conversion predicted in the simulations. This fact may be related to the higher carbon content and heavier molecular weight of the polyolefin derived volatiles. In the case of the PET, the experimental H₂ concentrations are above the equilibrium ones, but this difference must be attributed to the experimental error. The results reported in Fig. 3b also reveal the higher potential of polyolefins for H₂ production, which is associated with their higher carbon and hydrogen contents.

Fig. 4 shows the evolutions of the experimental and calculated results obtained for the conversion and H₂ concentration in the reforming step when different biomass/plastic ratios are used in the feed. As observed in the previous results, a clearly lower conversion was predicted by the simulation. In the case of the experimental values, a clearly lower conversion was observed for high HDPE contents. This result is due to the higher effective space time in the experiments performed with biomass. Thus, although the same mass of catalyst per feed mass unit was used, the biomass has much lower carbon content. Furthermore, a significant fraction of the carbon in the original biomass is converted to char, and therefore not reformed. Accordingly, the carbon moles treated per catalyst mass unit are remarkably lower when biomass is reformed than when HDPE is reformed. Experimental and calculated H₂ concentrations showed a similar evolution with feed composition. Thus, a clear peak is observed when the feed is composed of 75% plastic and 25% biomass. This kind of synergetic effect has already been reported in the literature in the joint valorization of biomass and plastics in different processes [79–81].

The comparison of experimental and simulation results under different conditions and feeding plastics of different nature and plastic/biomass mixtures reveals the adequacy of this simulation approach for the prediction of steam reforming results. In the following sections, the simulations are extended to predict the process performance under oxidative steam reforming conditions and, finally, to determine the most

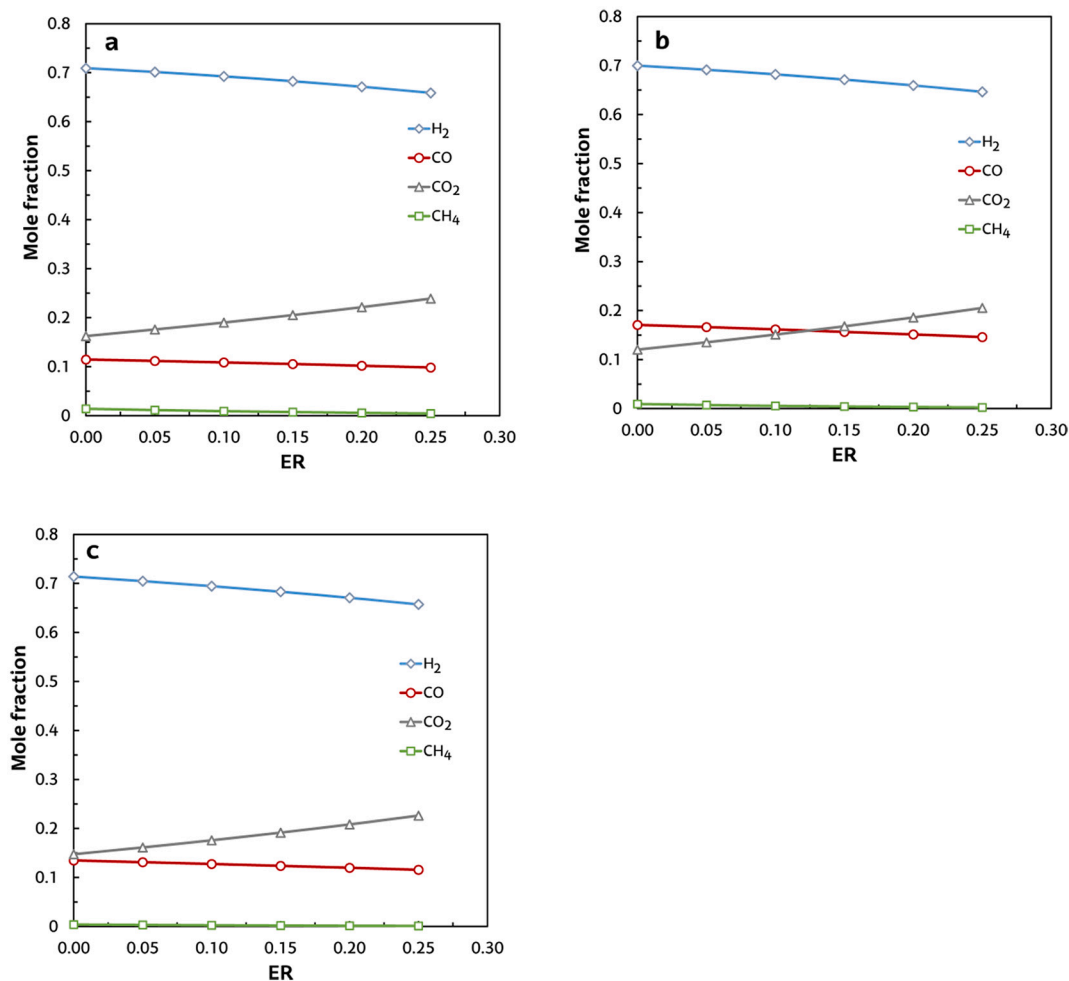


Fig. 5. Evolution of gas product composition (on a dry basis) with ER under different operating conditions, S/P = 4 and 650 °C (a), S/P = 3 and 700 °C (b) and S/P = 4 and 700 °C (c).

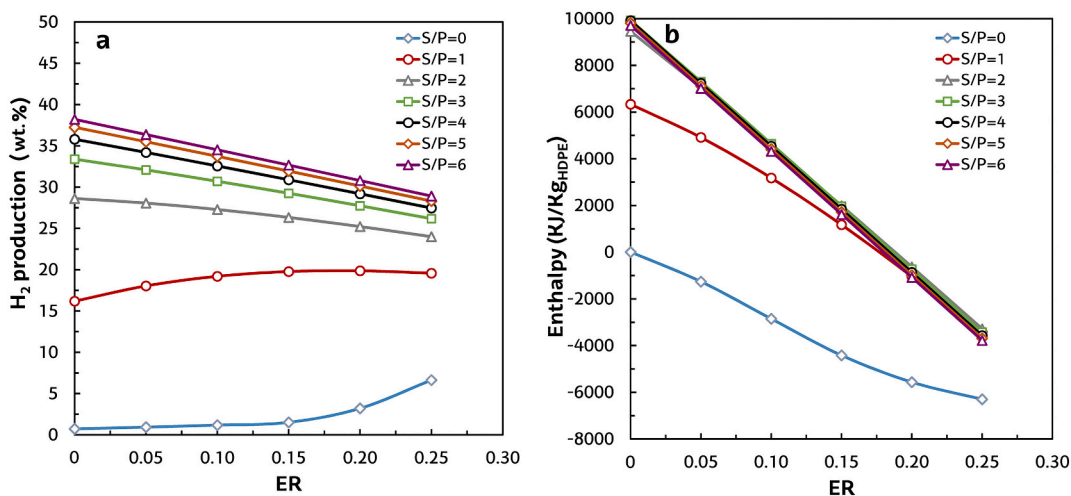


Fig. 6. Effect of ER on H₂ production (a) and reaction enthalpy (b), operating at 700 °C and with different S/P ratios.

suitable conditions and the potential of this process for the valorization of waste plastics.

3.2. Simulation of HDPE pyrolysis and in line oxidative reforming

This section deals with a detailed evaluation of HDPE valorization by pyrolysis and in line oxidative steam reforming. The influence of the main operating parameters was studied to understand their effect on the

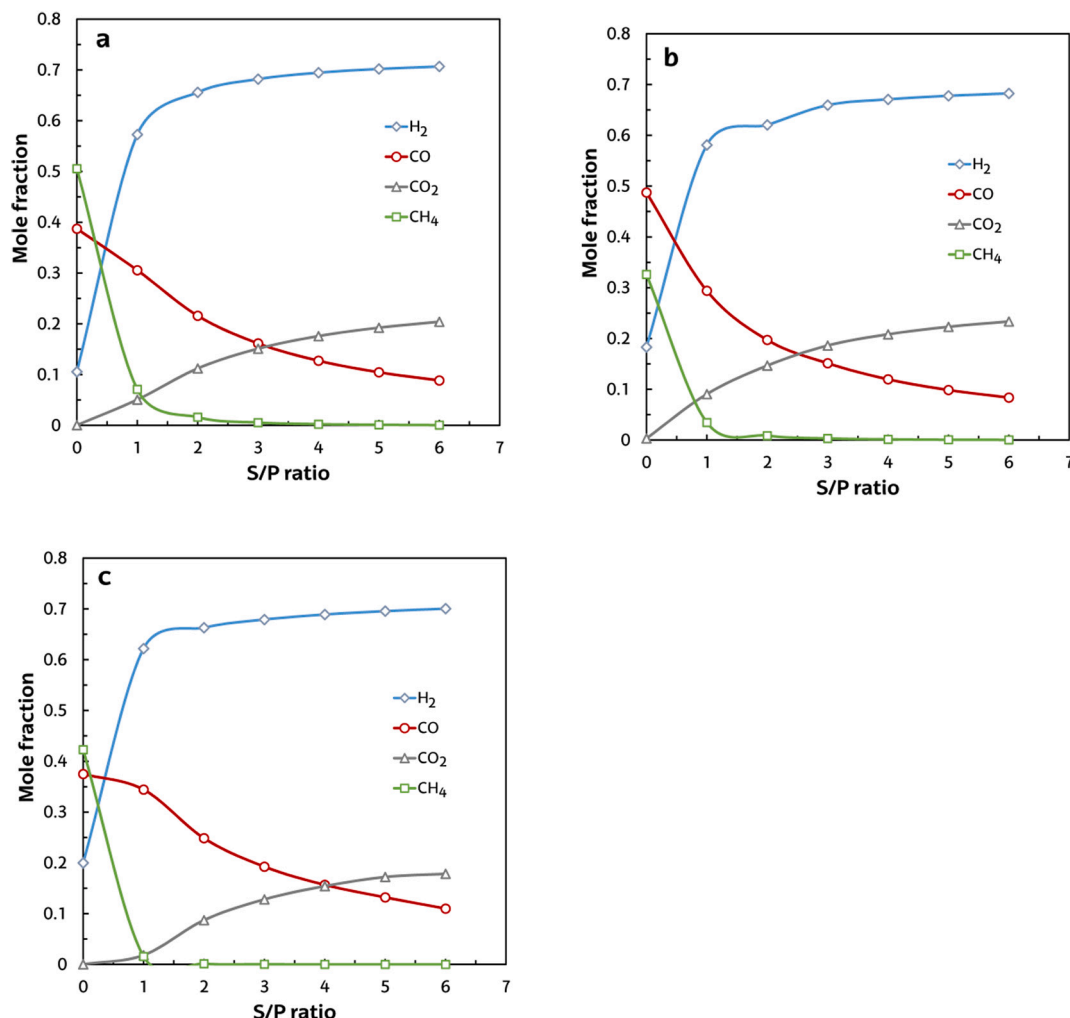


Fig. 7. Evolution of the gaseous stream composition (on a dry basis) with S/P ratio under different operating conditions, ER = 0.1 and 700 °C (a), ER = 0.2 and 700 °C (b) and ER = 0.1 and 800 °C (c).

process performance, i.e., the effect of temperature in the 500 to 800 °C range, S/P ratio between 0 and 6 and ER from 0 to 0.25.

Fig. 5 shows the effect of oxygen co-feeding on the composition of the gaseous stream obtained in the reforming of HDPE pyrolysis volatiles under different conditions. An increase in ER leads to similar trends in the gas composition in all the simulations. Thus, H₂ and CO concentrations decrease due to their partial oxidation (Eq. Eqn 5–7), whereas that of CO₂ increases. It should be noted that the relatively high temperatures and S/P ratios used in the simulations lead to almost full conversion of CH₄, with its mole fraction being below 0.02, even under steam reforming conditions (ER = 0).

The modification in ER leads to a remarkable effect on the H₂ production potential. Thus, as observed in Fig. 6a, the values obtained by operating with high S/P ratios decrease almost linearly with ER. The H₂ production values decrease by more than 20% when ER is increased from 0 to 0.25 in the simulations performed with high S/P values. However, a different trend is observed in the simulations with the S/P ratios of 0 and 1, which is explained by the insufficient steam available under these conditions for shifting the steam reforming reactions (Eq. (2)). Thus, O₂ incorporation caused CO₂ formation and the subsequent H₂ production by means of dry reforming of CH₄ and other hydrocarbons (Eq. (4)).

Moreover, the incorporation of O₂ into the reaction environment greatly modified the overall reforming reaction enthalpy (ΔH_r) (Fig. 6b). Thus, the contribution of oxidation reactions (Eqs. (5–7)) turned the

highly endothermic overall reaction at high S/P ratios to an exothermic one when an ER ratio of 0.25 is used. Operating under steam reforming conditions (ER = 0) at 700 °C, the reaction enthalpy was close to 10,000 kJ/kg_{plastic} for S/P values in the 2 to 6 range, and much lower using a S/P ratio of 1, as there was not enough steam to complete the reforming of the plastic derived hydrocarbons. It is to note that autothermal reforming conditions, i.e., $\Delta H_r = 0$, were reached with an ER of around 0.18 for moderate and high S/P values. This value is higher than that required for biomass pyrolysis volatiles (ER = 0.13) under similar conditions [60], and is explained by the higher carbon content of waste plastic derived volatiles, and therefore the higher energy requirement of the steam reforming reactions.

These results clearly show the potential interest of pyrolysis and in line oxidative steam reforming of HDPE, as H₂ productions of around 30 wt% can be obtained operating under autothermal regime. It should be noted that this value is much higher than those reported in the plastic steam gasification under optimum conditions, up to 18 wt% [22,25,27], and slightly lower than those obtained in the pyrolysis-steam reforming, between 34 and 37 wt% [40,41,43,82].

The influence of steam concentration on the gas product composition under different ER ratios and temperatures is shown in Fig. 7. Operating without external steam incorporation (S/P = 0), the gaseous product stream has a high CH₄ concentration, with the H₂ formed being associated with dry (Eq. (4)) and steam reforming (Eq. (2)) reactions promoted by the CO₂ and the steam formed in the combustion reactions

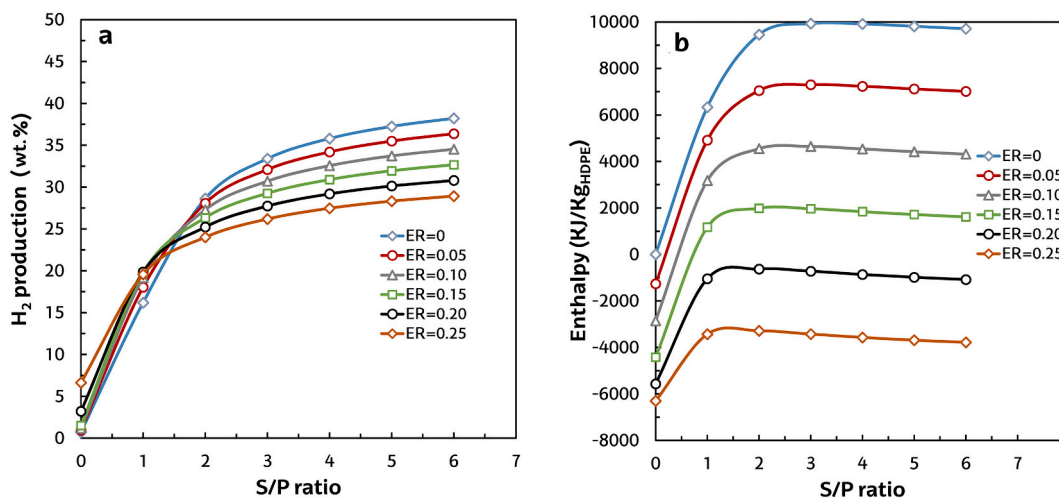


Fig. 8. Effect of S/P ratio on H₂ production (a) and reaction enthalpy (b), operating at 700 °C and with different ER values.

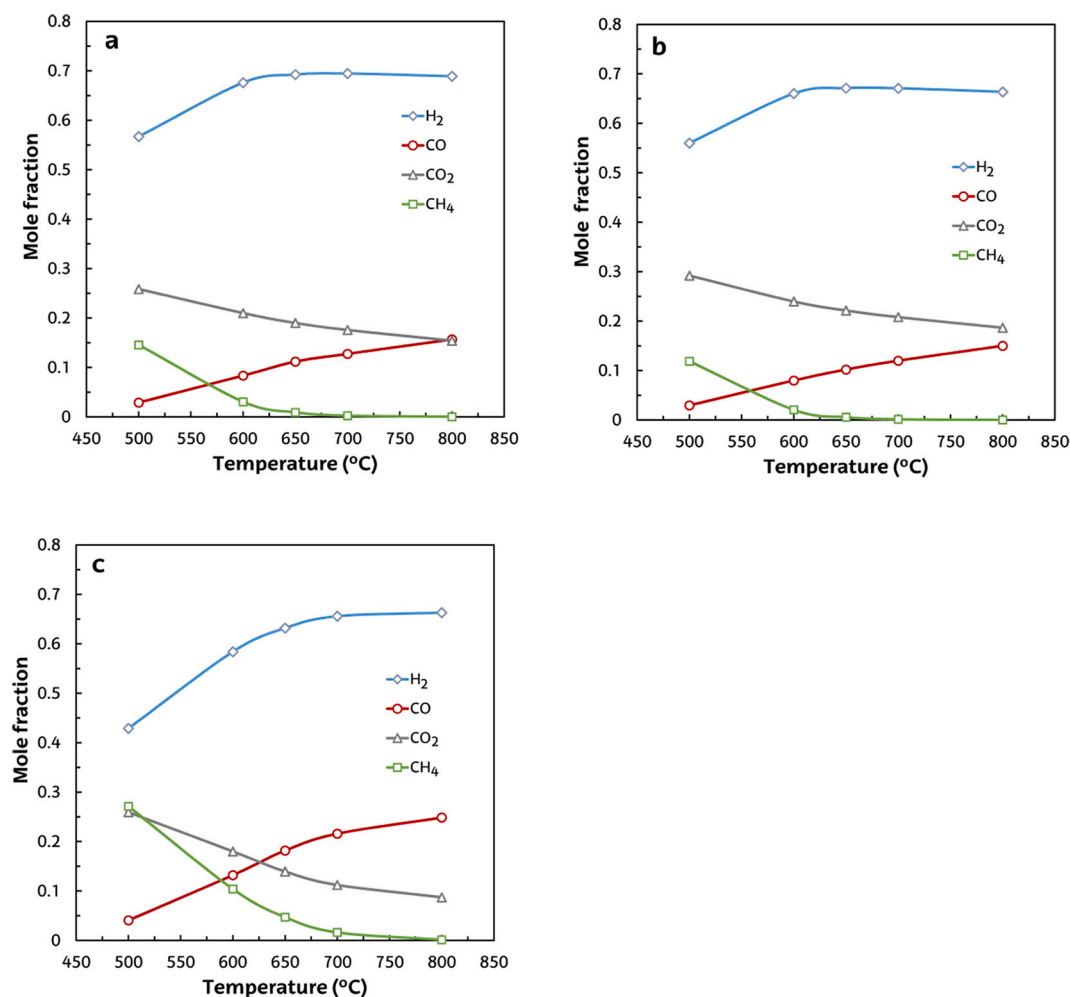


Fig. 9. Evolution of the gaseous stream composition (on a dry basis) with temperature under different operating conditions, S/P = 4 and ER = 0.1 (a), S/P = 4 and ER = 0.2 (b) and S/P = 2 and ER = 0.1 (c).

(Eqs. (5–7)). An increase in steam concentration contributes to shifting the equilibria of CH₄ steam reforming and WGS reaction towards the formation of CO₂ and H₂ with the subsequent reduction in CO concentration. The same effect of S/P ratio on the gas composition has been previously reported in the pyrolysis-steam reforming of waste plastics

[43,76,77] and steam gasification processes [25,78].

As observed in Fig. 8a, an increase in S/P ratio has a positive effect on H₂ production, reaching a production higher than 38 wt% with a S/P ratio of 6 at 700 °C and ER = 0. Although a S/P ratio slightly higher than 2 provides enough steam for the conversion of CH₄ by means of steam

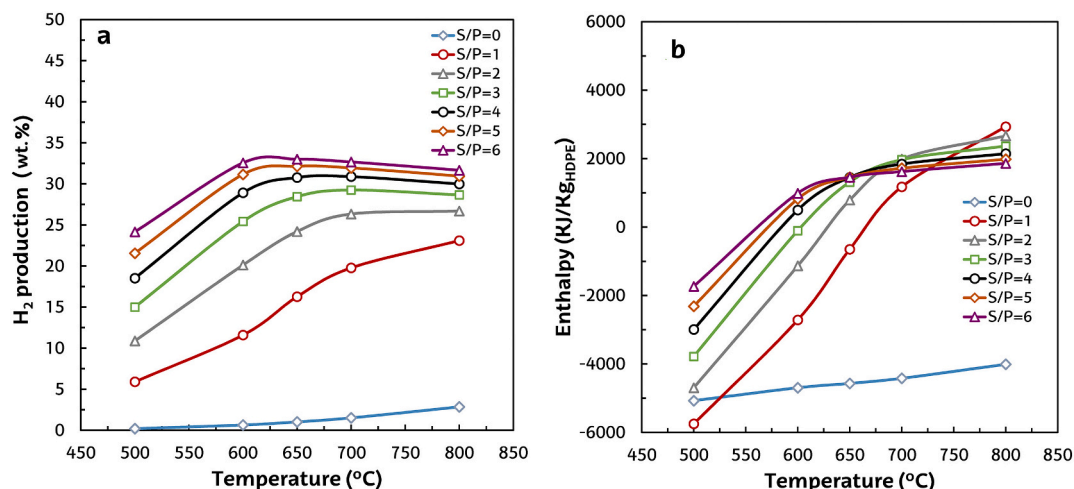


Fig. 10. Effect of temperature on H₂ production (a) and reaction enthalpy (b) operating with an ER ratio of 0.15 and different S/P ratios.

reforming (Eq. (2)), additional steam in the feed shifts the WGS reaction (Eq. (3)) equilibrium, and higher H₂ productions are therefore obtained.

The aforementioned effect of S/P ratio on the steam reforming (Eq. (2)) and WGS (Eq. (3)) reactions is also evident when the evolution of reaction enthalpy is analyzed (Fig. 8b). Thus, reaction enthalpy initially increases with S/P ratio until endothermic reforming reactions are completed, and further increases in the steam concentration promote the exothermic WGS reaction, with the subsequent reduction in the energy required in the reforming step. It is to note that the S/P values required to reach the ceiling enthalpy are lower when the ER is increased, as oxygen addition contributes to carbon conversion, and lower amounts of steam are therefore required to complete reforming.

Therefore, steam concentration has a major impact on the performance of the reforming process by improving gas composition, H₂ production, and even reaction enthalpy. Furthermore, it also has certain operational advantages, such the increase in the reforming reaction rate and the attenuation of coke deactivation by enhancing in situ coke gasification [48,84,85]. However, the steam flow rate conditions the process energy requirements associated with steam production and heating, and should be carefully considered [53,86]. Interestingly, oxygen co-feeding may reduce the steam requirements in the reforming step.

Finally, the effect of temperature on the reforming of HDPE pyrolysis volatiles was analyzed. The evolution of the gaseous stream composition under different S/P and ER conditions in the 500 to 800 °C range is shown in Fig. 9. This evolution is explained by the opposite effect temperature has on CH₄ steam reforming (Eq. (2)) and WGS (Eq. (3)) reactions. Thus, the former reaction is highly endothermic and the equilibrium shifts towards the formation of CO and H₂ at high temperatures. However, given the exothermic nature of the later, the reverse WGS is enhanced when reforming temperature is raised, with the subsequent reduction in H₂ and CO₂ concentrations [87]. Therefore, high non-converted CH₄ concentrations are obtained at 500 °C, but an increase in temperature leads to almost full conversion of CH₄. Furthermore, CO/CO₂ ratio is also remarkably affected, with a clear increasing trend as temperature is raised.

Fig. 10a shows the effect of temperature on H₂ production using an ER of 0.15 and different S/P ratios. At the lower temperature range, H₂ production increases with temperature due to the improvement in the reforming reaction extent, but a further increase in temperature leads to a peak in the 600–700 °C range for high S/P values. In spite of the interesting results obtained at moderate temperatures, such as 600 °C, it should be noted that the results obtained in this study are under thermodynamic equilibrium conditions. In this respect, the remarkable kinetic effect of temperature should also be considered, and therefore full

scale operation may require operating at higher temperatures to ensure a suitable reaction rate and high reforming conversions.

Fig. 10b shows the effect of temperature on reaction enthalpy operating with an ER of 0.15 and S/P values in the 0 to 6 range. It should be noted that the results are greatly influenced by the ER values used. Thus, at 500 °C, the reforming conversion is rather low and the contribution of oxidation reactions (Eqs. (5–7)) leads to an overall exothermic reaction. An increase in the process temperature turns the energy balance to an endothermic reaction due to the higher extent of reforming reactions. Nevertheless, there is a positive effect of the S/P ratio on the WGS reaction (Eq. (3)) equilibrium at high temperatures, as reaction enthalpies are lower as the S/P ratio is higher due to the exothermic nature of WGS reaction.

3.3. Optimization of operating conditions for the oxidative steam reforming of plastic pyrolysis volatiles

This section deals with the ascertainment of the most suitable values of temperature, ER and S/P for the steam reforming of different plastics and biomass/plastic mixtures. The optimum ranges of these variables must consider certain facts. In the case of temperature, practical aspects must be considered apart from those involving H₂ production potential and reaction enthalpy. Thus, previous experimental studies dealing with HDPE pyrolysis steam reforming clearly showed that high temperatures increased the reaction rate, and therefore volatile conversion and product yields [43]. In the same line, an increase in temperature also improved the stability of the catalyst, with a lower deactivation rate and coke deposition [85,88,89]. Based on these studies, 700 °C was determined as a suitable temperature for the reforming of plastic derived volatiles. It is to note that, a further increase in temperature causes a significant reduction in H₂ production due to the negative impact on the WGS reaction and, furthermore, it may also condition the stability of the catalyst due to sintering problems [90] and increase in energy demand.

According to simulation and experimental results, an increase in S/P ratio has a positive effect on H₂ production by shifting the WGS reaction. However, the energy efficiency of the process is reduced when operating with high S/P ratios, as the amount of water to be vaporized is high, as well as the unreacted steam fraction to be condensed after the reforming step. In order to strike a balance between H₂ production and energy efficiency, steam conversion is the factor directly affected by the S/P ratio. An analysis of the simulation results shows that a steam conversion of around 50% causes a change in the trend of S/P impact on H₂ production. Thus, an increase in S/P ratio when conversion is below 50% causes a significant improvement in H₂ production, whereas an increase in S/P when conversion is above 50% leads to a minor

Table 2
Optimum conditions for the oxidative steam reforming of plastic and mixtures pyrolysis volatiles.

	HDPE	PP	PS	PET	Mixture	Biomass	HDPE (25)/ Biomass (75)	HDPE (50)/ Biomass (50)	HDPE (75)/ Biomass (25)
S/P	2.0	2.0	3.0	0.8	2.0	0.4	0.8	1.1	1.5
ER	0.190	0.190	0.160	0.105	0.185	0.090	0.115	0.135	0.150
H ₂ prod.	25.5	25.5	24.7	7.9	24.0	7.1	11.4	15.3	19.6
Gas composition (vol%)									
H ₂	64.0	64.1	61.5	49.4	63.3	55.4	60.0	61.9	63.5
CO	20.4	20.4	18.0	25.9	20.3	23.8	21.8	21.8	20.9
CO ₂	14.6	14.6	20.1	24.1	15.5	20.2	17.5	15.4	14.6
CH ₄	0.9	0.9	0.4	0.6	0.8	0.7	0.8	1.0	1.0

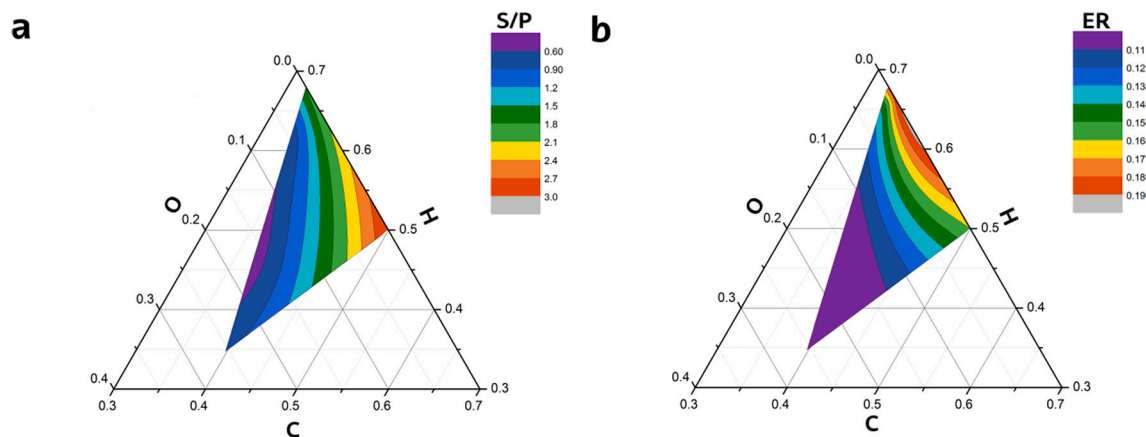


Fig. 11. Effect of the elemental (molar) composition of the pyrolysis volatile stream on the optimum S/P (a) and ER values (b) in the oxidative steam reforming of plastics and mixtures.

improvement in H₂ production, and therefore to an increase in the non-reacted steam fraction. Accordingly, the criterion of 50% steam conversion was selected to tune the S/P ratio. At the same time, the ER value must be fixed to overcome one of the main challenges of the reforming step, i.e., its high endothermicity. Thus, the ER value required for operating under autothermal conditions is the most suitable one. Therefore, the simulation of the reforming of different plastics and plastic mixtures was carried out at 700 °C, with ER and S/P being varied to attain autothermal operation at a steam conversion of 50%.

Table 2 shows the optimum operating values determined following the aforementioned criteria for the reforming of waste plastics, plastic mixtures and biomass/plastic mixtures. As observed, these values remarkably vary depending on the composition feedstock to be treated. Thus, the higher carbon content of the polyolefin derived volatiles than those derived from biomass or PET requires higher S/P ratios to complete steam reforming reactions, and higher ER values must be used to attain autothermal operation due to the contribution of endothermic reforming relations. It is to note that the optimum S/P value for PS was even higher due to the greater carbon content of this plastic. PET is the polymer that requires the lowest S/P and ER values. This fact is not only related to its considerable oxygen content (33.3%), but also to the formation of a carbonaceous residue in the pyrolysis step of this plastic, which leads to a reduction in the amount of the volatile stream to be reformed, and therefore to lower steam and oxygen requirements. Biomass has also a rather high oxygen content (44.6%) and a significant fraction of its carbon content is retained in the char formed in the pyrolysis step. Thus, the lower amount of carbon in the feed to the reforming step explains the lower ER and S/P values reported in Table 2. It should be noted that both ER and S/P parameters are based on the feed into pyrolysis step and not on the pyrolysis volatiles. Accordingly, the amount of char or solid residue formed in the pyrolysis step has a great influence on the values of these parameters. In the joint valorization of HDPE and biomass, an increase in the polymer content in the feed leads

to an increase in the steam and oxygen requirements for operating under optimum conditions. Thus, the higher carbon content of HDPE pyrolysis volatiles per mass unit in the feed means a higher amount of steam needed to ensure their full reforming. Furthermore, more oxygen must also be fed to account for the energy requirements associated with the higher extent of steam reforming reactions.

The composition of the pyrolysis volatile stream has also great influence on the gaseous stream composition at the outlet of the reforming step. The highest H₂ concentrations are obtained in the reforming of polyolefin derived volatiles followed by those formed in the pyrolysis of PS. However, the presence of oxygenates in the biomass and PET products leads to a reduction in H₂ concentration and an increase in those of CO and CO₂.

In order to ascertain the effect the pyrolysis stream composition has on the optimum conditions for the oxidative steam reforming, the optimum values of S/P and ER are summarized in Fig. 11a and b, respectively. It should be noted that molar compositions of pyrolysis volatiles are plotted on the sides of the ternary figures, and both ER and S/P are referred to the feed into the pyrolysis step and not to the volatile stream into the reforming step. Fig. 11a shows that a higher carbon content in the pyrolysis volatiles involves a higher steam requirement in the reforming step. However, an increase in the content of both oxygen and hydrogen leads to the opposite effect, with the influence of the latter being less significant. Similarly, an increase in carbon content is also associated with higher ER values, as more oxygen in the feed is required to balance the endothermic reactions involving carbon steam reforming.

4. Conclusions

The strategy based on plastic pyrolysis and line reforming pursues the development of an efficient and sustainable process for H₂ production. Oxygen co-feeding to the reforming step may contribute to overcoming the main challenges of this process, which are those associate

with high energy requirements and fast catalysts deactivation. In this paper, a detailed simulation study was carried out using the thermodynamic equilibrium approach based on the Gibbs free energy minimization. On the one hand, the role played by temperature, S/P ratio and ER was analyzed in the reforming of HDPE pyrolysis volatiles. On the other hand, the optimum conditions were determined for the oxidative reforming of the products derived from the pyrolysis of HDPE, PP, PS, PET, their mixture and biomass/HDPE mixtures. The composition of the pyrolysis products has a remarkable impact on the optimum process conditions. Thus, an increase in carbon content in the pyrolysis volatiles causes an increase in the optimum S/P and ER values. The results obtained are clear evidence of the potential of pyrolysis and oxidative steam reforming for the valorization of different waste plastics. In fact, operation under autothermal conditions and with suitable S/P ratios allows obtaining high H₂ productions. Thus, feeds of polyolefins and PS lead to yields of around 25 wt%, that of PET to 8 wt% and the one of 50:50 mixture of biomass and HDPE to 15%.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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