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A sequential process for hydrogen production based on continuous HDPE fast pyrolysis and in-line steam reforming

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Abstract

A continuous process has been developed consisting in the flash pyrolysis (500 ºC) of high density polyethylene (HDPE) in a conical spouted bed reactor (CSBR) followed by steam reforming in a fluidized bed reactor (Ni commercial catalyst). The effect reforming temperature in the 600-700 ºC range, space time from 2.8 to 20.8 g_{cat} min g_{HDPE}^{-1} and steam/plastic ratio between 3 and 5 have on product yields and gas composition has been studied. The continuous pyrolysis-reforming process performs well, with no operational problems and attaining complete HDPE conversion. Under the optimum conditions, i.e., 700 ºC, space time 16.7 g_{cat} min g_{HDPE}^{-1} and steam/plastic of ratio 5, the H_2 yield was 92.5 % of that corresponding to stoichometry, which accounts for a H_2 production of 38.1 g per 100g of HDPE in the feed.

Keywords: hydrogen; pyrolysis; reforming; plastic waste; conical spouted bed; Ni catalyst

Introduction

World production of plastics in 2013 was estimated to be 299 million tons, with an annual growth of 3.9 % [1], which is a consequence of their use in numerous applications (packaging, building and construction, automotion, electricity and electronics, agriculture, consumer and household appliances). However, a significant proportion of post-consumer plastic wastes end up in the waste upstream causing a large number of environmental hazards. Accordingly, the development of new valorization technologies is required for minimizing the landfill or incineration of waste plastics.

Amongst waste plastic valorization routes, thermochemical processes have best perspectives for their implantation and, in fact, they have been developed to pilot and demonstration scale [2, 3]. Pyrolysis is an interesting option for the recovery of fuels, chemicals and monomers from waste plastics [4-8], and consequently has been widely studied using several reactor designs, such as batch reactors, fluidized beds, spouted beds, screw kilns, etc. [4]. Furthermore the gasification of waste plastics [9-12] or its cogasification with other feedstocks, such as coal or biomass [13-16], has also been studied.

The studies dealing with the direct production of H_2 from waste plastics by reforming have been carried out following two main strategies: i) gasification with a reforming catalyst arranged in situ [17, 18] and ii) pyrolysis and in line reforming [19-24]. The latter strategy provides clear advantages compared to the direct gasification strategy due the lower operating temperature. Thus, the energy efficiency of the process is improved and, moreover, the sintering of the reforming catalyst is avoided.

The main aim of this study is the proposal of a novel strategy for H_2 production from high density polyethylene (HDPE) by pyrolysis in a conical spouted bed reactor (CSBR) and in-line reforming on a Ni catalyst in a fluidized bed reactor (Figure 1). The great novelty of

this strategy lies in the use of an original two-reactor-in-series configuration operating in continuous regime, instead of the most common batch reactors, to which correspond almost all the results reported in the literature. Moreover, the reactors used are characterized by high heat and mass transfer rates, and therefore may operate under similar conditions to those of industrial reactors. The use of two reactors in-line allows for the independent optimization of the catalytic step. Thus, the effect temperature, space time and steam/plastic ratio have on the reforming of HDPE pyrolysis volatiles has been addressed.

The pyrolysis step has been carried out in a CSBR, which is an original gas-solid contact method that performs well for plastic flash pyrolysis. Thus, a vigorous cyclic movement of the particles together with a high heat transfer rate, which are the features of this reactor, minimize bed agglomeration problems caused by fused plastic [25]. The absence of operational problems in the pyrolysis step ensures a stream of homogeneous composition throughout time, which is essential for a suitable operation in the subsequent reforming process.

Moreover, the use of a fluidized bed reactor for the catalytic steam reforming step avoids the operational problems observed in fixed bed reactors due to severe coke formation. The better performance of the fluidized bed reactor for the minimization of coke formation has been previously reported in the reforming of pyrolysis oils derived from both biomass [26, 27] and plastics [28].

Figure 1

2. Experimental section

2.1. Materials

The HDPE was provided by Dow Chemical (Tarragona, Spain) in the form of chippings (4 mm). The main properties of the polymer are as follows: average molecular weight, 46.2 kg mol^{-1}; polydispersity, 2.89, and density, 940 kg m^{-3}. The higher heating value, 43 MJ kg^{-1}, has been determined by differential scanning calorimetry (Setaram TG-DSC-111) and isoperibolic bomb calorimetry (Parr 1356).

The reforming catalyst has been provided by Süd Chemie (G90LDP catalyst) and its chemical formulation is based on NiO, $CaAl_2O_3$ and Al_2O_3. The catalyst has the form of perforated rings (19x16 mm) with a metallic phase of Ni supported on Al_2O_3, which is doped with Ca, with the NiO content being 14 %. This catalyst was ground and sieved to 0.4-0.8 mm, which is the suitable particle size to attain stable fluidization regime.

The physical properties of the catalysts have been determined by N_2 adsorption-desorption (Micromeritics ASAP 2010). The adsorption-desorption isotherm of this catalyst have already reported elsewhere [29, 30]. This material has a limited porous structure with a BET surface area of 19 m^2 g^{-1} and an average pore diameter of 122 Å.

The temperature programmed reduction (TPR) of the catalyst has been measured by AutoChem II 2920 Micromeritics [29, 30]. The TPR showed a main peak at 550 ºC associated with NiO reduction, which interacts with α-Al_2O_3. Moreover, another peak is observed at 700 ºC, which is probably related to $NiAl_2O_4$ according to the composition given by the provider. In order to ensure the complete reduction of NiO prior to the reforming reaction, the catalyst has been subjected to an in situ reduction process at 710 ºC for 4 h under a 10% vol. H_2 stream.

2.2. Equipment and reactors

Pyrolysis and in line steam reforming runs have been carried out by continuously feeding HDPE in a bench scale plant whose scheme is shown in Figure 2. The plant is provided

with a CSBR for the pyrolysis step and a fluidized bed reactor for the reforming step arranged in-line.

The design of the CSBR is based on previous knowledge acquired in hydrodynamic studies [31] and on the successful application of this technology to the pyrolysis and gasification of different solid wastes, such as biomass [32-34], plastics [11, 35] and waste tyres [36, 37]. In fact, this technology has been scaled up to 25 kg/h for biomass pyrolysis [38].

A detailed description of the CSBR design including a scheme can be found elsewhere [11]. Its main dimensions are as follow: height of the conical section, 73 mm; diameter of the cylindrical section, 60.3 mm; angle of the conical section, 30 º; diameter of the bed bottom, 12.5 mm, and diameter of the gas inlet, 7.6 mm. A radiant oven of 1250 W heats the pyrolysis reactor and its lower section, which acts as a gas preheater and is filled with an inert ceramic material that increases the surface area for heat transfer. Two K-type thermocouples are located inside the reactor, one in the bed annulus and the other one close to the wall.

The reforming step is carried out in a fluidized bed reactor with an internal diameter of 38.1 mm and a total length of 440 mm. This reactor is located inside a 550 W radiant oven that provides the energy needed to maintain the reaction temperature, which is controlled by a thermocouple placed in the catalyst bed.

In order to avoid the condensation of steam and the volatiles formed in the pyrolysis reactor on the interconnection pipes between pyrolysis and reforming processes, both reactors are located within a forced convection oven maintained at 270 ºC. Moreover, a high-efficiency cyclone and a sintered steel filter (5 μm) are located inside the forced convection oven downstream the pyrolysis and the reforming steps, respectively. The aim of the cyclone is

to retain the fine sand particles entrained from the CSBR and that of the filter to recover elutriated catalyst fines from the fluidized bed reactor.

Figure 2

The plant is provided with a plastic feeding system that allows for continuous operation. The feeding system consists of a vessel equipped with a vertical shaft connected to a piston placed below the material bed. Raising the piston, at the same time as the whole system is vibrated by an electric engine, the feeding system discharges the plastic through a pipe to the reactor. This pipe is cooled with tap water to avoid plastic melting and blocking the system. Moreover, a very small nitrogen flow rate introduced into the vessel stops steam entering the feeding vessel. The system is able to feed up to 5 g min^{-1} of HDPE.

Water has been fed into the CSBR by means of a Gibson 307 pump, which allows a precise measuring of the flow rate, and has been vaporized by means of an electric cartridge placed inside the forced convection oven. Moreover, N_2 is used as fluidizing agent during the heating process and its flow rate is controlled by a mass flow controller that allows feeding up to 20 L min^{-1}.

The gases formed in the reforming reactor circulate through a volatile condensation system consisting of a condenser (cooled with tap water) and a coalescence filter, which ensure the total condensation and retention of the non-reacted steam and HDPE derived products.

2.3. Experimental conditions

The conical spouted bed reactor contains 50 g of silica sand with a particle diameter in the 0.3-0.35 mm range. The bed in the steam reforming step is made up of a mixture of reforming catalyst and inert sand, with the mass being 25 g in all the experiments. Therefore, the catalyst/sand mass ratio was that corresponding to the space time studied.

The particle size of the catalyst was in the 0.4-0.8 mm range and that of inert sand in the 0.3-0.35 mm range. The particle sizes in the spouted and fluidized beds were delimited in the hydrodynamic studies carried out under reaction conditions (at 500 and 700 ºC, respectively) in order to guarantee suitable spouting and fluidization behaviour in the corresponding steps. It is remarkable that this point is crucial for a suitable operation of the pyrolysis and reforming process. The same gas stream (steam + HDPE derived volatiles) crosses both reactors and satisfactory operating regimes must be attained in both gas-solid contact technologies.

Water flow rate is 3 mL min^{-1} in all the conditions studied, which corresponds to a steam flow rate of 3.73 NL min^{-1}. The experiments performed at different temperatures and space times were carried out by continuously feeding 0.75 g min^{-1} of HDPE, i.e., a steam/plastic (S/P) mass ratio of 4 (steam/carbon (S/C) molar ratio of 3.1).

In the runs for the analysis of the effect of steam/plastic ratio the water flow rate was kept constant in order to ensure the same hydrodynamic performance in the spouted and fluidized bed reactors (steam acts also as a fluidizing agent in both reactors). However, the plastic mass flow rate was modified to attain the S/P ratio desired, with the mass flow rate being 1 and 0.6 g min^{-1} in the experiments performed with S/P ratios of 3 and 5, respectively. S/P ratios below 3 are not advisable as severe coke formation takes place in the reforming step [28].

The effect of space time on the reforming step was studied by varying the amount of catalyst, with the plastic feed rate being 0.75 g min^{-1} in these experiments. The space time was varied between 2.8 to 20.8 g_{cat} min g_{HDPE}^{-1}. The space time values mentioned are given based on the plastic fed into the pyrolysis reactor.

The pyrolysis of HDPE (first step) has been carried out at 500 ºC, given that this temperature ensures complete degradation of the plastic and avoids defluidization problems [25]. In addition, a negligible effect of pyrolysis temperature on the subsequent reforming step was reported by Czernik and French [22], and therefore the lowest allowable temperature (500 ºC) has been selected in this study. In the reforming step, the effect of temperature has been studied in the 600-700 ºC range. In this case, the main temperature limitation is the deactivation of the catalyst by Ni sintering, with the maximum advisable temperature being 700 ºC.

The conditions of the experimental runs in the reforming step (second one) are set out in Table 1.

Table 1

All the runs have been performed in continuous mode for several minutes in order to ensure steady state process. Moreover, the runs have been repeated at least 3 times under the same conditions (with fresh catalyst) in order to guarantee reproducibility of the results.

2.4. Product analysis

The volatile stream leaving the reforming reactor has been analysed on-line by means of a GC Varian 3900 provided with and HP-Pona column and a flame ionization detector (FID). The sample has been injected into the GC by means of a line thermostated at 280 ºC, once the reforming reactor outlet stream has been diluted with an inert gas. The non-condensable gases have been analyzed on-line in a micro GC (Varian 4900) and in this case the samples have been taken once the stream has crossed the condenser and the coalescence filter. Nevertheless, in the experiments aimed to determine the effect of steam on the pyrolysis of HDPE (section 3.1) the waxes are retained in a coalescence filter and their yield was determined by weight the filter prior and subsequent to use.

2.5. Reaction indices

Conversion and individual product yields have been considered for the assessment of process results. Plastic conversion has been defined similarly as carbon conversion efficiency in gasification processes; that is, the ratio between the moles of C recovered in the gaseous product and those fed in the polymer:

$$X_{HDPE} = \frac{C_{Gas}}{C_{HDPE}} 100 \quad (1)$$

The yield of C containing individual compounds is defined by mass unit of plastic in the feed:

$$Y_i = \frac{F_i}{F_{HDPE}} 100 \quad (2)$$

where F_i and F_{HDPE} are the molar flow rates of product i and plastic, respectively, both expressed in C equivalent moles.

The hydrogen yield was determined as a percentage of the maximum allowed by stoichiometry, which accounts for the hydrogen coming from the polymer and the steam:

$$Y_{H_2} = \frac{F_{H_2}}{F^0_{H_2}} 100 \quad (3)$$

where F_{H2} and F^0_{H2} are the hydrogen molar flow rates obtained and the maximum allowable by stoichiometry, respectively.

The following stoichiometry was considered:

$$C_n H_m + 2nH_2O \longrightarrow nCO_2 + (2n + m/2)H_2 \quad (4)$$

The volumetric yield has been obtained by adding the moles of the gaseous compounds formed in the reforming step, i.e. H_2, CO_2, CO, CH_4 and C_2-C_4 hydrocarbons, but steam was not considered, and therefore this parameter is given on a dry basis.

3. Results

3.1. First step: pyrolysis of HDPE

As observed in Figure 2, the steam required in the reforming step was introduced in the pyrolysis reactor, where it acts as a fluidizing agent. A previous study showed that steam behaves as an inert compound in the pyrolysis of HDPE at moderate temperatures (500 ºC) [29], with the results being similar to those reported by Elordi et al. [25] using nitrogen as fluidizing agent. Besides, Kaminsky et al. [39] operated at 700 ºC and reported small differences in the pyrolysis of waste plastics performed with steam and N_2 in a fluidized bed reactor.

The product stream obtained in the pyrolysis of HDPE in a conical spouted bed reactor is mainly composed of waxes (C_{21}^{+}) and diesel fraction (C_{12-20}), with their yields being 67 wt% and 25 wt%, respectively. Regarding the gas fraction (C_1-C_4), a low yield is obtained (1.4 wt%), with the main compounds being propylene and butenes. Similarly, the yield of hydrocarbons in the gasoline range is low (5.2 wt%) and mainly composed of isoparaffins and olefins, with the presence of aromatics being negligible.

The excellent features of the spouted bed reactor for the fast pyrolysis of plastics, namely, high heat transfer rate and vigorous movement and short residence time, allow for selectively obtaining waxes and diesel at low temperatures (500 ºC). Moreover, the absence of operational problems, especially bed defluidization due to agglomeration of bed particles coated with melted plastic, ensures a stream of homogeneous composition throughout time, which is essential for reproducible operation in the subsequent reforming reactor. In fact,

the upgrading of these long chain hydrocarbons by downstream thermal [40] or catalytic [35] processes has shown to be a feasible route for the valorisation of polyolefins.

3.2. Parametric study of the steam reforming step

The effect temperature, steam/plastic ratio and space time have on product yields and gas fraction composition has been analysed. In order to ascertain the influence of operating conditions on the reaction indices, the following reactions have been considered in the reforming step:

Steam reforming: eq. 4

Water gas shift (WGS): $CO + H_2O \Leftrightarrow CO_2 + H_2$ (5)

Methane steam reforming: $CH_4 + H_2O \Leftrightarrow CO + 3H_2$ (6)

Cracking (secondary reaction): $C_nH_m \rightarrow paraffins + olefins$ (7)

3.2.1. Effect of temperature

The effect of temperature on product yields and compositions has been studied in the 600-700 ºC range. Concerning the operating conditions, a relatively high space time (16.7 g_{cat} min g_{HDPE}^{-1}) and S/P ratio (4) have been established to avoid operational problems related to the low conversion of waxes in the feed.

The main gaseous products obtained in the reforming step are: H_2, CO_2, CO, CH_4 and light hydrocarbons (C_2-C_4), mainly made up of ethylene, ethane, propylene and propane. The non-reformed liquid products have been group into C_5^+ fraction.

Figure 3 shows the evolution of HDPE conversion (eq. 1) with temperature. As observed, the conversion is higher than 94 % in the range studied. In addition, an increase in

temperature favours the reforming reaction kinetics, reaching a conversion of 98 % at 700 ºC, with the yield of C_5^+ compounds being 2 %. High conversions involve an increase in the volumetric gas yield, reaching a value of 5.73 $Nm^3\ kg_{HDPE}^{-1}$ at 700 ºC, with this production being much higher than that obtained in the steam gasification of different plastics (between 1 and 2.5 $Nm^3\ kg_{plastic}^{-1}$) [9, 11, 41, 42].

The increase in conversion with temperature, common in endothermic reactions, is consistent with the trend reported for the catalytic steam reforming of municipal solid wastes [43] and is explained by the positive effect of temperature on the reforming of waxes and light hydrocarbons, eq. 4, and methane, eq. 6, but also on the endothermic cracking reactions, eq. 7.

Figure 3

Figure 4a shows the evolution of the individual compound yields with the reforming temperature. As observed, H_2 yield increases from 78.1 % at 600 ºC to 85.7 % at 700 ºC. At 700 ºC, the mentioned H_2 yield means a production of 37.3 g H_2 per 100 g of HDPE in the feed. The H_2 production reported by Czernik and Frech in the pyrolysis-reforming of polypropylene (PP) was slightly lower, 34 g per 100 g of polymer [22]. Based on the H_2 mass balance, approximately 63 % of this H_2 is formed from steam and the remaining 37 % from the polymer.

Furthermore, an increase in temperature favours the formation of CO, reaching a yield of 29.2 % at 700 ºC. The effect of temperature on the CO_2 yield is limited; that is, there is only a slight reduction in the range studied.

In spite of the very low yield of CH_4, C_2-C_4 and C_5^+ in the temperature range studied, a slight reduction in their yield is observed as temperature is increased. Thus, at 700 ºC the yield of CH_4, C_2-C_4 and C_5^+ are 0.8, 0.7 and 1.8 %, respectively. This result confirms that

the selective reforming of these compounds is enhanced over their formation by cracking. Moreover, temperature contributes to CO formation because WGS (eq. 5) is an exothermic reaction, and accordingly its equilibrium shifts towards CO formation by increasing temperature.

Furthermore, the effect of temperature on the composition of the gaseous products (Figure 4b) is limited. In fact, H_2 concentration increases only from 68 % at 600 ºC to 70 % at 700 ºC. The CO_2 concentration decreases slightly, being 20.9 % at 700 ºC. The effect of temperature on CO concentration is more significant due to the fact that temperature hinders WGS reaction, with CO concentration increasing from 6.8 at 600 ºC to 9.0 % at 700 ºC. As was previously mentioned, the reforming of plastic derived hydrocarbons, CH_4, C_2-C_4 and C_5^+ is almost complete, especially as temperature is raised. It should be noted that the H_2 yield in Figure 4a is based on the maximum allowable by stoichometry, but those of the other compounds are based on the amount of HDPE in the feed. Accordingly, the summation of all the yields in Figure 4a is not 100, but the yields of the carbon containing compounds account for this value.

Figure 4

The higher H_2 yield (85.7 %) obtained in this study under the same reforming conditions as those in a previous study carried out a fixed bed reactor (81.5 %) [29] highlights the higher efficiency of the fluidized bed reactor in the reforming step. The better performance of the fluidized bed reactor is related to the mixing regime of the catalyst particles [28]. This regime promotes isothermicity of the bed which is essential in a highly endothermic process as steam reforming. Moreover, it enhances in situ coke gasification, hindering the formation and growth of carbonaceous deposits and avoiding bed blockage.

The great differences in operating strategies, reactors, experimental conditions and feed properties hinder a comparison of this study's results with those in the literature for H_2 production from waste plastics. He et al. [18] studied the effect of temperature (700-900 ºC) in the continuous catalytic steam gasification of PE in a fixed bed reactor on a NiO/Al_2O_3 catalyst. They obtained the maximum H_2 concentration (37 %) operating at 900 ºC. The research group headed by Prof. Yoshikawa studied continuous pyrolysis and in line reforming of plastics on a Ru catalyst in a two-step process based on two fixed bed reactors [23, 24]. These authors did not observed a significant effect of reforming temperature on the gaseous stream composition in the 580-680 ºC range when feeding PP and polystyrene (PS), and they reported H_2 concentrations of the same order as those in this study (around 70 %). The process developed by the team headed by Prof. Williams is also based on two fixed beds for pyrolysis and reforming steps, with both being in batch regime [20, 21, 44]. These authors reported a positive effect of temperature when studying the pyrolysis-reforming of PP on $NiCeO_2/Al_2O_3$ and Ni/ZSM-5 catalysts, with the maximum H_2 content being of around 65 % at 900 ºC [20, 44]. The continuous process proposed by Czernik and French is made up of two fluidized bed reactors for pyrolysis and reforming steps [22]. They fed PP and operated at 800 ºC on a Ni commercial catalyst, which allowed obtaining a H_2 yield of 80 % of the maximum stoichometric one.

3.2.2. Effect of space time

The effect of space time on the reforming of HDPE volatiles has been studied between 2.8 and 20.8 g_{cat} min g_{HDPE}^{-1}. In these runs, reforming temperature was 700 ºC and S/P 4. Figure 5 shows a significant effect of space time on the conversion of HDPE volatiles from 2.8 (68.3 %) to 8.3 g_{cat} min g_{HDPE}^{-1} (97.5 %). A further increase in space time hardly increases conversion, which is almost complete for a space time of 20.8 g_{cat} min g_{HDPE}^{-1}. In

fact, total conversion is not reached for the latter value of space time due to gas by-passing in the fluidized bed reactor.

As a result of the intensification of reforming reactions (eqs. 4 and 6) and WGS (eq. 5), an increase in space time causes an increase in H_2, CO_2 and CO yields and, furthermore, a decrease in those of CH_4, C_2-C_4 and C_5^+ (Figure 6a). The enhancement of reforming reactions is explained by the water reacted, which increases from 0.79 kg kg_{HDPE}^{-1} for 2.8 g_{cat} min $g_{HDPE}^{-1}$to 2.20 kg kg_{HDPE}^{-1} for the highest space time studied.

An increase in space time to 8.3 g_{cat} min g_{HDPE}^{-1} causes a significant increase in H_2 (73.8 %) and CO_2 (69.3 %) yields, which also applies to process conversion (Figure 5). The effect on CO yield is less pronounced, with this yield being 23.2 % for a space time of 8.3 g_{cat} min g_{HDPE}^{-1}, which means that an increase in space time selectively promotes WGS reaction. There is a significant reduction in the yield of CH_4, and especially in those of C_2-C_4 and C_5^+, i.e., in the case of C_2-C_4 fraction it decreases from 27.2 % for the lowest space time studied to 3.8 % for 8.3 g_{cat} min g_{HDPE}^{-1} and in the case of C_5^+ compounds from 31.7 % to 2.4 %

Space times higher than 8.3 g_{cat} min g_{HDPE}^{-1} hardly affect product yields. Nevertheless, in the case of H_2, its yield continues increasing, reaching a value of 86.7 % for the maximum space time studied (20.8 g_{cat} min g_{HDPE}^{-1}). The effect high space times have on CO and CO_2 yields is negligible.

The significant effect of space time on the individual yields of gaseous products has also been observed in the pyrolysis and reforming of plastics [20] and in the gasification and reforming of municipal solid waste (MSW) [41-43], which is explained by the enhancement of reforming and WGS reactions.

The effect of space time on the gaseous stream composition is less pronounced (Figure 6b). H_2 concentration is around 70 % in the space time range studied, similarly to that of CO, which remains almost constant at a value of 8 %. However, the CO_2 content in the gaseous stream increases with space time, whereas that of CH_4 and C_2-C_4 decreases, being negligible (below 0.3 %) for space times higher than 8.3 g_{cat} min g_{HDPE}^{-1}. The aforementioned effect of space time on the gaseous stream composition clearly shows that space time favours reforming and WGS reactions, although the extension of the latter at 700º C is conditioned by the thermodynamic equilibrium.

Figure 5

Figure 6

3.2.3. Effect of steam/plastic ratio

The effect of the S/P ratio (and consequently of the steam partial pressure) has been studied between 3 and 5, with the remaining main operating conditions being as follows: 700 ºC and space time 16.7 g_{cat} min g_{HDPE}^{-1}. An increase in steam partial pressure in the reaction environment increases the reaction rate of reforming and WGS steps, which is evidenced by the high conversion values obtained. As observed in Figure 7, conversion takes values above 98 %, reaching a value of 99.6 % for a S/P ratio of 5. Thus, the gas yield significantly increases in the S/P range studied, from 4.99 Nm^3 kg^{-1}_{HDPE} for a S/P ratio of 3 to 5.84 Nm^3 kg^{-1}_{HDPE} for S/P = 5. It should be noted that there is also an increase in the amount of water reacted per kg of plastic in the feed from 1.87 to 2.31 kg kg_{HDPE}^{-1} when S/P ratio was raised from 3 to 5, respectively.

Figure 7

As observed in Figure 8a, an increase in S/P ratio causes an increase in H_2 and CO_2 yields, but a reduction in those of CO, CH_4, C_2-C_4 and C_5^+. Apart from the previously mentioned kinetic effect, this fact is also due to the effect of steam partial pressure by shifting the WGS reaction equilibrium. Thus, for a S/P ratio of 5, H_2 and CO_2 yields are as high as 92.5 % and 80.9 %, correspondingly. The previously mentioned H_2 yield accounts for a production of 38.1 g of H_2 per 100 g of HDPE in the feed. Furthermore, CO yield decreases to 18.1 %, and those of CH_4, C_2-C_4 and C_5^+, which are low for other S/P ratios, decrease to negligible values when operating with a S/P of 5.

Figure 8

Figure 8b shows the effect of S/P ratio on the concentration of the gaseous products. H_2 and CO_2 concentrations increase moderately with S/P ratio to values of 72.7 % and 22.2 %, respectively, for a S/P of 5. However, the CO content in the gaseous stream shows a sharp decrease from 12.8 to 4.9 % in the range studied. The concentration of gaseous hydrocarbons is very low due to the relatively high space time used.

In spite of the positive effect attained on process conversion and H_2 yield by increasing the S/P ratio, the value of this parameter should be carefully considered as its increase causes a significant reduction in the energy efficiency of the process.

A qualitatively similar effect of S/P ratio has been observed in the pyrolysis-reforming [21, 45] of different plastics in a batch process and has also been widely described in the steam gasification of polymeric materials [11, 28, 46] and MSW [41, 42].

4. Conclusions

The pyrolysis in a CSBR and in line reforming of HDPE in a fluidized bed reactor has been proven to be an alternative for the production of H_2 from plastics. The separation of

pyrolysis and reforming steps has several practical advantages, and the use of a fluidized bed reactor for the reforming step has shown a better performance than a previously studied fixed bed reactor by avoiding bed blockage by coke deposition.

A Ni commercial catalyst is highly active, attaining an almost complete conversion for space times higher than 8.3 g_{cat} min g_{HDPE}^{-1} at 700 ºC with a S/P ratio of 4. Temperature, space time and S/P ratio greatly influence product yields and gas composition. An increase in these parameters promotes HDPE derived volatile reforming, reaching a H_2 yield of 92.5 % of the maximum stoichometric value for a space time of 16.7 g_{cat} min g_{HDPE}^{-1}, 700 ºC and a S/P ratio of 5. This yield means a H_2 production of 38.1 g per 100g of HDPE in the feed.

An increase of reforming temperature from 600 to 700 ºC improves conversion from 94.5 to 98.1 % and H_2 yield, reaching a volumetric gas production of 5.73 Nm^3 kg_{HDPE}^{-1} at 700 ºC. However, WGS reaction equilibrium is hindered, and therefore CO content in the gaseous product stream increases. Moreover, an increase in S/P ratio shifts reforming and WGS reactions improving process conversion and H_2 yield.

The results of this study, obtained with continuous HDPE feed, evidence the interest of the strategy proposed for the large scale valorisation of the plastics contained in MSW. Apart from the implantation of this technology, the valorisation of other plastics in the MSW should also be contemplated.

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References

1. plastics, Plastics Europe, Plastics – the Facts, 2014-15; An analysis of European plasticsproduction, demand and waste data. (2015).

2. E. Butler, G. Devlin, K. McDonnell, Waste Polyolefins to Liquid Fuels via Pyrolysis: Review of Commercial State-of-the-Art and Recent Laboratory Research, Waste Biomass Valorization 2 (2011) 227-255.

3. S.M. Al-Salem, P. Lettieri, J. Baeyens, Recycling and recovery routes of plastic solid waste (PSW): A review, Waste Manage. 29 (2009) 2625-2643.

4. S.L. Wong, N. Ngadi, T.A.T. Abdullah, I.M. Inuwa, Current state and future prospects of plastic waste as source of fuel: A review, Renewable Sustainable Energy Rev. 50 (2015) 1167-1180.

5. P.J. Donaj, W. Kaminsky, F. Buzeto, W. Yang, Pyrolysis of polyolefins for increasing the yield of monomers' recovery, Waste Manage. 32 (2012) 840-846.

6. L.J. Yin, D.Z. Chen, H. Wang, X.B. Ma, G.M. Zhou, Simulation of an innovative reactor for waste plastics pyrolysis, Chem. Eng. J. 237 (2014) 229-235.

7. S.M. Al-Salem, L.G. Papageorgiou, P. Lettieri, Techno-economic assessment of thermo-chemical treatment (TCT) units in the Greater London area, Chem. Eng. J. 248 (2014) 253-263.

8. S.M. Al-Salem, P. Lettieri, J. Baeyens, The valorization of plastic solid waste (PSW) by primary to quaternary routes: From re-use to energy and chemicals, Prog. Energy Combust. Sci. 36 (2010) 103-129.

9. V. Wilk, H. Hofbauer, Conversion of mixed plastic wastes in a dual fluidized bed steam gasifier, Fuel 107 (2013) 787-799.

10. U. Arena, L. Zaccariello, M.L. Mastellone, Tar removal during the fluidized bed gasification of plastic waste, Waste Manage. 29 (2009) 783-791.

11. A. Erkiaga, G. Lopez, M. Amutio, J. Bilbao, M. Olazar, Syngas from steam gasification of polyethylene in a conical spouted bed reactor, Fuel 109 (2013) 461-469.

12. J.M. Toledo, M.P. Aznar, J.A. Sancho, Catalytic air gasification of plastic waste (polypropylene) in a fluidized bed. Part II: Effects of some operating variables on the quality of the raw gas produced using olivine as the in-bed material, Ind. Eng. Chem. Res. 50 (2011) 11815-11821.

13. I.I. Ahmed, N. Nipattummakul, A.K. Gupta, Characteristics of syngas from co-gasification of polyethylene and woodchips, Appl. Energy 88 (2011) 165-174.

14. J. Alvarez, S. Kumagai, C. Wu, T. Yoshioka, J. Bilbao, M. Olazar, Hydrogen production from biomass and plastic mixtures by pyrolysis-gasification, Int. J. Hydrogen Energy 39 (2014) 10883-10891.

15. G. Lopez, A. Erkiaga, M. Amutio, J. Bilbao, M. Olazar, Effect of polyethylene co-feeding in the steam gasification of biomass in a conical spouted bed reactor, Fuel 153 (2015) 393-401.

16. F. Pinto, C. Franco, R.N. Andre, C. Tavares, M. Dias, I. Gulyurtlu, I. Cabrita, Effect of experimental conditions on co-gasification of coal, biomass and plastics wastes with air/steam mixtures in a fluidized bed system, Fuel 82 (2003) 1967-1976.

17. P. Friengfung, E. Jamkrajang, S. Sunphorka, P. Kuchonthara, L. Mekasut, NiO/dolomite catalyzed steam/O2 gasification of different plastics and their mixtures, Ind. Eng. Chem. Res. 53 (2014) 1909-1915.

18. M. He, B. Xiao, Z. Hu, S. Liu, X. Guo, S. Luo, Syngas production from catalytic gasification of waste polyethylene: Influence of temperature on gas yield and composition, Int. J. Hydrogen Energy 34 (2009) 1342-1348.

19. C. Wu, P.T. Williams, Hydrogen production by steam gasification of polypropylene with various nickel catalysts, Appl. Catal. B 87 (2009) 152-161.

20. C. Wu, P.T. Williams, Effects of Gasification Temperature and Catalyst Ratio on Hydrogen Production from Catalytic Steam Pyrolysis-Gasification of Polypropylene, Energy Fuels 22 (2008) 4125-4132.

21. C. Wu, P.T. Williams, Pyrolysis-gasification of post-consumer municipal solid plastic waste for hydrogen production, Int. J. Hydrogen Energy 35 (2010) 949-957.

22. S. Czernik, R.J. French, Production of hydrogen from plastics by pyrolysis and catalytic steam reform, Energy Fuels 20 (2006) 754-758.

23. T. Namioka, A. Saito, Y. Inoue, Y. Park, T.j. Min, S.a. Roh, K. Yoshikawa, Hydrogen-rich gas production from waste plastics by pyrolysis and low-temperature steam reforming over a ruthenium catalyst, Appl. Energy 88 (2011) 2019-2026.

24. Y. Park, T. Namioka, S. Sakamoto, T.j. Min, S.a. Roh, K. Yoshikawa, Optimum operating conditions for a two-stage gasification process fueled by polypropylene by means of continuous reactor over ruthenium catalyst, Fuel Process. Technol. 91 (2010) 951-957.

25. G. Elordi, M. Olazar, G. Lopez, M. Artetxe, J. Bilbao, Product Yields and Compositions in the Continuous Pyrolysis of High-Density Polyethylene in a Conical Spouted Bed Reactor, Ind. Eng. Chem. Res. 50 (2011) 6650-6659.

26. A. Remiro, B. Valle, B. Aramburu, A.T. Aguayo, J. Bilbao, A.G. Gayubo, Steam reforming of the bio-oil aqueous fraction in a fluidized bed reactor with in situ CO2 capture, Ind. Eng. Chem. Res. 52 (2013) 17087-17098.

27. P. Lan, Q. Xu, M. Zhou, L. Lan, S. Zhang, Y. Yan, Catalytic steam reforming of fast pyrolysis bio-oil in fixed bed and fluidized bed reactors, Chem. Eng. Technol. 33 (2010) 2021-2028.

28. T. Tsuji, A. Hatayama, Gasification of waste plastics by steam reforming in a fluidized bed, J. Mater. Cycles Waste Manage. 11 (2009) 144-147.

29. A. Erkiaga, G. Lopez, I. Barbarias, M. Artetxe, M. Amutio, J. Bilbao, M. Olazar, HDPE pyrolysis-steam reforming in a tandem spouted bed-fixed bed reactor for H_2 production, J. Anal. Appl. Pyrolysis 116 (2015) 34-41.

30. G. Lopez, A. Erkiaga, M. Artetxe, M. Amutio, J. Bilbao, M. Olazar, Hydrogen Production by High Density Polyethylene Steam Gasification and In-Line Volatile Reforming, Ind. Eng. Chem. Res. 54 (2015) 9536-9544.

31. M. Olazar, M. San Jose, A. Aguayo, J. Arandes, J. Bilbao, Design Factors of Conical Spouted Beds and Jet Spouted Beds, Ind. Eng. Chem. Res. 32 (1993) 1245-1250.

32. A. Erkiaga, G. Lopez, M. Amutio, J. Bilbao, M. Olazar, Influence of operating conditions on the steam gasification of biomass in a conical spouted bed reactor, Chem. Eng. J. 237 (2014) 259-267.

33. J. Alvarez, M. Amutio, G. Lopez, I. Barbarias, J. Bilbao, M. Olazar, Sewage sludge valorization by flash pyrolysis in a conical spouted bed reactor, Chem. Eng. J. 273 (2015) 173-183.

34. A. Erkiaga, G. Lopez, M. Amutio, J. Bilbao, M. Olazar, Steam gasification of biomass in a conical spouted bed reactor with olivine and g-alumina as primary catalysts, Fuel Process. Technol. 116 (2013) 292-299.

35. M. Artetxe, G. Lopez, M. Amutio, G. Elordi, J. Bilbao, M. Olazar, Light olefins from HDPE cracking in a two-step thermal and catalytic process, Chem. Eng. J. 207-208 (2012) 27-34.

36. G. Lopez, M. Olazar, M. Amutio, R. Aguado, J. Bilbao, Influence of Tire Formulation on the Products of Continuous Pyrolysis in a Conical Spouted Bed Reactor, Energy Fuels 23 (2009) 5423-5431.

37. G. Lopez, M. Olazar, R. Aguado, J. Bilbao, Continuous pyrolysis of waste tyres in a conical spouted bed reactor, Fuel 89 (2010) 1946-1952.

38. J. Makibar, A.R. Fernandez-Akarregi, M. Amutio, G. Lopez, M. Olazar, Performance of a conical spouted bed pilot plant for bio-oil production by poplar flash pyrolysis, Fuel Process. Technol. 137 (2015) 283-289.

39. W. Kaminsky, B. Schlesselmann, C. Simon, Olefins from polyolefins and mixed plastics by pyrolysis, J. Anal. Appl. Pyrolysis 32 (1995) 19-27.

40. M. Artetxe, G. Lopez, G. Elordi, M. Amutio, J. Bilbao, M. Olazar, Production of Light Olefins from Polyethylene in a Two-Step Process: Pyrolysis in a Conical Spouted Bed and

Downstream High-Temperature Thermal Cracking, Ind. Eng. Chem. Res. 51 (2012) 13915-13923.

41. J. Wang, G. Cheng, Y. You, B. Xiao, S. Liu, P. He, D. Guo, X. Guo, G. Zhang, Hydrogen-rich gas production by steam gasification of municipal solid waste (MSW) using NiO supported on modified dolomite, Int. J. Hydrogen Energy 37 (2012) 6503-6510.

42. J. Li, S. Liao, W. Dan, K. Jia, X. Zhou, Experimental study on catalytic steam gasification of municipal solid waste for bioenergy production in a combined fixed bed reactor, Biomass Bioenergy 46 (2012) 174-180.

43. S. Luo, Y. Zhou, C. Yi, Syngas production by catalytic steam gasification of municipal solid waste in fixed-bed reactor, Energy 44 (2012) 391-395.

44. C. Wu, P.T. Williams, Hydrogen Production from the Pyrolysis/Gasification of Polypropylene: Influence of Steam Flow Rate, Carrier Gas Flow Rate and Gasification Temperature, Energy Fuels 23 (2009) 5055-5061.

45. C. Wu, P.T. Williams, Hydrogen production from the pyrolysis-gasification of polypropylene: Influence of steam flow rate, carrier gas flow rate and gasification temperature, Energy Fuels 23 (2009) 5055-5061.

46. A. Donatelli, P. Iovane, A. Molino, High energy syngas production by waste tyres steam gasification in a rotary kiln pilot plant. Experimental and numerical investigations, Fuel 89 (2010) 2721-2728.

Figure captions

Figure 1. Diagrammatic representation of the pyrolysis-reforming process.

Figure 2. Scheme of the laboratory scale pyrolysis-reforming unit.

Figure 3. Effect of reforming temperature on HDPE conversion. Reforming conditions: space time, 16.7 g_{cat} min g_{HDPE}^{-1}; S/P ratio, 4.

Figure 4. Effect of reforming temperature on the yields of products (a) and their concentration on the gas fraction (on a dry basis) (b). Reforming conditions: Space time, 16.7 g_{cat} min g_{HDPE}^{-1}; S/P ratio, 4.

Figure 5. Effect of reforming space time on HDPE conversion. Reforming conditions: 700 ºC; S/P ratio, 4.

Figure 6. Effect of reforming space time on the yields of products (a) and their concentration on the gas fraction (on a dry basis) (b). Reforming conditions: 700 ºC; S/P ratio, 4.

Figure 7. Effect of S/P ratio on HDPE conversion. Reforming conditions: 700 ºC; space time, 16.7 g_{cat} min g_{HDPE}^{-1}.

Figure 8. Effect of S/P ratio on the yields of products (a) and their concentration on the gas fraction (on a dry basis) (b). Reforming conditions: 700 ºC; space time, 16.7 g_{cat} min g_{HDPE}^{-1}.

Table 1. Experimental conditions in the parametric study of the steam reforming step.

Temperature (ºC): 600, 650 and 700 (space time, 16.7 g_{cat} min g_{HDPE}^{-1}; steam/plastic ratio, 4)
Space time (g_{cat} min g_{HDPE}^{-1}): 2.8, 4.2, 8.3, 12.5, 16.7 and 20.8 (700 ºC; steam/plastic ratio, 4)
Steam/plastic ratio: 3, 4 and 5 (700 ºC; space time, 16.7 g_{cat} min g_{HDPE}^{-1})