(RESEARCH ARTICLE)

Analysing the effects of process parameters on HDPE pyrolysis and in-line reforming

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Abstract

This study presents a comprehensive parametric investigation focusing on the pyrolysis and in-line reforming of High-Density Polyethylene (HDPE) at zero time on stream. The research explores the impact of varying operating parameters, specifically examining the effects of temperature, space time, and steam/plastic (S/P) ratio on conversion, hydrogen production, and product yields. The temperature was varied within the range of 600–750 °C, demonstrating notable influence on conversion efficiency and hydrogen production. Additionally, the effect of space-time (2.8–20.8 g catalyst min $gHDPE^{-1}$) was thoroughly evaluated, revealing substantial improvements in both conversion and hydrogen yields. Moreover, the S/P ratio of 1 to 3 was investigated, showcasing significant enhancements in hydrogen and CO_2 yields with increasing steam partial pressure. The study provides valuable insights into optimizing the process parameters for HDPE pyrolysis and in-line reforming, which are crucial for achieving efficient conversion and enhancing hydrogen production.

Keywords: Pyrolytic Conversion; African apple seed; Catalyst; High-Density Polyethylene (HDPE); Low-Density Polyethylene (LDPE); Activated Carbon

1. Introduction

Pyrolysis may turn petroleum-derived plastics into gasoline. Pyrolysis breaks plastic molecules into gas, oil, and solid residue by heating them to high temperatures in an oxygen-free atmosphere. The environment benefits from this technique since it reduces plastic trash in landfills and seas. It supplies alternate transportation and energy fuels. Population increases, fast economic development, urbanization, and lifestyle changes drive plastic garbage production and consumption. Plastic's short lifespan accelerates everyday garbage processing. Plastic output worldwide is 300 million tons annually and rising (Heikkinen et al., 2004). Plastics are made from petrochemical hydrocarbons with biodegradable flame retardants, stabilizers, and oxidants. Although there are several ways to recycle plastic garbage, most poor countries choose open or landfill disposal (Bernando, 2011). Landfills with plastic garbage attract rats and insects that carry illnesses. Recycling programs may cost more owing to labour, transportation, and upkeep (Prabir, 2010). Due to increased urbanization, especially in cities, landfill land is decreasing.

Population expansion, urbanization, and increasing industrialization have raised energy and environmental pollution concerns. These causes have increased fossil fuel usage and pollution. To lessen our dependence on petroleum derivatives, significant expenditures have been made in the quest for alternative or optional fuels (Dogan et al., 2012). Increased waste plastic manufacturing, which accounts for a large amount of solid waste in industrialized and emerging nations, is a worry. Cleaning automobiles of plastic garbage is complex, and plastic output is rising. Plastics make up over 80% of solid garbage. Not adequately handled, this may harm the ecosystem (Dogan et al., 2012).

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To solve this challenge, waste-to-energy methods are being investigated as fuel alternatives. Waste products are converted into energy to power vehicles or create electricity. This method reduces fossil fuel use and landfill trash (Murugan et al, 2008).

Besides waste-to-energy methods, alternative fuels for internal combustion engines are being investigated. Alcohol, biodiesel, and plastics are fuels. These fuels have significant drawbacks but may reduce our dependence on conventional fuels and their environmental effect (Murugan et al, 2008).

Finding alternative fuels and waste-to-energy methods is crucial to reduce fossil fuel use and pollution. These tactics are complex, but they provide promise for a sustainable future. Individuals, governments, and companies must collaborate to improve the earth for future generations (Dogan et al, 2012).

Energy may be generated by recycling landfill or incinerator waste (Murugan et al., 2008). Most plastic garbage is landfilled or stored, requiring huge geographical area. Reusing and landfilling may harm humans and the environment. Few waste plastics are recycled into new products like black-top street filters or raw materials for recovered elastic, phony reefs, or barriers. waste plastic might be an energy asset (Leung & Wang, 2003).

Thus, plastic garbage may be suitable for heated removal (Karatas et al, 2013). This makes them ideal for hot cycles like pyrolysis and gasification (Portofino et al, 2013). Regular and polybutadiene elastic are the most prevalent plastics (Williams, 2013). Besides energy and carbon, many materials may be reused. This study will utilize standard pyrolysis units to transform waste plastics into gas and fuel oil and analyze their physiochemical qualities. Pyrolysis is a popular way to turn waste plastic into solid, liquid, or gaseous fuels. Pyrolysis decomposes plastic trash at 300–900°C without oxygen to generate liquid oil gas and solid char (Kukreja, 2009). Pyrolysis thermally decomposes long-chain organic compounds in inert atmospheres with or without a catalyst. Controlling heat flow and pressure reduces organic material chains (Masanet et al., 2002). Pyrolysis produces tars, fumes, and char after a longer residence period and less intense heat (Fakhrhoseini & Dastanian, 2013). Pyrolysis does not need flue gas cleaning since it is often treated before use (Bridgwater, 2012). Additionally, it creates critical components for petrochemical and petroleum refining operations, which might compromise petroleum processing reliability (Heikkinen et al., 2004). At 500–650°C, pyrolysis produces valuable tars (liquid oils and waxes) with 75–80% yields. Pyrolysis is greener than landfilling because it decreases greenhouse gas (GHG) emissions, particularly carbon dioxide (CO_2). Pyrolysis provides greater environmental advantages than other municipal solid waste treatments. In an inert, oxygen-free atmosphere, pyrolysis does not produce dioxins through product interactions with oxygen (Abnisa et al., 2014; Zannikos et al., 2013; Hernandez et al., 2007; Heikkinen et al., 2004). Pyrolysis provides a high-calorific fuel that may be utilized in gas engines to create power and heat (Ahmad et al., 2014). Pyrolysis, like other thermochemical techniques (TCT) like hydrogenation, has a high internal rate of return (IRR) of over 30% in industrial economies of scale schemes (Park et al., 2012; Hong et al., 1993). The non-condensable percentage of pyrolysis-produced gases has a high CV and may lower the plant's energy needs (Abnisa & Wan Daud, 2014). Pyrolysis is cheaper than other treatment techniques because it needs fewer feedstock pre-treatment processes. Pyrolysis will be compared to various thermal and catalytic plastic solid waste chemical treatment processes in the study's comparative assessment. Feeds, catalysts, and process parameters strongly affect pyrolysis. This research will describe and objectively analyze the pyrolytic conversion of waste plastic utilizing African apple seed base activated carbon as catalyst to understand the process and its significant effects on the end products.

2. Material and methods

2.1. Material

The raw materials (waste Low Density Polyethylene (LDPE) and High-Density Polyethylene (HDPE) plastic) used for the catalytic pyrolysis process were sourced from Liberation Stadium Road, GRA Phase IV, Port Harcourt, Rivers State.

Below are the list of materials and tools used during the experimental procedure.

- Low Density Polyethylene (LDPE) plastic
- High-Density Polyethylene (HDPE) plastic
- Digital Weighing Balance (OHAUS Scout pro 2000 g),
- Mechanical Stirrer (JENWAY 1000 Hot Plate and Stirrer ST15 OSA, UK),
- SVAC2 Compact Vacuum Drying oven,
- 1.7 Cubic Foot, 240 °C, Model SVAC2,
- Model F6018,

- Thermo Scientific Thermolyne A1 Premium Muffle Furnace - 208V-FEI-QUANTA 200.
- African Star Apple seed shell.
- Mercury-in-glass Thermometer (GH Zeal LTD, 76 mm 0-360 °C),
- Conical Flask (250 mL),
- Measuring Cylinder,
- Beaker (500 mL),
- Retort Stand, Pipette (25 mL), Plastic containers for samples, Mortar pestle, Spatula, Stopwatch.
- De-ionized water and Phosphoric acid solution (14.7 M, available in the laboratory)

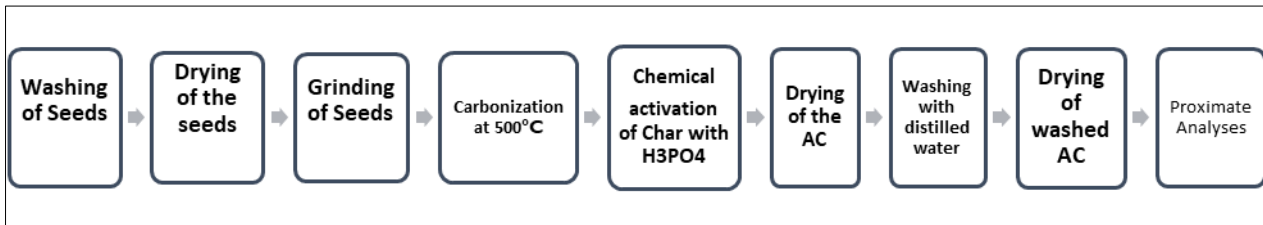## 2.2. Process Description for Activated Carbon production

Figure 1 Flowchart of procedures for producing activated carbon from African star apple

- Removal and drying of seed husks: The seed kernels of the African star apple were physically torn apart from fleshy fruit, retrieved, and washed to remove grease and debris, and then dried for three days in the sunlight, after which it was dehydrated in an oven at temp 105 °C for 3 hours to ensure all effective removal of all water residue in the seeds.
- Grinding: The dried precursor was separated into three sample shells and ground using mortar and pestle, and then the ground kernels were ground further to make particle size of -6 to +40 mesh.
- Preparation of activated carbon: Accurately weighed samples of dried African Star Apple seed shells were carbonized in crucibles at 500 °C in the furnace. The charcoal product obtained was ground and sieved to 2mm size. A solution of known concentrations of 0.8 M of Phosphoric acid (H3PO4) was made. Three separate 10g portions of the African Star apple samples were stirred and left to be soaked separately in 100 mL of 0.8 M H_3PO_4, respectively, for 24 hours. The sample was labeled ABD1 before being heated in the oven at 105 °C for 2 hours. The activated product was then cooled to 27 °C and washed with warm distilled water until it reached a pH of 7 to remove any undiluted residue of phosphoric acid after which the precursor was dried in an oven at a temperature of 105 0C for 1 hour. Finally, the dried antecedent was ground and sieved to get a molecule size of 125-150µm. It was stored in plastic containers for further use.

2.3. Gasification of HDPE and LDPE using activated carbon as catalyst

Gasification involves feeding, two reaction zones, char separation, and quenching. A distributor separates the bubbling fluidized bed gasifier and tar-cracking reactor reaction zones. The bubbling fluidized bed reactor's low freeboard length was intended to remove coke from the distributor's surface via impact physically. AC-filled packed bed reactors fracture tar. Fluidized bed reactor (380 mm height, 160 mm inner diameter) and tar-cracking reactor (height: 430 mm, inner diameter: 160 mm). The tar-cracking reactor has a greater diameter than the fluidized bed reactor to maximize gas contact time with the active carbon bed and avoid active carbon sweeping from the reactor. Due to their simplicity and controllability, electric heaters are employed to heat both reactors in the bench scale set-up. Commercial operations cannot adopt them for economic reasons. Tar cracking processes are endothermic, thus energy is needed. In the UOS two-stage gasification process, the fluidized bed gasifier directly linked to the tar-cracking reactor provides most of the energy for tar cracking. Tar cracking may employ fluidized bed gasifier oxygen when air or oxygen is gasified. In real-world UOS two-stage gasification applications, a dual loop gasification system may provide energy for fluidized bed gasifier steam gasification. The char separation system uses a cyclone and hot filter to separate particles bigger than 10 and 2 µm from syngas. The quenching system uses water-cooled condensers. Finally, EPs may clear tar in certain runs.

2.4. Physicochemical properties of the pyrolysis oil

Table 1 shows ASTM techniques used to compare the diesel fuel generated by pyrolyzing waste polymers (HDPE and LDPE) to diesel fuel.

Table 1 Test method for LDPE and HDPE

Parameter	Method
Density	ASTM D4052
Calorific value (mJ/kg)	ASTM D240
Cetane number	D613-84
Water content (mg/g)	ASTM D6304
Flash point	ASTM D93
Acid number (mg KOH/g)	IP 139
Kinematic viscosity @ 40	D445-04E02
Ash content	IP 391
Aromatic content (%)	IP 391
Pour point	D97-05A
Carbon content (wt.%)	ASTM D5291
Hydrogen content (wt.%)	ASTM D5291
Oxygen content (wt.%)	ASTM D5622
Sulphur content (wt.%)	ASTM D5453
Nitrogen content (mg/kg)	ASTM D4530
Carbon residue (wt.%)	ASTM D4530
LHV (MJ/kg)	ASTM D240

2.4.1. Experiment conditions

All tests except Run had feed rates of 8.3 g/min and gasification times of 60 min (240 min). The fluidized bed gasifier and tar-cracking reactor reaction temperatures were 790 and 840 °C for all runs. Natural olivine was 2200 g and active carbon 1500 g. Steam was heated to 600 °C before entering the gasifier. Steam was supplied at 12.5–20.8 g/min, resulting in a S/F of 1.5–2.5 and 2.8–4.6 Umf (calculated minimum fluidization velocity). The S/F was determined using Eq. (3):

$$\frac{S}{F} = \frac{m_s}{m_f} \;\ldots\ldots\ldots\ldots 1$$

Where *mS and mF* are the mass flow rates of steam and feed material (g/min), respectively. The contact time (*tc*) between the syngas and the active carbon bed in the tar-cracking reactor was calculated using Eq. (4):

$$t_c = \frac{V_{ac} \times (1-\varepsilon)}{V_g \times \frac{T_{rxn}}{T_0}} \ldots\ldots\ldots\ldots 2$$

where Vac is the active carbon bed volume in the tar-cracking reactor (m3), is its voidage (0.55 in this research), Vg is the volumetric flow rate of generated gas (m3/s), and Trxn and To are the reaction and outlet temperatures (K). Contact time was estimated at 1 s. Table 3 lists additional reaction conditions. Runs 1 and 2 examined how AC affected syngas quality without and with AC. Run 2 revealed AC's tar removal and hydrogen production roles. Runs 2–4 examined how the S/F affected syngas composition and gasification efficiency. S/F rose from 1.5 (Run 2) to 2.5. (Run 4). EP-free Run 5. Runs 2 and 5 showed that EP-free and EP-containing syngas differed in quality. In Runs 1–5, a hook-type distributor was employed between the fluidized bed gasifier and tar-cracking reactor. In Runs 6–8, mesh distributors were employed. Dolomite grains (800 g) were placed above the mesh-type distributor as a guard bed to prevent AC from dropping through the mesh pores. The mesh-type distributor was used to study how it resists coke formation. Fig. 3 shows hook- and mesh-type distributors. Run 7 used in-situ AC regeneration. A 20-minute feeding break was used to regenerate. The AC received 10 min of steam during in-situ regeneration. Comparing Runs 3 and 7 showed how in situ

AC regeneration affected syngas quality and textural qualities. Run 8 was a 4-hour operation with steam-regenerated AC every 20 minutes. Condensed, cryogenic, and carbon conversion efficiency.

tar removal efficiency (CTRE) was calculated for each run to evaluate the performance of the UOS two-stage gasification process as follows:

$$CGE\ (\%) = \frac{V_g \times LHV_g}{M_f \times LHV_f} \times 100 \ \ldots\ldots\ldots\ldots\ldots 3$$

All gasification products were split into syngas, char, condensate liquid, and tar. Condensate liquid was the result without condensed tar. The difference in weight of condensers, tubes, and EP before and after gasification was measured by measuring condensed tar. After collecting liquid, it was evapourated in a 105 °C oven for 24 h to separate condensed liquid from tar. Condensed tar was the remainder's weight. A calorimeter (Model 6100, Parr) assessed the energy balance by measuring the calorific values of char, condensate liquid, and condensed tar. Gas chromatography (GC: 7890A, Agilent Instruments)-thermal conductive detector (TCD) and GC-flame ionization detector (FID) were used to evaluate syngas for N_2, H_2, CO, CH_4, CO_2, and light hydrocarbons using argon as carriers. TCD Carboxen 1000 and HP-plot Al_2O_3/KCl columns were utilized (FID). This research used GC-FID to assess syngas' tar content, defined as hydrocarbons with a molecular weight greater than benzene. Brunauer–Emmett–Teller (BET) surface area and pore size analyzers analyzed AC's specific surface areas and pore size distributions (BELSORP mini II).

Table 2 Condition for steam gasification

Parameter	HDPE	LDPE
Activated carbon	1000 g	1000 g
Tar-cracking reactor temp. (°C)	800	800
Steam to fuel ratio (S/F)	2.5	2.5
Gasification time (min)	60	60
Fluidized bed reactor temp. (°C)	790	790

3. Results and discussion

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 –750 °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:

- Temperature in the pyrolysis step has been 600 °C;
- A high space time of 16.7 $g_{catalyst}$ min g_{HDPE}^{-1} (corresponding to 12.5 g of catalyst);
- Steam/ plastic (S/P) ratio of 2.5.

These conditions have been established 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 $g_{catalyst}$ min g_{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 favoured 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 (C_2 ▬ 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 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 2 (a and b) shows the evolution of gaseous products yields with temperature. To quantify the results obtained in the reforming step, some reaction indices have been defined.
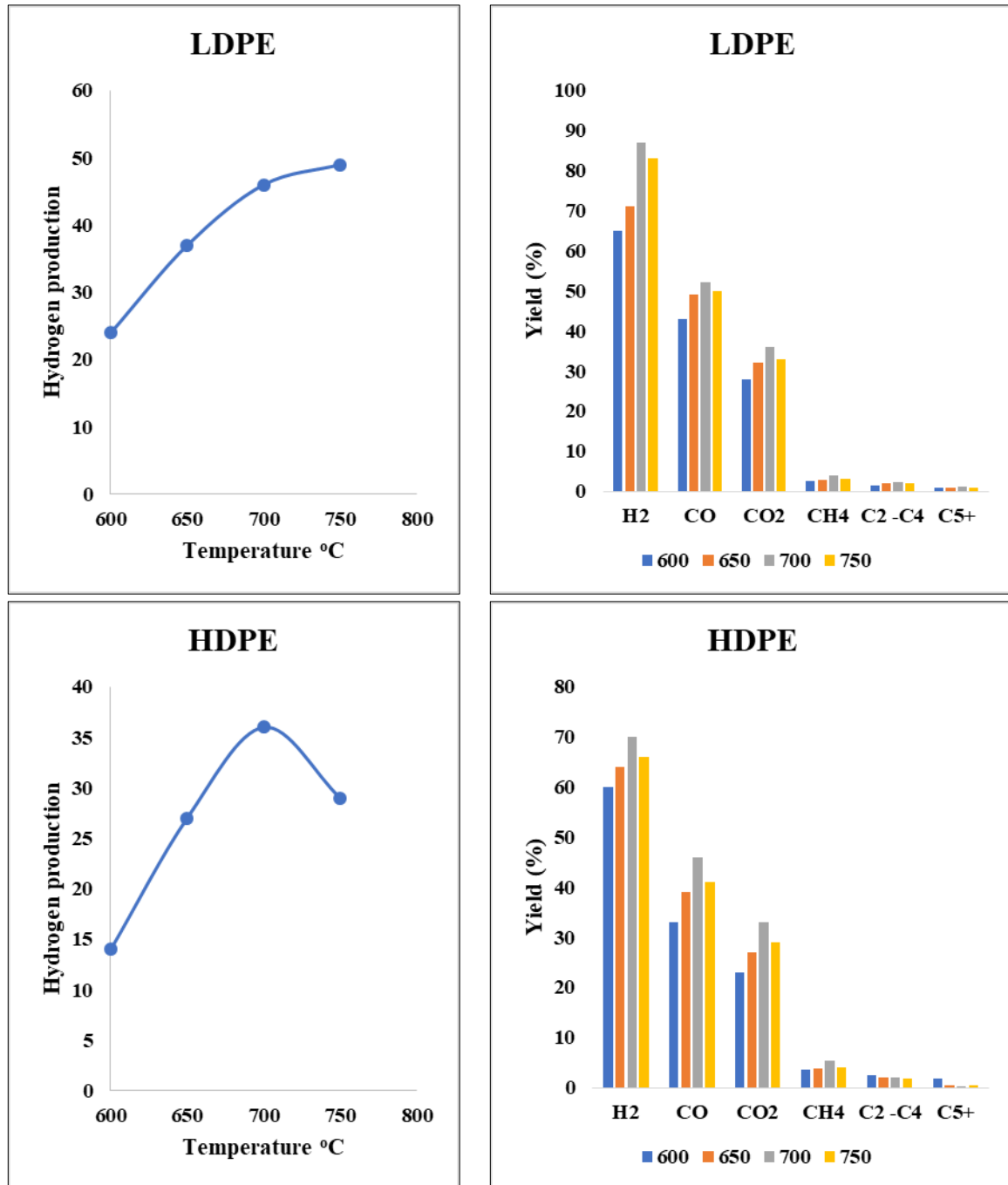
Figure 2 (a) Evolution of HDPE conversion and hydrogen production with temperature; (b) effect of reforming temperature on product yields. Reaction conditions: $T_{pyrolysis}$, 500°C; space time, 16.7 $g_{catalyst}$ min g_{HDPE}^{-1} and S/P ratio: 4

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. 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 (Seo *et al.,* 2003), 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 favoured, 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 Bagri and Williams (2001), 34 wt.%, in their study of pyrolysis-reforming of HDPE. The increase in conversion and hydrogen production with temperature in the catalytic steam reforming of municipal solid wastes (Abbas-Abadi et al., 2013) is explained because all the endothermic steps involved are favoured: (i) initial pyrolysis of waste; (ii) char 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 –750°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 4b 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 750 °C. Simultaneously, it is observed that temperature increase favours the formation of CO, obtaining a yield of 29.2% at 750 °C. The effect of temperature on the CO_2 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 favours the reforming of waxes, light hydrocarbons and CH_4. Thus, although CH_4, $C_2 — C_4$, and C_{5+} 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 considered that the WGS reaction is exothermic, and therefore its thermodynamic equilibrium shifts 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 – 20.8 g. catalyst min $g_{HDPE –1}$ 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:

- Temperature in the pyrolysis step, 600 °C;
- Temperature in the reforming step, 700 °C;
- S/P ratio, 4. As in the previous section, the effect of space time on the conversion, H_2 production and gaseous products yields has been studied.

Figure 3 shows the evolution with space time of conversion and H_2 production (Figure 3a) and of the products yields (Figure 3 b). As observed in Figure 3 a, there is a sharp increase in conversion when space time is increased from 2.8 (68.3%) to 8.3 g catalyst min $g_{HDPE –1}$ (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 g catalyst min $g_{HDPE –1}$. Regarding H_2 production, it increases from 19.5 wt.% at 2.8 to 40.5 wt.% at 20.8 g catalyst min $g_{HDPE –1}$. The production of hydrogen increases more significantly in the space time range from 2.8 to 8.3 g catalyst min $g_{HDPE –1}$, whereas in the 8.3 – 20.8g catalyst min $g_{HDPE –1}$ range the increase is milder. Figure 3b shows the effect space time in the 2.8 – 20.8 g catalyst min $g_{HDPE –1}$ range has on product yields. By enhancing the extent of reforming reactions and WGS reactions, the increase in space time increases the yields of H_2, CO_2 and CO, whereas it decreases the yields of CH_4, $C_2 — C_4$ and C_{5+}. An increase in space time (Figure 3 a) from 2.8 to 8.3 g catalyst min $g_{HDPE –1}$ leads to a pronounced increase in the yield of H_2 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 g catalyst min $g_{HDPE –1}$. Therefore, it seems that increasing space time in this range the WGS reaction is selectively favoured. It is also important to highlight the decrease in the yields of CH_4, $C_2 — C_4$ and C_{5+}, especially in the case of $C_2 — C_4$ 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 g catalyst min $g_{HDPE –1}$ range. For space times higher than 8.3 g catalyst min $g_{HDPE –1}$ 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 g catalyst min $g_{HDPE –1}$. On the other hand, an increase in space time from 8.3 to 16.7 g catalyst min $g_{HDPE –1}$ 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 (Kyong et al., 2002) and the gasification and reforming of municipal solid waste, which is explained by the enhancement of the reforming and WGS reactions.
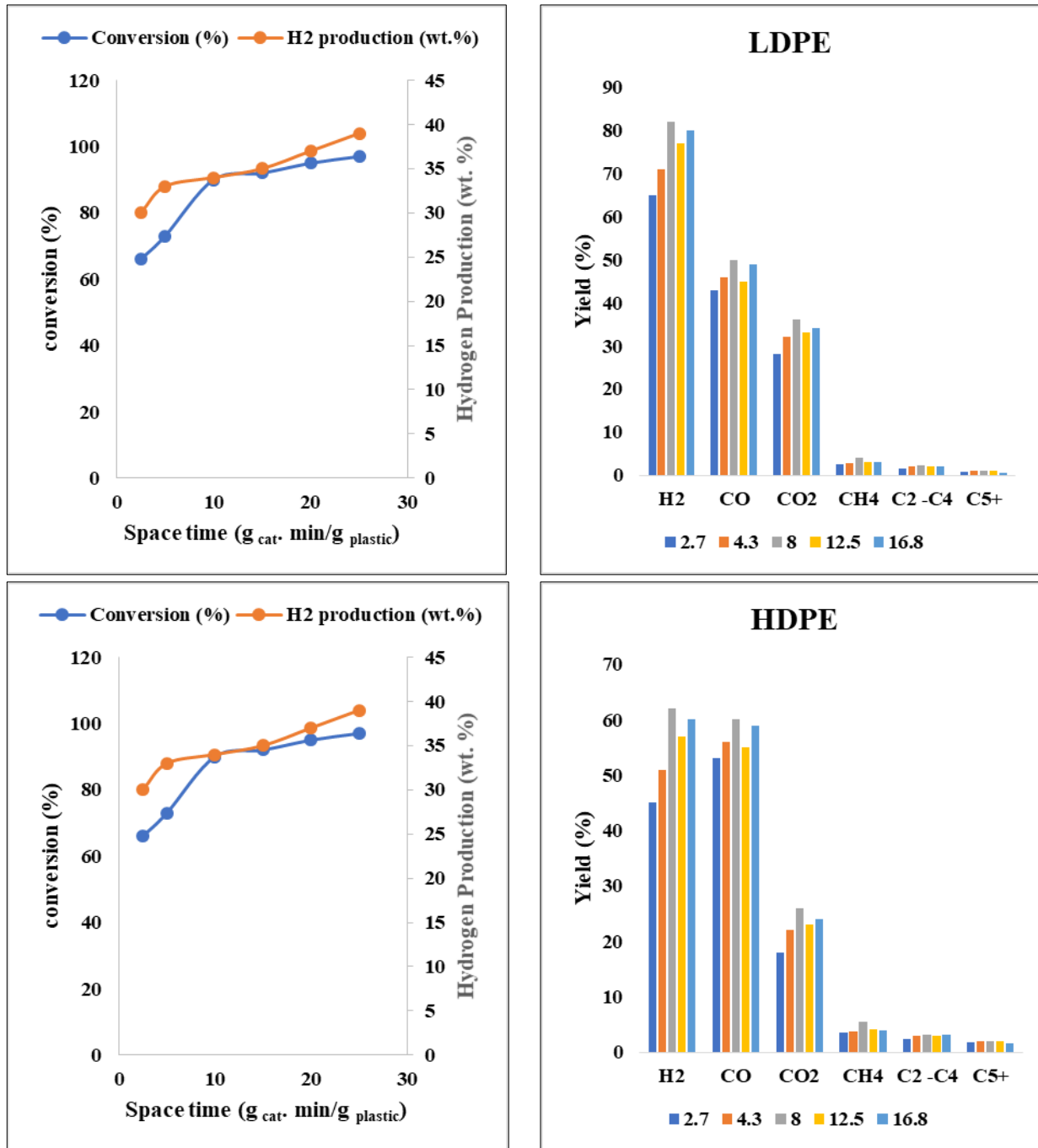
Figure 3 (a) Evolution of HDPE conversion and hydrogen production with space time; (b) effect of space time on product yields. Reaction conditions: $T_{pyrolysis}$, 500°C; $T_{reforming}$, 700°C; and S/P ratio, 4

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

In this section, the effect S/P ratio in the 1-3 range has on conversion, H_2 production and products yields at zero time on stream is shown. The operating conditions selected to carry out this study have been the following:

- Temperature of the pyrolysis step, 500 °C;
- Temperature of the reforming step, 700 °C;
- Space time, 16.7 $g_{catalyst}$ min g_{hdpe}^-.

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 H_2 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 conversions 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 32.0 wt.% for a S/P ratio of 3 to 39.5 wt.% for a S/P ratio of 5. Figure 4.5b 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 H_2 and CO_2 yields and a decrease in those of CO, CH_4, C_2 ▬ C_4, and C_{5+}. This effect is due to the higher concentration of steam in the reaction environment, which favours the displacement of both hydrocarbon reforming reactions and the WGS reaction. By favouring all the reactions involved in the reforming, an increase in the S/P ratio enhances the yield of H_2 and CO_2, up to 92.5 and 80.9 % for a ratio of 5. Consequently, the yield of CO decreases to 18.1 %. The yields of CH_4, C_2–C_4, and C_{5+}, which are small for a S/P ratio of 4, decrease until becoming insignificant. As observed, an increase in the 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 HDPE and LDPE, which is a widely proven fact in the gasification of different polymeric materials.
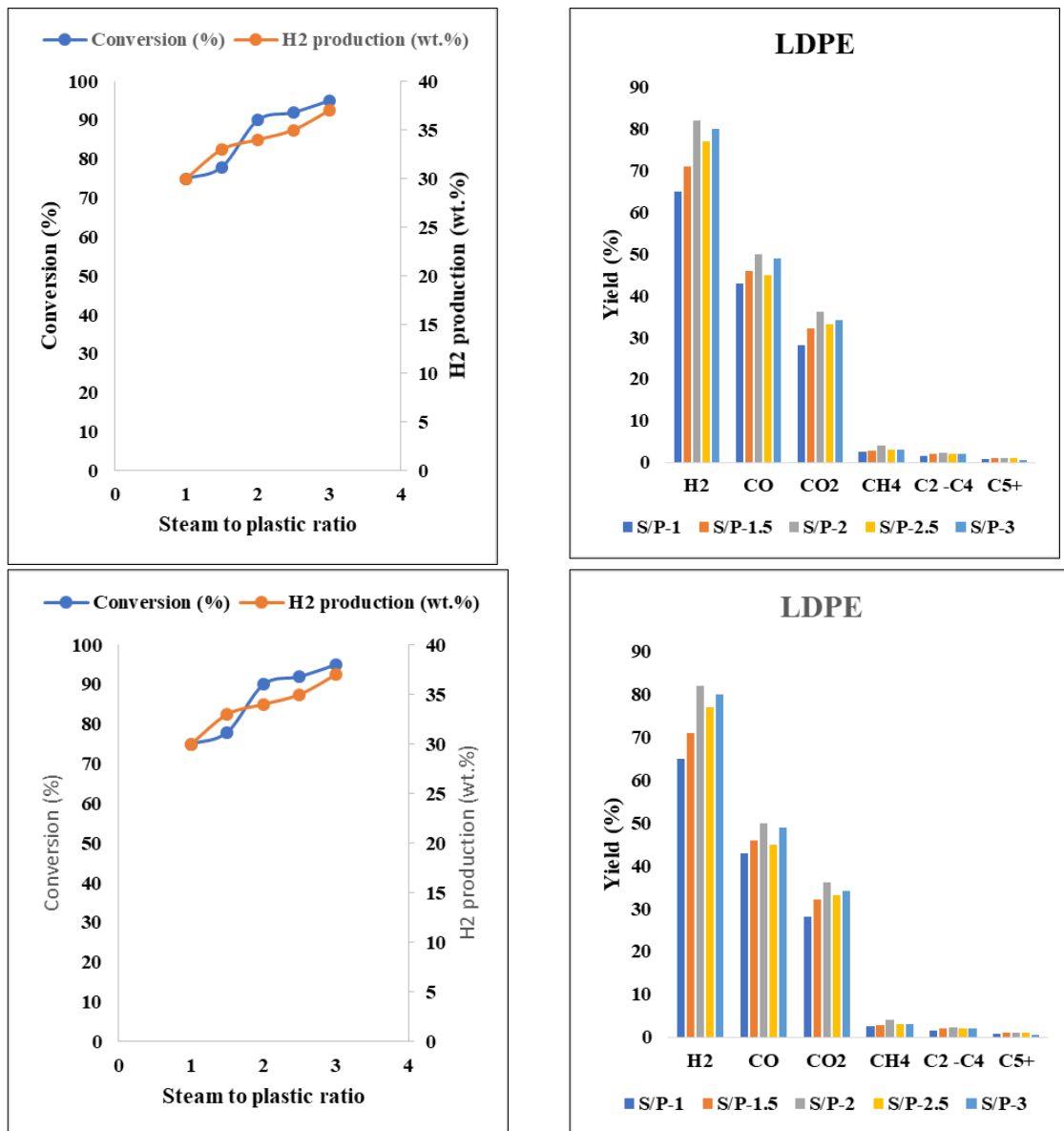

Figure 4 Effect of steam/plastic (S/P) ratio

4. Conclusion

In conclusion, this research underscores the critical influence of various parameters on HDPE pyrolysis and in-line reforming. The effect of temperature within the 600–750°C range showcased its pivotal role in conversion efficiency and hydrogen production. Higher temperatures favored endothermic reforming reactions, resulting in increased hydrogen production. Furthermore, the space-time parameter, reflecting catalyst mass relative to HDPE mass, significantly impacted conversion and hydrogen yields, emphasizing the importance of catalyst efficiency. Additionally, the steam/plastic (S/P) ratio demonstrated a substantial influence, with higher ratios favoring the reforming and water-gas shift reactions, enhancing hydrogen and CO_2 yields. Striking a balance in the S/P ratio is crucial to maintaining energy efficiency while maximizing hydrogen production. This study provides valuable insights for optimizing HDPE pyrolysis and reforming processes, offering a pathway towards enhanced hydrogen production and sustainable utilization of plastic waste.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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