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Light olefins from HDPE cracking in a two-step thermal and catalytic process

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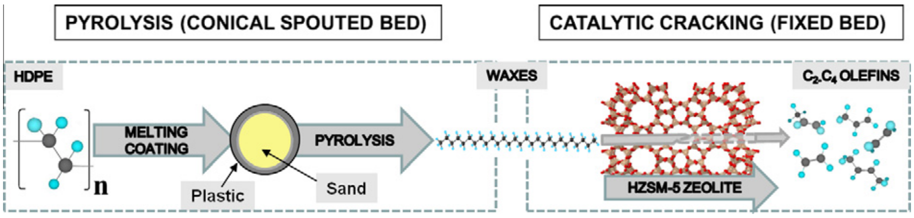
HIGHLIGHTS

- ▶ The two-step reaction system allows working with a continuous feed of HDPE.
- ▶ The product stream obtained in the pyrolysis step is mainly composed of waxes.
- ▶ The low residence time in the catalytic reactor avoids by-product formation.
- ▶ High yield of C_2–C_4 olefins (62.9 wt.%) at 550 °C and 8 g_{cat} min g_{HDPE}^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

The continuous catalytic pyrolysis of high density polyethylene (HDPE) has been carried out in a two-step reaction system involving a pyrolysis conical spouted bed reactor followed by a catalytic fixed bed reactor. The good performance of the conical spouted bed reactor has allowed using a low temperature in thermal cracking (500 °C) without defluidization problems, obtaining a volatile stream with a 90 wt.% overall yield of C_{12}–C_{20} and waxes in the first step. The effect of the second-step operating conditions on product yields and composition has been studied using a catalyst based on a HZSM-5 ($SiO_2/Al_2O_3 = 30$) zeolite. The influence of temperature in the 350–550 °C range and space–time in the 0–8 g_{cat} min g_{HDPE}^{-1} range has been studied. An increase in temperature or space–time gives way to an increase in the yield of light olefins, reaching a value of 62.9 wt.% at 550 °C and 8 g_{cat} min g_{HDPE}^{-1}, with the individual yields of ethylene, propylene and butenes being 10.6, 35.6 and 16.7 wt.%, respectively. Although the yield of single-ring aromatics increases when both variables studied are increased, the maximum yield obtained was lower than 13 wt.%. The yield of waxes (the main product in the first step) is negligible even at low temperatures or spaces-times, which evidences the efficiency of the catalytic step.

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1. Introduction

Current plastic consumption has been quantified at 100 kg per capita/year and is expected to increase to 140 kg per capita/year by 2015 [1]. In Europe, the Waste Framework Directive (Council Directive 2008/98/EC) provides a legal basis for the waste management hierarchy with the aim of increasing waste management recovery targets and, therefore, promoting recycling.

Nowadays, energetic valorisation (incineration) is the most widely used method of thermal treatment, although it has considerable environmental limitations and is considered a temporary solution until tertiary recycling technologies become feasible. The thermal and catalytic cracking of waste plastic is considered one of the most feasible large-scale recycling methods, since waste plastic is a valuable source of liquid and gas fuels, as well as chemicals [1–5]. Cracking technologies have become highly developed, especially for valorising polyolefin (2/3 of waste plastic), and they are eco-friendly. Therefore, cracking technologies continue to provide an excellent opportunity for research.

The main difficulty facing waste plastic cracking processes is related to the sticky nature and low thermal conductivity of plastic materials. Therefore, an adequate choice of reactor is essential for minimizing the physical step limitations prior to devolatilization

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[6]. The plastic must melt and then coat the sand in order to provide the maximum contact surface for facilitating the transfer of volatiles to the gas phase. Della Zassa et al. [7] highlight the importance of separating the melting step from the pyrolysis step to improve heat and mass transfer between phases and minimize plastic degradation to carbonaceous material. Given that fluidized bed reactors attain high heat and mass transfer rates, they can operate under isothermal conditions and have been extensively used in plastic pyrolysis, even with continuous plastic feeding [8–11].

Previous studies have reported the good performance of the conical spouted bed reactor (CSBR) for the continuous pyrolysis of HDPE [12]. The plastic is fed into the reactor as solid particles and, prior to the cracking reactions, the plastic melts and coats the sand and/or catalyst particles contained in the bed. The vigorous cyclic movement of the particles in the CSBR facilitates their uniform coating with fused plastic, improving heat and mass transfer and avoiding the defluidization problems occurring in the pyrolysis of plastics in fluidized bed reactors [13]. Furthermore, the CSBR is very versatile operating in a wide range of gas residence time, from spouting conditions (gas residence time around 1 s) to dilute spouting (jet spouted bed) conditions (gas residence time around 20 ms) [14], and therefore, minimizing the secondary reactions, such as overcracking to produce methane and condensing light olefins to give polyaromatics (PAH).

Consequently, the CSBR is especially suitable for the selective production of waxes (C_{21+}) without defluidization problems [12]. These waxes are suitable for dissolving in vacuum gas oil and co-feeding into catalytic cracking units (FCC) [15], given that they contribute to increasing C_2–C_4 olefin yield and their cracking causes a synergistic effect on the cracking of vacuum gas oil [16,17].

Furthermore, the cyclic movement of particles that is characteristic of spouted beds gives way to low segregation, which is a great advantage of the CSBR reactor for using the catalyst in situ [18,19]. The use of an acid catalyst lowers the activation energy and, therefore, allows decreasing the pyrolysis temperature and increasing the selectivity of high interest products [20,21]. The use of HZSM-5 catalysts in polyolefin pyrolysis in fluidized bed reactors has been studied by several authors with the aim of obtaining a product stream composed mainly of light olefins or a gasoline fraction with low aromatic content [22–26]. In situ pyrolysis of HDPE on HZSM-5 catalysts in a CSBR reactor has also been studied [27,28]. Due to their strong acidity, HZSM-5 zeolites are highly active for cracking, isomerisation and aromatization reactions taking place by carbocation intermediates [5], whereas their shape-selectivity in the microporous structure hinders hydrogen transfer reactions and polyaromatic generation and contributes to increasing C_2–C_4 olefin selectivity with low coke generation [29]. Moreover, the three-dimensional structure of the HZSM-5 zeolite facilitates coke precursor diffusion towards the outside of the zeolite structure, which is enhanced by the high nitrogen flow rate used in the pyrolysis process in a CSBR [30].

The high yield and selectivity of waxes in a CSBR has allowed their downstream transformation by thermal cracking in a multitubular reactor at high temperatures. A high yield of C_2–C_4 olefins has been obtained, reaching a value of 76 wt.% at 900 °C, with the individual yields of ethylene, propylene and butenes being 39.8, 19.2 and 17.2 wt.%, respectively, with a low yield of aromatics (5.5 wt.%) [31].

In this study, the volatiles formed in the thermal cracking of HDPE in a CSBR (mainly waxes) have been converted in a catalytic step in a fixed bed reactor, using a HZSM-5 zeolite catalyst for the selective production of light olefins. The influence of second-step operating conditions (temperature and space–time) on product yield and composition has been studied in order to optimize the catalytic step for maximizing light olefin production.

The two-step system (thermal and catalytic) allows using different temperatures and contact times in each step. This strategy has been studied using a batch pyrolysis reactor and an in-line fixed bed catalytic reactor with an acid catalyst for obtaining monomers or fuels [32–34]. Moreover, the two-step operation has been applied to plastic gasification for obtaining H_2, using an in-line fixed bed reactor with a reforming catalyst [35].

2. Material and methods

2.1. Experimental equipment and conditions

The HDPE was supplied by the Dow Chemical Company (Tarragona, Spain) in the form of cylindrical pellets (4 mm). The properties specified by the supplier 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 kJ kg^{-1}, has been measured by differential scanning calorimetry (Setaram TG–DSC 111) and isoperibolic bomb calorimetry (Parr 1356).

Fig. 1 shows a scheme of the bench-scale plant used in this study. The solid feed system consists of a vessel equipped with a vertical shaft connected to a piston placed below the material bed. The plastic is fed into the reactor by raising the piston while the whole system is vibrated by an electric motor. A very small N_2 flow rate introduced into the vessel stops the volatile stream entering the feeding vessel. The plastic feed rate can be varied from 0.2 to 5 g min^{-1} (1 g min^{-1} in this study). The pipe that connects the feeding system with the reactor is cooled with tap water to avoid the plastic melting and clogging the system.

The dimensions of the conical spouted bed reactor used guarantee bed stability in a wide range of operating conditions and were established according to previous hydrodynamic studies [36,37]. A similar reactor has been used for the pyrolysis of different materials, such as other plastic materials (polystyrene, polymethylmethacrylate and polyethylene terephthalate) [38–40], scrap tyres [41], and lignocellulosic biomass [42]. The bed was made up of 50 g of sand (0.3–0.4 mm) and nitrogen was used to fluidize the bed. The nitrogen flowrate was 20% above that required for the minimum spouting velocity (5 L min^{-1} under ambient conditions), which ensures the vigorous movement of the sand enhances heat and mass transfer in the bed and maintains the bed isothermal. Temperature (500 °C) was controlled by a thermocouple placed in the bed. The average residence time of the volatile product ranges from approximately 30 milliseconds in the spout zone to 500 milliseconds in the annulus.

The pyrolysis volatiles formed (mainly waxes) are fed in-line to the catalytic fixed bed reactor placed in a forced convection oven kept at 270 °C to avoid the condensation of the heavy products. The fixed bed is a cylindrical stainless steel reactor, with an internal diameter of 13.1 mm and a total length of 305 mm. The residence time in this reactor is of around 30 milliseconds. Upstream from the catalytic fixed bed reactor, a high efficiency cyclone is placed inside the oven to retain the fine sand particles entrained from the bed. The catalytic bed consists of 8 g (sand + catalyst), with the amount of catalyst (1–2 mm) being 0, 4, 6 and 8 g, corresponding to the values of space–time of 0, 4, 6 and 8 g_{cat} min $g_{HDPE}{}^{-1}$, respectively. A K-type thermocouple is used to control and monitor the temperature in the reactor and the runs have been carried out at 350, 400, 450, 500 and 550 °C. The continuous runs have been held for 5 h to obtain enough liquid for its subsequent analysis and to qualitatively assess the significance of catalyst deactivation by coke deposition.

The products formed in the catalytic step circulate through a volatile condensation system. It consists of a double-shell tube condenser cooled with tap water, a Peltier cooler and a

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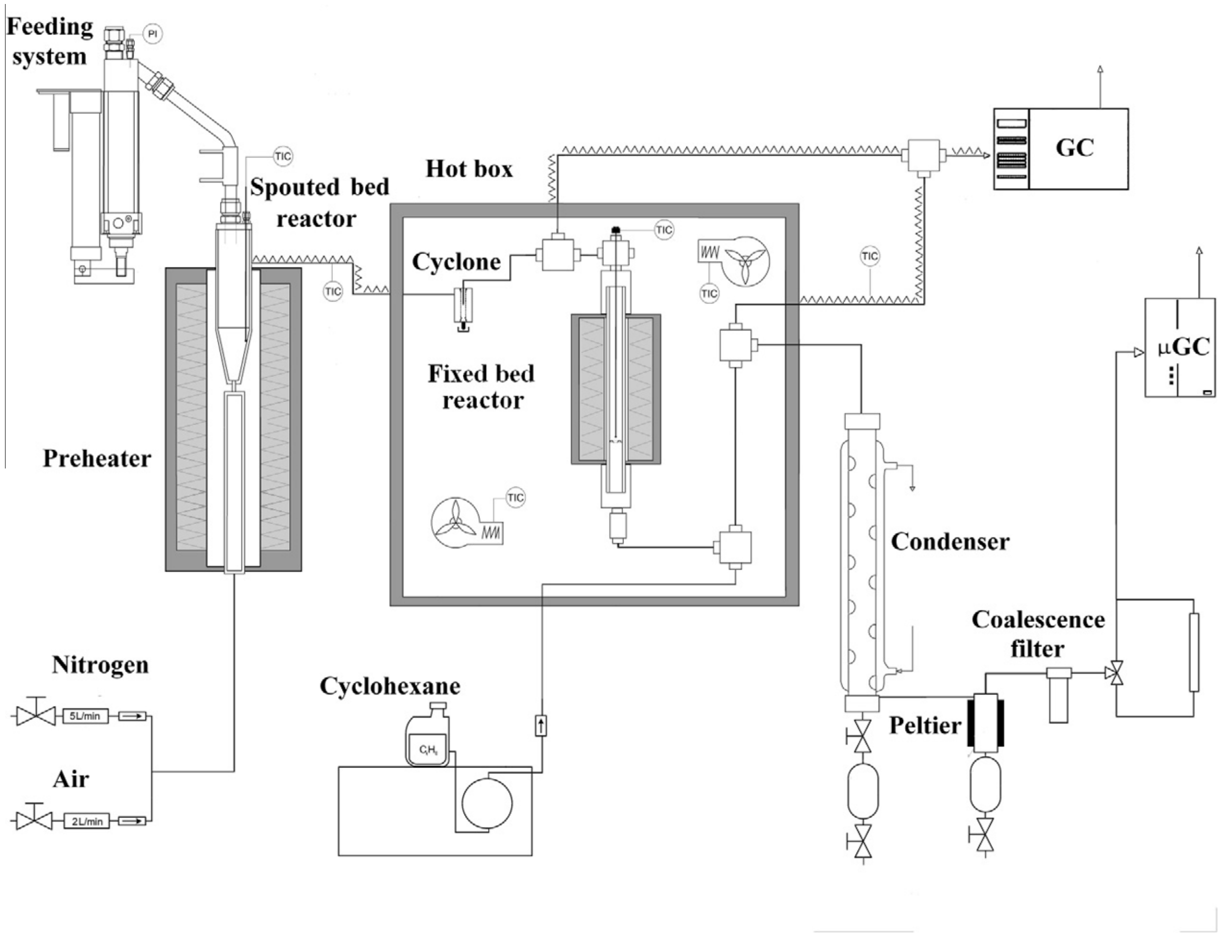

Fig. 1. Scheme of the pilot plant used for the two-step thermal and catalytic process.

coalescence filter to ensure the total condensation of volatile hydrocarbons.

The product stream leaving the pyrolysis and catalytic reactors has been analyzed by an on-line Varian 3900 chromatograph connected by means of a line thermostated at 280 °C to avoid the condensation of heavy products. Cyclohexane (not formed in the process) has been used as an internal standard to validate the mass balance, which has been fed into the product stream at the outlet of the catalytic reactor. Furthermore, the non-condensable gases have been analyzed by means of a micro GC Varian 4900, which allows detailed quantification to be made of the product stream. The liquid compounds (dissolved in acetone to avoid the clogging of the GC–MS injector) have been identified by means of a GC–MS spectrometer (Shimadzu 2010-QP2010S) provided with a DB-1MS column. The gaseous compounds have been identified by means of a micro GC–MS spectrometer (Varian 490-Agilent 5975B). The micro GC has four channels equipped with different columns: channel A, OV-1; channel B, Stabilwax; channel C, molecular sieve MS5A; channel D, PPQ. The columns connected to the mass spectrometer are OV-1 (for nonpolar compounds) and Stabilwax (especial for polar compounds).

In order to ensure the reproducibility of the results, the on-line GC analysis of the product stream has been repeated twice for each time on stream, with the differences observed being below 5%. The overall mass balances for carbon and hydrogen have been carried out by monitoring the polymer fed into the reactor and the hydrocarbons at the outlet of the two-step process. An internal standard (cyclohexane) has been used to validate the mass balance, whose closure was above 95% in all the runs carried out.

2.2. Catalyst

A catalyst based on HZSM-5 zeolite with a SiO_2/Al_2O_3 ratio of 30 has been used, supplied by Zeolyst International (Kansas City, USA). The HZSM-5 zeolite has been supplied in ammonium form and, therefore, prior to agglomeration it has been calcined at 550 °C to obtain the acid form. The zeolite (25%) has been agglomerated by wet extrusion with bentonite (Exaloid, 30%) and inert alumina (Martinswerk, 45%). The agglomeration generates mesopores and macropores in the catalyst particles, which attenuate the deactivation of the catalyst because the coke formed inside the HZSM-5 zeolite structure is deposited on its outside and, consequently, external pore blockage is minimized [29,43]. Finally, the catalyst has been calcined at 575 °C for 2 h to eliminate the strong acid sites (hydrothermally unstable) of the HZSM-5 zeolite by dehydroxylation [44]. The selection of the HZSM-5 zeolite is based on previous results obtained operating with the catalyst in situ in the pyrolysis reactor. This catalyst has low deactivation by coke deposition [29,30] and a high selectivity for the production of C_2–C_4 olefins. However, the HY zeolite is suitable for the production of C_5–C_{11} hydrocarbons, but its deactivation is faster, and Hβ zeolite performance is midway between HZSM-5 and HY [45,46].

The catalyst's main properties have been measured (Table 1). The physical properties (BET surface area, average pore diameter and pore volume distribution) have been measured by N_2 adsorption–desorption (Micromeritics ASAP 2010). The acid properties of the catalyst have been obtained by NH_3 adsorption–desorption. The values of total acidity and average acid strength have been obtained by monitoring the differential adsorption of

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Table 1
Catalyst properties.

BET surface area ($m^2\ g^{-1}$)	182
Av. pore diameter (Å)	84
Pore volume distribution (%)	
<20/20<dp(Å)<500/>500	4.5/27.5/68.0
Total acidity ($mmol_{NH3}\ g^{-1}$)	0.14
Average acid strength (kJ mol_{NH3}^{-1})	150
Acidity levels by TPD (%)	
<280/280<T(°C)<420/>420	34/52/14

NH_3 simultaneously by calorimetry and thermogravimetry in a Setaram TG–DSC 111 [28,30]. The curve for temperature programmed desorption of NH_3 has been obtained by connecting a Blazer Instruments mass spectrometer (Thermostar) on-line to a Setaram TG–DSC 111, and an acid site classification has been established according to the following desorption levels: weak acidity 150–280 °C; average acidity 280–420 °C and strong acidity 420–550 °C.

3. Results and discussion

3.1. Pyrolysis of HDPE at 500 °C (first step)

The continuous pyrolysis of HDPE in a CSBR has been carried out at 500 °C. This temperature is suitable for avoiding defluidization problems and attaining a maximum yield of waxes (C_{21+}) [12]. Table 2 shows the yields of the product fractions obtained, which have been grouped into six different lumps: light olefins (C_2–C_4), light alkanes (C_1–C_4), single-ring aromatics, non-aromatic C_5–C_{11} compounds, C_{12}–C_{20} hydrocarbons and waxes (C_{21+}).

Given the low residence time of the gases in the spouted bed reactor and the low pyrolysis temperature used, the product stream obtained in the pyrolysis step is composed mainly of C_{12}–C_{20} hydrocarbons and waxes, with the overall yield being 90 wt.%. Furthermore, the other products obtained (non-aromatic C_5–C_{11} hydrocarbons, light olefins and alkanes) can be upgraded by cracking. Methane and aromatics are refractory to cracking but their yield is very low. These results are similar to those obtained by Elordi et al. [12] in a conical spouted bed reactor and to those obtained in a fluidized bed reactor at the same temperature [47]. The yield of waxes is higher in a CSBR, given there is no defluidization or char formation.

Table 2
Yields (wt.%) of the product fractions obtained in the continuous pyrolysis of HDPE.

Product fractions	Yield (wt.%)
Light olefins (C_2–C_4)	**1.15**
Ethylene	0.08
Propylene	0.50
Butenes	0.57
Light alkanes (C_1–C_4)	**0.35**
Methane	0.03
Ethane	0.07
Propane	0.08
Butanes	0.18
Non-aromatic C_5–C_{11}	**5.58**
Paraffins	0.34
Isoparaffins	2.50
Naphthenes	0.19
Olefins	2.56
Aromatic C_6–C_{11}	**0.28**
C_{12}–C_{20}	**25.64**
Diolefins	3.22
Olefins	13.07
Paraffins	9.35
Waxes (C_{21+})	**67.0**
C_{21}–C_{40}	29.5
C_{40+}	37.5

Based on the mechanisms reported in the literature, polyolefin thermal cracking takes place at 500 °C through two mechanisms [48]: (i) random scission of the links of melted macromolecules coating the sand particles to yield long chain hydrocarbons; (ii) chain-end scission of oligomers to yield low molecular weight products. The high heat and mass transfer rate between phases in the conical spouted bed reactor promotes the first mechanism, with a high wax formation rate [12]. Besides, the low residence time of the waxes in the reactor minimizes depolymerisation reactions. Consequently, the conical spouted bed reactor strikes a balance between volatilisation and decomposition mechanisms, corresponding to a selective production of waxes. Moreover, it should be noted that apart from the good quality of the product stream obtained for the downstream catalytic cracking, continuous operation allows obtaining a constant stream at the outlet of the first step, which is essential to ensure an accurate study of the influence of second-step operating conditions.

3.2. Effect of space–time on the catalytic cracking of pyrolysis volatiles (second step)

Fig. 2, corresponding to 500 °C, shows that an increase in space–time from 0 to 8 g_{cat} min g_{HDPE}^{-1} gives way to a complete transformation of the waxes, with an increase in the yield of light olefins (from 0.4 wt.% to 57.9 wt.%), light alkanes (from 0.68 wt.% to 11.4 wt.%) and single-ring aromatics (from 0.1 wt.% to 12.4 wt.%). The yield of C_{12}–C_{20} hydrocarbons is lower than 4 wt.% when space–time is 8 g_{cat} min g_{HDPE}^{-1} and the yield of non-aromatic C_5–C_{11} hydrocarbons peaks for a low value of space–time.

It should be noted that a high yield of diesel fraction (C_{12}–C_{20}) is obtained in the run carried out without catalyst, i.e. 50 wt.% of the HDPE in the feed. Consequently, this operating mode is a suitable strategy for maximizing the yield of diesel fraction and obtaining an interesting product for refineries. The interest of the second catalytic step lies in the selective production of light olefins at low temperatures. Polyolefins and other residual feeds, such as lignocellulosic biomass derivatives [49,50], may contribute to meeting the increasing C_2–C_4 olefin demand (currently obtained by steam cracking of naphtha and in FCC units) [51].

Polyolefin catalytic cracking takes place through two carbocationic mechanisms [52]: (i) the classical bimolecular mechanism (or

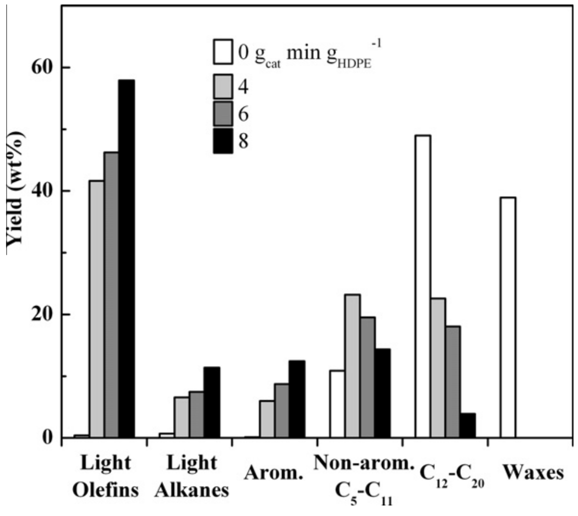

Fig. 2. Effect of space–time on product fraction yields.

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β-scission); (ii) the monomolecular or proteolytic mechanism, through carbonium ions. The mechanism controlling catalytic cracking will be one or the other depending on the number of carbon atoms in the reactant, the type of bonds (olefinic or paraffinic), the reaction conditions, and the shape selectivity of the catalyst and its acid properties (surface density, acid strength of the sites and Bronsted/Lewis ratio). Shape selectivity, moderate acid strength and the low hydrogen transfer capacity of the HZSM-5 zeolite are suitable properties for enhancing the proteolytic cracking of polyolefins and minimizing bimolecular reactions, such as olefin oligomerization-cracking to produce paraffins and olefin cyclization and condensation to form coke [53,54].

The results obtained (Fig. 2) evidence the good performance of the HZSM-5 zeolite to selectively obtain C_2–C_4 olefins (reaching a yield of 58 wt.% for 8 g_{cat} min $g_{HDPE}{}^{-1}$) with a low yield of aromatics (12.5 wt.%). Apart from catalyst properties, the system proposed also helps to minimize undesired secondary reactions due to its suitable features, as are: (i) the low residence time in the thermal and catalytic steps; (ii) the low concentration of the volatiles in the fixed bed reactor, which are diluted on the high nitrogen flow rate used in the pyrolysis step. These characteristics give way to a higher C_2–C_4 olefin selectivity than other studies in which a HZSM-5 zeolite is used in a fluidized bed reactor [22–26] or pyrolysis volatiles are transformed on a HZSM-5 catalyst in an in-line batch reactor [32,34]. Furthermore, the insignificant methane formation evidences the expediency of operating at low temperatures (500 °C) and short residence times to hinder olefin overcracking reactions.

Elordi et al. [27,28] obtained similar results in the in situ catalytic pyrolysis of HDPE in a conical spouted bed reactor on a HZSM-5 at 500 °C. However, the amount of catalyst used was 3–4 times higher than the amount of catalyst used in this study. A comparison of these two strategies (catalyst in situ or in-line) operating by continuously feeding HDPE shows the two-step system is more efficient, given that all the catalyst is used in the transformation of a crackable volatile stream. In the single-step process, the physical steps of melting and coating, the pyrolysis process (thermal cracking) and catalytic cracking all take place on the catalyst, which means reactions compite on the same acid sites.

Fig. 3 shows the effect of space–time on the individual yields of gas compounds (light olefins and light alkanes). The main compound in the gas fraction is propylene, recording an individual yield of 32 wt.% for a space–time of 8 g_{cat} min $g_{HDPE}{}^{-1}$. Furthermore, the individual yields of ethylene and butenes increase as space–time is increased, with their values for 8 g_{cat} min $g_{HDPE}{}^{-1}$ being 9.4 wt.% and 16.5 wt.%, respectively.

Although the yields of light alkanes increase as space time is increased due to the enhancement of hydrogen transfer reactions, the effect of space time is less significant. Moreover, these yields are lower than the yields of light olefins in the whole range studied.

Fig. 4 shows the effect of space–time on the yields of gasoline compounds (non-aromatic C_5–C_{11} and single-ring aromatic compounds) ordered according to the number of carbon atoms (Fig. 4a) and type of bond (Fig. 4b).

The yields of C_5, C_6 and C_{11} compounds decrease as space–time is increased, whereas the yield of C_7, C_8 compounds increase. According to the type of bond, an increase in space–time gives way to an increase in aromatic compounds and a decrease in the yield of paraffin and olefin compounds in the gasoline fraction. These trends are due to the olefinic nature of C_5 and C_6 compounds (easily crackable) and to the aromatic nature of C_7 and C_8 compounds, whose formation is enhanced by cyclization and aromatization secondary reactions when space–time is increased. This effect of space time has been observed by other authors in the pyrolysis of polyolefins in a batch reactor and in in-line catalytic cracking on a HZSM-5 catalyst [32–34].

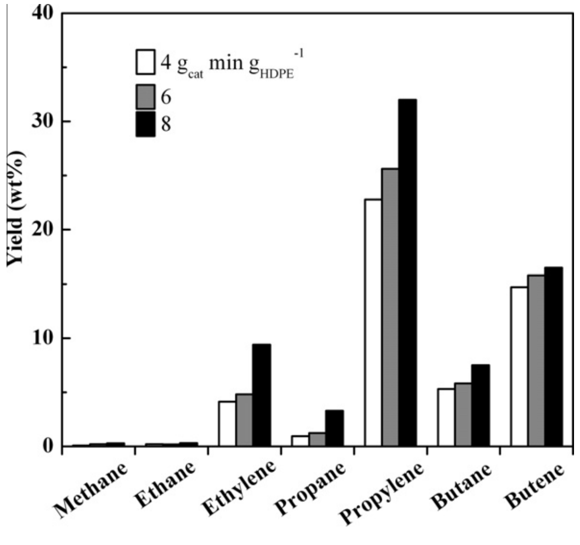

Fig. 3. Effect of space–time on the individual yields of C_1–C_4 compounds.

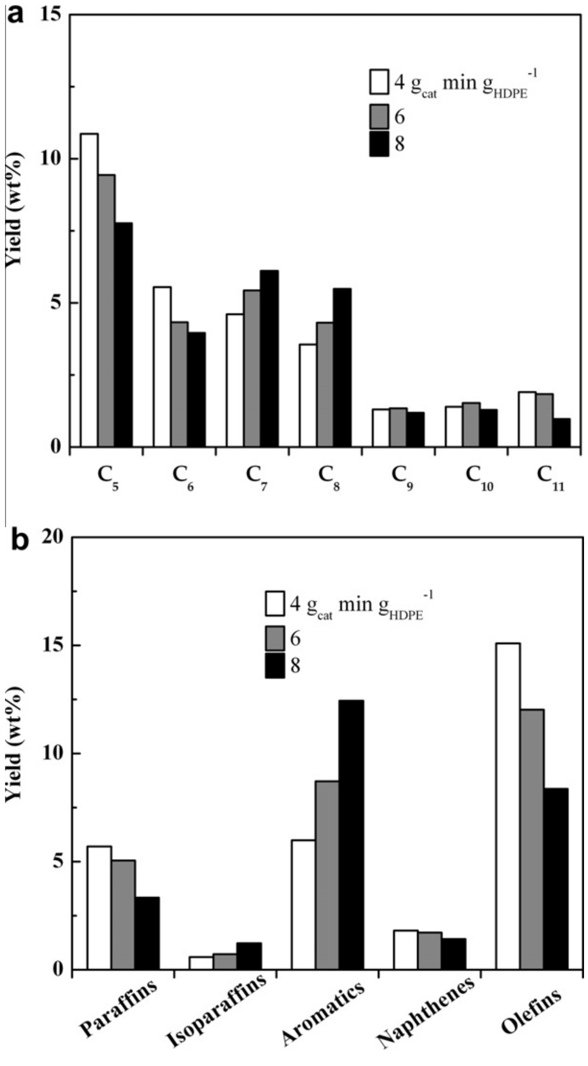

Fig. 4. Effect of space–time on the yields of the different fractions in the gasoline lump according to the number of carbon atoms (a) and chemical bond (b).

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The main aromatic compounds of the gasoline fraction are toluene and xylenes, with individual yields for a space–time of 8 g_{cat} min g_{HDPE}^{-1} being 4 wt.% and 3.3 wt.%, respectively. The yield of benzene increases as space–time is increased, but the maximum yield obtained is lower than 1 wt.%.

3.3. Effect of temperature on the catalytic cracking of pyrolysis volatiles (second step)

The effect of temperature on the yields and compositions of products fractions has been studied using a space time of 8 g_{cat} min g_{HDPE}^{-1}, with the aim of avoiding the operating problems caused by the formation of waxes at low temperatures.

The influence of temperature on product fraction yields is shown in Fig. 5. A significant effect of temperature has been observed. Thus, the yield of light olefins increases from 31.5 wt.% at 350 °C to 62.9 wt.% at 550 °C, due to the monomolecular cracking of non-aromatic C_5–C_{11} compounds, whose yield decreases from 46.3 wt.% at 350 °C to 11 wt.% at 550 °C. Below 450 °C, an increase in temperature also enhances the cracking of C_{12}–C_{20} fraction, whose yield is low in the whole range studied due to the high space–time used. Moreover, the yield of single-ring aromatic compounds increases when temperature is raised, from 3.4 wt.% at 350 °C to 13 wt.% at 550 °C, due to the enhancement of hydrogen transfer reactions. The effect of temperature on light alkane yield is less significant, peaking at 450 °C. Thus, a temperature increase in the range below 450 °C gives way to the formation of light alkanes by hydrogen transfer from olefins, whereas a temperature increase in the range above 450 °C enhances cracking reactions to produce mainly ethylene. This effect of temperature on product yields is similar to that observed by Mastral et al. [24] in the catalytic degradation of HDPE on a HZSM-5 zeolite in a fluidized bed reactor in the 350–450 °C temperature range. These authors attribute this effect to the endothermicity of β scission reactions. However, at temperatures between 450 °C and 550 °C, they observed a decrease in the yield of the light olefin fraction by enhancing secondary reactions, such as isomerisation, hydrogen transfer or Diels–Alder reactions. These secondary reactions are also observed in the in-line catalytic transformation on HZSM-5 zeolite of the polyolefin pyrolysis volatiles obtained in a batch reactor [32–34], being explained by the higher residence time used favouring unwanted secondary reactions.

Regarding the gas fraction (Fig. 6), the light olefin fraction is composed mainly of propylene. The yield of propylene increases as temperature is increased, reaching a value of 35.5 wt.% at 550 °C. Furthermore, the yield of ethylene increases when temperature is increased, from 0.8 wt.% at 350 °C to 10.5 wt.% at 550 °C, whereas the yield of butene (18 wt.%) remains almost constant. The main compound in the lump of light alkanes is butane, with a yield of 6.5 wt.% at 550 °C. The yields of methane and ethane are very low (below 0.4 wt.%), which is attributed to the low residence time in the reactor minimizing not only bimolecular cracking reactions to produce methane and ethane but also hydrogen transfer reactions to produce light alkanes from light olefins.

As observed, an increase in temperature not only enhances the overall yield of light olefins but also influences the individual selectivity of the three light olefins. At low temperatures, the main components in the light olefin fraction are butenes, whereas as temperature is raised, the selectivity of propylene is increased and propylene becomes the main compound in the light olefin fraction even at 450 °C. Moreover, the ethylene/propylene ratio increases as temperature is raised. This olefin redistribution is due to an olefin cracking-oligomerization mechanism in the presence of a HZSM-5 zeolite, which enhances ethylene selectivity as temperature is increased [55].

Fig. 7 shows the effect of temperature on the yield of gasoline compounds (non-aromatic C_5–C_{11} and single-ring aromatic compounds) ordered according to the number of carbon atoms (Fig. 7a) and type of bond (Fig. 7b). As temperature is raised, the yields of C_5 and C_6 olefins decrease due to their olefinic nature, i.e. cracking is enhanced as temperature is raised. Furthermore, as a consequence of cracking reactions, the yields of paraffins, isoparaffins and naphthenes in the C_5–C_{11} fraction steadily decrease as temperature is increased. Moreover, an increase in temperature enhances olefin oligomerization and subsequent condensation to produce toluene and xylenes, with their yield at 550 °C being 4 wt.% and 3 wt.%, respectively. Other authors report a greater effect of temperature on the yield of aromatic compounds when a catalyst based on HZSM-5 zeolite is used in situ in a fluidized bed reactor [25] or in a conical spouted bed reactor [27]. This difference is explained by the lower residence time of the catalytic step used in this work, which minimizes secondary reactions, especially oligomerization and condensation reactions to produce aromatics. Consequently, the yield of PAH compounds is negligible, which is highly significant for blending the C_5–C_{11} fraction in the gasoline pool, and even from an environmental point of view.

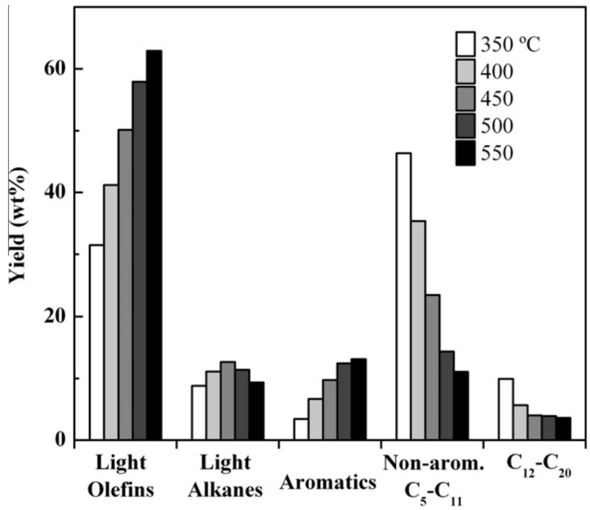

Fig. 5. Effect of temperature on product fraction yields.

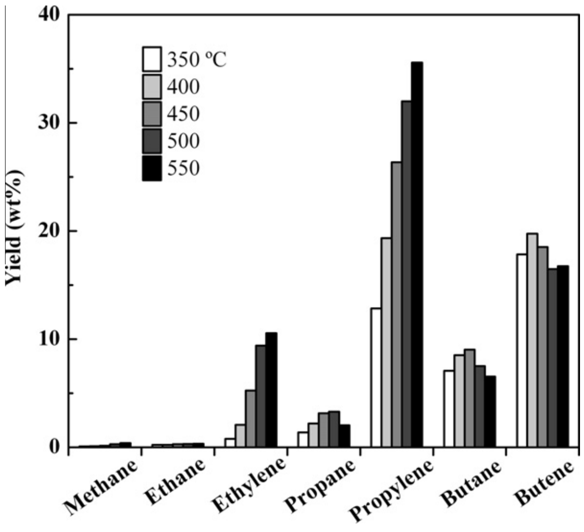

Fig. 6. Effect of temperature on the individual yields of C_1–C_4 compounds.

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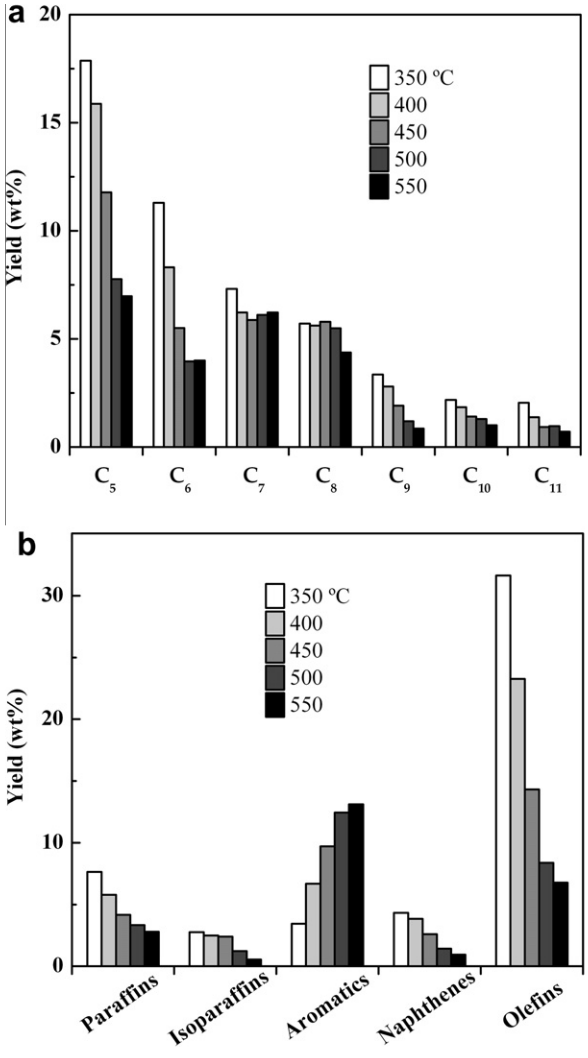

Fig. 7. Effect of temperature on the yields of the different fractions in the gasoline lump according to the number of carbon atoms (a) and chemical bond (b).

It should be noted that deactivation is low when operating at 500 °C for 5 h (results not shown here) and insignificant below this temperature. The coke deposited on the catalyst used for 5 h (300 g of HDPE) at 500 °C is below 1 wt.%. This is due to: (i) the reaction conditions (separate thermal and catalytic steps, complete conversion of waxes (main coke precursors), moderate temperature in the catalytic step and low residence time of the compounds in the reactor); (ii) the HZSM-5 zeolite properties, given that they improve the flow of coke precursors towards the outside of the zeolite crystals. In previous studies operating with the catalyst in the pyrolysis reactor, a better performance in terms of coke deposition of the HZSM-5 zeolite has been proven in relation to other zeolites (Hβ and HY). The latter are characterized by their wider micropores favouring the growth of coke precursors towards condensed structures [29,30]. The slow deactivation with the catalyst used in this work implies longer times on stream to study the deactivation using both strategies (catalyst in situ or in the second step) and to determine the coke nature and its location in the catalyst structure.

4. Conclusions

The two-step (thermal and catalytic) reaction system proposed is an interesting and versatile technology for HDPE valorization (and probably for other polyolefins), given that it allows reaching high yields of light olefins with rather low values of temperature and space–time. These results are due to: (1) the good performance of the conical spouted bed reactor for continuous thermal cracking to produce a product stream composed mainly of waxes; (2) HZSM-5 zeolite activity and selectivity for transforming waxes into hydrocarbons with high olefin selectivity.

An increase in space–time and temperature has a significant effect on product distribution, i.e. it increases the yield of light olefins and decreases the yield of C_{12+} hydrocarbons or non-aromatic C_5–C_{11} fraction. Furthermore, an increase in space–time and temperature enhances secondary reactions and, therefore, the yield of the single-ring aromatic fraction.

However, the low residence time used in both steps and the low concentration of the volatiles in the catalytic fixed bed reactor allows minimizing the secondary reactions to obtain a high yield of light olefins (62 wt.%) and a low yield of secondary reaction products, such as single-ring aromatic products (13 wt.%), even at 550 °C and 8 g_{cat} min ${g_{HDPE}}^{-1}$.

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