Conversion of HDPE into Value Products by Fast Pyrolysis Using FCC Spent Catalysts in a Fountain Confined Conical Spouted Bed Reactor

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Continuous catalytic cracking of polyethylene over a spent fluid catalytic cracking (FCC) catalyst was studied in a conical spouted bed reactor (CSBR) with fountain confiner and draft tube. The effect of temperature (475–600 °C) and space-time (7–45 g_{HDPE} min g_{cat}^{-1}) on product distribution was analyzed. The CSBR allows operating with continuous plastic feed without defluidization problems and is especially suitable for catalytic pyrolysis with high catalyst efficiency. Thus, high catalyst activity was observed, with waxes yield being negligible above 550 °C. The main product fraction obtained in the catalytic cracking was made up of C7–C11 hydrocarbons, with olefins being the main components. However, its yield decreased as temperature and residence time were increased, which was due to reactions involving cracking, hydrogen transfer, cyclization, and aromatization, leading to light hydrocarbons, paraffins, and aromatics. The proposed strategy is of great environmental relevance, as plastics are recycled using an industrial waste (spent FCC catalyst).

Introduction

The excellent properties of plastic materials, such as light weight, resistance to corrosion, color, transparency, versatility, or low cost,[1] have led to their use by everyone around the world on a daily basis. Thus, overall plastic production reached 368 million tons in 2019, with polyolefin plastics accounting for almost 50% of the total amount produced.[2] This huge annual plastic production is causing serious environmental problems due to their short usage time, low biodegradability, and high amount landfilled. In fact, from the 17.8 million tons of plastic waste collected in Europe in 2018, 18.5% was sent to landfills, 39.5% used for energy recovery, and 42% was recycled.[3] Nevertheless, the microplastics and nanoplastics generated in waste management, as it involves cost-effective and well-known technologies. However, mechanical recycling requires the separation of plastics according to their nature and often causes final product quality problems due to the thermal and mechanical degradation undergone by the material.[7–9] Another alternative currently used for plastic waste management involves energy recovery. However, this option is not consistent with the guidelines set out in the circular economy, that is, the life of the material is not extended as much as possible. In addition, even though plastic waste is a suitable feedstock for energetic recovery due to its high calorific value, the emission of greenhouse gases, as well as harmful gases and particles to the environment,[10,11] makes this plastic valorization alternative questionable.

In 2015, the European Commission established an action plan based on a circular economy, which pursues a transformation from the old linear model to the circular model in which the waste is reintroduced into the production cycle, thereby minimizing the amount of waste generated.[6] Although general guidelines for plastics recycling had already been proposed in this first global plan, the European Commission established a specific strategic plan for plastics in another report on circular economy in 2018, in which guidelines were given for producing, using, and recycling plastics.[5] This plan sets the goal of recycling all packaging plastics by 2030. In view of the proposed strategy and taking into account that part of packaging plastics is used in the food industry, Matthews et al. stated the need for new recycling technologies to reduce the impact of the strategy proposed by the European Commission on food safety.[6] Thus, the European Commission remarked the pressing need to develop and scale up innovative chemical recycling processes to prevent plastic waste and microplastics pollution. Mechanical recycling is the most common procedure for plastic management, as it involves cost-effective and well-known technologies. However, mechanical recycling requires the separation of plastics according to their nature and often causes final product quality problems due to the thermal and mechanical degradation undergone by the material.[7–9] Another alternative currently used for plastic waste management involves energy recovery. However, this option is not consistent with the guidelines set out in the circular economy, that is, the life of the material is not extended as much as possible. In addition, even though plastic waste is a suitable feedstock for energetic recovery due to its high calorific value, the emission of greenhouse gases, as well as harmful gases and particles to the environment,[10,11] makes this plastic valorization alternative questionable.
In this scenario, thermochemical conversion technologies for plastics waste recycling represent promising alternatives, as they allow producing fuels and high value-added chemicals, and therefore boosting circular economy by reintroducing these wastes into the production cycle. In addition, pyrolysis addresses one of the disadvantages of mechanical recycling, as it is suitable for treating mixtures of plastics of different nature. Regarding the impact on climate change and the depletion of fossil resources, pyrolysis shows clear benefits over energy recovery. Thus, pyrolysis has demonstrated 50% lower impact on climate change according to the life cycle assessment carried by Jeswani et al. The main problems of plastic waste pyrolysis are related to the endothermicity of the process and the low thermal conductivity of plastic materials. Thus, a suitable pyrolysis reactor must ensure a high heat transfer rate to the polymer particles to attain their fast heating and melting and high degradation rates, and therefore minimize the secondary reactions associated with excessively high residence times in the reactor. However, the heat transfer limitations within both the solid and the fused polymer involve a major challenge in the design of the pyrolysis reactor. Therefore, the selection of the reactor is a key factor for ensuring bed isothermicity, with fluidized and conical spouted bed reactors (CSBR) being those with best performance, as they allow high heat and mass transfer rates between phases.

Besides, the physical steps of plastic fusion and coating of sand and/or catalyst particles by the molten plastic occur prior to the devolatilization and cracking steps in the process of plastic pyrolysis. Given the sticky nature of the molten plastic, control of these physical steps is essential to avoid bed defluidization by the formation of fused plastic aggregates. Thus, the thickness of the molten plastic on the particle must be below a critical value, which leads to high amounts of beds required in fluidized bed reactors, and therefore large reactor volumes and high gas flow rates and energy requirements. The CSBR proved to be a very interesting alternative to fluidized beds, since the vigorous movement of the particles in the bed minimizes the formation of large plastic aggregates, avoiding bed defluidization even under conditions of maximum stickiness. In addition, recent modifications of this reactor, such as the incorporation of a draft tube and a fountain confiner, allowed increasing the turbulence of the particles in the bed, and therefore operating under vigorous fluidization regimes, that is, fountain-enhanced regime. These conditions promote a great fountain expansion with a remarkable increase in fountain height (see Figure 1), favoring the contact between the bed particles (sand or catalyst) and the plastic-derived volatiles, as well as improving heat transfer rates. Thus, the CSBR reactor with draft tube and fountain confiner not only allows operating with lower gas flow rates and smaller particle sizes without fine particle entrainment, but also enhances the efficiency of the catalyst due to better contact between the volatiles and the catalyst. Figure 1 shows a scheme of the fountain confined conical spouted bed operating under vigorous fluidization.

Thermal pyrolysis of polyolefins has been widely studied in the literature and occurs mainly via random radical scission mechanism, and so the product stream contains a wide range of components from permanent gases to solid waxes. In this scenario, the use of catalysts has been proposed to increase selectivity towards specific products of interest. Among the different catalysts, HZSM-5, H6, HY, and HUSY zeolites have been the most studied for plastic pyrolysis, since they have proven to be more effective than catalysts with lower acid density and strength, such as amorphous silica-alumina or MCM-41. Thus, due to the acidity and shape selectivity of zeolite catalysts, polyolefin pyrolysis can be directed towards a narrow product distribution, that is, polyolefin catalytic cracking over HZSM-5 zeolite leads to a product stream composed by mainly light olefins, whereas cracking over HY zeolite leads to liquid hydrocarbons, and over H6 to an intermediate product distribution. Spent fluid catalytic cracking (FCC) catalysts have also shown considerable cracking activity in the pyrolysis of plastics, with the additional advantage of avoiding the landfill disposal of this spent catalyst. In fact, landfilling of this catalyst is becoming more and more expensive and difficult due to its concentration of metals (rare earth, vanadium, or nickel) and the need of pretreatments prior to deposition. Thus, instead of using it as cement additive or recovering the metals, reusing it as cracking catalyst is a highly interesting alternative.

The main aim of this study is to analyze the performance of a novel reactor configuration, a CSBR provided with a draft tube and fountain confiner, in the catalytic pyrolysis of high-density polyethylene (HDPE) over a spent FCC catalyst. Moreover, the effect of operating conditions (space-time and temperature) on the product distribution obtained is analyzed in detail. Thus, the suitability of the new reactor configuration will be assessed for HDPE catalytic pyrolysis using fine catalyst particles in situ. The optimum hydrodynamic conditions for stable operation have been set in a previous study, which allow operating with continuous plastic feed without bed defluidization problems caused by formation of plastic aggregates. The development of a process for HDPE catalytic pyrolysis on spent FCC catalyst is
of great significance from an environmental and sustainability viewpoint, with excellent perspectives for full-scale implementation. This strategy takes advantage of the residual cracking activity of an industrial waste (FCC catalysts) to convert waste plastics into valuable fuels and chemicals.

Experimental Section

Materials

The spent FCC catalyst used in this work was previously used in the FCC unit at Petronor Refinery in Somorrostro, Spain. The spent FCC catalyst was sieved to a particle size in the 90–150 μm range for use in the CSBR. These catalysts are designed for the FCC unit in refineries to comply with certain features: (i) activity for cracking macromolecules; (ii) resistance to attrition; (iii) hydrothermal stability; (iv) metal tolerance; (v) low coke deposition; and (vi) fluidizability. Thus, the FCC catalyst is composed of HY zeolite (16 wt %) and various additives, such as silica, alumina, and clay, which provide meso- and macropores to the catalyst to improve its properties for use in the FCC unit. The HY zeolite is a 12-membered-ring zeolite with three-dimensional pore structure and pore channels of 7.4 × 7.4 Å,[44] and therefore its shape selectivity only allows the diffusion of molecules smaller than C₄ hydrocarbons.[45] The spent catalyst used in this case has been collected in the purge at the exit of the FCC unit regenerator. Therefore, the catalyst also contains several metal oxides (Fe, MgO, NiO, Ca, Na₂O, TiO₂, MnO, P₂O₅, and V₂O₅) in its structure, which have been accumulated on the catalyst in the consecutive reaction-regeneration cycles in the refinery unit. The catalyst's main physical and acid properties are summarized in Table 1. The physical properties (Brunauer-Emmett-Teller (BET) surface area, micropore area, average pore diameter, and pore volume distribution) have been measured by N₂ adsorption-desorption (Micromeritics ASAP 2010). The acid properties of the catalyst have been obtained by NH₃ adsorption-desorption. The values of total acidity and average acid strength have been obtained by monitoring the differential adsorption of NH₃, simultaneously by calorimetry and thermogravimetry in a Setaram TG-DSC 111.[38] As observed in Table 1, the spent FCC catalyst maintains the physical properties after use in the refinery unit, with the values of BET surface area and micropore area being 143 and 103 m² g⁻¹, respectively. Moreover, the total acidity (124 μmol NH₃ g⁻¹) and the average acid strength (105 kJ mol⁻¹ NH₃) are evidence that the catalyst has still moderate acidity for use in cracking reactions.

Table 1. Physical and acid properties of the spent FCC catalyst used.

| Property                           | Value     |
|-----------------------------------|-----------|
| BET surface area [m² g⁻¹]          | 143       |
| Sₘicroporous [m² g⁻¹]              | 103       |
| average pore diameter [Å]         | 101       |
| <20/20 < dp(Å) < 500 [Å]          | 5.7:7.6:86.7 |
| total acidity [μmol NH₃ g⁻¹]       | 124       |
| average acid strength [kJ mol⁻¹ NH₃] | 105    |

Equipment and experimental design

Dow Chemical Company (Tarragona, Spain) supplied the HDPE used in this study. The HDPE provided is in the form of cylindrical pellets with their average diameter being 4 mm. Dow Chemical Company provided its main properties (average molecular weight: 46.2 kg mol⁻¹; polydispersity: 2.89; density: 940 kg m⁻³), and the higher heating value (43 kJ kg⁻¹) was measured by isoperibolic bomb calorimetry (Parr 1356).

Figure 2 shows the experimental equipment used for the continuous catalytic cracking of HDPE over the spent FCC catalyst. This bench scale plant is composed of the following elements: (i) solid feeding system; (ii) gas feeding system; (iii) CSBR; (iv) gas cleaning system; (v) condensation system; and (vi) gas analysis devices. HDPE was continuously fed (1 g min⁻¹) into the reactor by means of the solid feeding system, which allowed HDPE continuous feeding from 0.5 to 5 g min⁻¹. The feeding system consists of a vessel equipped with a vertical shaft connected to a piston placed below the bed material. As the piston rises, the plastic is fed into the reactor through a pipe cooled with tap water to avoid HDPE melting before entering the reactor (see Figure 2). A N₂ flow rate of 7 L min⁻¹, controlled by a mass flow meter, was used (4 times that corresponding to the minimum spouting velocity). It should be noted that this value was established based on previous hydrodynamic studies.[26] This gas flow rate ensures operation under enhanced fountain regime conditions. In this hydrodynamic regime, the fountain height is equal to that of the confiner, where there is

Figure 2. Scheme of the bench-scale plant used for catalytic cracking of HDPE over the spent FCC catalyst.
great turbulence and excellent gas–solid contact, which is of great relevance to improve catalyst efficiency. Further information about this hydrodynamic regime and the gas and solid circulation patterns can be found elsewhere.[25,26] Nitrogen was preheated to the reaction temperature by means of a preheater.

The main element of the experimental unit is the CSBR, whose good performance for continuous pyrolysis and gasification of biomass, municipal solid waste, and tires[27,28] has already been proven. In this case, the reactor is provided with a fountain confiner and a draft tube, which allows operating in a wide range of operating conditions with stable spouting. The design of the reactor, fountain confiner, and draft tube is based on previous hydrodynamic studies.[23–25] Thus, the main reactor dimensions are summarized in Table 2. The bed was made of sand (0.2–0.3 mm) and catalyst (90–150 μm), with its total amount being 150 g, and the amounts of catalyst 7, 15, 30, and 45 g, corresponding to the values of space-time of 7, 15, 30, and 45 gcat min-gHDPE⁻¹, respectively. The plastic feed rate remained constant in all the runs (1 g min⁻¹). Accordingly, the space time was adjusted by varying the amount of catalysts in the bed. Pyrolysis temperature was measured by a thermocouple placed in the bed and product distribution was monitored throughout the pyrolysis process at 475, 500, 550, and 600°C. The experiments to study the effect of temperature were performed using a space time of 15 gcat min-gHDPE⁻¹.

The volatiles formed in the reactor cross a gas cleaning system, which consists of a high efficiency cyclone and a 25 μm sintered steel filter to retain the particles contained in the gas stream. Both are placed inside a forced convection oven maintained at 300°C to avoid the condensation of heavy compounds prior to their chromatographic analysis. The condensation system consists of a double-shell tube condenser cooled with tap water and coalescence filters, which ensure full cleaning of permanent gases before their analysis by chromatographic techniques. The product stream leaving the gas cleaning system was analyzed on-line by an Agilent 7890 chromatograph. The Agilent 7890 GC was equipped with a flame ionization detector (FID) and a HP PONA column. Additional information of the chromatographic method can be found elsewhere.[29] The sample was driven to this equipment through a line thermostated at 230°C to avoid the condensation of any heavy product. Cyclohexane (not formed in the process) was used as an internal standard to validate the mass balance closure. This compound was fed into the product stream at the outlet of the sintered steel filter. Furthermore, the non-condensable gases were also analyzed by G.A.S. Compact GC⁶ chromatograph, which is provided with two detectors [FID and thermal conductivity detector (TCID)] and three columns (MXT-Q Bond, MXT-Msieve 5A, and RT-Q-Bond), which allow analyzing in detail the product stream obtained. The liquid compounds collected in the condensation system were identified by means of a GC-MS (Shimadzu 2010-QP2010S) provided with a DB-1MS column. To improve the condensation of the most volatile products, the product stream was bubbled through cyclohexane to condense and collect these compounds within the solvent. The GC analysis was carried out subsequently to at least 10 min continuous operation to ensure steady state conditions, and each run has been carried out at least 5 times to ensure reproducibility of the results. The experimental error under these conditions was below 4% in all cases.

### Results and Discussion

#### Effect of space-time on product distribution

Figure 3 shows the effect of space-time on the product distribution obtained in the continuous catalytic pyrolysis of HDPE at 550°C using the spent FCC catalyst. To ease the understanding of the results, the products have been grouped into four categories: C₁–C₄ gas fraction (light olefins and light alkanes); C₅–C₁₁ hydrocarbons; C₁₂–C₁₈ hydrocarbons; and C₁₉+. Waxes are made up of long-chain hydrocarbons (linear or branched) heavier than C₁₉, which are solid compounds at room temperature. As observed in Figure 3, the spent FCC catalyst has still significant cracking activity, as the yield of waxes, which are thermal pyrolysis products formed by primary devolatilization reactions,[30–32] is negligible above 15 gcat min-gHDPE⁻¹. The catalytic activity of the spent FCC catalyst is enhanced by this reactor configuration, that is, the joint use of a draft tube and a fountain confiner in the CSBR allows operating with smaller catalyst particles and therefore promoting catalyst efficiency. On the one hand, as the catalyst particle is finer, external surface by mass unit is higher, which improves the contact between the molten plastic and the catalyst, and therefore accelerates the degradation rate.[26,29,30] On the other hand, a vigorous fluidization pattern (enhanced fountain regime) was attained with great development of the fountain region, which greatly increases the contact between the plastic derived volatiles and the catalyst, thereby improving the cracking efficiency.[27,28] Moreover, the volatiles formed are forced to flow down from the fountain top to the lower end of

| Table 2. Main dimensions of the reactor, fountain confiner, and draft tube. |
|------------------------|---------|
| **Dimension**          | **Value** |
| total height of the reactor | 340 mm  |
| height of the conical section | 205 mm  |
| diameter of the cylindrical section | 123 mm  |
| bottom diameter         | 20 mm   |
| gas inlet diameter      | 10 mm   |
| fountain confiner diameter | 80 mm   |
| total length of the draft tube | 82 mm  |
| draft tube diameter     | 10 mm   |
| height of the entrainment zone | 25 mm  |
| angle of the conical section | 28°    |

![Figure 3. Effect of space-time on the product distribution obtained in the catalytic pyrolysis of HDPE over the spent FCC catalyst.](image-url)
the confiner, which increases their contact time with the catalyst and, therefore, the catalyst performance. Thus, although waxes are the main products using a space-time of $7 \, \text{g}_{\text{cat}} \text{min g}_{\text{HDPE}}^{-1}$, light hydrocarbons are obtained with space-times above $15 \, \text{g}_{\text{cat}} \text{min g}_{\text{HDPE}}^{-1}$, with the C$_5$–C$_{11}$ fraction being the main one. It should be pointed out that the use of a space-time of $7 \, \text{g}_{\text{cat}} \text{min g}_{\text{HDPE}}^{-1}$ showed a limited cracking activity when compared with the results obtained in the thermal pyrolysis of the same plastic in a CSBR.$^{[68]}$ However, an increase in space-time from 7 to 15 g$_{\text{cat}}$min g$_{\text{HDPE}}^{-1}$ reduces the yield of waxes from 66 wt% to zero, whereas the yield of C$_1$–C$_4$ gas fraction, C$_5$–C$_{11}$ hydrocarbons, and C$_{12}$–C$_{18}$ hydrocarbons increases considerably from 9.6, 17.9, and 6.4 wt% to 25.5, 56.4, and 18.1 wt%, respectively. Moreover, a space-time above 15 g$_{\text{cat}}$min g$_{\text{HDPE}}^{-1}$ leads to severe cracking, with the yield of C$_1$–C$_4$ gas fraction increasing to 28.6 wt% in detriment of the C$_5$–C$_{11}$ hydrocarbon fraction, which decreases to 51.6 wt% when a space time of 45 g$_{\text{cat}}$min g$_{\text{HDPE}}^{-1}$ is used.

As aforementioned, the FCC catalyst consists of HY zeolite agglomerated with various binders and promoters. Thus, the main active component of the catalyst is the zeolite HY, although the surface of the matrix will also provide acidity and the large compounds will be pre-cracked in the meso- and macropores of the matrix.$^{[64,65]}$ Consequently, an increase in space-time leads mainly to more accessible zeolite active sites in the reaction medium, favoring catalytic cracking over thermal cracking and increasing the yield of light hydrocarbons. Similarly as in this study, Abbas-Abadi and Haghighi$^{[62]}$ reported that an increase in space-time when catalyst/polymer ratio is low leads to an increase in the liquid yield, whereas an increase when this ratio is above 20 wt% causes the cracking of liquid products to gaseous ones. Akpanudoh et al.$^{[63]}$ observed the same trend in PE cracking over USY zeolite. That is, below 7% acidity value the lack of acid sites causes incomplete polymer conversion to liquid products, but above 7% acidity the liquid yield decreases due to excessive cracking, leading to an increase in the gas yield.

The effect of space-time on the individual gas products is shown in Figure 4. As observed, the gas fraction is mainly composed of light olefins, with butene being the main compound in the space-time range studied. Besides, an increase in space-time above $7 \, \text{g}_{\text{cat}} \text{min g}_{\text{HDPE}}^{-1}$ affects mostly ethylene, propylene, and butene yields, but hardly affects their selectivity. The catalytic cracking takes place by the formation of carbocations over the acid sites and their subsequent cracking by random or preferentially end-chain cracking, which leads to the formation of light olefins.$^{[7]}$ Thus, an increase in space-time from 15 to 45 g$_{\text{cat}}$min g$_{\text{HDPE}}^{-1}$ increases the yield of ethylene from 0.9 to 1.8 wt%, propylene from 7.9 to 8.6 wt%, and butenes from 9.7 to 11.2 wt%. However, although bimolecular cracking is not sterically limited inside HY pores, a low extent of hydrogen transfer reactions is observed, which is presumably due to the moderate acidity of the FCC spent catalyst. Thus, the maximum yields of butane, propane, ethane, and methane are 5.7, 1.1, 0.7, and 0.6 wt%, respectively.

Figure 5 shows the effect of space-time on C$_5$–C$_{11}$ hydrocarbons ordered according to their carbon atom number (Figure 5a) and chemical structure (Figure 5b). As observed, the C$_5$–C$_{11}$ fraction is made up of mainly olefin hydrocarbons, which account for more than 35 wt% when space-time is higher than $7 \, \text{g}_{\text{cat}} \text{min g}_{\text{HDPE}}^{-1}$. Furthermore, space-time has no considerable

![Figure 4. Effect of space-time on the individual gaseous (C$_1$–C$_4$) compounds.](image)

![Figure 5. Effect of space-time on C$_5$–C$_{11}$ compounds sorted according to their (a) carbon atom number and (b) chemical structure.](image)
Effect on the nature of C₂–C₁₁ hydrocarbons. Thus, the main compounds are C₅ and C₆ olefins formed by the primary cracking of the polymer, and they hardly undergo secondary reactions, such as hydrogenation to form paraffins or cyclization and aromatization reactions to form aromatic compounds. It should be noted that this aromatic fraction includes valuable chemicals, such as BTX (benzene, toluene, and xylenes). However, the yield of aromatics obtained (8 wt%) is slightly higher than that commonly observed in the thermal pyrolysis of HDPE at 550 °C, which is presumably due to the cyclization and aromatization reactions promoted to a certain extent within the zeolite pores by HY shape selectivity. This high concentration of olefins and relatively low concentration of aromatics in the C₅–C₁₁ fraction is characteristic of the spent FCC catalyst, which is mainly explained by the low hydrogen transfer capacity of this catalyst, also observed in the C₅–C₄ fraction composition.

The main drawback of the C₅–C₁₁ fraction for incorporating into the refinery gasoline pools lies in its high olefin content. Its content in the gasoline is limited to 18 vol% by the EU legislation to avoid polymerization and the subsequent gum formation problems. However, the low aromatic content and the abundance of sulfur (limited to 35 vol% and 10 ppm, respectively) makes this fraction interesting for incorporation into the refinery gasoline pool, even though it may require a mild upgrading to reduce olefin content. Moreover, the research octane number (RON) index of the C₅–C₁₁ hydrocarbon fraction is in the 88–90 range, with the value increasing slightly from 88.4 to 90.0 when space-time is increased from 7 to 45 gₚₚ/min HDPE⁻¹, which is consistent with the similar composition of the C₅–C₁₁ fraction obtained in all runs.

**Effect of temperature on product distribution**

Figure 6 shows the effect of temperature when operating with a space-time of 15 gₚₚ/min HDPE⁻¹ on the product distribution obtained in the pyrolysis of HDPE over the FCC catalyst. The CSBR allows operating in continuous mode at low temperatures without defluidization problems. Thus, this technology ensures a vigorous cyclic movement of bed material, which avoids the formation of large agglomerates of molten plastic with the particles. Besides, when a catalyst is used in situ, cracking takes place with lower activation energy and higher reaction rate, and thus at lower temperature. Accordingly, continuous PE catalytic pyrolysis can be carried out at 475 °C without operational problems. However, a high wax yield (49.5 wt%) is still obtained at 475 °C, whose conversion is enhanced as temperature and, therefore, the cracking activity of FCC spent catalyst, is increased. Thus, above 500 °C, waxes are almost fully cracked, with their yield being negligible above 550 °C. As observed in Figure 6, the cracking of waxes leads mainly to the formation of C₅–C₁₁ hydrocarbons, reaching a maximum yield of 61.2 wt% at 500 °C. Nevertheless, an increase in temperature from 500 to 600 °C leads to severe cracking reactions enhancing the formation of C₅–C₄ gas fraction due to the cracking of C₅–C₁₁ hydrocarbons. Thus, the gas yield increases from 19.8 to 27.8 wt% and that of the C₅–C₄ fraction decreases from 61.2 to 54.1 wt% when temperature is increased from 500 to 600 °C. Temperature hardly affects the yield of C₁₁–C₁₅ that is, this yield increases slightly at low temperatures and is almost constant when temperature is increased above 500 °C.

This effect of temperature on product yields in the catalytic pyrolysis of HDPE is explained by the endothermic nature of the cracking reactions. Thermal pyrolysis of polyolefins involves significant differences in the reaction mechanisms and in the chemical structure of the degradation products, as is the case of highly branched polypropylene (PP)-derived hydrocarbons in relation to those obtained from PE. However, these differences are less significant under catalytic pyrolysis conditions. Santos et al. also observed that temperature has great effect on the product distribution obtained in the thermal and catalytic cracking. Thus, they observed incomplete PE and PP degradation using USY catalyst at 400 °C and an increase in the liquid and gaseous fractions as temperature is increased, which is due to the enhancement of C=C bond cracking at high temperatures. Lin and Yang carried out PP pyrolysis in a fluidized bed reactor over a FCC catalytic pyrolysis in the 330–450 °C range. Although they observed a solid residue even at the highest temperature studied (presumably due to incomplete PP conversion), they reported similar trends to those obtained in this work for the gas and liquid fractions. Thus, the main product fraction obtained was the C₁₁–C₁₅ one, which they attributed to the primary products from the cracking of the large hydrocarbons formed in the PP volatilization step. Besides, they also observed that an increase in temperature led to a more severe cracking of these primary products, thereby decreasing the liquid yield to form C₅–C₄ hydrocarbons.

Figure 7 shows the effect of temperature on the C₁₁–C₁₅ gas fraction. As observed in the temperature range studied, the gas fraction is mainly formed by light olefins, with butene being the main compound, whose yield increases from 4.4 to 10.4 wt% when temperature is raised from 475 to 600 °C. Likewise, the yield of ethylene and propylene increases when temperature is increased, reaching maximum values of 2.4 and 8.7 wt%.
respectively, at 600°C. An increase in temperature not only increases the yield of the three light olefins but also has certain influence on their selectivity. Thus, the ethylene/butene ratio increases from 0.03 to 0.23 when temperature is increased from 475 to 600°C. This olefin redistribution is related to oligomerization-cracking reactions occurring in the presence of the acid catalyst, as ethylene selectivity is favored by an increase in both catalyst acidity and temperature.[74,75]

Regarding the light paraffins fraction, an overall low yield of this fraction is observed due to the low extent of hydrogen transfer reactions, which are limited by the moderate acidity of the FCC catalyst. However, butane and propane yields reach maximum values of 5.4 and 1.0 wt% at 550°C and decrease to 3.9 and 0.5 wt%, respectively, when temperature is raised to 600°C. In contrast, the yields of methane and ethane increase as temperature is increased, with that of methane yield being especially remarkable at 600°C. Methane and ethane formation is due to the overcracking at high temperatures, which is a general trend observed by other authors in the catalytic pyrolysis of different plastics and mixtures of plastics over FCC catalysts.[40,76,77]

The effect of temperature on C₉₋C₂₅ hydrocarbons is shown in Figure 8, ordered according to their carbon atom number (Figure 8a) and chemical structure (Figure 8b). It can be observed that the C₉₋C₁₁ fraction is mainly composed of olefin hydrocarbons, with their yield being higher than 20 wt% above 500°C. On the one hand, it can be clearly seen that an increase in temperature from 475 to 500°C (the temperature range in which the cracking of waxes is enhanced, Figure 6) leads to the formation of mainly olefin hydrocarbons as primary products in the catalytic cracking of waxes over the spent FCC catalyst. Although to a lower extent, this temperature increase from 475 to 500°C also enhances hydrogen transfer, Diels-Alder cyclization, and aromatization reactions to form paraffins, naphthenes, and aromatics. On the other hand, an increase in temperature above 500°C not only favors the cracking of C₉₋C₁₁ hydrocarbons to give light hydrocarbons (C₁₋C₄ fraction), but also secondary aromatization reactions. Thus, an increase in temperature from 500 to 600°C not only favors the cracking of C₉₋C₁₁ hydrocarbons to give light hydrocarbons (C₁₋C₄ fraction), but also secondary aromatization reactions. Thus, an increase in temperature from 500 to 600°C decreases the yield of olefins, paraffins, isoparaffins, and naphthenes from 24.0, 3.5, 5.8, and 5.8 wt% to 21.8, 3.2, 3.8, and 4.0 wt%, respectively, whereas the yield of aromatic hydrocarbons remains almost constant (i.e., it increases slightly from 8.1 to 8.6 wt%).

The results obtained in this work are consistent with other studies of HDPE pyrolysis over FCC catalysts. Abbas Abadi et al.[78] studied HDPE catalytic pyrolysis in a stirred reactor over an FCC catalyst and observed that the carbon number distribution shifts to lighter hydrocarbons as temperature is increased. Thus, they obtained a maximum gas yield (19.2 wt%) at 510°C, which was the maximum temperature studied. Besides, the liquid fraction obtained was mainly composed of olefin hydrocarbons, and the aromatic fraction increases when temperature is raised as consequence of Diels-Alder cyclization and aromatization reactions. The amount of aromatics they obtained (9.6 wt% at 510°C) is slightly higher than that obtained in this work, presumably due to the higher residence time used.

Figure 7. Effect of temperature on the individual gaseous (C₁₋C₄) compounds at 15 g<sub>cat</sub>·min<sup>-1</sup>·g<sub>HDPE</sub>⁻¹.

Figure 8. Effect of temperature on C₄₋C₁₁ compounds sorted according to their (a) carbon atom number and (b) chemical structure at 15 g<sub>cat</sub>·min<sup>-1</sup>·g<sub>HDPE</sub>⁻¹.
As mentioned above, the main drawback for incorporating the C5–C11 fraction obtained into the refinery gasoline pools lies in its high olefin content, which is limited by the UE legislation to 18 vol%.[66] Accordingly, this fraction may be processed in hydrocracking units for reducing aromatic and olefin content.[113] In this case, the RON index[69] of the C5–C11 fraction obtained is in the 87–88 range and is hardly influenced by the reaction temperature. Thus, temperature affects the yield of products but only has a slight influence on the composition of the C5–C11 fraction.

Mechanism for HDPE catalytic cracking over an FCC catalyst

Catalytic pyrolysis of HDPE occurs through the following general steps:[18] (i) polymer melting; (ii) coating of catalyst particles with fused plastic; (iii) fused plastic pyrolysis; and (iv) catalytic cracking of fused plastic and pyrolysis volatiles. Moreover, secondary reactions in the gas phase may also take place in the waste plastics catalytic pyrolysis. However, the conditions attained in the CSBR (i.e., short residence times, high heating rates, and relatively low reaction temperatures) limit the extent of these secondary reactions.[67,79]

Prior to the cracking steps involving the molten plastic, in-situ catalytic cracking of HDPE involves the physical steps of plastic melting and coating of catalyst particles by the fused plastic. These physical steps are conditioned by the low thermal conductivity of the polymer and the sticky nature of the fused plastic material. Therefore, a suitable reactor is essential for operating in continuous mode without operational problems and ensuring high reaction rates.[12] Moreover, the type of reactor also plays an important role on the catalytic steps, that is, the contact of the fused plastic with the catalyst particles, as well as the residence time and the contact time of the volatiles formed with the catalyst are key factors on the catalyst efficiency.

![Image of a diagram](https://www.chemsuschem.org/articles/2021/14/0889/fig9.png)

**Figure 9.** Main reaction pathways in the HDPE catalytic cracking.

The CSBR provided with a draft tube and a fountain confiner used in this work has excellent features for plastics catalytic cracking involving both the physical and the catalytic cracking steps. Thus, it eases fast melting and degradation without operational problems. Moreover, the use of the fountain confiner leads to the following advantages in the cracking steps: (i) allows working with fine catalyst particles (90–150 μm in this study), favoring the contact between the catalyst particles and the fused plastic; and (ii) improves the cracking in the fountain region by forcing the volatiles formed to flow down from the fountain top to its bottom before leaving the confiner.[25,27,61]

Elordi et al.[38] carried out the catalytic pyrolysis of HDPE over a spent FCC catalytic in a CSBR with neither fountain confiner nor draft tube. They agglomerated the spent FCC catalyst with bentonite to increase its particle size and avoid the entrainment of fine catalyst particles. Thus, they used a space-time of 30 g cat min g HDPE⁻¹, which corresponds to 6 wt% of HY zeolite. Concerning the amount of HY zeolite in each case, the space-time value of 30 g cat min g HDPE⁻¹ used by Elordi et al.[38] involves a similar amount as the value of 15 g cat min g HDPE⁻¹ used in this work. Therefore, an increase in the volatile residence time within the reactor and the contact time of the catalyst with the polymer-derived pyrolysis volatiles in the fountain (associated with the use of the fountain confiner) significantly increases the catalytic efficiency. Thus, approximately 10 wt% waxes have been obtained without the fountain confiner at 500 °C, which are almost completely cracked using a fountain confiner, as proven in this study.

Regarding the cracking steps involving the molten HDPE (summarized in Figure 9), the molten plastic macromolecules that have coated the bed particles (sand and FCC catalyst) will be cracked mainly via random scission mechanism[80] to yield long-chain hydrocarbons or via end-chain scission to yield lighter hydrocarbons.[29,37] The first one is the main pathway of thermal cracking and leads to waxes, which are HDPE pyrolysis
primary products. This formation of primary products via random scission or end-chain scission mechanism also occurs when a catalyst is used in situ, as the fused HDPE coating the particles initiates its cracking via thermal mechanism. On the other hand, catalytic cracking starts through the formation of a carbenium ion by the addition of a hydride ion to an olefin on Brensted acid sites or the abstraction of a hydride ion to a paraffin on Lewis acid sites. The mechanism of cracking (thermal and catalytic) also includes the reactions of isomerization, hydrogen transfer, cyclization, aromatization, or condensation with their enhancement or inhibition being conditioned by the operating conditions, acidity, and the shape selectivity of each catalyst.

In this study, an increase in space-time and temperature not only enhances the initial pathways of devolatilization and cracking of waxes but also the secondary reactions of cracking, isomerization, hydrogen transfer, cyclization, and aromatization, which leads to the formation of light hydrocarbons, isoparaffins, paraffins, naphthenes, and aromatic compounds, respectively. However, the moderate acidity of the FCC catalyst limits the extension of these secondary reactions. Thus, the combination of the features of the spent FCC catalyst and the suitable operating conditions and features of the CSBR equipped with fountain confiner allow the conversion of waste polyolefins to valuable hydrocarbons, as are light olefins and liquid fuels in the gasoline and diesel ranges.

Conclusions

The excellent performance of the conical spouted bed reactor (CSBR) has been proven for continuous catalytic pyrolysis of high-density polyethylene (HDPE) over a spent fluid catalytic cracking (FCC) catalyst with high selectivity towards gases (C<sub>1</sub>–C<sub>4</sub>) rich in light olefins and gasoline fraction (C<sub>5</sub>–C<sub>11</sub>). The good features of this reactor, such as the vigorous cyclic movement of the particles in the bed and the high heat and mass transfer rates, are enhanced by the use of a fountain confiner and a draft tube. Besides, the use of these devices allows handling fine catalyst particles in the bed without elutriation problems, which considerably improves the contact between the catalyst and the fused plastic material. Moreover, the fountain confiner increases the volatile residence time within the reactor, thus increasing catalyst efficiency.

The catalytic activity of the spent FCC catalyst for HDPE cracking has been proven. In fact, the yield of waxes (thermal cracking primary products) is negligible above 550 °C when a space-time of 15 g<sub>ppm</sub>min g<sup>-1</sup> HDPE is used. Moreover, the obtained products have a remarkable commercial interest, as is the case of light olefins, especially propylene and butenes, and liquid fuels in the range of gasoline and diesel. Besides, a considerable effect of space-time has been observed, mainly enhancing the cracking reactions as space-time is increased and therefore increasing the yield of C<sub>1</sub>–C<sub>4</sub> gases by cracking of C<sub>5</sub>–C<sub>11</sub> hydrocarbons. However, in the range studied, space-time hardly affects the secondary reactions of isomerization, hydrogen transfer, cyclization, and aromatization.

Temperature significantly affects the primary cracking reactions, as well as the secondary reactions. On the one hand, in the lower range of temperature, an increase in this variable leads to the enhancement of mainly cracking reactions, with the yield of waxes being almost negligible at 500 °C. In addition, an increase in isoparaffins, paraffins, naphthenes, and aromatics with temperature is evidence that it enhances isomerization, hydrogen transfer, cyclization, and aromatization reactions. Besides, an increase in temperature above 550 °C enhances oligomerization-cracking reactions, with the selectivity of ethylene being especially increased among the three light olefins. A slight increase in light paraffins is also observed at high temperatures, which is evidence of overcracking reactions.

Acknowledgements

This work was carried out with the financial support from Spain’s ministries of Science, Innovation and Universities RTI2018-101678-BIO00(MCIU/AEI/FEDER, UE) and RTI2018-098283-J000(MCIU/AEI/ FEDER, UE) and Science and Innovation (PID2019-107357RB-I00 (MCI/FEDE, UE)), the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 823745, and the Basque Government (IT1218-19 and KK-2020/00107).

Conflict of Interest

The authors declare no conflict of interest.

Keywords: heterogeneous catalysis · pyrolysis · sustainable chemistry · waste plastics · waste valorization

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