

## **Co-cracking of high-density polyethylene (HDPE) and vacuum gasoil (VGO) under refinery conditions**

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### **ABSTRACT**

The co-cracking of a 5 wt% of high-density polyethylene (HDPE) dissolved in vacuum gasoil (VGO) under conditions similar to those of the industrial fluid catalytic cracking (FCC) has been studied. The main goal has been to assess the effect of the co-feeding of waste plastic on attained conversion, as well as on the yield and composition of the products, given its interest for the subsequent refinery processes focused on the production of fuels. The products have been grouped in fractions: dry gas (C<sub>1</sub>-C<sub>2</sub>); liquefied petroleum gas (C<sub>3</sub>-C<sub>4</sub>), naphtha (C<sub>5</sub>-C<sub>12</sub>), light cycle oil (C<sub>13</sub>-C<sub>20</sub>), heavy cycle oil (C<sub>20+</sub>) and coke. Obtained results expose a significant synergy in the co-cracking, obtaining with the HDPE/VGO blend a higher conversion at 560 °C, together with higher yield of naphtha and concentration of light olefins. The synergy is based on the fast formation of intermediate alkylcarbenium ions at high temperature. Naphtha has been extensively characterized obtaining higher contents of n-paraffins and olefins and lower of iso-paraffins and aromatics in the cracking of the HDPE/VGO blend. This last characteristic increases the interest of the naphtha obtained in the co-cracking to be included in the gasoline pool of the refinery.

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**Keywords:** plastic; recycling; waste management; waste refinery; catalytic cracking;  
FCC unit

## 1. Introduction

The high production rates of plastics, estimated in ca. 9 billion tons between 1950 and 2017, and the fact that recycling and energy recovery rates are still very low, in 2017 just the 7.2 and 9.6 wt% of the worldwide generated plastic waste was recycled and incinerated, respectively; entail such a waste disposal rate that causes irreversible damages to natural ecosystems [1]. Furthermore, the incineration of plastics releases dangerous substances such as heavy metals, dioxins and furanes that have been associated with adverse health effects [2]. On the other hand, Jambeck et al. [3] have estimated that 250 million tons of mismanaged plastic waste would reach the oceans by 2025 with unpredictable effects in the health of marine life and, consequently, in human health [4]. Barnes [5] has assessed the economic difficulties to revert this situation stressing the necessity to invest in innovative technology solutions. To assess the magnitude of the problem, the Ocean Cleanup organization has made a feasibility study obtaining that € 492–708 billion investment is required to rid 70 million tons of plastic from oceans in the following 10 years [6].

Thermochemical routes, i.e., pyrolysis and gasification of plastics, has already acquired good levels of technological development [7,8]. Comparing both routes, pyrolysis offers some advantages over gasification, since it allows for the direct production of fuels or for the recovery of the monomers by using simple technologies with reduced environmental impact [7,9,10]. Indeed, pyrolysis can be used to valorize different types of plastics and by adjusting the operating conditions the selective production of different fractions can be obtained: C<sub>1</sub>–C<sub>4</sub> (gases), C<sub>5</sub>–C<sub>10</sub> (no aromatics), aromatics and waxes [11,12]. Furthermore, by means of selecting an appropriate acid catalyst, e.g., HZSM-5, H $\beta$  or HY zeolites, and proper operating conditions, high yields of fuels can be obtained [13–17], as well as intensify the recovery of the monomers [18–20]. On the other hand, with

reforming catalysts the valorization of plastics is aimed at H<sub>2</sub> production [21]. For the viability of these latter catalytic processes, the regenerability of the catalyst is a key factor [22].

Several arguments can be given to explain why these technologies have not yet been implemented on a commercial-scale. Firstly, proposed pyrolysis technologies are very diverse and have been mainly studied at laboratory and pilot plant-scale. Moreover, obtained pyrolysis oil must be subjected to an additional hydroreforming stage prior to its use as automotive fuel [23]. However, main causes are related to the necessity of finding the economic viability of proposed initiatives, which requires the commercialization of obtained fuels and chemicals.

According to given restraints for the valorization of waste plastics and keeping in mind that plastics are petroleum-derived products, an interesting and pragmatic solution is to valorize them inside the well-established petrochemical industry using conventional and already depreciated refinery units [24]. This way, the products obtained in the valorization of plastics would be commercialized together with the common high-quality fuels. Inside the conventional refinery scheme, fluid catalytic cracking (FCC) and hydroprocessing units are the most suitable ones for a large-scale upgrading of these feedstocks without causing any remarkable negative impact on the yield and composition of the products. Indeed, hydroprocessing are widely recognized as versatile units [25] and it has been extensively checked in laboratory-scale reactors that hydroprocessing can treat feedstocks of different nature, such as aromatic refinery streams [26], scrap tires pyrolysis oil (STPO) [27] or plastics dissolved in different streams [28]. Nonetheless, hydroprocessing is a highly expensive process since it demands high hydrogen pressures and temperatures, which justifies the reluctance to invest in hydroprocessing units in refineries and to treat non-conventional feedstocks in these units. On the contrary, FCC units, with average

capacities of 50 thousand barrels per day, can be commonly found in almost all the refineries. Besides, their characteristic integration of reaction and regeneration units, as well as the innovations performed in the catalyst design for more than 70 years, increase their capacity to treat alternative feedstocks [29,30]. The advantages of the valorization of waste plastics in a refinery (waste refinery) and, specifically, of polyolefins in industrial FCC units are summarized in [Table 1](#). Furthermore, refineries may comply with a social function within the circular economy strategy and could benefit from economical compensations or tax deductions for contributing to environmental care and protection.

Table 1

The co-cracking of plastics together with conventional refinery streams has been investigated in literature by mainly using polyolefins, following different strategies and with different laboratory-scale reactors, i.e., batch, fixed and fluidized bed reactors. This way, some authors have investigated the co-cracking of polyolefin-derived waxes, i.e., C<sub>21+</sub> stream obtained by fast pyrolysis of polyolefins at low temperature. Arandes et al. [31] have studied the co-cracking of polypropylene (PP) pyrolysis waxes and light cycle oil (LCO). Rodríguez et al. [32] have observed a higher synergy in the co-cracking of high-density polyethylene (HDPE) pyrolysis waxes and vacuum gasoil (VGO), as VGO is more crackable than LCO. However, the co-cracking of dissolved plastics has attracted more attention, as the prior stage of pyrolysis is not required. Various authors have employed as solvents pure hydrocarbons with the aim of studying the cracking mechanism of the plastic. This strategy has been followed by de la Puente et al. [33] with a blend of low-density polyethylene (LDPE) and toluene and by Wong et al. [34] with a blend of LDPE and benzene. In a pioneering work of co-cracking of plastics and a refinery stream, Ng [35] obtained a high gasoline yield using a HDPE/VGO blend as feedstock. It has been also studied the co-cracking under FCC unit conditions of different blends, such

as LDPE/VGO [36,37], PP/LCO [38], polystyrene/LCO and polystyrene-polybutadiene/LCO [39,40]. Most of the works that study the cracking of plastic/refinery stream blends are focused on the comparison of the yields of the main product fractions, i.e., dry gas, LPG, naphtha, LCO, HCO and coke, with those obtained in the cracking of VGO. However, to make the co-feeding of plastics to FCC units a reality, an extensive experimentation is required, delving into the effect of the co-feeding on the composition of product fractions. In particular, the effect on the naphtha fraction, whose formation is a key parameter in the economy of the FCC unit, as it affects the operation of the subsequent separation and reforming stages required to adapt the quality of the final products to legal restrictions.

In this work, we have assessed the capacity of the FCC unit to treat the plastic waste dissolved in a refinery stream. For this purpose, a laboratory-scale FCC riser simulator reactor operating under conditions (catalyst, temperature, catalyst/oil ratio and reaction time) similar to those used in industrial FCC units has been used. The aim of the work is to study the influence of adding HDPE (5 wt%) to a conventional FCC unit feed (VGO) on the yields and distribution of the product fractions. Additionally, the detailed analysis done to gaseous (dry gas and LPG) and, specifically, naphtha fractions (whose composition has been in-deep characterized) allows for performing a valorization of the synergy of the co-cracking and of the effect of the co-feeding of the HDPE on the composition of these fractions and their interest for refinery. Moreover, given the versatility of the refinery units, the effect of two variables of great incidence, i.e., temperature and catalyst to oil ratio, has been investigated.

## **2. Material and methods**

### **2.1 Feedstocks**

The vacuum gasoil (VGO) has been supplied by Petronor Refinery (Muskiz, Spain) from the feedstock to its own FCC unit. It consists on a blend of gasoils from different units: atmospheric and vacuum distillation, visbreaker, hydrotreater and coker units. [Table 2](#) summarizes the main physicochemical properties of the VGO, which have been measured by techniques described in detail elsewhere [32]. According to the results shown in [Table 2](#), VGO is a highly aromatic feedstock, with similar content in mono-, di- and poly-aromatics (20.88, 16.36 and 23.94 wt%, respectively). The simulated distillation analysis (ASTM D2887 Standard) reveals that VGO has a 5 wt% of light cycle oil (LCO) (216-350 °C) and a 95 wt% of heavy cycle oil (HCO) (> 350 °C). The high-density polyethylene (HDPE) has been supplied by Dow Chemical (Tarragona, Spain) in the form of 4 mm pellets. In deep characterization of this HDPE has been carried out following the procedures detailed elsewhere [28] and its main properties are summarized in [Table 2](#).

The HDPE/VGO blend has been prepared by continuously stirring for 120 min at 60 rpm at a temperature of 80 °C, conditions well established in literature to prepare blends with up to 10 wt% of the polymer [41]. Moreover, Marcilla et al. [42] have studied the increase of the melting point and viscosity of the feedstock when increasing the amount of LDPE dissolved in VGO. Therefore, the chosen weight fraction of the polymer in the blend has been of 5 wt%, as it ensures that no obstruction will occur in the injection system. Furthermore, it would not be reasonable the co-feeding of a higher amount of plastics into a FCC unit as the capacity of this unit is much higher than the availability of waste plastic.

Table 2

## 2.2 FCC catalyst

In this work, a commercial equilibrium FCC catalyst (previously spent in refinery) has been used. The catalyst, provided by Petronor Refinery (Muskiz, Spain), with a content

of 13.8 wt% of Y zeolite has been widely characterized by several techniques described in detail elsewhere [26]. Its main properties are collected in [Table S1](#) in the Supplementary Material. It is remarkable that this catalyst has a higher apparent bulk density ( $0.9 \text{ g cm}^{-3}$ ), which has been measured according to ASTM D1895 Standard, than that of fresh FCC catalysts (commonly in the  $0.8\text{--}0.85 \text{ g cm}^{-3}$  range) due to the metal deposition that takes place during the consecutive reaction-regeneration cycles in the FCC unit [43]. The average particle size has been determined by ASTM E1382 Standard. The X ray diffraction assays (XRD) were carried out using a Philips X'Pert PRO equipment and have been used to estimate the unit cell size of the zeolite (ASTM D3942 Standard) with the reflection angles corresponding to those of spent catalysts (Al:  $23.5$ ,  $26.9$  and  $31.2^\circ$ ; Si:  $28.5^\circ$ ).

Textural properties, pore size distribution and micropore volume have been determined using  $\text{N}_2$  adsorption-desorption isotherms recorded at  $-196^\circ\text{C}$  in a Micromeritics ASAP 2010 equipment after degasification at  $150^\circ\text{C}$  during 8 h. Besides, the pore size distribution has been estimated from  $\text{N}_2$  adsorption isotherm branch by BJH method, whereas the micropore volume has been calculated by t-plot method. The content of metals of the catalyst was measured in a Thermo X7-11 quadrupolar mass spectrometer (Q-ICP-MS) provided with Xt interphase and concentric nebulizer.

Total acidity and average acidic strength have been measured from  $\text{NH}_3$  temperature-programmed desorption (TPD) analyses. The data have been collected in TG-DSC Setaram 111 calorimeter attached to a Balzers Quadstar 422 mass spectrometer according to the experimental procedure described elsewhere [44]. The Brønsted/Lewis (B/L) acidic site ratio has been determined by Fourier transform infrared spectroscopy (FTIR) of pyridine adsorbed in a Thermo Nicolet 6700 FTIR provided with SPECAC transmittance cell connected to a vacuum pump [28].



### 2.3 Reaction equipment and product analysis

The equipment employed for experimental runs is a fluidized batch CREC riser simulator reactor patented by de Lasa [45], which can reproduce at laboratory-scale the conditions of the industrial FCC unit [46,47] as it has been described in detail elsewhere [48].

The experimental runs have been carried out with both raw VGO and HDPE/VGO blend (5 wt% of plastic) at 500-560 °C, with a catalyst/oil (C/O) mass ratio of 3–7  $\text{g}_{\text{cat}} \text{g}_{\text{feed}}^{-1}$  and a reaction time of 6 s, conditions characteristic of the industrial FCC unit. For these runs, once the reaction temperature is achieved, the feedstock is manually injected into the system. The feedstock vaporizes immediately and, once the reaction time is elapsed, products are sent to an Agilent Technologies 7890A gas chromatograph (HP-PONA, 50 m  $\times$  0.2 mm  $\times$  0.5  $\mu\text{m}$ ) equipped with a FID detector by means of a vacuum pump. To ensure both the soundness and reproducibility of the data, at least 3 repeats for each one of the experiments have been performed.

The reaction products have been grouped in lumps according to their boiling point range as follows: dry gas ( $\text{C}_1\text{--}\text{C}_2$ ), liquefied petroleum gases (LPG,  $\text{C}_3\text{--}\text{C}_4$ ), naphtha ( $\text{C}_5\text{--}\text{C}_{12}$ ), light cycle oil (LCO,  $\text{C}_{13}\text{--}\text{C}_{20}$ ) and heavy cycle oil (HCO,  $\text{C}_{20+}$ ) and coke. Besides, the products have been also grouped by their chemical nature and number of carbon atoms. The amount of coke deposited in the catalyst has been measured by temperature programmed oxidation (TPO) in a TA Instruments TGA-Q 5000 thermobalance connected in line to a Thermostar mass spectrometer to monitor the generation of  $\text{CO}_2$  during coke combustion. Research octane number (RON) of the naphtha fraction has been obtained according to its composition determined by means of chromatographic methods [49].

The yield of each lump  $i$  has been defined as the mass ratio of each particular fraction referred to the total mass fed:

$$\text{Yield of lump}_i \text{ (wt\%)} = \frac{\text{mass of lump}_i}{\text{total mass fed}} \cdot 100 \quad (1)$$

Furthermore, as it is commonly done in the FCC catalytic cracking unit, the conversion has been determined as the sum of the yields of the dry gas, LPG, naphtha and coke fractions.

### 3. Results and discussion

#### 3.1. Conversion and yields

Figure 1 compares the conversion obtained in the cracking of the HDPE/VGO blend with that obtained with the VGO at different temperatures and C/O ratios. The ranges of conversion attained are wider for the blend (37.9–65.7 wt%) than for the VGO (41.4–62.7 wt%). The biggest differences are found at the lightest and harshest operating conditions (500 °C, 3 g<sub>cat</sub> g<sub>feed</sub><sup>-1</sup> and 560 °C, 7 g<sub>cat</sub> g<sub>feed</sub><sup>-1</sup>, respectively). Under the medium severity conditions (530 °C, 5 g<sub>cat</sub> g<sub>feed</sub><sup>-1</sup>) the conversion obtained is similar for both feedstocks, i.e., 53.3 and 53.4 wt% for the HDPE/VGO blend and VGO, respectively. It is noticeable that at 560 °C and with high C/O ratio (7 g<sub>cat</sub> g<sub>feed</sub><sup>-1</sup>) the conversion obtained in the cracking of the HDPE/VGO blend is remarkably higher than that obtained in the cracking of VGO.

Figure 1

The evolution of product yields with conversion is shown in Figure 2. The use of conversion as a variable allows monitoring the evolution of the results with the reaction extent, which is a technique commonly done in studies of catalytic cracking [50–52]. As

it has been observed, an increase in the severity of the reaction conditions, i.e., temperature and C/O ratio, brings an increase in the yields of dry gas, LPG, naphtha and coke fractions, while reduces the yields of LCO and HCO fractions. Hence, it can be established that LCO and HCO fractions, which are the majority in the composition of the feedstocks, are cracked to form lighter compounds. Attending to the effect of both variables, it can be seen that temperature has a higher resemblance on the results than C/O ratio, which is a common result obtained in the cracking under refinery conditions of various feedstocks, such as VGO and HDPE pyrolysis waxes [32]. It must be highlighted that the decrease with conversion of the yield of the HCO fraction observed in [Figure 2e](#) is less pronounced for the HDPE/VGO blend. This fact is a consequence of the low cracking rate of the HDPE at low temperatures [53,54]. Equally, Marcilla et al. [42] have demonstrated by means of thermogravimetric analysis of a LDPE/VGO blend that the decomposition of the VGO occurs at lower temperature than that of the LDPE. Thus, in conditions of low conversion, i.e., low temperature and C/O ratio, the reactivity of the HDPE/VGO blend is smaller than that of the VGO, since the chains of HDPE contribute to attenuate the cracking of the heavy compounds of the VGO.

On the contrary, the slope of the yield of the LCO fraction ([Figure 2d](#)) is slightly higher for the blend, which reveals the high reactivity, within this fraction, of the oligomer chains derived from the cracking of the chains contained in the HCO fraction. However, at higher conversions the differences between the yields of the LCO and HCO fractions ([Figure 2d](#) and [e](#), respectively) disappear for both feedstocks and the yields converge on a value of 58 wt%. This tendency reveals that the crackability of the HDPE and VGO compounds is similar at higher values of temperature and C/O ratios.

The yields of dry gas, LPG and naphtha fractions ([Figure 2a](#), [b](#) and [c](#), respectively) increase with conversion, but the slope followed by the blend in the case of LPG and

naphtha fractions is higher. This points out that the co-feed of HDPE favors the formation of these fractions, while disfavoring the formation of dry gases. Therefore, avoiding the over-cracking of the molecules within the LPG and naphtha fractions.

To explain the results of the co-cracking displayed in [Figure 2](#) there should be taken into account not only the notorious differences, but also the common aspects of the cracking mechanisms of dissolved HDPE chains and of the components of the VGO. This way, it is well established in the literature that thermal cracking of the HDPE occurs by free radical mechanism [55], whereas in presence of an acid catalyst it occurs through a carbocationic mechanism requiring a lower activation energy and leading to the rapid formation of a secondary alkylcarbenium ion by protonation of the free radicals [56]. Alkylcarbenium ions are intermediates of sequential skeletal rearrangements and  $\beta$ -scission reactions, which leads to the formation of a smaller alkylcarbenium ion and an olefin [57]. Likewise, alkylcarbenium ions are also the active intermediates in the carbocationic cracking mechanism of the components of the VGO, but they are obtained through the cracking of aliphatic chains and of lateral chains of the aromatic compounds, being less relevant the formation of olefins by ring opening reactions [58]. Consequently, the formation of alkylcarbenium ions, which depends on the length of the chain and branching degree of the components, is of special relevance.

The aforementioned results of the [Figure 2](#), with a lesser extent of reaction for the blend than for the VGO at low temperature, seem to indicate that the olefins that constitute the dissolved HDPE chains require higher temperature for the formation of the alkylcarbenium ions than the olefins obtained from some components of the VGO. Nonetheless, at higher temperature the chains of olefins obtained by thermal cracking of the HDPE are shorter, hence being faster the rate of the carbocationic cracking mechanism. In the same way, the cracking mechanism of the components of the VGO are

avored by a high concentration of HDPE-derived alkylcarbenium ions in the reaction medium. However, it cannot be dismissed the possibility that the results could be affected by the different diffusivity of the dissolved HDPE chains and of the components of the VGO. Indeed, Al-Sabawi et al. [59] have highlighted the diffusional limitations of the bulky components of the VGO below 550 °C.

On the other hand, even though coke formation increases with the reaction extent, a minor coke formation (Figure 2f) has been obtained with the blend. Due to this difference, at low conversion levels, the catalyst will predictably suffer a minor deactivation. Furthermore, this fact is in concordance with the major difference in the conversion and product distribution above these conditions of low conversion, in which the coke yield is more than 1 wt% smaller for the blend. The lower yield of coke can be justified, mainly, because of the reduction in the concentration of poly-aromatics derived from the co-feeding of HDPE, as well as for the increase of the H/C ratio derived from the hydrogenated nature of the chains of polymer that attenuates the rate of coke condensation reactions [60].

Figure 2

### 3.2 Yield of components of the gas products

The effect of temperature and C/O ratio on the yields of the main components of the gas fraction (dry Gas and LPG fractions) in the cracking of the HDPE/VGO blend and of the VGO is shown in Figure 3. It can be seen that an increase in temperature favors both thermal and catalytic cracking, as well as the over-cracking of the intermediates, disfavoring at the same time the hydrogen-transfer reactions. Consequently, the yields of C<sub>1</sub>–C<sub>3</sub> and butane (n- and i-C<sub>4</sub>) (Figure 3a-c and Figure 3d-f, respectively), which are products of the over-cracking, increase; whereas the yields of butenes (c-, i- and t-C<sub>4</sub>)

(Figure 3g-i), mainly formed by hydrogen-transfer reactions, reduce at higher temperatures. On the other hand, an increase of the C/O ratio, with less relevance than temperature favors the yields of all the products in the C<sub>1</sub>-C<sub>4</sub> range, except for propylene (C<sub>3</sub><sup>-</sup>) at 560 °C (Figure 3c) and cis and trans-butene (c- and t-C<sub>4</sub><sup>-</sup>) (Figure 3g-i) with an opposite evolution.

When comparing the results obtained with both feedstocks, the co-feeding of HDPE increases the yields of olefins, as well as the yields of propane and n-butane. The highest yield of iso-butene (i-C<sub>4</sub><sup>-</sup>) (Figure 3g-i) is in concordance with the importance of the isomerization of olefins observed by Kumar et al. [61] in the cracking of HDPE. Besides, this difference between the yields of iso-butene (i-C<sub>4</sub><sup>-</sup>) and of the remaining butenes (c- and t-C<sub>4</sub><sup>-</sup>), increases feedstocks at higher temperatures because the hydrogen-transfer reactions are disfavored, as checked by Passamonti et al. [62] in the cracking of VGO.

Figure 3

Given the relevance of the light olefins for the petrochemical industry, the olefinicity of the C<sub>3</sub> and C<sub>4</sub> families obtained with both feedstocks has been compared in Table 3. It can be seen that, at low-severity cracking conditions the olefinicity is higher in the cracking of the VGO. However, if severity increases this trend is reversed, turning higher the olefinicity of the LPG fraction obtained in the cracking of the HDPE/VGO blend. Moreover, an increase in the C/O ratio provokes a reduction of the C<sub>3</sub> olefinicity in the cracking of the blend. On the other hand, the effect over C<sub>4</sub> olefinicity is not well defined. Conversely, an increase in temperature causes an increase of both olefinicities in the cracking of the blend because of the boosting of the over-cracking reactions within the naphtha fraction.

Table 3

### 3.3 Composition of the naphtha fraction

To understand the results of the behavior of the HDPE in the cracking of the HDPE/VGO blend, it should be considered that the cracking of polymers commonly leads to olefins with a high level of isomerization [61] and high selectivity to C<sub>3</sub>-C<sub>4</sub> and C<sub>5</sub>-C<sub>12</sub> products, which correspond to molecules within the LPG and naphtha fractions, respectively. Furthermore, aromatics will be later formed by cyclization reactions of olefins and subsequent dehydrogenation of produced naphthenes, whereas paraffins are products of hydrogen-transfer reactions of olefins. According to these hypotheses, the major hydrocarbon family in naphtha fraction (Figure 4, which correspond to 560 °C) is the olefinic one, followed by (in this order) the aromatic, iso-paraffinic, n-paraffinic and naphthenic family. When comparing these results with those obtained at 500 and 530 °C (depicted in Figure S1 in the Supplementary Material) an increase in temperature arouses the concentration of olefins, since their formation from heavier olefins is favored. Moreover, high temperatures mitigate the conversion of olefins into paraffins by means hydrogen-transfer reactions. On the contrary, an increase in the C/O ratio causes a decrease in the concentration of both olefins and naphthenes and an increase in the concentration of paraffins and aromatics, because the higher amount of acidic sites promotes the hydrogen-transfer reactions.

Figure 4

Studying the composition of the family of n-paraffins of the naphtha fraction (Figure 5a at 560 °C and Figure S2 at 500 and 530 °C) it is observed that its concentration decreases as the number of carbon atoms increases, achieving the minimum values for the C<sub>10</sub> paraffins. Therefore, the C<sub>5</sub> are the main n-paraffins, with the maximum concentration value of 3.1 wt% at 500 °C and  $7 \text{ g}_{\text{cat}} \text{ g}_{\text{feed}}^{-1}$  (Figure S2a). Additionally, the concentration

of all the n-paraffins decreases when increasing the temperature, since the cracking of the heaviest ones is favored; leading to the formation of lighter n-paraffins and olefins in the range of dry gas and LPG fractions. Besides, the hydrogen-transfer reactions, responsible of conversion of olefins into n-paraffins, are disfavored. Conversely, an increase in the C/O ratio causes an increase in the concentration of n-paraffins, since the hydrogen-transfer reactions are selectively favored. Observed effects of the temperature and C/O ratio are in concordance with those obtained in the catalytic cracking of HDPE [54] and of the LDPE/VGO blend [63].

The distribution of iso-paraffins (Figure 5b at 560 °C and Figure S3 at 500 and 530 °C) is, also, in decline in order from lowest to highest number of carbon atoms, being the highest concentration that of C<sub>5</sub> iso-paraffins (9.8 wt%) at 500 °C and 7 g<sub>cat</sub> g<sub>feed</sub><sup>-1</sup> (Figure S3a). Similarly to what it happens for the n-paraffins, the temperature favors the cracking of all the iso-paraffins and an increase in the C/O ratio favors its formation by hydrogen-transfer reactions.

The concentration of olefins (Figure 5c at 560 °C and Figure S4 at 500 and 530 °C) also decreases as the molecular weight increases, although a minimum is observed for the C<sub>9</sub> olefins at 530 (Figure S4b) and 560 °C (Figure 5c). The increase of C<sub>5</sub>–C<sub>8</sub> olefins can be attributed to their formation from the LCO and HCO fractions, where the oligomers from primary cracking of diluted HDPE are. Their formation is more favored than their cracking to olefins in the LPG and dry gas fractions. Thus, the well-known greater crackability of olefins of higher molecular weight is ratified. On the other hand, an increase of C/O ratio favors the cracking of the olefins, becoming secondary the role of the hydrogen-transfer reactions, which can be the responsible for the increase of the concentration C<sub>10</sub> olefins when increasing not also the temperature, but also the C/O ratio.



In [Figure 5d](#) (corresponding to 560 °C) and in [Figure S5](#) (corresponding to 500 and 530 °C) it is observed that the C<sub>8</sub>–C<sub>12</sub> aromatics are majority in this family of the naphtha fraction at the whole range of operating conditions studied. An increase in temperature favors the cracking of the side chains of aromatics increasing the concentrations of C<sub>6</sub> and C<sub>7</sub> aromatics. On the other hand, an increase in the C/O ratio leads to an increase in the concentration of all the aromatics since their formation from hydrogen-transfer reactions is favored. The exception can be found for C<sub>10</sub>–C<sub>12</sub> aromatics at 500 °C ([Figure S5a](#)), for which, the cracking of their side chains is favored to a greater extent when the C/O ratio is increased.

Figure 5

#### 3.4. Comparison of the naphtha from cracking of the HDPE/VGO blend and of the VGO

There are two remarkable facts when the composition of the naphtha fraction obtained in the cracking of the HDPE/VGO blend is compared with that of the VGO ([Figure 6](#) at C/O = 7 g<sub>cat</sub> g<sub>feed</sub><sup>-1</sup> and [Figure S6](#) at C/O = 3 and 5 g<sub>cat</sub> g<sub>feed</sub><sup>-1</sup>): (i) there is a big difference between the concentrations of all the hydrocarbon families; and (ii) the reaction conditions have a qualitatively similar effect for both feedstocks. It can be seen that the co-feeding of HDPE causes a remarkable increase in the concentration of n-paraffins and olefins, comparing with the naphtha obtained in the cracking of the VGO, and a decrease in the concentration of iso-paraffins, naphthenes and aromatics. Thus, the concentration of olefins in the naphtha fraction obtained in the cracking of the blend is 16.5 wt% higher, whereas the concentration of aromatics 14.2 wt% lower. Indeed, the biggest differences of 22.6 and 17.3 wt% respectively, have been obtained at the highest temperature (560 °C) and lower C/O ratio (3 g<sub>cat</sub> g<sub>feed</sub><sup>-1</sup>) ([Figure S6c](#)). This fact clearly reveals the selectivity

of the conversion of the HDPE diluted in the feedstock to lineal paraffins and olefins under FCC conditions.

As it has been pointed out, there is a similar qualitative effect of the reaction conditions for the both feedstocks. As the temperature arouses, the concentration of the olefins increases, whereas the rest of the hydrocarbon families decreases, except that of aromatics, which remains almost constant. For both feedstocks, an increase in the C/O ratio leads to an increase on the concentration of n-paraffins, to a greater extent than that of iso-paraffins (in particular at 500 °C) and to a decrease in the concentration of olefins, as hydrogen-transfer reactions are promoted [64]. This fact, together with the greater reaction rate of Diels-Alder cyclization reactions, justify the increase in the concentration of aromatics in the cracking of the HDPE/VGO blend at higher C/O ratios. Although, this increase is lower in the naphtha obtained in the cracking of VGO cracking, in which the concentration of olefins is lower.

#### Figure 6

The concentration of n-paraffins is higher for the HDPE/VGO blend than for the VGO for the whole range of investigated reaction conditions (Figure 7a-c at  $C/O = 7 \text{ g}_{\text{cat}} \text{ g}_{\text{feed}}^{-1}$  and Figure S7 at  $C/O = 3$  and  $5 \text{ g}_{\text{cat}} \text{ g}_{\text{feed}}^{-1}$ ) since the catalytic cracking of HDPE, which occurs by means of carbocationic mechanisms, leads to a wide distribution of paraffins. Although the distribution of the naphtha fractions obtained with both feedstocks decreases with the number of carbon atoms, the distribution of the blend is more homogeneous. This indicates that a lesser redistribution by selective over-cracking in decreasing order of molecular weight has occurred. An increase in temperature causes an overall decrease of the concentration of all the n-paraffins, whereas an increase in the C/O ratio increases them. Thus, the biggest differences are obtained at 500 °C and  $7 \text{ g}_{\text{cat}} \text{ g}_{\text{feed}}^{-1}$

<sup>1</sup> (Figure 7a) and the smallest at 560 °C and 3 g<sub>cat</sub> g<sub>feed</sub><sup>-1</sup> (Figure S7a), which are the conditions at which the hydrogen-transfer reactions are more and less favored, respectively.

The concentration of iso-paraffins also shows a wide distribution (Figure 7d-f at C/O = 7 g<sub>cat</sub> g<sub>feed</sub><sup>-1</sup> and Figure S8 at C/O = 3 and 5 g<sub>cat</sub> g<sub>feed</sub><sup>-1</sup>), although it is narrower for the naphtha obtained in the cracking of the HDPE/VGO blend. Individual concentrations are lower in this case, except for the family of C<sub>7</sub> at 7 g<sub>cat</sub> g<sub>feed</sub><sup>-1</sup> (Figure 7d-f), which is consistent with the high yield of iso-paraffins in the cracking of VGO and with the linear nature of the parent oligomers found in the LCO and HCO fractions of the HDPE. Furthermore, the individual concentration of iso-paraffins decreases with temperature for both feedstocks as hydrogen-transfer reactions are mitigated, whereas increases with C/O ratio because, this time, hydrogen-transfer reactions are boosted.

On the other hand, the difference between individual concentrations decreases when the number of carbon atoms is increased, due to the greater crackability of the high-molecular weight iso-paraffins. Hence, the biggest differences are observed for the C<sub>5</sub> ones, as they are ca 4.6 % higher for the VGO than for the blend, achieving the highest difference (7.4 %) at 500 °C and 7 g<sub>cat</sub> g<sub>feed</sub><sup>-1</sup> (Figure 7d). Once again, these results expose the relevance of the hydrogen-transfer reactions in the distribution of the compounds within the naphtha fraction.

### Figure 7

The concentration of olefins (Figure 8a-c at C/O = 7 g<sub>cat</sub> g<sub>feed</sub><sup>-1</sup> and Figure S9 at C/O = 3 and 5 g<sub>cat</sub> g<sub>feed</sub><sup>-1</sup>) is higher in the naphtha obtained in the cracking of the HDPE/VGO blend for all the numbers of carbon atoms. The biggest difference is obtained for the C<sub>6</sub> olefins with an average value of 6 % and a maximum value of 7.5 % (at 560 °C and 3 g<sub>cat</sub>

$\text{g}_{\text{feed}}^{-1}$ ) (Figure S9c). On the other hand, the differences in the concentration of  $\text{C}_5\text{--C}_7$  olefins are maximized with temperature, whereas the differences for the  $\text{C}_8\text{--C}_{10}$  ones are reduced. As  $\text{C}/\text{O}$  ratio increases the differences in the concentration of the  $\text{C}_6\text{--C}_9$  olefins decrease, while the concentration of  $\text{C}_5$  and  $\text{C}_{10}$  olefins shows a maximum at  $\text{C}/\text{O} = 5 \text{ g}_{\text{cat}} \text{ g}_{\text{feed}}^{-1}$  (Figure S9d-f).

Although the concentration of  $\text{C}_7\text{--C}_{12}$  aromatics is higher in the naphtha obtained in the cracking of the VGO (Figure 8d-f at  $\text{C}/\text{O} = 7 \text{ g}_{\text{cat}} \text{ g}_{\text{feed}}^{-1}$  and Figure S10 at  $\text{C}/\text{O} = 3$  and  $5 \text{ g}_{\text{cat}} \text{ g}_{\text{feed}}^{-1}$ ), higher concentrations of benzene have been obtained in cracking of the blend. This result is presumably related to the dehydrogenation of the naphthenes produced by Diels-Alder cyclization reactions of olefins. On the other hand, the more abundant aromatic compounds for both feedstocks are the  $\text{C}_9$  ones, showing at the same time the biggest difference (ca. 4.6 %) between them. An increase in temperature and in  $\text{C}/\text{O}$  ratio provokes bigger differences between the aromatic concentrations in both naphthas, which depicts a bigger effect of this variables over the cracking and dehydrogenation reactions in the cracking of the VGO. Individually, the biggest difference is found for the  $\text{C}_9$  aromatics at  $530 \text{ }^\circ\text{C}$  (Figure 8e and Figure S10b,e).

### Figure 8

In Table 4, the values for the isoparaffinicity, olefinicity and olefin branching indexes, as well as the octane number (RON) are shown for the naphtha fraction obtained in the cracking of both feedstocks at different temperatures and  $\text{C}/\text{O}$  ratios. It can be seen that the isoparaffinicity of the naphtha fraction obtained in the cracking of the HDPE/VGO blend diminishes when increasing the number of carbon atoms; therefore, the maximum isoparaffinicity is reached for  $\text{C}_5$  at  $560 \text{ }^\circ\text{C}$  and  $7 \text{ g}_{\text{cat}} \text{ g}_{\text{feed}}^{-1}$ . At these conditions, the isoparaffinicity of the  $\text{C}_6$  and  $\text{C}_7$  molecules also meets its maximum value. However,

comparing the isoparaffinicity of the naphtha from both feedstocks, it can be confirmed that in the cracking of the blend the promotion of isomerization and hydrogen-transfer reactions is lesser than in the cracking of the VGO. Thus comparing the values obtained with both feedstocks, the isoparaffinicity of the naphtha obtained in the cracking of the blend cracking is remarkably lower than that of the VGO. This way, the maximum value obtained with the blend has been of 3.44 (for C<sub>5</sub> at 500 °C and 5 g<sub>cat</sub> g<sub>feed</sub><sup>-1</sup>), whereas for the VGO has been of 10.81 (for C<sub>6</sub> at 530 °C and 5 g<sub>cat</sub> g<sub>feed</sub><sup>-1</sup>).

Conversely, the olefinicity indexes of the naphtha from the cracking of the blend are higher than those from the cracking of VGO. In both cases, they increase with temperature and decrease with C/O ratio, since the hydrogen-transfer reactions are, respectively, disfavored and favored. Thus, the maximum C<sub>5</sub> and C<sub>6</sub> olefinicity values are reached at 560 °C and 3 g<sub>cat</sub> g<sub>feed</sub><sup>-1</sup> with values of 0.85 and 0.71, respectively, in the cracking of the HDPE/VGO blend and of 0.71 and 0.62, respectively, in the cracking of the VGO.

Table 4

Since the commercial interest of branched olefins is higher, the isoolefinicity index of naphtha is quite important. At 3 g<sub>cat</sub> g<sub>feed</sub><sup>-1</sup> the isoolefinicity values of both naphthas are similar. However, as C/O ratio increases the reduction of the index is more significant in the case of the naphtha obtained with the blend. Hence, the values at 7 g<sub>cat</sub> g<sub>feed</sub><sup>-1</sup> are remarkably lower than those of the naphtha from the cracking of the VGO. On the other hand, the isoolefinicity index of C<sub>5</sub> and C<sub>6</sub> families, i.e., the main ones, in general, decreases with temperature for both feedstocks.

The RON of the naphtha obtained in the cracking of the blend is, in general, lower than that obtained in the naphtha from the cracking of the VGO. In both cases, RON increases with temperature and shows a dissimilar behavior with C/O ratio. The same experimental

conditions ( $560\text{ }^{\circ}\text{C}$  and  $5\text{ g}_{\text{cat}}\text{ g}_{\text{feed}}^{-1}$ ) are required to achieve the maximum RON with both feedstocks, 105.6 with the HDPE/VGO blend and 105.5 with the VGO.

To sum up, the naphtha produced in the cracking of the HDPE/VGO blend has a remarkably different composition than that obtained with the VGO, despite the fact that just a 5 wt% of HDPE has been co-fed. Although the naphtha from the blend has a higher concentration of linear paraffins and olefins, has a lower concentration of iso-paraffins, which is compensated by the advantage of a lower concentration of aromatics. Therefore, its incorporation into the gasoline pool requires a less severe hydrotreatment in refinery than the naphtha fraction obtained in the cracking of the VGO.

It should be pointed out that aforementioned results about the composition of the gaseous and naphtha fractions, together with the effect of the temperature and C/O ratio on the composition of these fractions, are supplementary to those obtained in the scarce literature about the cracking of polyolefins dissolved in VGO [36,37]. Additionally, our results consolidate a favorable opinion about the prospects of this initiative, which can be applied without any additional issue than those commonly faced in refinery when different crude oils are treated or when secondary refinery streams, e.g., distillation residues or LCO, are co-fed together with VGO to FCC unit. Indeed, given the high contents of heavy molecules, metals and heteroatoms in these secondary refinery streams, these feeds produce more uncertainty than those expected with the co-feeding of polyolefins.

### 3.5. Economic interests of recycling plastics in FCC units

The use of refinery units for the large-scale recycling of wastes requires prior economic and technology studies. This work, which corresponds to the last mentioned ones, pursues the goal of assessing the incidence of co-feeding wastes in the yields and composition of obtained products. However, this type of studies may be complemented with other aspects

different from those studied in this work, such as the incidence of the co-feeding of polyolefins in the regeneration section of the FCC unit. On the other hand, economic studies are required to quantify the magnitude of the incentives that refineries will get to assume such a modification of the conventional feedstock. A detailed economic study requires accurate economic data of the costs derived from collection, segregation and transport stages of the waste plastics, as well as of the costs derived from the different reaction and separation stages involved in the production of fuels. Hence, this type of study is out of the scope of the present work. Nonetheless, the global economic aspects of the use of FCC units to valorize plastics are commented below, which complement the advantages collected in [Table 1](#).

Firstly, the recycling of polyolefins implies an increase of the availability of feedstock to FCC unit, together with a consequent save of crude oil. In addition, given the high capacity of FCC units (a standard unit treats 50 thousand barrels per day), the co-feeding of a 5 wt% of plastics studied in this work, will allow to valorize ca. 400 tons of polyolefins per day and to save the same amount of the current feedstock (VGO) and crude oil. As previously demonstrated, the co-feeding of a 5 wt% of plastics has not a negative incidence on the yield and composition of the products and, predictably, it will not require unconventional modifications of the operating conditions of the FCC unit, neither on the subsequent separation and reforming units. Moreover, the gradual co-feeding of new streams to conventional units is a strategy commonly followed by refineries. Indeed, FCC units are commonly depreciated and they are periodically (every 4 or 5 years) submitted to inspection and upgrade, being the period prior to inspection stage the selected one to treat new feeds. Likewise, the co-feeding of polyolefins would be initially tested in refinery with small concentrations. Therefore, it should be noted that

the results obtained in this work with a 5 wt% of polyolefins correspond to an extreme situation.

Furthermore, the effect of the co-feeding of polyolefins on the composition of the streams of products entails a reduction in the consumption of hydrogen and promotes the upgrading of secondary refinery streams in FCC units. This way, the co-cracking of polyolefins leads to the formation of more olefinic naphtha and LCO fractions, with a lower content of aromatics. Consequently, the hydrotreating of these product streams will require less severe conditions than those required by the products obtained in the cracking of conventional feeds. This fact implies a lower hydrogen consumption in hydrotreatment units and, predictably, the possibility of feeding higher contents of aromatic refinery streams, such as cuts from atmospheric distillation or cocker units, to FCC unit.

Economic profits derived from the reduction of emissions of pollutants must be also expected. Likewise, a lower crude oil consumption will bring about a positive environmental incidence given the reduction of carbon dioxide emissions that extraction and transport stages of the crude oil entail. This reduction of emissions will come with the corresponding tax rate reductions for the countries in charge of the oil exploration activity, leading to a presumably lower price of the barrel of crude oil.

In short, it consists on a technically viable initiative that for its industrial implementation must fulfill the interests of the society, in conjunction with the economic interests of the plastic recycling and oil refining sectors. The latter, is a private, mature and technologically consolidated sector, which has its own well-defined market submitted to severe regulations. However, this is a promising opportunity for refining sector to improve their society image by assuming the recycling of materials produced within the petrochemical industry. On the other hand, it could be expected that large-scale plastic



recycling will improve the economic viability of the waste plastics collection, segregation and transport enterprises, which made up a heterogeneous and less consolidated sector that commonly depends on local and regional institutions. Moreover, national institutions must supply economic motivation during the transition period towards the industrial implementation of the initiative to promote the coordination between the different implied industrial sectors.

#### **4. Conclusions**

The co-cracking under refinery conditions of a 5 wt% of HDPE with VGO has a remarkable effect on the conversion, distribution of products and composition of the LPG and naphtha fractions, showing positive synergies for their posterior valorization in refinery. Even though the presence of dissolved HDPE attenuates the cracking of the heavy components of the VGO in conditions of low severity (500 °C), this attenuation is reduced when the severity of the cracking increases resulting in a greater conversion of the blending at 560 °C and  $7 \text{ g}_{\text{cat}} \text{ g}_{\text{feed}}^{-1}$ . Additionally, the co-feeding attenuates the over-cracking reactions within the LPG and naphtha fraction. Hence, their yields are higher than those of the cracking of the VGO, whereas the yield of dry gases is lower. On the other hand, as HDPE dilution increases the H/C ratio and decreases the content of poly-aromatics in the feed, the yield of coke decreases.

The increase of the yield of the LPG fraction is a consequence of the increase of the yields of propylene and butenes. In addition, the co-feeding of HDPE has an important effect on the composition of the naphtha fraction, by increasing the concentration of n-paraffins and olefins. Even though the octane rating is lower when decreasing the concentration of iso-paraffins and aromatics, its composition is more favorable for its posterior

incorporation into the refinery gasoline pool because it requires a less severe hydrotreatment than the naphtha fraction obtained in the cracking of the VGO.

Consequently, obtained results expose the capacity of the FCC unit to recycle plastics, especially polyolefins, by means of its solution and co-cracking with typical feedstocks, such as VGO, improving the quality of obtained products. Other strategies to include the FCC unit in the valorization of plastics, such as that of combining a first stage of fast pyrolysis with the subsequent stage of co-cracking of the waxes, have the attractive aspect of performing the pyrolysis in geographically delocalized units. However, the simplicity of the co-cracking of dissolved polyolefins is a favorable factor for the industrial implementation of this initiative.

### **Acknowledgements**

This work has been carried out with financial support of the Ministry of Science, Innovation and Universities (MICINN) of the Spanish Government (grant RTI2018-096981-B-I00), the Basque Government (grant IT1218-19), the European Union's ERDF funds and the European Commission (HORIZON H2020-MSCA RISE-2018. Contract No. 823745).

The authors also acknowledge Petronor Refinery for providing the VGO and the catalyst used in this work.

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**Table 1.** Advantages of the co-cracking of polyolefins in refinery FCC units.

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***Properties of the FCC units***

Are commonly installed in refineries and are already depreciated units

Have a remarkable capacity (50 thousand barrels per day in a standard unit)

Have undergone great technological innovations in the reaction, stripping and regeneration sections, with the aim of increasing the versatility to treat different feeds (secondary refinery streams, among others)

Equilibrium catalysts are designed to treat heavy-molecular weight feeds to ensure high selectivity towards gasoline

Equilibrium catalysts may undertake numerous reaction-regeneration cycles

***Processing dissolved plastics in refineries***

Additional facilities are those required for dissolving polyolefins

The valorization of waste plastics is centralized in a refinery (waste-refinery)

The product streams may be incorporated into the pools of fuels

Already depreciated separation and reforming units are used

Final fuels may be marketed together with the current ones

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**Table 2.** Main properties of the vacuum gasoil (VGO) and the high-density polyethylene (HDPE).

Properties	VGO	HDPE
Density at 15 °C (kg L <sup>-1</sup> )	0.9272	0.9403
IBP-FBP (°C)	190–598	–
Average molecular weight (g mol <sup>-1</sup> )	405.3	46,200
Dispersity	–	2.89
Higher heating value (MJ kg <sup>-1</sup> )	42	43
Elemental analysis (wt%)		
C	86.60	86.00
H	12.00	14.00
N	0.23	–
S (ppm)	11700	–
Composition (wt%)		
Paraffins	8.49	–
Naphthenes	29.16	–
Mono-aromatics	20.88	–
Di-aromatics	16.36	–
Poly-aromatics	23.94	–

**Table 3.** Comparison of the olefinicity of the C<sub>3</sub>-C<sub>4</sub> families of LPG fraction obtained in the cracking of the HDPE/VGO blend and of the VGO at different temperatures and C/O ratios. The standard deviation of the results in triplicate experimental replicates is below  $\pm 2\%$  of the average value.

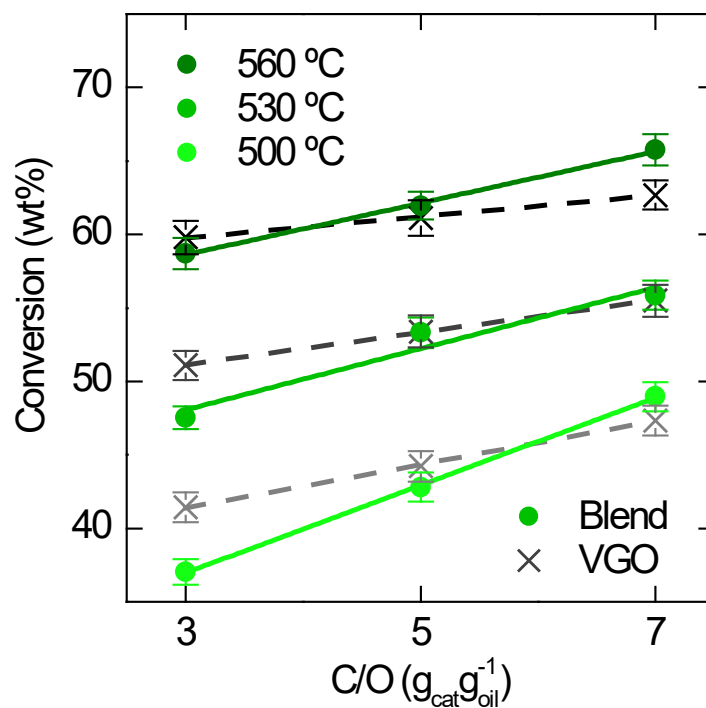
Olefinicity	T (°C)	HDPE/VGO			VGO		
		C/O=3	C/O=5	C/O=7	C/O=3	C/O=5	C/O=7
C <sub>3</sub> <sup>=</sup> / C <sub>3 Total</sub>	500	0.73	0.75	0.61	0.82	0.78	0.68
	530	0.75	0.77	0.75	0.80	0.76	0.68
	560	0.80	0.79	0.71	0.82	0.75	0.76
C <sub>4</sub> <sup>=</sup> / C <sub>4 Total</sub>	500	0.43	0.46	0.39	0.58	0.47	0.27
	530	0.59	0.60	0.61	0.55	0.50	0.37
	560	0.79	0.66	0.66	0.76	0.62	0.56

**Table 4.** Comparison of the different quality indexes of the naphtha obtained in the cracking of the HDPE/VGO blend and in the cracking of the VGO at different temperatures and C/O ratios. The standard deviation of the results in triplicate experimental replicates is below  $\pm 2\%$  of the average value.

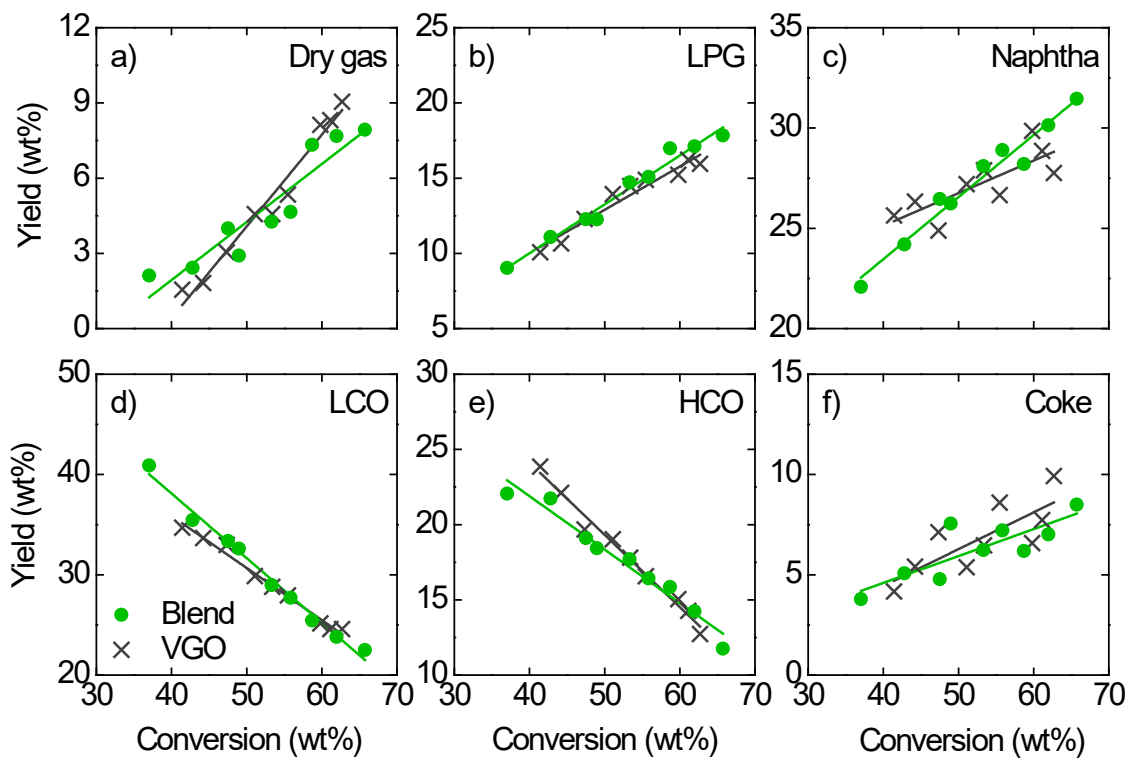
Isoparaffinicity	T (°C)	HDPE + VGO			VGO		
		C/O=3	C/O=5	C/O=7	C/O=3	C/O=5	C/O=7
i-C <sub>5</sub> /n-C <sub>5</sub>	500	1.89	3.44	3.22	7.46	8.67	9.09
	530	2.03	2.79	3.30	7.22	8.86	9.11
	560	1.62	2.88	3.81	6.20	6.93	7.31
i-C <sub>6</sub> /n-C <sub>6</sub>	500	1.89	2.91	2.44	7.89	8.91	7.10
	530	2.13	2.56	2.63	9.42	10.81	8.87
	560	2.49	2.67	2.92	7.83	6.86	6.76
i-C <sub>7</sub> /n-C <sub>7</sub>	500	1.93	1.67	1.61	10.20	9.10	6.32
	530	2.11	1.71	1.79	10.70	7.96	7.77
	560	2.06	1.93	2.11	7.94	6.31	5.21
i-C <sub>8</sub> /n-C <sub>8</sub>	500	1.10	0.43	0.47	5.54	5.04	2.43
	530	0.76	0.65	0.38	3.32	4.16	2.90
	560	1.16	1.48	1.03	3.24	2.99	3.32
<b>Olefinicity</b>							
C <sub>5</sub> <sup>=</sup> /C <sub>5</sub>	500	0.72	0.50	0.41	0.56	0.36	0.24
	530	0.77	0.61	0.53	0.61	0.43	0.34
	560	0.85	0.72	0.64	0.71	0.55	0.46
C <sub>6</sub> <sup>=</sup> /C <sub>6</sub>	500	0.68	0.46	0.43	0.46	0.28	0.25
	530	0.68	0.55	0.51	0.53	0.39	0.37
	560	0.71	0.64	0.59	0.62	0.57	0.52
<b>Branching of olefins</b>							
i-C <sub>5</sub> <sup>=</sup> /n-C <sub>5</sub> <sup>=</sup>	500	1.42	1.07	0.43	1.45	1.35	1.28
	530	1.41	1.02	0.65	1.18	1.25	1.04
	560	0.88	0.60	0.62	1.10	0.92	0.67
i-C <sub>6</sub> <sup>=</sup> /n-C <sub>6</sub> <sup>=</sup>	500	0.95	0.31	0.10	1.08	0.90	0.62
	530	0.84	0.44	0.15	0.67	0.63	0.33
	560	0.37	0.13	0.11	0.40	0.25	0.25
i-C <sub>7</sub> <sup>=</sup> /n-C <sub>7</sub> <sup>=</sup>	500	0.58	0.14	0.14	0.27	0.18	0.38
	530	0.99	0.22	0.13	0.32	0.42	0.34
	560	0.38	0.16	0.13	0.38	0.40	0.37
<b>RON</b>							
	500	100.2	97.6	98.9	102.0	101.6	103.3
	530	101.0	100.8	101.1	103.9	103.8	105.2

Isoparaffinicity	T	HDPE + VGO			VGO		
	(°C)	C/O=3	C/O=5	C/O=7	C/O=3	C/O=5	C/O=7
	560	103.9	105.6	105.1	105.4	105.5	105.2

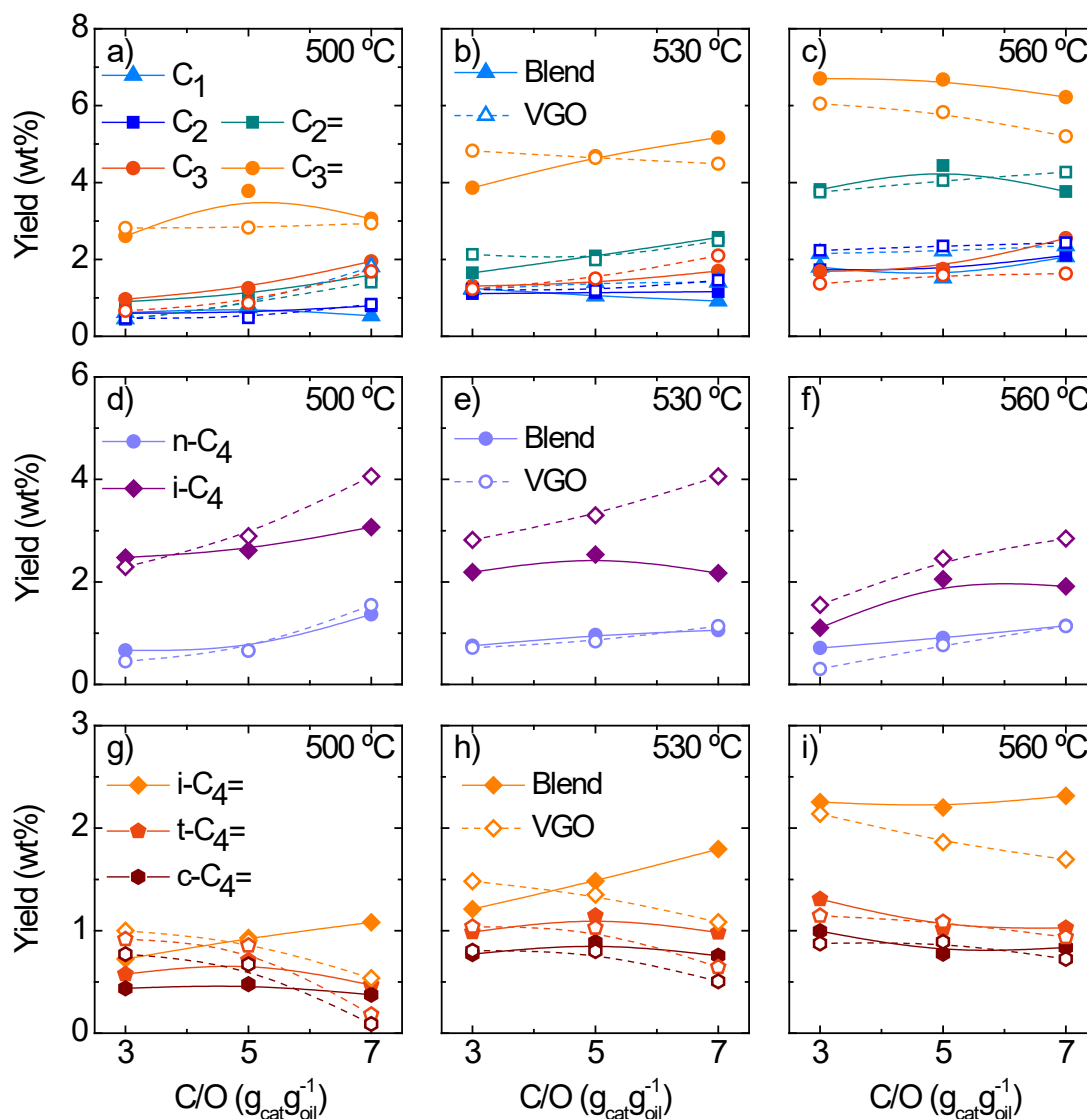




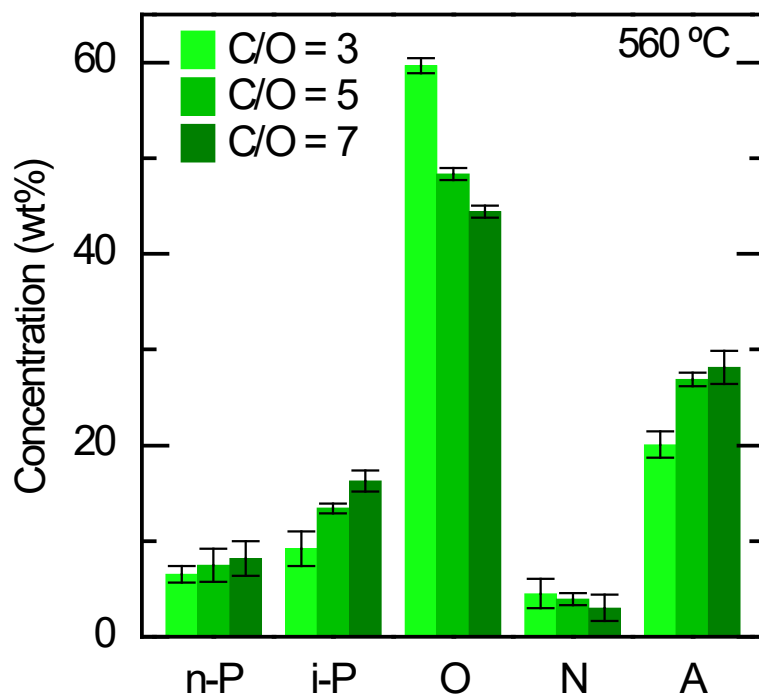
**Figure 1.** Evolution of conversion with C/O ratio in the cracking of the HDPE/VGO blend (green dots) and raw VGO (grey crosses) at different temperatures. The error bars represent the standard deviation of triplicate experimental replicates.



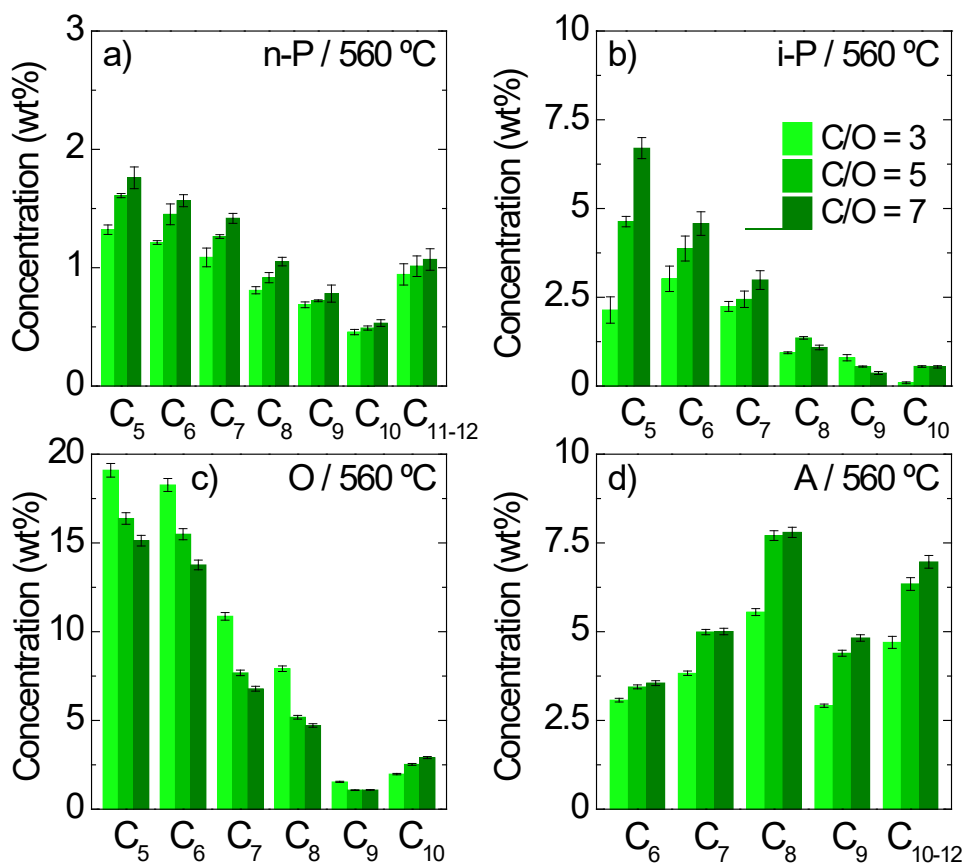
**Figure 2.** Evolution with conversion of the yields of dry gas (a), LPG (b), naphtha (c), LCO (d), HCO (e) and coke (f), in the cracking of the HDPE/VGO blend (green dots) and VGO (grey crosses). Reaction conditions: 500-560 °C; C/O ratio, 3-7  $\text{g}_{\text{cat}} \text{g}_{\text{feed}}^{-1}$ . The standard deviation of the results in triplicate experimental replicates is below  $\pm 2\%$  of the average value.



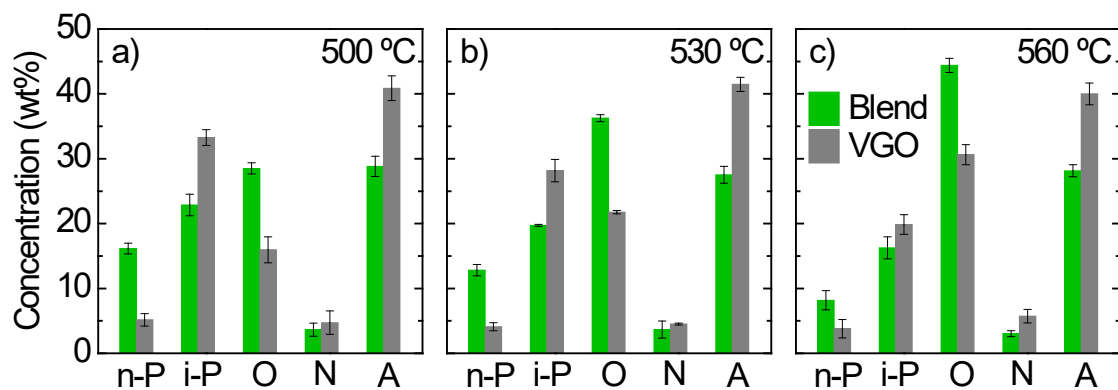
**Figure 3.** Evolution with C/O ratio of yields of C<sub>1</sub>-C<sub>3</sub> gases (a, b and c, which correspond to 500, 530 and 560 °C, respectively), butanes (d-f) and butenes (g-i), in the cracking of the HDPE/VGO blend (stuffed symbols) and VGO (empty symbols). The standard deviation of the results in triplicate experimental replicates is below  $\pm 2\%$  of the average value.



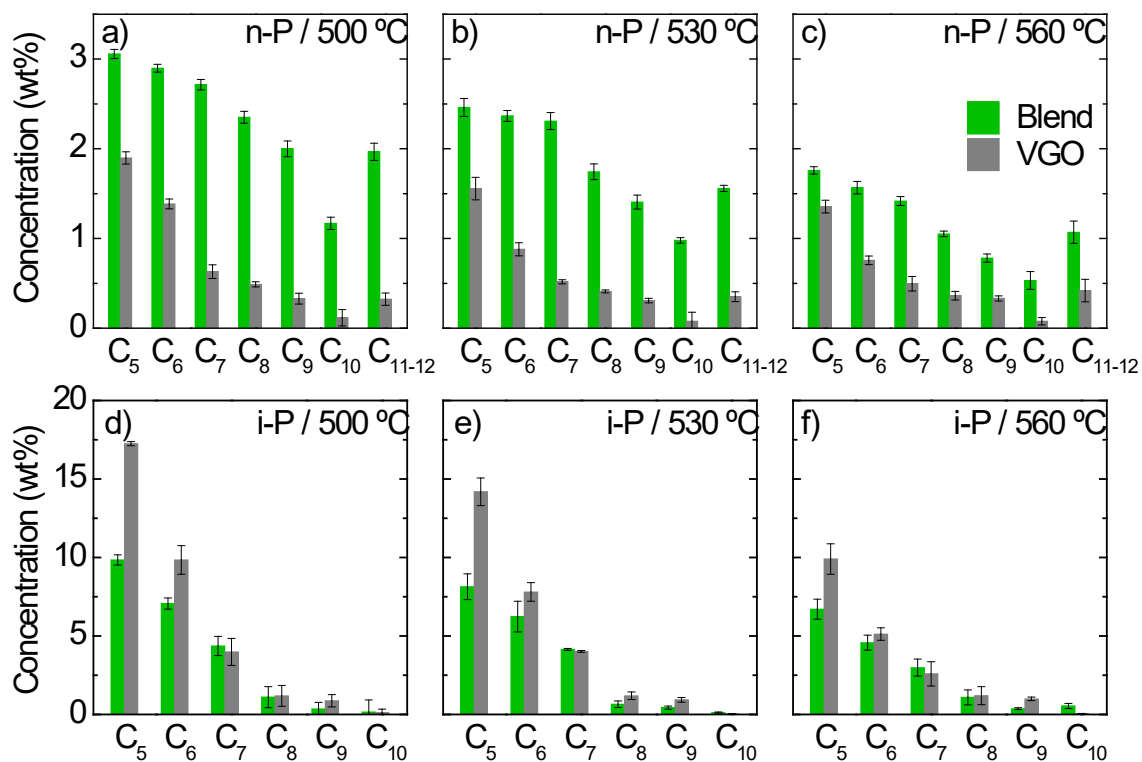
**Figure 4.** Effect of the C/O ratio on the composition of the naphtha fraction (concentration of hydrocarbon families) in the cracking of the HDPE/VGO blend at 560 °C. Key: n-P, paraffins; i-P, iso-paraffins; O, olefins; N, naphthenes; and, A, aromatics. The error bars represent the standard deviation of triplicate experimental replicates.



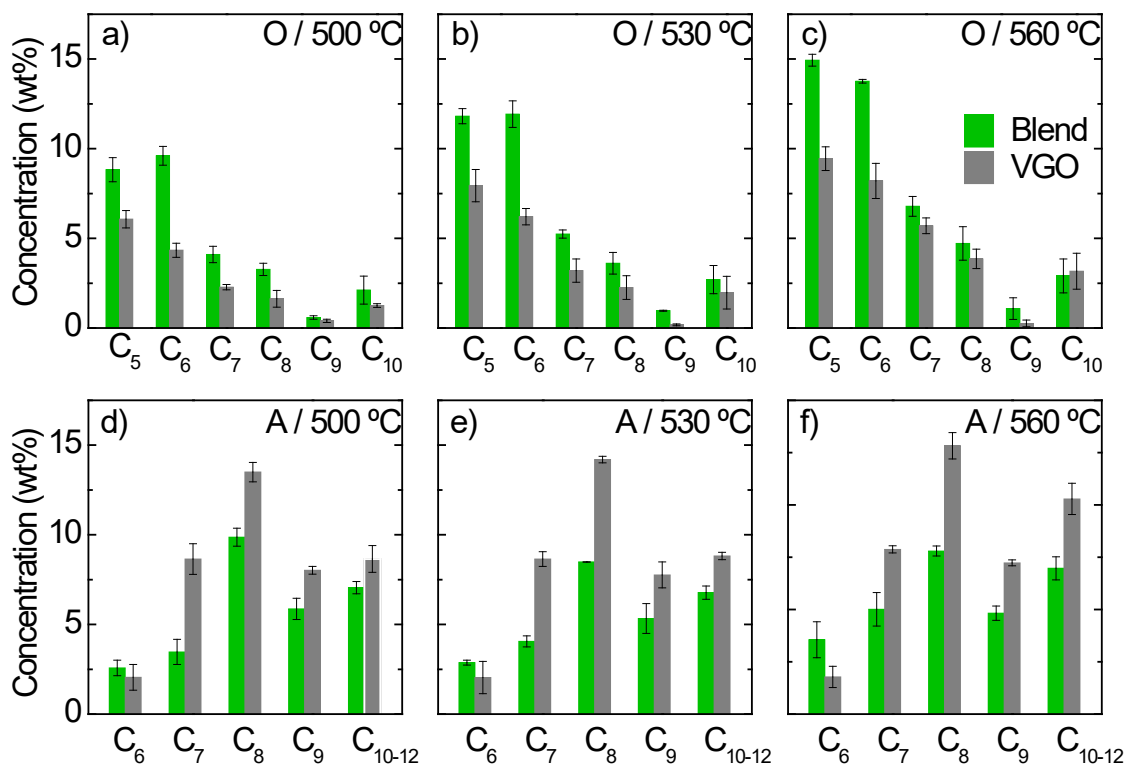
**Figure 5.** Effect of the C/O ratio on the composition of the n-paraffins (a), iso-paraffins (b), olefins (c) and aromatics (d) (grouped according to their number of carbon atoms) of the naphtha fraction obtained in the cracking of the HDPE/VGO blend at 560 °C. Key: n-P, paraffins; i-P, iso-paraffins; O, olefins; N, naphthenes; and, A, aromatics. The error bars represent the standard deviation of triplicate experimental replicates.



**Figure 6.** Comparison of the composition of the naphtha fraction obtained in the cracking of the HDPE/VGO blend of the VGO at a temperature of 500 °C (a), 530 °C (b) and 560 °C (c) and C/O ratio of 7  $\text{g}_{\text{cat}} \text{g}_{\text{feed}}^{-1}$ . Key: n-P, paraffins; i-P, iso-paraffins; O, olefins; N, naphthenes; and, A, aromatics. The error bars represent the standard deviation of triplicate experimental replicates.



**Figure 7.** Comparison of the composition of the n-paraffins (a-c) and iso-paraffins (d-f) in the naphtha fraction obtained in the cracking of the HDPE/VGO blend of the VGO at a temperature of 500 °C (a, d), 530 °C (b, e) and 560 °C (c, f) and C/O ratio of  $7 \text{ g}_{\text{cat}} \text{ g}_{\text{feed}}^{-1}$ . Key: n-P, paraffins and i-P, iso-paraffins. The error bars represent the standard deviation of triplicate experimental replicates.



**Figure 8.** Comparison of the composition of the olefins (a-c) and of the aromatics (d-f) in the naphtha fraction obtained in the cracking of the HDPE/VGO blend of the VGO at a temperature of 500 °C (a, d), 530 °C (b, e) and 560 °C (c, f) and C/O ratio of 7  $\text{g}_{\text{cat}} \text{g}_{\text{feed}}^{-1}$ . Key: O, olefins; and, A, aromatics. The error bars represent the standard deviation of triplicate experimental replicates.