Thermal and catalytic pyrolysis of a real mixture of post-consumer plastic waste: an analysis of the gasoline-range product

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Abstract

In this work, the thermal and catalytic pyrolysis of different types of plastic waste and a real mixture were investigated in a fixed-bed reactor over different catalysts (CaO, MgO, HY, HZSM-5). Important differences in gas, liquid, and solid yields were found as a function of polymer type. The highest gas yield was obtained with expanded polystyrene (52.3 %), and the maximum oil production with high-impact polystyrene (33.9 %), while polypropylene film led to the highest char release (17.5 %). Regarding the composition of the liquid oil, high-impact polystyrene showed the highest yield of gasoline-range product (426 g per kg of pyrolyzed plastic), mainly composed of aromatics compounds (90 %). The addition of catalysts increased the gas yield to the detriment of the oil produced. The effect was more evident for zeolite-type catalysts, i.e., the gas yield raised from 43.3 (non-catalytic) to 51.5 % (HZSM-5). Low influence on the oil composition, i.e., gasoline-range product, was detected. This can be explained by the fast deactivation of catalysts because of coke deposition. Only an increase in the fraction of gasoline in liquid oil was observed when low-cost catalysts (CaO and MgO) were used, without significant changes in the composition of this product.

Keywords: Plastic waste; Pyrolysis; Catalysts; Gasoline-range product; Hydrocarbon types.

1. INTRODUCTION

Today, the benefits of plastics are unquestionable: low cost, lightweight, aseptic, durable, resistant, and easy to mold. Unlike metals, they do not rust or corrode; most photodegrade and slowly break down into small fragments known as microplastics. Since the 1950s, their production, which relies heavily on fossil hydrocarbons, has overtaken the manufacture of any material due to the global shift from making durable plastics to single-use ones, which are discarded by the same year of manufacture [1]. According to recent estimations in Europe, only one-third of the collected post-consumer plastic waste (10.2 Mt) was sent to recycling facilities but over 23 % (6.9 Mt) was still sent to landfill [2]. Depositing plastic waste in a landfill does not mean eliminating the problem, but rather it can generate another one in the future. In this sense, plastic buried deep in landfills can leach harmful chemicals that spread into the soil and water. Also, some recent works have shown that microplastics that are generated in a landfill without sufficient protection can be transferred to the environment and could have a very negative effect on ecosystems [3–5]. The European Strategy for Plastics in a Circular Economy [6] proposes a series of key measures to improve the economy and quality of plastic recycling and reduce waste and littering, among which are: favor the use of recycled plastics and reuse and recycling against the landfilling or incineration, eradicate illegal and non-compliant landfills and use economic instruments to increase the cost of landfilling and incineration.

Although many sorting processes have been implemented, only plastic waste, especially rigid plastics composed of one type of polymer, can be recycled through mechanical procedures. However, many more contaminated or mixed dirty plastics and plastics made of multi-materials that cannot be mechanically recycled for technical or economic reasons are accumulated in landfills [7]. Chemical recycling offers a solution for these unrecovered plastic wastes incorporating them as secondary raw materials in different industrial ecosystems. Chemical recycling is, therefore, a complementary solution to mechanical recycling, as it can be used to process a broader scope of plastic waste that is currently unsuitable for mechanical recycling.

Pyrolysis is one of the most investigated chemical recycling technologies for the plastic waste [8]. In the last few years, many studies about the pyrolysis of different plastic waste have been published. Most pyrolysis studies have been carried out with individual plastics and mixtures. Particularly, thermal conversion by pyrolysis of polyethylene (PE),

both high density polyethylene (HDPE) and low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PCV), individually and in mixtures have been deeply examined [9–17]. For example, Rodríguez Lamar et al. [9] investigated the kinetic thermal pyrolysis of PP, HDPE, and LDPE. Also, the liquid fractions obtained from the pyrolysis were characterized according to ASTM standards and by gas chromatography. Williams and Williams [10] analyzed the thermal pyrolysis of mixed plastics to simulate the plastic composition of municipal solid waste (MSW) found in Europe and the interaction between polymers was investigated. Costa et al. [11] also examined the thermal pyrolysis of a plastic mixture derived from MSW containing PE, PP, PS, and small amounts of PET and PVC. The liquid fractions were analyzed using the gas chromatography-mass spectrometry technique and the effect of the presence of the different types of polymers on the hydrocarbons produced was discussed. Also, Singh et al. [12,13] analyzed the effect of heating rates, the residence time of volatiles in the reactor, and pyrolysis temperature on product yield and its composition on the pyrolysis of a post-consumer plastic waste mixture also composed of PE, PP, PS, PET, and PVC. Other authors analyzed the pyrolysis of PP under atmospheric and vacuum pressure at different temperatures and heating rates and reported volatiles composition as a function of pyrolysis conditions [14]. Recently, Rodríguez-Luna et al. [15] investigated the pyrolysis of HDPE in a two-step process to increase pyrolysis oil yield. The sequential process used in this study consisted of two pyrolysis steps, one focused on wax production and the other on oil yield operating parameters optimized based on statistical analysis. Other studies examined the effect of different types of plastic waste (PE, PP, PS, and PET) and their mixtures on the yield and quality of produced liquid oil from the pyrolysis process [16], even working with real streams of plastic waste rejected from the industrial plant [17].

In most cases, crude pyrolysis oils cannot be used directly, and many studies emphasized the need to upgrade the pyrolysis oils [18]. In this sense, fractional distillation, commonly used to separate petroleum oils, can be used to upgrade oil properties/composition. Some authors as Wiriyaumpaiwong and Jamradloedluk [19], studied the distillation of two pyrolytic oil samples derived from the pyrolysis of PE and mixed plastic wastes. Also, extensive research on producing determined valuable compounds from plastic waste pyrolysis has been widely conducted. For example, Jung

et al. [20] and Sarker and Rashid [21] pyrolyzed PE and PP under various reaction conditions and analyzed the content of benzene, toluene, and xylenes (BTX aromatics), which are very important petrochemical materials, in the oil product. For both PE and PP materials, it was found that the BTX aromatics content increased with the reaction temperature. Other authors examined the potential of liquid oil samples derived from the pyrolysis of plastic film waste as automotive diesel fuel. Distilled pyrolysis liquids in the diesel range and the liquid fractions were characterized according to automotive diesel standards [22]. Also, Baena-González et al. [23] reported compounds and materials that can be recovered from the distillation of pyrolysis oil obtained from PS. Other researchers completed a study to optimize liquid products obtained through refinery distillation bubble cap plate column [24]. These authors found important differences in product yield and characterization on each tray depending on the pyrolysis temperature. In addition, Demirbas [25] and Dobó et al. [26] pyrolyzed three plastic wastes (PE, PP, and PS) and their mixtures to obtain valuable gasoline-range hydrocarbons from the pyrolytic oil. Other researchers studied the hydrogen production from PE, PP, PS, and PET and their mixture [27].

Other options for improving the properties and composition of pyrolysis oils are co-pyrolysis and the use of catalytic materials in the process. Regarding co-pyrolysis, it is thermal pyrolysis involving two or more different materials as feedstock; in this option, the mixing ratio of the materials is one of the most important influencing factors. Regarding catalytic pyrolysis, although a wide variety of catalysts has been investigated, mainly zeolites (predominantly HZSM-5 and HY) with remarkable acidic character, high surface area, and high pore volume. Also, available low-cost materials such as bentonite or metal oxides (CaO and MgO) have been extensively applied in both in-situ and ex-situ catalytic pyrolysis patterns [28,29]. The lower cost of these materials compared to synthetic zeolites makes them competitive for real applications at a large scale. For example, some authors have enhanced the formation of benzene, toluene, and ethylbenzene (BTE) aromatics by using the ammonium-type ZSM-5 zeolite as a catalyst in the pyrolysis of expanded polystyrene (EPS) [30]. Elordi et al. [31] also used HZSM-5 supported on bentonite and alumina to pyrolyze HDPE, LDPE, and PP. Also, PE, PP, PS, and PET were catalytically pyrolyzed by Xue et al. [32]. The authors found differences in product distribution and composition at in-situ and ex-situ configurations and reported positive synergies between PE and PS or PE and PET. A simulated mixture

of plastics representing the plastic mixture found in municipal solid waste was pyrolyzed using spent zeolite from a fluid catalytic cracker (FCC) and HY, and HZSM-5 acidic zeolites [33], and authors reported that aromatic contents of oils increased with the presence of catalysts as well as increased the bed temperature. Especially, HY acidic zeolite promoted the formation of low molecular weight aromatic hydrocarbons. Also, co-pyrolysis of polycarbonate (PC) with PS was conducted to produce aromatic hydrocarbons using HZMS-5 as a catalyst [34]. A reaction temperature of 700 °C reaches a maximum content of aromatic hydrocarbons, and co-pyrolysis of PC with PS produced more monocyclic aromatic hydrocarbons. Other researchers studied the catalytic pyrolysis of individual PE, PP, PS, and PET and its mixture in the presence of CaO under a steam atmosphere. Authors reported that CaO enhanced the gas and liquid production from mixtures, and the wax content derived from PE and PP was reduced [35]. MgO and CaO were also used as catalysts for the pyrolytic conversion of PE and PP. These low-cost catalysts improved the conversion to liquid products, decreasing the gas and char yields and producing liquid results in the gasoline, diesel, and kerosene range was achieved [36].

Although thermal and catalytic pyrolysis of plastics is being studied individually and in blends, including by co-pyrolysis, few studies have been determined the possible interactions and synergic effects of the combination of polymers, especially coming from real post-consumer waste plastic that at the present time are being sent to landfills. In this work, the thermal and catalytic pyrolysis of a real mixture of post-consumer plastic waste comes from the rejected plastic fraction of non-selective collection of MSW was investigated over low-cost basic materials (CaO and MgO) and commercial acid zeolites (HZSM-5 and HY). The product yields of liquid oil of thermal and catalytic pyrolysis of individual plastics and the real mixture of plastics were analyzed. Analysis of hydrocarbon types in the gasoline-range product was specially examined in both thermal and catalytic pyrolysis. Specifically, the comparison performed between results of the evaluation of gasoline-range product derived from plastic pyrolysis of individual plastics and the real mixture is especially innovative. To the best of our knowledge, the present study is among the first ones to deeply investigate the influence of the polymer and catalyst, which can certainly affect the pyrolysis products, on the gasoline-range product.

2. MATERIALS AND METHODS

2.1. Raw material

The mixture of plastic waste used in this study came from the rejected plastic fraction of a mechanical biological treatment (MBT) plant in Granada (Spain). The mixture was composed of rigid polypropylene (PP), expanded polystyrene (EPS), high impact polystyrene (HIPS), polypropylene film (PP film), and polyethylene film (PE film). Before thermal and catalytic pyrolysis experiments, these polymeric fractions were identified by Near Infrared Spectroscopy (NIR) using a portable Panatec Thermo Scientific microPhazir AG analyzer with a wavelength range of 20400 – 1600 nm, separated, and subjected to a size reduction process (1-3 mm). Particularly, the received raw material showed an average composition (wt. %) of 56.10% of PP, 12.65% of PP film, 12.65% of PE film, 10.05% of EPS, and 8.55% of HIPS. Information about characteristics such as proximate and elemental analysis can be found in previous works [37,38] and a summary is provided in Table 1.

Table 1. Characteristics of raw materials. Data from [37,38].

	Analysis	PP	PP film	PE film	EPS	HIPS
Proximate	Moisture, %	0.00	0.20	1.00	0.00	1.80
	Volatile matter, %	99.3	99.0	95.5	99.8	88.9
	Ash content, %	0.70	0.70	1.00	0.10	7.60
	Fixed carbon, %	0.00	0.10	2.40	0.10	1.70
Elemental	C, %	82.92	83.54	77.61	91.69	66.47
	H, %	14.47	13.95	11.91	8.28	7.63
	N, %	0.16	0.12	0.10	0.11	0.14
	S, %	0.00	0.00	0.00	0.00	0.00
	O, %	1.75	1.69	10.38	0.00	17.84

2.2. Preparation and characterization of the catalysts

Available low-cost catalysts, CaO and MgO materials, were supplied by Scharlab S.L. and PanReac, respectively. The commercial acidic zeolites used were HZSM-5 zeolite (zeolyst ZSM-5, SiO_2/Al_2O_3 mole ratio = 30) and Y-zeolite (zeolyst Y, hydrogen, SiO_2/Al_2O_3 mole ratio = 5.2) both supplied by Alfa Aesar.

The catalysts were calcined under an air atmosphere at 550 ºC for 3.5 h in a muffle furnace (Nabertherm, L 3/11/B180 Model) before using to stabilize their chemical, structural and morphological properties. Although commercial catalysts used in this contribution are well-characterized by manufacturers, the morphological modifications of the samples after calcination were analyzed, i.e., surface area and pore volume by N_2 adsorption-desorption isotherms conducted at -196 ºC in an ASAP2429 device from Micromeritics. The total surface area was determined by the BET method, the total pore volume by the N_2 uptake at $P/P_0\sim0.99$, the microporous surface and pore volume from the t-plot method, and the average pore size from the DFT method.

2.3. Pyrolysis reactor and pyrolysis conditions

The pyrolysis experiments were performed on a horizontal laboratory-scale fixed-bed tubular reactor (internal diameter 4 cm and length 34.25 cm) R50/250/12 model of Nabertherm made of stainless steel 316 and integrated with a flowmeter to regulate the inert nitrogen flow, see **Figure 1**. The experiments were carried out with approximately 20 g of plastic waste placed in a closed 316 stainless steel tube (internal diameter of 27.25 cm and 30.6 cm of length) with a chimney hole at a heating rate of 10 ºC·min^{-1} from room temperature to 500 ºC determined as optimum temperature for maximize liquid yield in a previous work [39] and with a constant flow rate of 0.8 L·min^{-1} of N_2. Reached pyrolysis temperature, kept the reactor at this temperature for 60 min. Then, the pyrolysis test was finished; the reactor was cooled under a low nitrogen flow of 0.2 L·min^{-1} until room temperature was achieved. When used, the catalyst (1 g) was placed in a basket at the outlet line of the reactor but within the radiant zone.
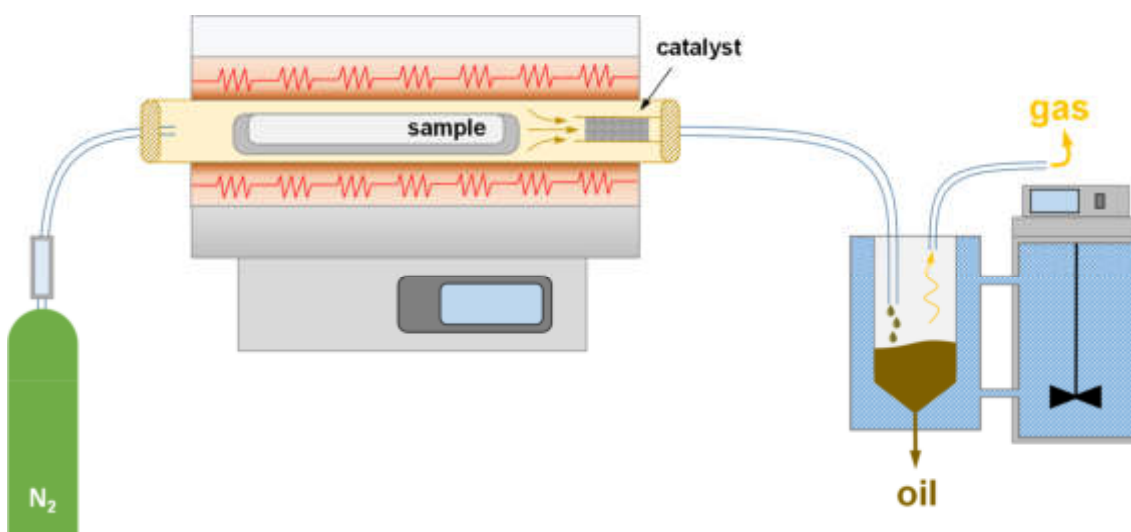

Figure 1. Representation of the installation used for the pyrolysis experiments.

Regarding the sampling of the products, the liquid fraction was collected using an ore-weighted glass receiver submerged in a liquid bath at -7 ºC, and the solid product was taken from the steel tube when the reactor was cooled.

The solid residue and the liquid products were directly weighted, and their yields were determined according to the following equations (gas yield by difference to 100%):

$$\eta_l = \frac{m_l}{m_m} \cdot 100 \qquad\qquad (1)$$

$$\eta_s = \frac{m_s}{m_m} \cdot 100 \qquad\qquad (2)$$

$$\eta_g = 100 - (\eta_l + \eta_s) \qquad\qquad (3)$$

where m_m, m_l and m_s are the weights of the plastic sample, liquid, and solid products, respectively, and η_l, η_s and η_g are the yields of liquid, solid, and gases, respectively. Experiments were conducted in triplicate, and the average value obtained led to a relative standard deviation inferior to 5 %.

2.4. Liquid product analysis

2.4.1. Analytical procedure

The identification of the components of the liquid fraction was carried out by gas chromatography (Agilent 8860 model) coupled to a triple-quadrupole mass spectrometer detector (Agilent 5977 model) with analysis scan speed ≤ 20000 Da·s^{-1} and ionization energy by the electronic impact of 70 eV. The column used was a Phenomenex with a nonpolar phase ZB-5ms (30 m, 0.25 mm internal diameter, and 0.25 µm of fill thickness). The oven temperature was programmed in two modes with initial temperatures of 40 and 42 ºC for 5 and 4 min, injector temperature of 240 ºC in both ways, and final temperatures of 240 and 320 ºC for 6 and 4 min with 15 and 6 ºC·min^{-1} gradients, respectively. The samples were weighed and diluted in 1 mL of chloroform and injected in split mode (10:1 for gasoline-range product and 5:1 for pyrolytic oil) at a constant flow of Helium of 1 mL·min^{-1}.

2.4.2. Simulated distillation (SD)

The determination the distribution of the boiling range of the compounds identified in the chromatograms of the gasoline fraction and pyrolytic oils was performed using D7096-19 and D2887-19a standard test methods of ASTM, respectively [40,41]. Synthetic mixtures of pure liquid hydrocarbons encompassing the boiling range of both

analytical techniques were used to determine reference retention times. The referential compounds were also confirmed using the National Institute of Standards and Technology (NIST) mass spectrum library database (NIST 08).

To calculate the boiling point based on the retention time of the compounds in the samples, the referential times and boiling points of the referential compounds were used according to the following equation:

$$BP_x = \left(\frac{BP_2 - BP_1}{RT_2 - RT_1}\right) \cdot (RT_x - RT_1) + BP_1 \tag{4}$$

where BP_1, BP_2 and RT_1, RT_2 are the boiling point and retention times of referential compounds, and BP_x and RT_x are the boiling points and retention times of the compounds in the sample.

The boiling range distribution was reported as a function of weight percent distilled and the following products were analyzed according to ASTM designation D5154/D5154M-18 [42]: gasoline product, C_5 compounds through compounds boiling up to 216 ºC, the light cycle oil (LCO) product defined to have a boiling point range of 216 °C to 343 °C and the heavy cycle oil product (HCO) determined to have a minimum boiling point of 343 °C.

2.4.3. Hydrocarbon types in the gasoline-range product

The total concentration of total paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes, indans, tetralins and naphthalenes in the gasoline-range product was determined by the standard test method ASTM D2789-95 by mass spectrometry, based on the summation of characteristic mass fragments [43].

2.5. Coke deposition on the catalysts

Coke originates from undesirable side reactions and covers surface sites, ultimately blocking pores. It is a mixture of solid and non-volatile carbonaceous compounds which may include alkanes, alkenes or cyclic and aromatic molecules from feed or generated as an intermediate. To determine the coke yield on the catalysts, continued stripping and subsequent combustion of catalysts were carried out in a PerkinElmer TGA thermobalance STA6000 model. Approximately 20 mg of the spent catalyst was introduced in the thermobalance with a constant flow of 20 mL·min^{-1} of nitrogen from room temperature to 500 ºC at a heating rate of 15 ºC·min^{-1}. Then, the desired temperature was maintained for 30 min, followed by flash combustion up to 550 ºC. The weight

percentages of volatile products were calculated and added to their respective cuts in the liquid product. In contrast, the total mass of the non-volatile fraction of coke was calculated according to equation 5:

$$\eta_c = \frac{m_i - m_f}{m_f} \cdot 100 \tag{5}$$

where η_c is the coke yield, and m_i and m_f are the mass of the sample at the beginning and end of the combustion stage, respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization of the catalysts

Table 2 shows the textural characterization of the different catalysts analyzed by N_2 adsorption-desorption isotherms after thermal treatment at 550 ºC. According to the IUPAC classification of physisorption isotherms, depicted in **Figure S1**, all the materials studied can be classified as type IV whose capillary condensation is accompanied by hysteresis loops of type H3, for basic low-cost catalysts, i.e., CaO and MgO and type H4, for acid zeolite-type catalysts [44]. The surface area and pore volume of CaO displayed the typical low values reported in the literature, in which the temperature does not considerably affect the textural properties [45]. The surface area of MgO was higher than CaO, with a remarkable mesoporous character as deduced from the porous size distribution, see **Figure S2**. Although MgO can be prepared with a more developed surface area, the value obtained in this case for the commercial formula treated thermally is in accordance with the reported for some MgO prepared after precipitation of hydroxide precursor formulas [46]. The acid zeolite-type catalysts, HY and HZSM-5, gave the highest micropore volume and surface area values. Particularly, the hieratically HY zeolite led to an extraordinarily high surface area and well-developed microporosity, i.e., over 90%, as reported from some ordered zeolite structures [47]. In this case, the HY samples presented a high contribution of micropores of *ca.* 19 Å. The HZSM-5 displayed lower values within the range expected for this zeolite [48,49].

Table 2. Textural properties characteristics of the different catalysts.

catalyst	S_{BET} $(m^2 \cdot g^{-1})$	S_{MP} $(m^2 \cdot g^{-1})$	S_{ext} $(m^2 \cdot g^{-1})$	V_T $(cm^3 \cdot g^{-1})$	V_{MP} $(cm^3 \cdot g^{-1})$	Average pore size (Å)
MgO	58	2	56	0.131	< 0.001	90
CaO	5	0.1	5	0.011	< 0.001	90

HY	1384	1274	110	0.639	0.432	50
HZSM-5	488	440	48	0.204	0.147	31

S_{BET}: specific BET surface area; S_{MP}, micropores specific surface area by t-plot method; S_{EXT}: external specific surface area as the difference of S_{BET} and S_{MP}; V_T: total pore volume from N_2 uptake at $P/P_0 \sim 0.99$; V_{MP}: volume of micropores by t-plot method; average pore size by DFT method

3.2. Effect of type of polymer on thermal pyrolysis performance

3.2.1. Effect of type of polymer on product yields

Figure 2 shows the gas, liquid, and solid yields resulting from the pyrolysis of individual studied plastic waste. EPS was the polymer that produced the highest yield of gas (52.3%), followed by PP film (48.7%), PP (45.1%), PE film (38.1%), and HIPS (31.2%). Regarding the solid (char) yield, PP film, HIPS, and PE film were the plastic waste that generated more solids (17.5%, 13.4%, and 10.1%, respectively). About the liquid product, PP film generated a reduced amount of liquid (33.9%), while HIPS showed the highest liquid yield (55.5%). In addition, although some of the studied polymers (PP and PP film and EPS and HIPS) have the same thermoplastic base, significant differences in product yields were observed, perhaps due to different manufacturing processes; for example, EPS is prepared by impregnation with a blowing agent, such as isopentane, while HIPS is synthesized by emulsion polymerization in styrene-butadiene latex [50]. Also, the HIPS plastic sample used in this work mainly came from yogurt packaging, and it was pyrolyzed with all the other materials from yogurt labels, i.e., painted paper.

If the theoretical (calculated yield according to the quantities of polymers present in the mixture) and real (experimental result obtained) product yields are compared, gas and char yields decreased from 44.2% to 43.4% (about 1.9 %) and 8.1 to 6.3% (around 22.8 %), respectively. In contrast, the production of the liquid product increased from 47.7 to 50.4 %, approximately an increase of 5.6 %.
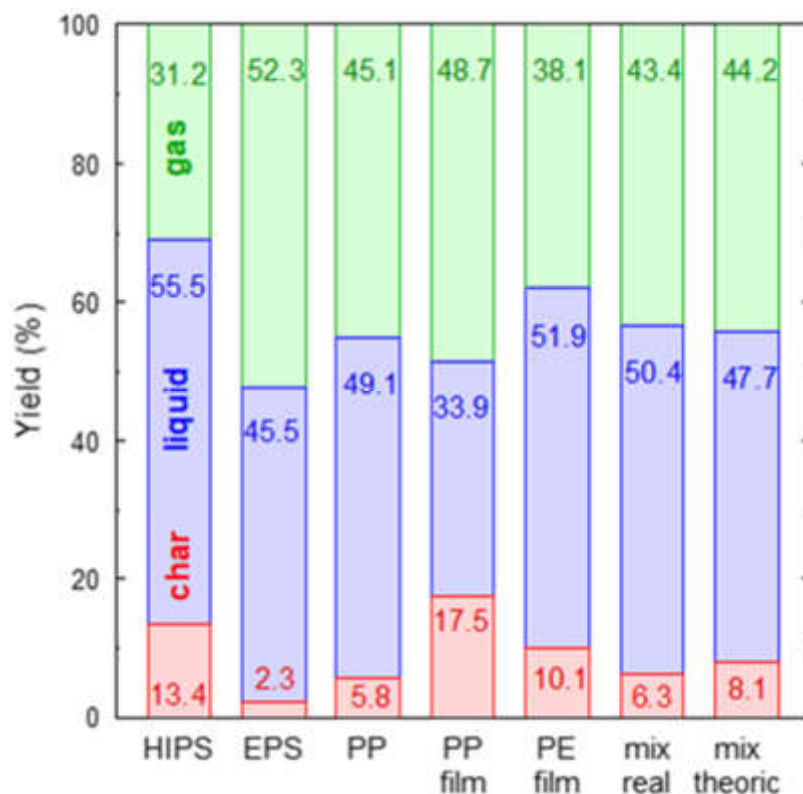
Figure 2. Gas, liquid, and solid yields as a function of polymer type.

In addition to the type of polymer (feedstock composition), other variables such as temperature, heating rate, particle size, use of catalyst, type of reactor, and type of system for the collection of the different products, can influence the product yields. Therefore, very different data can be found in the literature. **Table S1** summarizes product yields found by other researchers on thermal and catalytic pyrolysis of plastic waste. For example, in the thermal pyrolysis of EPS waste, Verma et al. Field [30] reported a maximum liquid yield of 94.4% at 650 ºC. Other authors, by pyrolyzing a mixture of HDPE, LDPE, PS, PP, PET, and PVC at 700 ºC, reported a liquid yield of around 75%, about 9 % of gas, and a char yield of approximately 2 % [10]. Also, Inayat et al. [51] pyrolyzed PS at 400 ºC and 500 ºC, obtaining around 64 % and 76 % of liquid product, respectively. Similarly, a study of thermal pyrolysis of LDPE, PP, and their mixtures was done by Anene et al. [52] in a batch pyrolysis reactor at 460 ºC, obtaining a liquid yield of 86 % for PP and a liquid yield of 96 % for LDPE. Additionally, López et al. [17] studied the pyrolysis of a complex combination of HDPE, PP, PS, EPS, PET, PVC, PE film, PP film, and other packing materials (blister, tetra-brick, Al film, Al, iron, etc.) at 500 ºC and obtained approximately the same yield data of liquid (53 %), gas (41.5 %),

and solid (5.5 %) than those reported here. Also, Williams and Williams [53], in the pyrolysis of LDPE, obtained a liquid yield of 45.3 % at 500 ºC.

3.2.2. Effect of type of polymer on simulated distillation boiling points

The simulated distillation curves of the liquid product obtained from the pyrolysis of the individual plastic wastes and their mixture are shown in **Figure 3**. Also, **Table 3** reports the yields of gasoline, light cycle oil (LCO), and heavy cycle oil (HCO) products (as a mass percentage). The trend of the curves suggested that liquid product from pyrolysis of HIPS presented lower volatilization temperatures since, in general, higher distilled mass fractions were reached at different temperatures, mainly between 130 ºC and 400 ºC. In opposition, the simulated distillation curve of PE film showed a low percentage of the gasoline-range product as higher boiling temperatures were needed to reach high distilled mass fractions; therefore, about 70% of the liquid was an HCO-range product. In addition, similar pattern curves were observed for PP, PP film, and the mixture of plastics with slight differences in yields of gasoline, LCO, and HCO-range products. Finally, EPS showed a different profile with similar product yields of gasoline and LCO-range and a lower yield of HCO-range.

Regarding the impact of the combination of the different plastic materials on gasoline, LCO, and HCO production, the mixture of plastic waste produced an average value of approximately 20 % more gasoline-range product than that which would be obtained as a proportional balance of the gasoline got from the individual plastic waste pyrolysis. Also, making the same evaluation, an average reduction of LCO and HCO of around 12 % and 14 % was observed from the theoretical data from mixing LCO and HCO produced from the individual plastic pyrolysis, respectively.
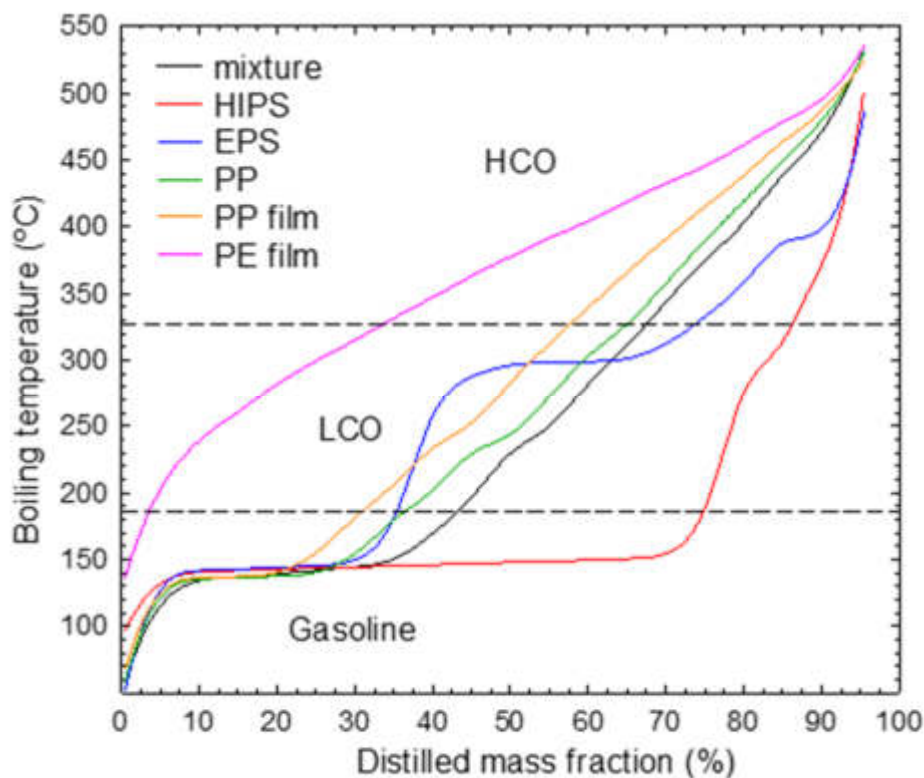
Figure 3. Boiling temperature as a function of distilled mass fraction (simulated distillation) of the liquid fraction from thermal pyrolysis of the mixed plastic waste and their residual polymers.

Table 3. Gasoline, LCO, and HCO products yields (mass %) in thermal pyrolysis (non-catalytic) of post-consumer plastic waste

Plastic-type	Gasoline-range	LCO-range	HCO-range
Mixture (theoretical)	39.7	25.2	35.1
Mixture (experimental)	47.7	22.1	30.2
HIPS	76.8	11.3	11.9
EPS	37.3	40.0	22.7
PP	42.4	25.3	32.2
PP Film	36.8	24.0	39.2
PE Film	7.2	23.3	69.5

Average values with a relative standard deviation inferior to 5%.

Finally, **Table 4** reports the yields of the different types of products obtained from each polymer and the mixture studied in this work. The major yield was observed for the gasoline-range product in oils from pyrolysis of HIPS, PP, and the mix of plastics with values ranging between 235.35 and 426.2 g·kg^{-1} plastic. However, deficient gasoline production (40 g·kg^{-1} plastic) was observed in liquid from PE film pyrolysis due to higher bottoms (HCO) output uncracked. In general, wax is the main product obtained in the thermal pyrolysis of polyolefins at moderate temperatures [53]. Consequently, many

authors have reported the greater production of waxes, depending on the thermal pyrolysis conditions, in the pyrolysis of the PE [54,55].

Regarding LCO-range product yield, it was higher in the liquid of thermal pyrolysis of EPS (222.0 g·kg⁻¹ plastic) and lower in the case of HIPS pyrolysis (62.7 g·kg⁻¹ plastic). Finally, HCO-range product values *ca.* 66.0 (HIPS) and 385.7 (PE film) g·kg⁻¹ plastic was found. As indicated before, a high amount of heavy products was expected for PE film pyrolysis since the "liquid" obtained as the product was wax.

Table 4. Gasoline, LCO, and HCO products yields (data in g·kg⁻¹ plastic) in thermal pyrolysis (non-catalytic) of post-consumer plastic waste.

Plastic-type	Gasoline-range	LCO-range	HCO-range
Mixture	240.4	111.4	152.2
HIPS	426.2	62.7	66.0
EPS	207.0	222.0	126.0
PP	235.3	140.4	178.7
PP Film	204.2	133.2	217.6
PE Film	40.0	129.3	385.7

Average values with a relative standard deviation inferior to 5%.

Dobó et al. [26] also studied the gasoline production from pyrolytic oil of different mixtures containing HDPE, LDPE, PP, and PS, representing the plastic demand in Hungary, the EU, and the world. The gasoline-range product was obtained by atmospheric distillation with a yield of 473−512 g·kg⁻¹ solid waste. These authors attributed the enhanced gasoline yield to the installation design that recirculates high boiling point components into the reactor for further molecule scission. The researchers also reported an increase in gasoline-range product yield when the proportion of PS was raised. This result has been observed by the high gasoline yield obtained for HIPS material in this work.

3.2.3. Effect of the type of polymer on hydrocarbon types in the gasoline-range product

The gasoline-range product has been analyzed in the type of polymer pyrolyzed. The simulated distillation curves of this product are shown in **Figure 4A**. For analogy with hydrocarbons present in crude petroleum, the gasoline-range product was first classified into three general types: paraffins, naphthenes, and aromatics (**Figure 4B**), and then, a more detailed categorization was performed into naphthalenes, indans, or tetralins, alkylbenzenes, paraffins, monocycloparaffins, and dicycloparaffins (**Figure 4C**).

Some significant differences were observed in the composition of the gasoline-range product obtained by thermal pyrolysis of different types of polymers. The yields of aromatics, paraffins, and naphthenes significantly varied between HIPS and EPS plastics and polyolefins (PP, PP film, PE film) and the mixture of plastics. Especially, thermal pyrolysis of HIPS and EPS showed a high yield of aromatic compounds, reaching a value of 89.8 % and 83.5 % in gasoline derived from HIPS and EPS materials, respectively. Conversely, PP, PP film, PE film, and the mixture of plastics showed a high yield of naphthenes with values ranging between 50.3 and 58.9 %.
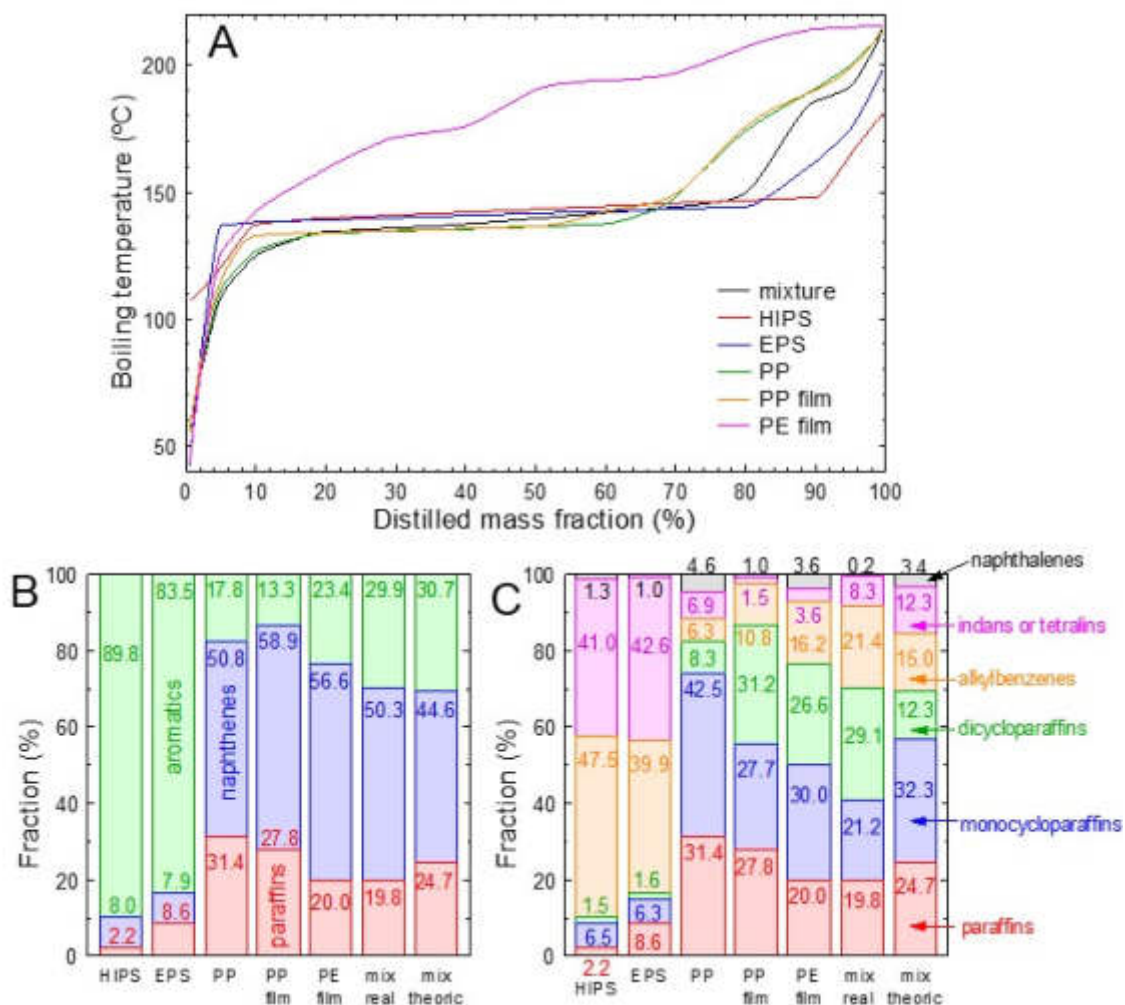
Figure 4. Simulated distillation (A), general hydrocarbon group distribution (B) detailed hydrocarbon groups (C) of the gasoline-range product obtained from the thermal pyrolysis of the mixed plastic waste and their individual components.

In gasoline-range products obtained from pyrolysis of different mixtures of LDPE, HDPE, PP, and PS, Dobó et al. [26] reported that between 11.13 and 15.14 % of paraffins, between 8.14 and 9.70 % of naphthenes and between 18.74 and 21.94 % of aromatics. Also, Miskolczi et al. [56], from the determination of the composition of liquid products

obtained from the thermal pyrolysis at 450 ºC of a mixture of HDPE (90 %) and PS (10 %), reported that gasoline-range product contained 46.1 % of paraffins and 11.9 % of aromatics.

Finally, the feasibility of plastic pyrolysis processes may be improved if the derived products are dissolved and converted into suitable feedstock streams for refinery process units. The main advantage is the use of amortized units and the subsequent treatment of the products together with ordinary refinery products [57]. In this sense, if the distribution of the gasoline-range derived products (total paraffins, naphthenes, and aromatics) is compared to the composition of commercial petroleum products, the gasoline of oil from pyrolysis of PP and PP film (paraffins: 27.8-31.4 %, naphthenes: 50.8-58.9 %, aromatics: 13.3-17.8 %) showed a very close composition to the heavy fossil naphtha and could be sent to a hydrotreatment or catalytic reforming to convert low-octane hydrocarbons into more valuable high-octane components, producing more valuable aromatics such as benzene, toluene, and xylenes (BTX). However, the composition results of the oils derived from thermal pyrolysis of HIPS (paraffins: 2.2%, naphthenes: 8.0%, aromatics: 89.8%) and EPS (paraffins 8.6%, naphthenes: 7.9%, aromatics: 83.5%) showed a more comparable composition of reformed naphtha which are directly available for the production of aromatic components [58].

3.3. Effect of type of catalyst on catalytic pyrolysis performance

3.3.1. Effect of type of catalyst on product yields

Figure 5 shows the effect of the presence of a catalyst on the product yields, including the coke deposition, obtained from the catalytic pyrolysis of the studied mixture of plastic waste. In general, an increase in the gas yield and a decrease in liquid output were detected. Especially the effect is more evident for zeolite-type catalysts (HY and HZSM-5). Regarding coke formation, similar coke deposition was observed for all tested catalysts (among 2.4-6.3 %). Coke is the main drawback in the catalytic pyrolysis of plastics. It is an effect that should be minimized since it inhibits the catalytic activity and increases the costs for the regeneration of the catalyst [59]. Xue et al. [32] in the ex-situ catalytic pyrolysis at 600 ºC of PE, PP, PET, and PS over HZSM-5 zeolite or Hidalgo et al. [36] in the catalytic pyrolysis of PE and PP over CaO and MgO reported similar coke deposition data.
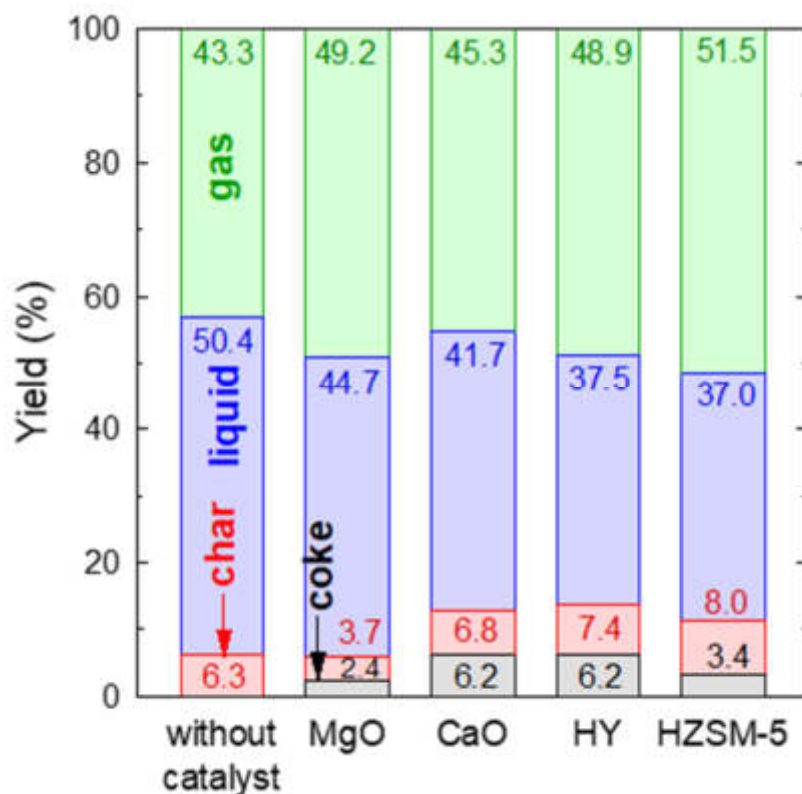
Figure 5. Gas, liquid, and solid yields as a function of catalyst.

Other authors also reported gases, liquid, and solid yields, of catalytic pyrolysis of different plastics (see **Table S1**). For example, Verma et al. [30] performed the catalytic pyrolysis of EPS waste at different feed/ZSM-5 ammonium catalyst ratios and, under the same experimental conditions of this work, obtained approximately 1 % of char, 26 % of gas, and 76 % of liquid products. Also, the catalytic pyrolysis of PS over MgO was performed at 500 ºC by Inayat et al. [51], leading to a liquid yield of approximately 90 %. Other researchers, using MgO and CaO as catalysts, reported conversion to liquid products during the pyrolysis of PE and PP between 57.3 and 79.6 % depending on the polymer and the catalyst used (PE-CaO: 57.3 %; PE-MgO: 71.8 %, PP-MgO: 78.6 %, PP-CaO: 83.8 %). Regarding the char yields, these authors reported yields of 10.3 % (PP-MgO), 6.6 % (PP-CaO), 21.5 % (PE-MgO), and 15% (PE-CaO) [36]. Anene et al. [52], in the catalytic pyrolysis of mixtures LDPE/PP at 460 ºC using a patented zeolite, found that an increase in PP proportions decreased the liquid yields and increased the gas formation. Their values were similar to those obtained in our work. Also, Miskolczi et al. [60] investigated the catalytic degradation of PE (90 %) and PS (10 %) in a batch reactor over FCC, ZSM-5, and clinoptilolite, between 410 – 450 ºC with 2 % of ZSM-5 at 430 ºC, reported a yield of solids of approximately 9 %, a liquid yield of 77 % and gas yield

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of 14 %. Other researchers, Onwudili et al. [33], carried out catalytic pyrolysis of a mixture of plastics, including HDPE (19.0%), LDPE (43.0 %), PP (8.0 %), PS (15.0 %) and PET (15.0 %), in a fixed bed reactor at 500 ºC over spent catalyst from FCC, HY, and HZSM-5 zeolites and obtained high liquid yields (FCC: 72 %, HY: 73 %, HZSM-5: 72 %). Finally, López et al. [17] studied catalytic pyrolysis over HZSM-5 with a complex mix of HDPE, PP, PS, EPS, PET, PVC, PE film, PP film, and other packing materials such as blister, tetra-brick, Al film, Al, iron, etc., at 440 ºC. Particularly 92.3 % of thermoplastics where PE film (50.55 %), which was the highest proportion, followed by HDPE (13.44 %), PP (9.63 %), PS (6.6 %), PP film (4.92 %) PVC (4.28 %) and PET (2.88 %). These authors obtained approximately an equivalent value of solid yield (6.5 %), a slightly low value of liquid yield (41.5 %), and a slightly higher yield of gases (49.9 %) than this work.

3.3.2. Effect of type of catalyst on simulated distillation boiling points

The simulated distillations of liquid products derived from thermal and catalytic pyrolysis of the mixture of plastics are shown in **Figure 6**. In all the liquids, the predominant product was gasoline, with yields between 57.7 % (MgO) and 45.3 % (HZSM-5 zeolite). Comparable gasoline yields were obtained by Hidalgo et al. [36] using MgO and CaO. Also, Anene et al. [52] in catalytic pyrolysis with zeolite at 460 ºC, obtained a similar gasoline yield (45.6 %).

The results also suggest that the main differences between the liquids of pyrolysis were obtained in LCO and HCO-range products. Especially, low-cost MgO and CaO catalysts reduced the volatilization temperature of the components of these products compared to those of thermal pyrolysis. However, both studied zeolite-type catalysts (HZSM-5 and HY) showed a lower distilled mass fraction for a determined boiling temperature until approximately 350 ºC and a very low increase of distilled mass fraction at temperatures higher than 350 ºC, if compared to the curve of the liquid obtained from the thermal pyrolysis, i.e., the non-catalytic test. Other authors, like Miskolczi et al. [60], did not find significant differences in the composition of the liquids obtained by catalytic pyrolysis of HDPE and PS over HZSM-5. The convenience of using LDPE, PP, PVC/LDPE, and PVC/PP in the hydrocracking unit of a refinery was investigated by Ucar et al. [61] over different catalysts at 425-450 ºC. For example, the blends of PE with vacuum gas oil (VGO) on HZSM-5 showed changes in distillation curves compared to the distillation

curve of the liquid obtained in the thermal pyrolysis, reducing or increasing the boiling points depending on the analyzed temperature.
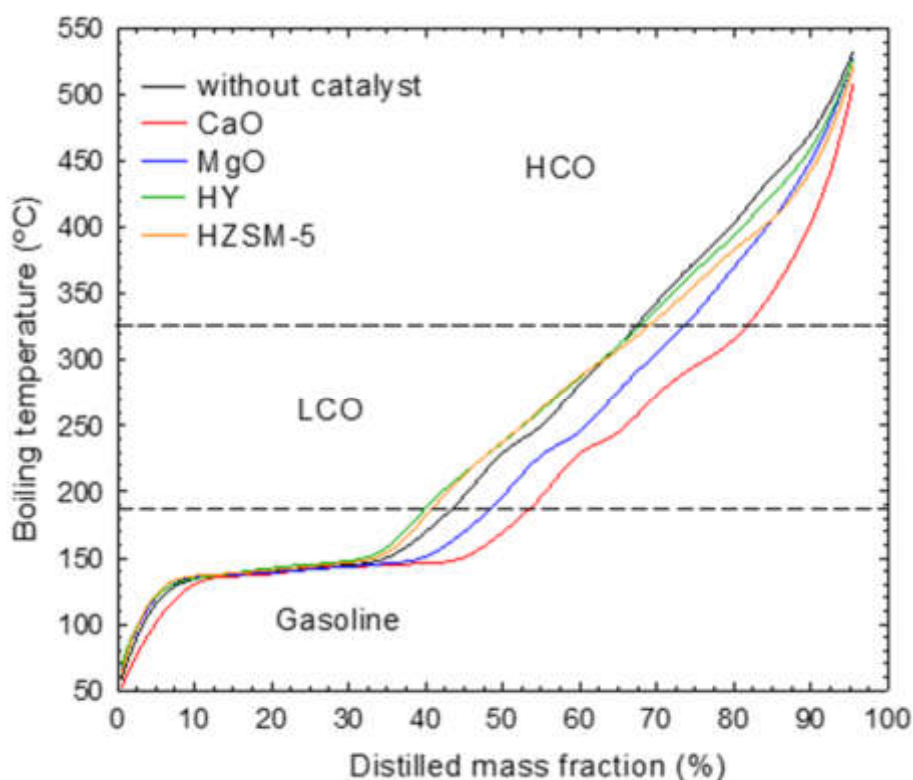

Figure 6. Boiling temperature as a function of the distilled mass fraction (simulated distillation) of the liquid fraction from catalytic pyrolysis of the mixed plastic waste.

If liquid yield was considered, the absolute data about product yields were calculated. **Table 5** reports the different products obtained from the pyrolysis of the mixture studied in this work over each catalytic material.

Table 5. Gasoline, LCO, and HCO products yields obtained from the mixture (data in g·kg^{-1} plastic) in thermal (non-catalytic) and catalytic pyrolysis

Catalyst	Gasoline-range	LCO-range	HCO-range
Without catalyst	240.5	111.2	152.3
MgO	241.0	113.5	62.9
CaO	236.2	104.6	106.1
HY	170.1	95.1	109.9
HZSM-5	167.3	101.5	101.0

Average values with a relative standard deviation inferior to 5%.

Table 5 shows that basic low-cost catalysts (CaO and MgO) had better performance on gasoline-range product generation than acid zeolite-type catalysts. Especially, MgO showed a similar yield of this type of product compared to the composition of liquid of non-catalytic test. If a deep comparison between thermal and

catalytic pyrolysis is performed, it can be observed that MgO and CaO transform heavier compounds (HCO-range product), increasing the fraction of lighter compounds in the liquid of pyrolysis. However, the great conversion of plastics to gas products in catalytic pyrolysis over acid zeolites reduces the yield of gasoline-range product, mainly attributed to micropores in the catalyst [62]. In conclusion, the differences in product yields would result from geometric constraints due to the shape selectivity of each catalytic material [63]. According to pores size distribution (**Figure S3**), starting at 50 Å radius, MgO and HY have additional pores volume than the other catalysts, which would allow higher bottoms (HCO) conversion, but HY has a significant reduction of volume between 100 to 300 Å radius that would not let it to break a larger number of bottoms like MgO (61.3 %); however, additional pore volume in the range of 15 to 20 Å in radius would convert more LCO (19.8 %) to gasoline, which in turn decomposes to gases through the micropores. This suggests that to crack LCO and HCO, the catalyst requires a bimodal pore size distribution [64]. Finally, among CaO and HZSM-5, which have a similar trend of pores distribution, the last one has more additional pore volume, and as a result, fewer LCO and HCO yields than those obtained by CaO are detected.

3.3.3. Effect of type of catalyst on hydrocarbon types in the gasoline-range product

Regarding the simulated distillation of the gasoline-range product, see **Figure 7A**, very low differences between thermal and catalytic pyrolysis were observed. Only a slight increase in the boiling point in the gasoline-range product generated by catalytic pyrolysis over CaO, if compared to the curve of the gasoline-range product obtained by thermal pyrolysis, was observed.

Concerning the hydrocarbon types, compared to the gasoline-range product obtained by thermal pyrolysis, no significant differences were observed in paraffins, naphthenes, and aromatics content, see **Figure 7B**. More specifically, **Figure 7C** shows that the catalysts marginally decreased the yield of monocycloparaffins, and dicycloparaffins and increased the output of alkylbenzenes and naphthalenes. For example, alkylbenzenes yield increased from 21.4 % for thermal pyrolysis to 26.3 % for catalytic pyrolysis over HZSM-5 or to 24.2 % when MgO was used as catalyst. However, no clear trend was found in indans or tetralins yields that changed between 7.8 % for catalytic pyrolysis over HY to 12.1 % over CaO. Also, changes in monocycloparaffins contents were very low, decreasing from 21.3 % for thermal pyrolysis (the highest value determined) to 18.9 % and 19.0 % (the lowest values determined) for catalytic pyrolysis over MgO and CaO,

respectively. These insignificant changes can be justified by the deactivation of the catalyst by coke deposition, which occurs preferably on the strong acid sites of zeolite-type catalysts [31]. The carbon deposition occurring in the micropores may block the access of the bio-oil compounds to acidic sites [62].
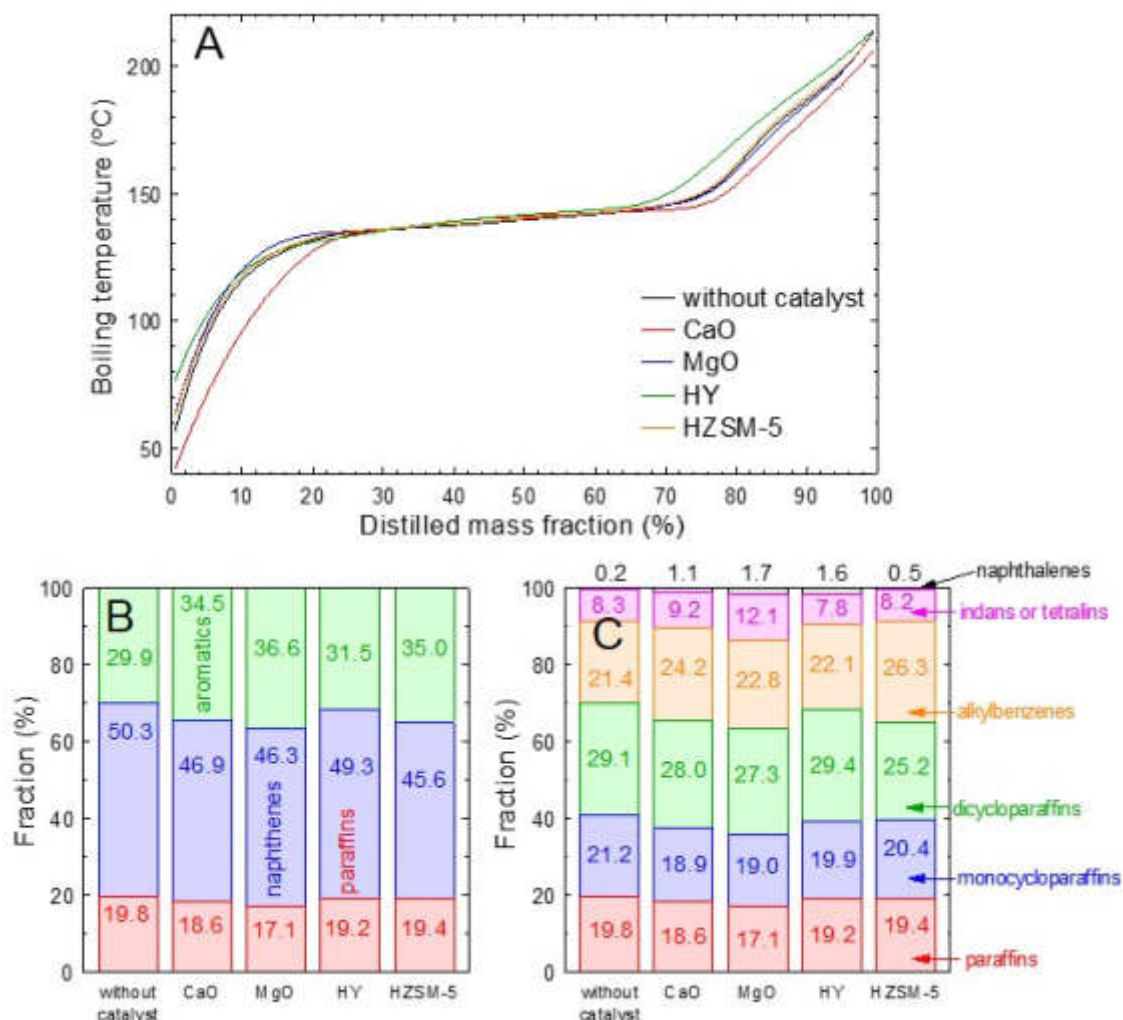

Figure 7. Simulated distillation (A), hydrocarbon group distribution (B), and hydrocarbon groups of the gasoline distribution (C) obtained from the catalytic pyrolysis of the mixed plastic.

4. CONCLUSIONS

The thermal and catalytic pyrolysis of a real mixture of post-consumer plastic waste representing the plastics present in the rejected fraction from municipal solid waste non-collected selectively was studied. Liquid oil from HIPS pyrolysis showed 76.8 % of the gasoline-range product. However, liquid from pyrolysis of PE film showed a very low percentage of this product (7.2 %). Significant variations were observed in the composition of the gasoline-range product obtained by thermal pyrolysis of different

types of polymers. The yields of aromatics, paraffins, and naphthenes considerably varied between polystyrene plastics (HIPS and EPS), polyolefins (PP, PP film, PE film), and the mixture of plastics. High aromatics production was observed for HIPS and EPS (89.8 % and 83.5 %) and more paraffins (from 20.0 to 31.4%) and naphthenes (between 50.8-58.9%) for polyolefins.

Regarding the catalytic tests, low-cost MgO and CaO promoted gasoline fraction in the liquid product (241.0 and 236.2 $g \cdot kg^{-1}$ plastic). However, very low differences between thermal and catalytic pyrolysis were observed in simulated distillation curves and the composition of the gasoline-range product. In future works, appropriate modifications of catalysts by thermal or hydrothermal procedures, with or without chemical treatment for changes of the framework, to increase their selectivity by cracking towards the gasoline-range product generation, effective ways to reduce coke deposition during catalytic pyrolysis and regeneration of the deactivated catalyst, could be studied.

Acknowledgements

REFERENCES

[1]   United Nation Environment Programme, SINGLE-USE PLASTICS: A Roadmap for Sustainability, Tara Canno, United Nations Environment Programe, 2018.

[2]   Plastics Europe, Plastics - the Facts 2021, (2021). https://plasticseurope.org/knowledge-hub/plastics-the-facts-2021/ (accessed April 11, 2022).

[3]   J. Sun, Z.R. Zhu, W.H. Li, X. Yan, L.K. Wang, L. Zhang, J. Jin, X. Dai, B.J. Ni, Revisiting Microplastics in Landfill Leachate: Unnoticed Tiny Microplastics and Their Fate in Treatment Works, Water Res. 190 (2021) 116784. https://doi.org/10.1016/J.WATRES.2020.116784.

[4]   Y. Su, Z. Zhang, D. Wu, L. Zhan, H. Shi, B. Xie, Occurrence of microplastics in landfill systems and their fate with landfill age, Water Res. 164 (2019) 114968.

https://doi.org/10.1016/J.WATRES.2019.114968.

[5]   Y. Wan, X. Chen, Q. Liu, H. Hu, C. Wu, Q. Xue, Informal landfill contributes to the pollution of microplastics in the surrounding environment, Environ. Pollut. 293 (2022) 118586. https://doi.org/10.1016/J.ENVPOL.2021.118586.

[6]   E. Commission, A European Strategy for Plastics in a Circular Economy, Comm. Commun.   –   Plast.   Strateg.   (2020). https://environment.ec.europa.eu/strategy/plastics-strategy_en#documents (accessed September 1, 2022).

[7]   J. Hopewell, R. Dvorak, E. Kosior, Plastics recycling: challenges and opportunities, Philos. Trans. R. Soc. B Biol. Sci. 364 (2009) 2115–2126. https://doi.org/10.1098/RSTB.2008.0311.

[8]   D.I. Collias, M.I. James, J.M. Layman, Circular Economy of Polymers: Topics in Recycling Technologies, American Chemical Society, Washington, DC, 2021. https://doi.org/10.1021/BK-2021-1391.

[9]   Y. Rodríguez Lamar, J. Noboa, A.S. Torres Miranda, D. Almeida Streitwieser, Conversion of PP, HDPE and LDPE Plastics into Liquid Fuels and Chemical Precursors by Thermal Cracking, J. Polym. Environ. 29 (2021) 3842–3853. https://doi.org/10.1007/S10924-021-02150-1.

[10] E.A. Williams, P.T. Williams, The Pyrolysis of Individual Plastics and a Plastic Mixture in a Fixed Bed Reactor, J. Chem. Technol. Biotechnol. 70 (1997) 9–20. https://doi.org/10.1002/(SICI)1097-4660(199709)70:1<9::AID-JCTB700>3.0.CO;2-E.

[11] P. Costa, F. Pinto, R. Mata, P. Marques, F. Paradela, L. Costa, Validation of the Application of the Pyrolysis Process for the Treatment and Transformation of Municipal Plastic Wastes, Chem. Eng. Trans. 86 (2021) 859–864. https://doi.org/10.3303/CET2186144.

[12] R.K. Singh, B. Ruj, A.K. Sadhukhan, P. Gupta, Impact of fast and slow pyrolysis on the degradation of mixed plastic waste: Product yield analysis and their characterization,   J.   Energy   Inst.   92   (2019)   1647–1657. https://doi.org/10.1016/J.JOEI.2019.01.009.

[13] R.K. Singh, B. Ruj, A.K. Sadhukhan, P. Gupta, Thermal degradation of waste plastics under non-sweeping atmosphere: Part 2: Effect of process temperature on product characteristics and their future applications, J. Environ. Manage. 261 (2020) 110112. https://doi.org/10.1016/J.JENVMAN.2020.110112.

[14] G.K. Parku, F.X. Collard, J.F. Görgens, Pyrolysis of waste polypropylene plastics for energy recovery: Influence of heating rate and vacuum conditions on composition of fuel product, Fuel Process. Technol. 209 (2020) 106522. https://doi.org/10.1016/J.FUPROC.2020.106522.

[15] L. Rodríguez-Luna, D. Bustos-Martínez, E. Valenzuela, Two-step pyrolysis for waste HDPE valorization, Process Saf. Environ. Prot. 149 (2021) 526–536. https://doi.org/10.1016/J.PSEP.2020.11.038.

[16] R. Miandad, M.A. Barakat, A.S. Aburiazaiza, M. Rehan, I.M.I. Ismail, A.S. Nizami, Effect of plastic waste types on pyrolysis liquid oil, Int. Biodeterior. Biodegradation. 119 (2017) 239–252. https://doi.org/10.1016/J.IBIOD.2016.09.017.

[17] A. López, I. de Marco, B.M. Caballero, M.F. Laresgoiti, A. Adrados, Pyrolysis of municipal plastic wastes: Influence of raw material composition, Waste Manag. 30 (2010) 620–627. https://doi.org/10.1016/j.wasman.2009.10.014.

[18] M.S. Qureshi, A. Oasmaa, H. Pihkola, I. Deviatkin, A. Tenhunen, J. Mannila, H. Minkkinen, M. Pohjakallio, J. Laine-Ylijoki, Pyrolysis of plastic waste: Opportunities and challenges, J. Anal. Appl. Pyrolysis. 152 (2020) 104804. https://doi.org/10.1016/J.JAAP.2020.104804.

[19] S. Wiriyaumpaiwong, J. Jamradloedluk, Distillation of Pyrolytic Oil Obtained from Fast Pyrolysis of Plastic Wastes, Energy Procedia. 138 (2017) 111–115. https://doi.org/10.1016/J.EGYPRO.2017.10.071.

[20] S.H. Jung, M.H. Cho, B.S. Kang, J.S. Kim, Pyrolysis of a fraction of waste polypropylene and polyethylene for the recovery of BTX aromatics using a fluidized bed reactor, Fuel Process. Technol. 91 (2010) 277–284. https://doi.org/10.1016/J.FUPROC.2009.10.009.

[21] M. Sarker, M.M. Rashid, Production of Aromatic Hydrocarbons Related Kerosene Fuel from Polystyrene and Polypropylene Waste Plastics Mixture by Fractional Distillation Process, Int. J. Appl. Chem. Sci. Res. 1 (2013) 1–10.

[22] A. Gala, M. Guerrero, B. Guirao, M.E. Domine, J.M. Serra, Characterization and Distillation of Pyrolysis Liquids Coming from Polyolefins Segregated of MSW for Their Use as Automotive Diesel Fuel, Energy and Fuels. 34 (2020) 5969–5982. https://doi.org/10.1021/ACS.ENERGYFUELS.0C00403.

[23] J. Baena-González, A. Santamaria-Echart, J.L. Aguirre, S. González, Chemical recycling of plastic waste: Bitumen, solvents, and polystyrene from pyrolysis oil,

Waste Manag. 118 (2020) 139–149. https://doi.org/10.1016/J.WASMAN.2020.08.035.

[24] R. Thahir, A. Altway, S.R. Juliastuti, Susianto, Production of liquid fuel from plastic waste using integrated pyrolysis method with refinery distillation bubble cap plate column, Energy Reports. 5 (2019) 70–77. https://doi.org/10.1016/J.EGYR.2018.11.004.

[25] A. Demirbas, Pyrolysis of municipal plastic wastes for recovery of gasoline-range hydrocarbons, J. Anal. Appl. Pyrolysis. 72 (2004) 97–102. https://doi.org/10.1016/J.JAAP.2004.03.001.

[26] Z. Dobó, G. Kecsmár, G. Nagy, T. Koós, G. Muránszky, M. Ayari, Characterization of Gasoline-like Transportation Fuels Obtained by Distillation of Pyrolysis Oils from Plastic Waste Mixtures, Energy and Fuels. 35 (2021) 2347– 2356. https://doi.org/10.1021/ACS.ENERGYFUELS.0C04022.

[27] I. Barbarias, G. Lopez, M. Artetxe, A. Arregi, J. Bilbao, M. Olazar, Valorisation of different waste plastics by pyrolysis and in-line catalytic steam reforming for hydrogen production, Energy Convers. Manag. 156 (2018) 575–584. https://doi.org/10.1016/J.ENCONMAN.2017.11.048.

[28] G. Fadillah, I. Fatimah, I. Sahroni, M.M. Musawwa, T.M.I. Mahlia, O. Muraza, Recent Progress in Low-Cost Catalysts for Pyrolysis of Plastic Waste to Fuels, Catalysts. 11 (2021) 837. https://doi.org/10.3390/CATAL11070837.

[29] S. Budsaereechai, A.J. Hunt, Y. Ngernyen, Catalytic pyrolysis of plastic waste for the production of liquid fuels for engines, RSC Adv. 9 (2019) 5844–5857. https://doi.org/10.1039/C8RA10058F.

[30] A. Verma, S. Sharma, H. Pramanik, Pyrolysis of waste expanded polystyrene and reduction of styrene via in-situ multiphase pyrolysis of product oil for the production of fuel range hydrocarbons, Waste Manag. 120 (2021) 330–339. https://doi.org/10.1016/J.WASMAN.2020.11.035.

[31] G. Elordi, M. Olazar, G. Lopez, M. Artetxe, J. Bilbao, Continuous polyolefin cracking on an HZSM-5 zeolite catalyst in a conical spouted bed reactor, Ind. Eng. Chem. Res. 50 (2011) 6061–6070. https://doi.org/10.1021/IE2002999.

[32] Y. Xue, P. Johnston, X. Bai, Effect of catalyst contact mode and gas atmosphere during catalytic pyrolysis of waste plastics, Energy Convers. Manag. 142 (2017) 441–451. https://doi.org/10.1016/J.ENCONMAN.2017.03.071.

[33] J.A. Onwudili, C. Muhammad, P.T. Williams, Influence of catalyst bed

temperature and properties of zeolite catalysts on pyrolysis-catalysis of a simulated mixed plastics sample for the production of upgraded fuels and chemicals, J. Energy Inst. 92 (2019) 1337–1347. https://doi.org/10.1016/j.joei.2018.10.001.

[34] J. Wang, J. Jiang, X. Wang, R. Wang, K. Wang, S. Pang, Z. Zhong, Y. Sun, R. Ruan, A.J. Ragauskas, Converting polycarbonate and polystyrene plastic wastes into aromatic hydrocarbons via catalytic fast co-pyrolysis, J. Hazard. Mater. 386 (2020) 121970. https://doi.org/10.1016/J.JHAZMAT.2019.121970.

[35] S. Kumagai, I. Hasegawa, G. Grause, T. Kameda, T. Yoshioka, Thermal decomposition of individual and mixed plastics in the presence of CaO or Ca(OH)$_2$, J. Anal. Appl. Pyrolysis. 113 (2015) 584–590. https://doi.org/10.1016/J.JAAP.2015.04.004.

[36] J.M. Hidalgo Herrador, M. Murat, Z. Tišler, J. Frątczak, H. de Paz Carmona, Direct Polypropylene and Polyethylene Liquefaction in CO$_2$ and N$_2$ Atmospheres Using MgO Light and CaO as Catalysts, Materials (Basel). 15 (2022) 844. https://doi.org/10.3390/MA15030844.

[37] M.A. Martín-Lara, A. Piñar, A. Ligero, G. Blázquez, M. Calero, Characterization and Use of Char Produced from Pyrolysis of Post-Consumer Mixed Plastic Waste, Water. 13 (2021) 1188. https://doi.org/10.3390/W13091188.

[38] L.M. Quesada Lozano, Desarrollo de tratamientos térmicos sostenibles para la valorización del plástico procedente de la fracción de rechazo de las plantas de tratamiento de residuos sólidos urbanos, Doctoral Thesis, University of Granada, 2021.

[39] M.F. Paucar-Sánchez, M. Calero, G. Blázquez, M.J. Muñoz-Batista, M.A. Martín-Lara, Characterization of liquid fraction obtained from pyrolysis of post-consumer mixed plastic waste: A comparing between measured and calculated parameters, Process Saf. Environ. Prot. 159 (2022) 1053–1063. https://doi.org/10.1016/J.PSEP.2022.01.081.

[40] American Society for Testing and Materials, Standard Test Method for Determination of the Boiling Range Distribution of Gasoline by Wide-Bore Capillary Gas Chromatography, in: ASTM Vol. 05.03 Pet. Prod. Liq. Fuels, Lubr. D6469 – D7398, 2021: pp. 1–15. https://doi.org/0.1520/D7096-19.2.

[41] American Society for Testing and Materials, Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography, in: ASTM Vol. 05.01 Pet. Prod. Liq. Fuels, Lubr. C1234 – D4176, 2021: pp. 1–35.

https://doi.org/10.1520/D2887-19AE02.

[42]   American Society for Testing and Materials, Standard Test Method for Determining Activity and Selectivity of Fluid Catalytic Cracking (FCC) Catalysts by Microactivity Test 1, in: ASTM Vol. 05.06 Gaseous Fuels; Coal Coke; Catal. Bioenergy Ind. Chem. From Biomass, 2022: pp. 1–9. https://doi.org/10.1520/D5154_D5154M-18.

[43]   American Society for Testing and Materials, Standard Test Method for Hydrocarbon Types in Middle Distillates by Mass Spectrometry, in: ASTM Vol. 05.01 Pet. Prod. Liq. Fuels, Lubr. C1234 – D4176, 2021: pp. 1–15. https://doi.org/10.1520/D2425-21.

[44]   M. Thommes, K. Kaneko, A. V. Neimark, J.P. Olivier, F. Rodríguez-Reinoso, J. Rouquerol, K.S.W.W. Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), Pure Appl. Chem. 87 (2015) 1051–1069.

[45]   R.D. Micic, M.S. Bosnjak Kiralj, S.N. Panic, M.D. Tomic, B.D. Jovic, G.C. Boskovic, Activation temperature imposed textural and surface synergism of CaO catalyst for sunflower oil transesterification, Fuel. 159 (2015) 638–645. https://doi.org/10.1016/J.FUEL.2015.07.025.

[46]   J.K. Bartley, C. Xu, R. Lloyd, D.I. Enache, D.W. Knight, G.J. Hutchings, Simple method to synthesize high surface area magnesium oxide and its use as a heterogeneous base catalyst, Appl. Catal. B Environ. 128 (2012) 31–38. https://doi.org/10.1016/J.APCATB.2012.03.036.

[47]   L.H. Chen, M.H. Sun, Z. Wang, W. Yang, Z. Xie, B.L. Su, Hierarchically structured zeolites: From design to application, Chem. Rev. 120 (2020) 11194–11294. https://doi.org/10.1021/ACS.CHEMREV.0C00016.

[48]   Y. Xu, S. Liu, X. Guo, L. Wang, M. Xie, Methane activation without using oxidants over Mo/HZSM-5 zeolite catalysts, Catal. Letters. 30 (1994) 135–149. https://doi.org/10.1007/BF00813680.

[49]   W. Zhang, D. Yu, X. Ji, H. Huang, Efficient dehydration of bio-based 2,3-butanediol to butanone over boric acid modified HZSM-5 zeolites, Green Chem. 14 (2012) 3441–3450. https://doi.org/10.1039/C2GC36324K.

[50]   J. Aguado and D. Serrano, Feedstock Recycling of Plastic Wastes, The Royal, Cambridge, 1999. https://doi.org/10.1039/9781847550804.

[51]   A. Inayat, K. Klemencova, B. Grycova, B. Sokolova, P. Lestinsky, Thermo-

catalytic pyrolysis of polystyrene in batch and semi-batch reactors: A comparative study, Waste Manag. Res. 39 (2020) 260–269. https://doi.org/10.1177/0734242X20936746.

[52] A.F. Anene, S.B. Fredriksen, K.A. Sætre, L.A. Tokheim, Experimental study of thermal and catalytic pyrolysis of plastic waste components, Sustainability. 10 (2018) 1–11. https://doi.org/10.3390/su10113979.

[53] P.T.. Williams, E.A. Williams, Fluidised bed pyrolysis of low density polyethylene to produce petrochemical feedstock, J. Anal. Appl. Pyrolysis. 51 (1999) 107–126. https://doi.org/10.1016/S0165-2370(99)00011-X.

[54] M. Predel, W. Kaminsky, Pyrolysis of mixed polyolefins in a fluidised-bed reactor and on a pyro-GC/MS to yield aliphatic waxes, Polym. Degrad. Stab. 70 (2000) 373–385. https://doi.org/10.1016/S0141-3910(00)00131-2.

[55] K. Takuma, Y. Uemichi, A. Ayame, Product distribution from catalytic degradation of polyethylene over H-gallosilicate, Appl. Catal. A Gen. 192 (2000) 273–280. https://doi.org/10.1016/S0926-860X(99)00399-3.

[56] N. Miskolczi, L. Bartha, G. Deák, B. Jóver, D. Kalló, Thermal and thermo-catalytic degradation of high-density polyethylene waste, J. Anal. Appl. Pyrolysis. 72 (2004) 235–242. https://doi.org/10.1016/J.JAAP.2004.07.002.

[57] G. Lopez, M. Artetxe, M. Amutio, J. Bilbao, M. Olazar, Thermochemical routes for the valorization of waste polyolefinic plastics to produce fuels and chemicals. A review, Renew. Sustain. Energy Rev. 73 (2017) 346–368. https://doi.org/10.1016/J.RSER.2017.01.142.

[58] M.R. Rahimpour, M. Jafari, D. Iranshahi, Progress in catalytic naphtha reforming process: A review, Appl. Energy. 109 (2013) 79–93. https://doi.org/10.1016/J.APENERGY.2013.03.080.

[59] V. Daligaux, R. Richard, M.H. Manero, Deactivation and Regeneration of Zeolite Catalysts Used in Pyrolysis of Plastic Wastes—A Process and Analytical Review, Catal. 2021, Vol. 11, Page 770. 11 (2021) 770. https://doi.org/10.3390/CATAL11070770.

[60] N. Miskolczi, L. Bartha, G. Deák, Thermal degradation of polyethylene and polystyrene from the packaging industry over different catalysts into fuel-like feed stocks, Polym. Degrad. Stab. 91 (2006) 517–526. https://doi.org/10.1016/j.polymdegradstab.2005.01.056.

[61] S. Uçar, S. Karagöz, T. Karayildirim, J. Yanik, Conversion of polymers to fuels in

a refinery stream, Polym. Degrad. Stab. 75 (2002) 161–171. https://doi.org/10.1016/S0141-3910(01)00215-4.

[62] J. Hertzog, V. Carré, L. Jia, C.L. Mackay, L. Pinard, A. Dufour, O. Mašek, F. Aubriet, Catalytic Fast Pyrolysis of Biomass over Microporous and Hierarchical Zeolites: Characterization of Heavy Products, ACS Sustain. Chem. Eng. 6 (2018) 4717–4728. https://doi.org/10.1021/ACSSUSCHEMENG.7B03837.

[63] C.H. Bartholomew, R.J. Farrauto, Fundamentals of Industrial Catalytic Processes, John Wiley and Sons, 2010. https://doi.org/10.1002/9780471730071.

[64] M.M. Mitchell, J.F. Hoffman, H.F. Moore, Chapter 9 Residual Feed Cracking Catalysts, Stud. Surf. Sci. Catal. 76 (1993) 293–338. https://doi.org/10.1016/S0167-2991(08)63832-X.