



Oil and gas production from the pyrolytic transformation of recycled plastic waste: An integral study by polymer families



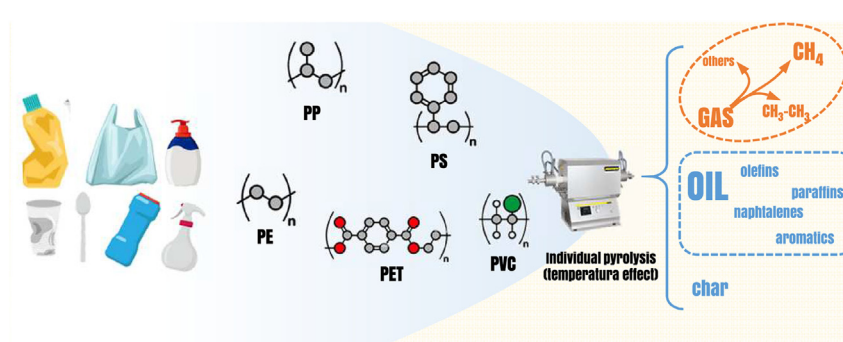
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HIGHLIGHTS

- The optimum pyrolysis temperature for oil production was ~ 500 °C in all the plastics.
- The oil from HIPS, EPS, PET, and PP displayed low molecular weight (C_5 - C_9).
- HIPS and EPS led to an oil with a high aromatic character, mainly composed of styrene.
- The oil from PE was the most diverse in terms of hydrocarbon types.
- Methane was the main compound released in the gases followed by ethane in importance.

GRAPHICAL ABSTRACT



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ABSTRACT

Different plastics recovered from a local urban solid waste plant were collected before landfilling, separated, and classified by families, i.e. polyethylene (PE), polypropylene (PP), high impact and expanded polystyrene (HIPS and EPS, respectively), polyethylene terephthalate (PET), and polyvinyl chloride (PVC). A systematic pyrolysis study was carried out to compare the different behavior registered in each plastic type, and an integral analysis of the produced oils and synthetic gas was conducted. In general terms, the oil yield followed the order $EPS > PP > PE > HIPS > PET > PVC$, reaching maximum values over 500 °C after 1 h of treatment. The oil from HIPS, EPS, PET, and PP was rich in light compounds, i.e., C_5 - C_9 hydrocarbons. Almost 100 % of the oil from HIPS and EPS pyrolysis was aromatic. The aromatic fraction was important in the case of PVC (57 %) and PET (45 %). PE produced an oil with the most varied distribution of compounds but rich in olefins (67 %). The analysis of the non-condensable composition of the gas showed that in all the pyrolysis gases methane was over 50 % (vol.), followed by ethane in importance. CO was produced in the case of PET.

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1. Introduction

Plastics are polymeric materials ubiquitous present in human modern life. Their versatility comes from the easiness to be molded, laminated, shaped, and tailored both physically and chemically. That means that there is plastic suitable for diverse applications used for packaging, building and construction clothing, agriculture, transport, and electronics among others. Currently,

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the annual consumption of plastics per person in developed countries is estimated at 50 and 68 kg (Thiounn and Smith, 2020).

The current economy of plastic can be labeled as linear under a dramatic rise in plastic waste that jeopardizes the exploitation of natural resources. A transition of the plastics economy from linear into a circular strategy, promoting the reuse, recycling, or use of waste plastic as a raw material. The recycling of plastics constitutes a mechanical process, in which the plastics are blended and inserted again into the plastic production chain (Schyns and Shaver, 2021). Unfortunately, not all types of plastics are flexible for such a purpose and many of them are discharged. In this case, chemical recycling is a plausible route to reduce the environmental impacts, promoting valorization and reduction of incineration or landfilling. Chemical recycling is the key to closing the loop of plastic recycling and includes hydrolysis and pyrolysis processes (Thiounn and Smith, 2020).

Pyrolysis is one of the most attractive techniques for the chemical recycling of plastics. This technology is based on the application of heat in the absence of oxygen. As consequence, the macromolecular structures of polymers are broken down into smaller molecules or oligomers, and sometimes monomeric units, giving as a result, diverse yields of liquid, gas, and a small proportion of a solid char (Qureshi et al., 2020). The produced liquid can be refined and used as a fuel, which can help to minimize the energy crisis (Wong et al., 2015). The quantities and characteristics of pyrolysis products depend on diverse factors, mainly temperature, time, or the presence of catalysts, among others (Panda et al., 2010; Maqsood et al., 2021). The presence of catalysts generally leads to enhanced lysis of the bonds, extending the pyrolysis process and/or reducing the temperature, raising the gas yield. For that reason, the control of the operational conditions results in great importance to enlarging oil production. In addition, the reactor design also affects the oil and gas yields. The heat supplying rate, the heat transfer mechanism, and the residence time are critical aspects bound to enlarging the production of pyrolysis products or a certain composition of a product (Jahirul et al., 2022; Soni et al., 2021). Three main groups of technological reactor solutions are available, slow pyrolysis, fast pyrolysis, and flash pyrolysis (Maqsood et al., 2021). Slow pyrolysis refers to those designs that imply a low heating rate, long solid and gas residence periods (minutes to hours), and low temperatures. Some examples are fixed-bed reactors and rotatory kilns. Although slow pyrolysis allows pyrolyzing particles of high size (5–50 mm), the high reaction time (300 to 3600 s) rises the energetic cost of the process (Maqsood et al., 2021). The drawbacks of slow mode can be faced with fast and flash pyrolytic reactors. Fast pyrolysis reactors are technically more complex, requiring residence time of fewer than 2 s, small and uniform particle size (<1 mm), high heating rates, and devices to hastily collect the released gas stream. Some examples of fast pyrolysis can be found in fluidized beds, conical spout beds, and circulating fluidized bed reactors (Matayeva et al., 2019). The fast pyrolysis can be taken to the limit in terms of operational conditions, leading to the known as flash pyrolysis, which conducts the process at high very high temperatures, and extreme heating rates, implying the shortest residence times (<1 s) and smallest particles size though (<0.2 mm). Flash pyrolysis can be conducted in both, fluidized and fixed-bed reactors (Maqsood et al., 2021).

The pyrolytic transformation of plastics into added-valued chemicals has been explored previously, mainly considering as raw materials high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP) or polystyrene (PS) (Jaafar et al., 2022; Santos et al., 2018). HDPE and PP lead to an oil rich in olefin compounds while PS leads to the formation of aromatic compounds up to three rings (Jaafar et al., 2022; Anene et al., 2018). To date, there is little information in the literature consider-

ing an integral study of the analysis of the oil and gas produced during the pyrolysis of plastic wastes collected from real residues classified by families. Much attention has been devoted to the oil fraction due to its potential application for the obtention of gasoline and diesel fractions. However, the energetic added value associated with the pyrolysis gases deserves study since they could contribute to reducing the energy consumption in the pyrolysis reactor by using it as fuel. HDPE, LDPE, PP, PS, PVC (polyvinyl chloride), and PET (polyethylene terephthalate) are reported as the most common municipal solid wastes in Europe in which PE outstands from the rest by the high consumption rates (Gebre et al., 2021). For that reason, this work introduces a systematic comparison of the pyrolysis of the different plastic families recovered from a non-recycled fraction of an urban solid waste plant before landfilling, including PE, PP, HIPS (high-impact polystyrene), EPS (expanded polystyrene), PVC, and PET among the plastic residues. The pyrolysis study was carried out individually to fully understand and compare the different behavior registered in each plastic type. The temperature during the thermal treatment was also studied between 450 and 525 °C. In each case, the oil yield was quantified and characterized by FTIR and GC-MS techniques for the identification of the compounds. Moreover, the evolution of the composition of the released gases in each case was analyzed.

2. Materials and methods

2.1. Materials

The materials used in this work were plastic residues collected from objects of common use collected from a treatment plant of urban solid waste, *Ecocentral* (Granada). The collected plastic waste was classified, washed, dried, and crushed to a size inferior to 1 mm and stored until use. As these plastics have already been processed, they incorporate different additives in their formulation, which may contribute to the characteristics and composition of the products obtained in the pyrolysis process. Table 1 shows the plastic waste origin, the elemental composition, and the heating value. The results of the proximate analysis characterization of the original plastic wastes are available in Table S1.

2.2. Pyrolysis tests

The pyrolysis tests were developed in a Naberthem horizontal furnace reactor, model R50/250/12. Fig. 1 shows a scheme of the experimental setup. The pyrolysis was carried out in an inert atmosphere of N₂ with a flow of 100 mL·min⁻¹, a heating rate of 20 °C·min⁻¹, and a residence time of 90 min. The holding temperatures were 450, 475, 500, and 525 °C. In all cases, about 40 g of crushed plastic was used. The exhaust gas coming from the tubular reactor was directed to a condensation system consisting of a glass bottle immersed in an ethylene glycol bath at -10 °C. The liquid fraction was collected and quantified in this bottle while the gas was sampled in bags. Once the operation was finished, the solid remaining in the reactor was removed and quantified to determine the char fraction. The gas fraction was determined by the difference. The pyrolysis tests were repeated in triplicate and the relative standard deviation of the yield percentage was inferior to 5 %.

2.3. Chemical characterization of the pyrolysis oils

The elemental analysis of the starting materials and the oil samples was determined using an Elemental Fison's Instrument, EA 1108 CHNS. The sample was oxidized at ca. 1400 °C in the presence of a catalyst (WO₃). The released gases (CO₂, H₂O, NO_x, SO_x, and

Table 1
Type, origin, and characteristics of the plastic waste used in this work.

Material	Source	Monomer formula	Elemental composition (%)						HHV (MJ·kg ⁻¹)
			C	H	N	S	O ²	Cl	
Polyethylene Film (PE)	Commercial bags	(C ₂ H ₄) _n	80.44	17.91	0.08	n.d. ³	1.57	n.d.	52.67
High Impact Polystyrene (HIPS ¹)	Food packaging	(C ₈ H ₈) _n	64.37	8.15	0.24	n.d.	27.24	n.d.	28.63
Expanded Polystyrene (EPS)	Styrofoam containers	(C ₈ H ₈) _n	90.32	9.66	0.02	n.d.	0	n.d.	44.48
Polypropylene (PP)	Food packaging	(C ₃ H ₆) _n	84.01	15.08	0.19	n.d.	0	n.d.	51.14
Polyethylene Terephthalate (PET)	Food packaging	(C ₁₀ H ₈ O ₄) _n	61.76	5.62	0.01	n.d.	32.61	n.d.	23.16
Polyvinylchloride (PVC)	Pipelines	(C ₂ H ₃ Cl) _n	32.70	5.23	0.03	n.d.	7.92	54.12	17.17

¹ includes paper label.

² by difference.

³ not detected.

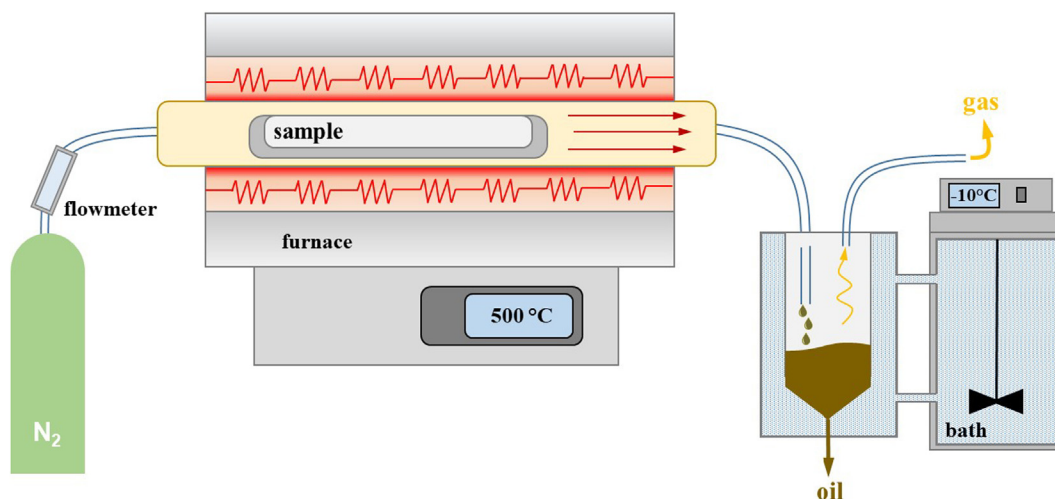


Fig. 1. Experimental pyrolysis setup.

unreacted O₂) flow through a zone packed with elemental copper kept at 860 °C leading to the capture of O₂ and the reduction of the organic nitrogen and sulfur to N₂ and SO₂. The final gases (CO₂, H₂O, N₂, and SO₂) are separated by gas chromatography and the quantification is conducted by thermal conductivity detection. The amount of oxygen is determined by the difference. From the results of elemental analysis, the high heating value (HHV) was calculated according to Dulong's equation (Kathiravale et al., 2003):

$$\text{HHV (MJ} \cdot \text{kg}^{-1}) = 33.77 \cdot C + 144.04 \cdot \left[\text{H} - \frac{\text{O}}{8} \right] + 9.40 \cdot S \quad (1)$$

where, C, H, O, and S are the mass fractions of carbon, hydrogen, oxygen, and sulfur.

Attenuated total reflectance Fourier transform Infrared (ATR-FTIR) was used for the qualitative structural determination of the oil samples. A Perkin-Elmer Spectrum 65 device was used, recording the spectra between 4000 and 400 cm⁻¹ with a resolution of 2 cm⁻¹.

The gas chromatography-mass spectrometry (GC-MS) technique was used for the identification of the compounds contained in the oil. The analyses were performed using an Agilent high-resolution GC, model 7890A, coupled to a Waters triple-quadrupole mass spectrometer, model micro GC. The operating conditions were: injector and transfer line temperature, 250 °C with the injector operating in split mode; carrier gas (He) flow of

1 mL·min⁻¹; nonpolar phase ZB-5MS capillary column, Phenomenex (30 m × 0.25 mm, ID 0.25 μm). The oven was programmed to hold at 40 °C for 4 min, increased to 280 °C at a rate of 6 °C·min⁻¹, and held at this temperature for 6 min. The operation conditions of the mass selective detector were as follows: interface temperature, 250 °C, full scan, 30–650 Da, and electron ionization energy, 70 eV. The identification of compounds was based on the mass spectrum library of the National Institute of Standards and Technology, using the NIST MS Search 2.0 software integrated with MassLynx V4.1 software with mass spectrum library NIST 08.

2.4. Analysis of the pyrolytic gases

The analysis of non-condensable gases was carried out by gas chromatography in an Agilent 990 Micro-GC system equipped with two channels and thermal conductivity detection. The first channel was connected to a molecular-sieve-coated Molsieve 5 Å column (20 m × 0.25 mm, ID 30 μm), for the quantification of O₂, N₂, CO, and CH₄. The second channel was connected to a PoraPLOT column (10 m × 0.25 mm, ID 8 μm), for the determination of ethane, ethylene, carbon dioxide, propane, *n*-butane, acetylene, and methyl acetylene. The released HCl in the case of PVC was trapped in an aqueous solution by bubbling the pyrolysis gas over water. The results of the gas analysis were expressed as a volume percentage of each compound concerning the total number of compounds analyzed on a free N₂ basis.

3. Results and discussion

3.1. Influence of temperature and plastic nature on the distribution of the products

Fig. 2 shows the results of the gas, oil, and char yields obtained during the pyrolysis of the different plastic tested (data available in Table S1). Different oil yields were obtained depending on the nature of the plastic used. Thus, concerning the liquid yield, the best results were obtained in the pyrolysis of EPS reaching a value of 66.0 % at 500 °C, while the lowest value was obtained with the pyrolysis of PVC, with a maximum value of 5.8 % at 475 °C. Similarly, the highest percentage of char is obtained from the pyrolysis of PVC (34.6 % at 450 °C), PET (24.1 % at 450 °C), and HIPS (11.4 % at 450 °C), while pyrolysis of PE, PP, and EPS produced almost no solid residue. Regarding the gas yields, the highest value was obtained from PVC (65.1 % at 525 °C) and the lowest value from EPS (33.0 % at 500 °C). In general terms, 500 °C can be selected as the optimum temperature for the maximum oil yield, except for PET and PVC whose highest values were reached at 475 °C.

On the one hand, the differences observed in the product's distribution are related to the type of polymer and the composition, as can also be seen by comparing the elemental analysis of the raw materials shown in Table 1. The char yield can be connected to the sum of the fixed carbon and ash, see Table S1. In this sense PET, with 13.8 % of fixed carbon, and PVC with 11.2 % of fixed carbon and 13.6 % of ash led to high char yields. HIPS was the third in importance in terms of char yield, a fact that can be explained based on the 7.6 % of ash content in the original plastic. The plastics with high carbon proportion lead to a high proportion of oil, as observed for EPS and PP. Different behavior can also be observed in the HIPS if compared to the EPS. The higher char percentage in the pyrolysis of the HIPS could be related to the presence of cellulose labeling accompanying the material. The interactions between PS and cellulose during the pyrolysis have been found to increase

the char yield and decrease the liquid yield, contributing to an increase in the char percentage (Sophonrat et al., 2018).

On the other hand, in general, an increase in the pyrolysis temperature favors the formation of oil until reaching a maximum at ca. 500 °C and a minimum of gas yield. After this maximum of oil production is reached, a further increase in the temperature affects negatively the oil yield but positively to the gas released, rising the gas percentage. This effect is more pronounced in some plastics. For example, if the temperature increases from 450 °C to 475 °C, the liquid yield in the pyrolysis of PE increases from 27.8 % to 40.4 % to detriment of the char generated; however, the gas yield was barely affected by the temperature. The same temperature rise in the pyrolysis of PP led to a rise in the oil yield from 41.4 % at 450 °C to 53.6 % at 500 °C. The released gas in PP reached a minimum of 500 °C to increase to 525 °C. The pyrolysis temperature of HIPS does not affect the yield; however, for the case of EPS the highest oil generated was at 500 °C which was correlated with a minimum gas percentage. A further temperature rising slightly increased the gas yield scarifying the oil performance.

These results are in good agreement with the already reported by previous works although diverse variables affecting the pyrolysis process may affect the results achieved. Table S3 shows some of the results reported in the literature at their optimum condition. It is also noteworthy to mention that the results vary considerably depending if the material tested was raw or wasted (Uebe et al., 2022). In the pyrolysis of PE, PP HIPS, and EPS, the oil yield was favored by an increase of the temperature, leading to 44.6, 61.9, 42.8 and 65.0 %, respectively at 500 °C, respectively; decreasing slightly as the temperature increased (Jaafar et al., 2022). The high value obtained in PS was justified by the aromatic structure, which is more difficult to break, reducing the formation of gases and favoring the formation of liquid. PET and PVC have been reported to decompose mainly into gaseous products at pyrolysis temperatures close to 500 °C (Anuar Sharuddin et al., 2016). PET favors gas production, while the pyrolysis of PVC is accompanied by a dehydrochlorination that generates a large amount of gas. Similar results in the pyrolysis of rigid PP, PE film, and a mixture of rigid PP and PE at 450 °C have been reported (Kusenberget al., 2022), whose yield values were 87 % of oil, 10 % of gas, and 3 % of char. These authors indicated that the introduction of other polymers such as PET or PVC would produce an increase in the solid fraction.

It should also be noted that the appearance of the liquid products is different depending on the type of polymer, see Table S1. The nature of the liquids products is mainly wax and liquid. PS pyrolysis produces mainly an oil with low viscosity. The pyrolysis of PET led to an oil with a great waxy appearance. For PE and PP, the oil products were mainly in the form of wax except for PP at low pyrolysis temperatures which was a liquid. Also, the color of the liquid obtained from the pyrolysis of PE, PP, PET, and PVC was light brown, yellowish, yellowish, and black, respectively. However, in the pyrolysis of HIPS and EPS, the color was brown and dark brown, respectively.

Given that, in general, the best results in terms of liquid yield have been obtained at 500 °C, this temperature was selected for a complete characterization of the oils obtained.

3.2. Elemental analysis and higher heating value of the oils obtained at 500 °C

Table 2 shows the elemental analysis and the higher heating value of the oil obtained in the pyrolysis of the different plastics. The oils obtained from PE and EPS have the highest carbon proportion, 84.3 %, and 83.2 % respectively. However, regarding hydrogen, PE and PP reached the highest percentages. The oil obtained from EPS and PP contains oxygen, i.e. 7.9 % and 8.8 % respectively. On the contrary, the oils obtained from PVC and PET have in their com-

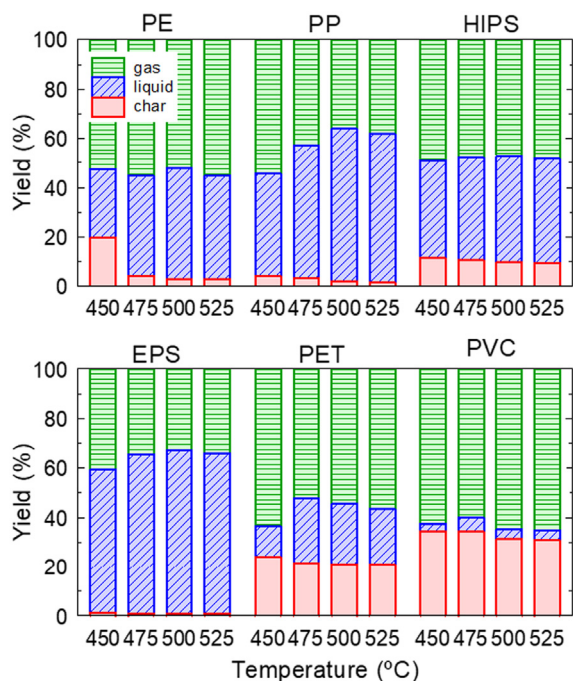


Fig. 2. Product yields (char, oil, and gases) obtained in the pyrolysis of the different plastic waste tested. Experimental conditions: 40 g of plastic, $Q_{N_2} = 100 \text{ mL}\cdot\text{min}^{-1}$; heating rate: $20 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$; holding temperature: 90 min.

Table 2
Elemental analysis and higher heating value of the oil obtained at 500 °C.

Material	Elemental composition (%)						HHV (MJ.kg ⁻¹)
	N	C	H	S	O	Cl	
HIPS	0.32	76.59	8.36	n.d.	14.73	n.d.	35.32
EPS	0.17	83.17	8.72	n.d.	7.94	n.d.	39.28
PE	0.30	84.28	13.79	n.d.	1.63	n.d.	48.06
PP	0.18	84.90	12.95	n.d.	1.97	n.d.	43.28
PVC	0.11	56.88	8.76	n.d.	34.09	0.16	18.45
PET	0.03	62.99	5.68	n.d.	31.30	n.d.	23.90

position a lower percentage of carbon or hydrogen, and a noteworthy amount of oxygen, i.e. 34.1 % and 34.3 % for PVC and PET respectively. It should be also noted the presence of chlorine in the oil from the pyrolysis of PVC. It is known that PVC decomposes in a two-stage mechanism. In the first stage, HCl gas is released and in the second stage, chlorinated hydrocarbons can be released, which are considered important contaminants in pyrolysis oil (Kusenberget al., 2022).

Regarding the calorific value of the oils produced, the values obtained follow the PE > PP > EPS > HIPS > PET > PVC, highlighting the low value obtained for PVC (18.45 MJ.kg⁻¹) or PET (23.90 MJ.kg⁻¹). These results are consistent with the elemental analysis and the HHV of the raw materials (see Table 1). Similar values for elemental analysis and HHV for the oil obtained from the pyrolysis of mixed plastic waste have been reported (Lee et al., 2021). The following HHV values have been found depending on the plastic used: 43.55 MJ.kg⁻¹ for PS oil, 43.70 MJ.kg⁻¹ for PP oil, 43.39 MJ.kg⁻¹ for LDPE oil, and 43.65 MJ.kg⁻¹ for HDPE oil (Budsaerechai et al., 2019). The calorific value of PET and PVC has been reported below 30 MJ.kg⁻¹ due to the presence of benzoic acid in PET and chlorinated compounds in PVC (Anuar Sharuddin et al., 2016).

For a better understanding of the elemental analysis, Figure S1 shows the Van Krevelen diagram in which the ratios H/C and O/C of the pyrolytic oils of this work are compared with other works and two reference fuels, i.e. gasoline and diesel. It is observed that the oil obtained from PE has the highest H/C ratio, while the oil obtained from the pyrolysis of PET has the lowest H/C value. The oils from the pyrolysis of PVC and PET led to the highest O/C ratio, given their higher oxygen proportion found in the elemental analysis, due presence of oxygenated compounds. Moreover, the highest H/C ratio is preferred for oil since it is generally characteristic of a higher fraction of paraffin groups; whereas a higher olefin, naphthene, or aromatics display a lower H/C ratio (Lee et al., 2021).

3.3. FTIR analysis of the oils obtained at 500 °C

The oils obtained from the pyrolysis of each plastic were analyzed by FTIR with the purpose of a qualitative analysis of the compounds present in each case. Fig. 3 shows the FTIR spectra of the oil obtained from each type of plastic, and Table 3 shows the correlation between the peak wavelength and the associated functional group. The FTIR spectra obtained for the pyrolysis oils differ significantly depending on the type of polymer. The peaks at 3082 and 3064 cm⁻¹ represent the stretching vibration of —OH (Kremer et al., 2021) and have been registered in the oils from HIPS and EPS. The presence of alkanes is detected in the range 2957–2855 cm⁻¹ with C—H stretching vibration and 1455–1377 cm⁻¹ with C—H asymmetric vibrations, mainly present in PE, PP, and PVC (Kremer et al., 2021; Singh et al., 2020; Kumar and Singh, 2013). The presence of alkenes can be attributed to the presence of a peak at 1648 cm⁻¹ (C=C stretching) which was mainly detected in PE, PP, and HIPS. The unsaturation can be also confirmed by the presence of peaks at 991 and 776 cm⁻¹ attributed

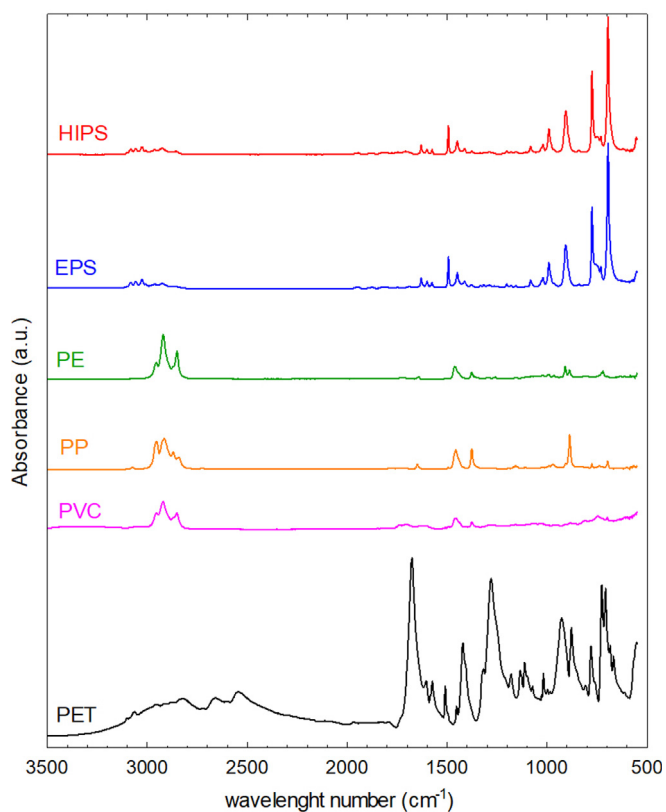


Fig. 3. FTIR spectra of the oil obtained at 500 °C from the different plastic wastes. Experimental conditions as shown in Fig. 2.

to C—H and CH₂ vibrations, respectively (Kremer et al., 2021; Singh et al., 2020; Kumar and Singh, 2013; Malik et al., 2022). The presence of aromatic groups leads to the definition of peaks at 1605–1495 cm⁻¹ corresponding to the aromatic C=C stretching, peaks within 1318–1280 cm⁻¹ due to the C—O stretch, peaks at 1217–1027 cm⁻¹ associated with the C—H in-plane deformation, or at 753–676 cm⁻¹ linked to the C—H out of plane deformation. The oils from HIPS, EPS, PVC, and PET defined aromatic bonds in their FTIR spectra (Budsaerechai et al., 2019; Kremer et al., 2021; Malik et al., 2022). Furthermore, the oil of PVC displays a peak at 605 cm⁻¹ that could correspond to the presence of halogenated compounds due to the chlorine present in this polymer (Torres et al., 2020; Chandran et al., 2019).

3.4. Composition of the oils obtained at 500 °C by GC-MS

The composition of the hydrocarbons contained in the oils obtained in the pyrolysis of each type of plastic was studied by GC-MS. The Total ion chromatogram (TIC) and the composition of hydrocarbons are shown in Fig. 4. The hydrocarbons were clas-

Table 3
Characteristic peaks of FTIR spectra of the oil obtained at 500 °C with each of the plastic waste indicating the bond and the corresponding functional group.

Bond	Functional Group	Wavelength (cm ⁻¹)	HIPS	EPS	PET	PVC	PE	PP
O—H stretch	Alcohols	3082	X	X				
O—H stretch	Alcohols	3064	X	X				
C—H stretch	Aromatics	3028	X	X				
C—H stretch	Alkanes	2957				X	X	X
C—H stretch	Alkanes	2924	X	X		X	X	X
CH— stretch	Alkanes	2870						X
C—H stretch	Alkanes	2855				X	X	X
C=O stretch	Aldehydes	1738					X	
C=O stretch	Aldehydes	1695			X	X		X
C=C stretch	Alkenes	1648					X	
C=C stretch in ring	Aromatics	1605	X	X	X	X		
C=C stretch in ring	Aromatics	1495	X	X				
C—H <i>asym</i>	Alkanes	1455	X	X	X	X	X	X
C—H <i>asym</i>	Alkanes	1377				X	X	X
C—O	Aromatics	1318			X			
C—O	Aromatics	1280			X			
C—H i-p	Aromatics	1217						
C—H i-p	Aromatics	1180			X			X
C—H i-p	Aromatics	1125			X			
C—H i-p	Aromatics	1071	X	X				
C—H i-p	Aromatics	1027	X	X	X	X	X	
C—H o-o-p	Alkenes	991	X	X			X	
C—H o-o-p	Alkenes	965					X	X
CH2 o-o-p	Alkenes	909	X	X			X	
CH2 o-o-p	Alkenes	888			X		X	X
C—H o-o-p	Alkenes	843						
C—H o-o-p	Alkenes	776	X	X	X		X	X
C—H o-o-p	Aromatics	753				X		
C—H o-o-p	Aromatics	729	X	X		X	X	
C—H o-o-p	Aromatics	712			X			
C—H o-o-p	Aromatics	695	X	X	X	X		X
C—Cl stretch	Halo compounds	605				X		

sified according to the length of their carbon chain into three groups, i.e. C₅–C₉, C₁₀–C₁₃, and >C₁₃. There are notable differences between the distributions of carbon number compounds in the oils derived from the different polymers. The oil obtained in the pyrolysis of PE displayed contained the highest proportion of heavy compounds. As can be seen in the TIC of the oil from PE, a wide range of multiple peaks attributable to compounds <C₁₃ was released. Nonetheless, the oil from PP, a polymer similar to PE, leads to a TIC chromatogram completely different, in which the contribution of light and moderate weigh compounds is comparable, with a low presence of hydrocarbons over C₁₃ if compared to PE. The pyrolysis of PE has been already reported to provide a high proportion of heavy compounds (Lee and Shin, 2007; Marcilla et al., 2009). Previous studies have reported similar behavior when comparing PE and PP pyrolysis oil products. The main hydrocarbons obtained from PE pyrolysis are hydrocarbons such as C₆–C₄₁ alkanes and C₈–C₄₁ 1-alkenes (C₈–C₄₁) whereas PP tends to produce lighter compounds, mainly C₄–C₂₄ alkenes, and dialkenes (Ding et al., 2021). As a consequence of the existence of tertiary carbon in the polymeric PP chain, which requires lower activation energy to break than the C–C in the PE chain, the pyrolysis of PP is likely to display more breaking points than the PE, explaining the great difference of products distribution (Zhang et al., 2022).

Regarding PS pyrolysis, either HIPS or EPS gave place to the release of light oils, rich in C₅–C₉ fraction, mainly composed of styrene. The release of aromatic compounds as a consequence of the styrene monomer has been proposed as the main pyrolysis rupture in PS (Budsareechai et al., 2019). In the case of PET, the oil was composed of light (C₅–C₉) and heavy compounds (>C₁₃), with a very low contribution of C₉–C₁₃ hydrocarbons. Finally, the oil from PVC showed a similar contribution of C₉–C₁₃ and >C₁₃ fractions.

The five most abundant compounds present in pyrolytic oil are summarized in Table 4. The pyrolysis of PE and PP gave oils with aliphatic nature, which is consistent with the already reported

studies (Aguado and Serrano, 2006; Ahmad et al., 2015; Sakata et al., 1999; Williams and Slaney, 2007). However, in the case of PE, the distribution of compounds is wide and diverse, mainly alkanes and 1-alkene. In the case of PP, 2,4-dimethyl-1-heptene was the hydrocarbon with the highest contribution. Regarding the composition of the oil from both HIPS and EPS, styrene appeared as the most relevant compound, i.e., 69.9 % for HIPS and 60.6 % for EPS. Moreover, the styrene was followed by alkylated benzenes. Styrene has been previously detected as the major compound in the pyrolysis PS by a large number of researchers (Kaminsky et al., 1995; Onwudili et al., 2009; Scott et al., 1990). However, under acid conditions, the PS lysis is more selective to ethylbenzene, also detected in this work but to a fewer extent than styrene (Soni et al., 2021). Regarding the pyrolysis oil of PET, ethylbenzene (4.7 %), benzaldehyde (18.8 %), and benzoic acid (6.5 %) were detected as the major compounds. The pyrolysis of PET displays a major route via the inner breakage of the monomer which gives place to the release of acetaldehyde and benzoic acid (Dimitrov et al., 2013). However, other derivatives of benzoic acid such as acethylbenzoic acid have been associated if the breakage of the bonds between the monomers takes place (Du et al., 2016). Finally, the oil from PVC contained aromatic compounds such as naphthalene and phenanthrene. These compounds are consistent with the literature, in which benzene, naphthalene, and other polycyclic aromatic hydrocarbons have been identified in the oil from PVC (Montaudo and Puglisi, 1991). The dehydrochlorination of PVC releases unsaturation bonds that promote the formation of aromatic compounds. The presence of labile bonds and defects in the PVC chain, random allylic chlorine atoms, and partial oxidation gives place to ketoalicyclic chlorine compounds, internal double bonds, and head-to-head structures (Soni et al., 2021).

The nature of the compounds in the oil was also classified into five categories, i.e. paraffins, isoparaffins, naphthenes, olefins, and aromatics to elucidate a potential application such as fuel for

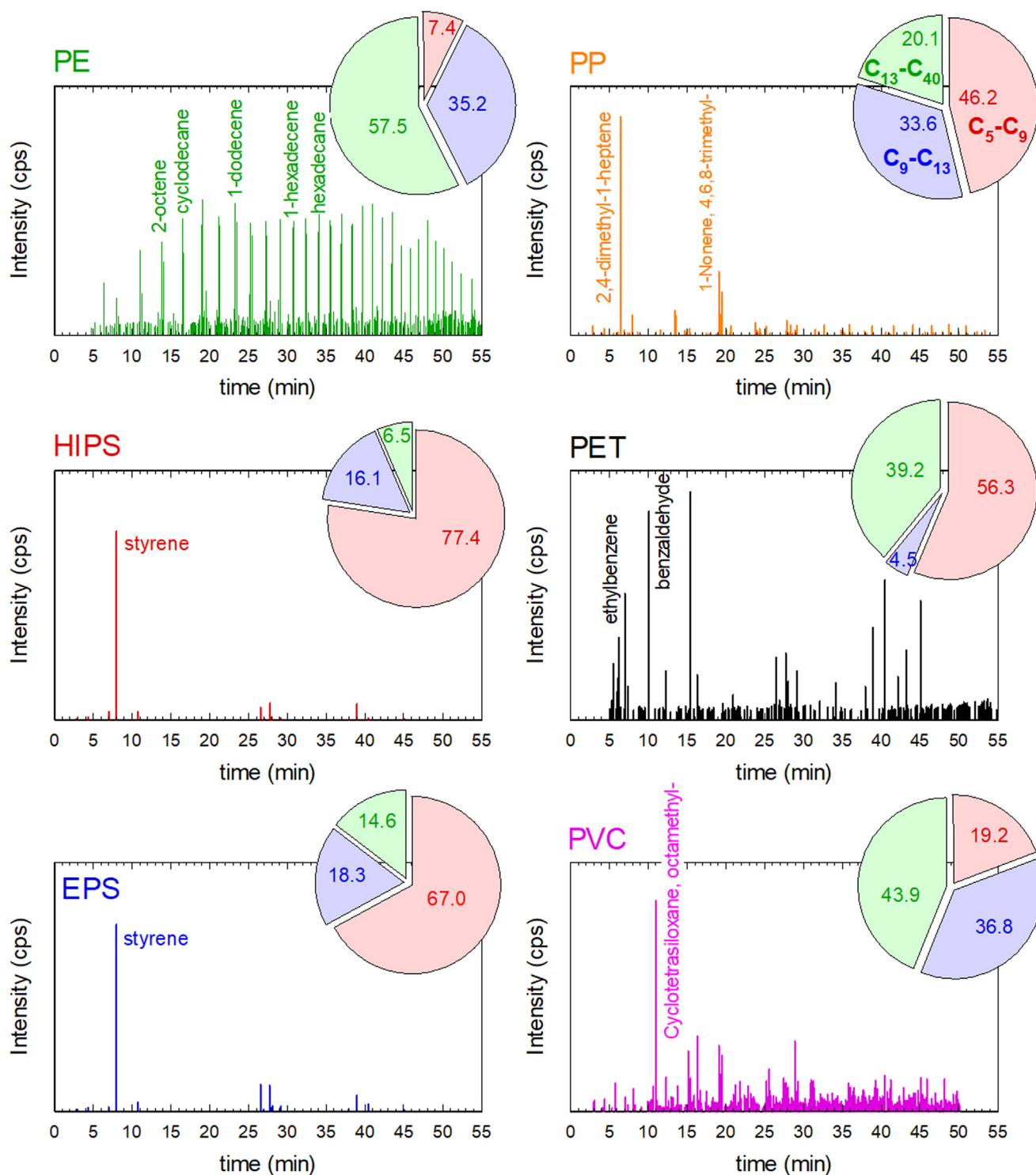


Fig. 4. Characterization of the pyrolysis oil at 500 °C by GC-MS. Total ion chromatogram and distribution by carbon by polymer families. Experimental conditions as shown in Fig. 2.

transport or organic synthesis. Fig. 5 shows the composition of the oil in these categories by type of plastic. The results were not similar for all polymers due to the different monomers of each case. The largest group in PE oil was paraffins (27 %) and isoparaffins (25 %). Similar paraffin distribution has been reported in the oil obtained from HDPE, i.e. 59.7 % of total paraffin (Ahmad et al., 2015). The PP oil also displayed a high proportion of olefins

(65.1 %). This considerable proportion of olefins is consistent with the pyrolysis mechanism. The pyrolysis of PE and PP takes place by random chain scission; giving as result, a broad hydrocarbon spectrum including polyolefins but no aromatics. The oil derived from PS, either HIPS or EPS, led to almost a complete presence of aromatics (~99.8 %) given by the release of the monomer, styrene. The oil derived from PET produced a complex spectrum of

Table 4
Hydrocarbons identified in the oil obtained in the pyrolysis at 500 °C.

Plastic precursor	Main hydrocarbons identified	Area (%)
PE	2-Octene (C ₈ H ₁₆)	2.97
	1-Dodecene (C ₁₂ H ₂₄)	2.00
	Hexadecane (C ₁₆ H ₃₄)	9.94
	1-Hexadecene (C ₁₆ H ₃₂)	3.23
	Nonadecane (C ₁₉ H ₄₀)	5.68
HIPS	Styrene (C ₈ H ₈)	69.88
	Benzene, 3-pentenyl-, (Z)- (C ₁₁ H ₁₄)	7.03
	Cyclopropylphenylmethane (C ₁₀ H ₁₂)	6.96
	Benzene, 1,1'-(1,3-propanediyl)bis- (C ₁₅ H ₁₆)	6.11
	Ethylbenzene (C ₈ H ₁₀)	3.21
EPS	Styrene (C ₈ H ₈)	60.57
	Benzene, 1,1'-(1,3-propanediyl)bis- (C ₁₅ H ₁₆)	8.56
	Benzene, 3-pentenyl-, (Z)- (C ₁₁ H ₁₄)	8.30
	Cyclopropylphenylmethane (C ₁₀ H ₁₂)	6.11
	1,2-Diphenylcyclopropane (C ₁₅ H ₁₄)	2.54
PET	Benzaldehyde(C ₇ H ₆ O)	18.82
	Benzoic acid (C ₇ H ₆ O ₂)	6.53
	Thiocarbamic acid, N, N-dimethyl,S-1,3-diphenyl-2-butenyl ester (C ₁₉ H ₂₁ NOS)	5.80
	1,1':3',1''-Terphenyl, 5'-phenyl-(C ₂₄ H ₁₈)	5.05
PP	Ethylbenzene (C ₈ H ₁₀)	4.71
	2,4-Dimethyl-1-heptene (C ₉ H ₁₈)	27.02
	1-Nonene, 4,6,8-trimethyl- (C ₁₂ H ₂₄)	22.42
	Cyclooctatetraene (C ₈ H ₈)	4.60
	1-Octene, 3,7-dimethyl- (C ₁₀ H ₂₀)	3.53
PVC	Cyclohexane, 1,3,5-trimethyl-2-octadecyl- (C ₂₇ H ₅₄)	3.06
	Cyclotetrasiloxane, octamethyl- (C ₈ H ₂₄ O ₄ Si ₄)	5.15
	Naphthalene (C ₁₀ H ₈)	2.47
	Naphthalene, 2-methyl- (C ₁₁ H ₁₀)	4.33
	Phenanthrene (C ₁₄ H ₁₀)	2.15
	1,1'-Biphenyl, 4-methyl- (C ₁₃ H ₁₂)	2.08

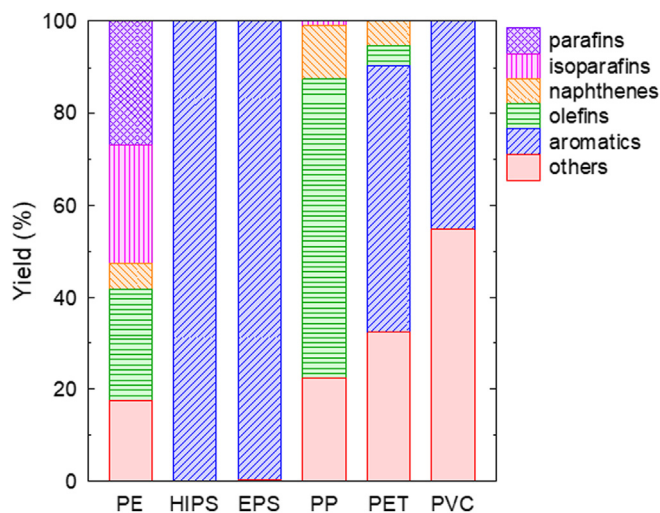


Fig. 5. Distribution of hydrocarbon by families during the pyrolysis at 500 °C of the different plastics. Experimental conditions as shown in Fig. 2.

hydrocarbons that included mainly aromatics (57.9 %), naphthenes (5.2 %), and olefins (4.4 %) groups. However, no paraffins were detected. The pyrolysis of PET is a complex process that releases different types of oxygenated aromatics, which can be degraded generally via decarboxylation and secondary reactions of the transformation products (Çit et al., 2010; Dhahak et al., 2020; Dzięcioł and Trzecznyński, 2001; Yoshioka et al., 2004; Artetxe et al., 2010). Finally, the oil from PVC provided a higher fraction of aromatics (45.3 %) and other uncategorized compounds (54.7 %), attributed to chlorinated compounds. According to the literature,

the decomposition of PVC occurs through three successive processes that include: (1) dehydrochlorination, in which takes place the conversion of PVC into intermediates and gaseous HCl; (2) breakdown of intermediates, i.e. conversion of intermediate compounds into polyene chain and other volatiles; and, (3) breakdown of polyene into aromatics (Gebre et al., 2021; López et al., 2011; Yu et al., 2016).

3.5. Composition of the gases obtained at 500 °C

Fig. 6 shows the evolution of the concentration (% vol, N₂-free) of the main compounds found in the pyrolytic gas as a function of the operation pyrolysis time for each of the tested plastics. Plastics are mainly composed of carbon and hydrogen, so when they decompose by pyrolysis they generate mainly hydrocarbon-containing gases. In this sense, methane, ethane, ethylene, propane, *n*-butane, propylene, or *n*-pentane, are usually the main gaseous products; accompanied by other permanent gases such as hydrogen. Carbon dioxide and carbon monoxide can be released due to the presence of oxygen in the structure of the polymer as in PET (Dhahak et al., 2019), or hydrochloric acid due to the chlorine presence in PVC (Gebre et al., 2021). Other compounds can be generated due to the impurities accompanying the plastics such as the labeling or by contact with other materials such as organic waste (Maqsood et al., 2021; Das and Tiwari, 2018).

As shown in Fig. 6, the nature of the compounds found in the pyrolysis of PE, PS, PP, PET, and PVC is similar; nevertheless, their percentage in the gas varies significantly depending on the type of polymer. The main compound found in the non-condensable gases from the pyrolysis of PE, HIPS, EPS, PP, and PVC was methane, which represents over 50 % and shows a maximum value between 40 and 80 min of operation time. However, in the pyrolysis of PET, the non-condensable gases initially contain a high percentage of carbon monoxide that decreases rapidly as the operation progresses, which may be due, as indicated above, to the presence of oxygen in the structure of the PET. Previous studies about the pyrolysis of PET recovered from municipal plastic waste have reported that during PET pyrolysis oxygen is released. This released oxygen further reacts with carbon to produce carbon monoxide and carbon dioxide. The CO profile decreased with the reaction time as it can react with the carbon to produce CO₂ (Singh and Ruj, 2016), as monitored in this work.

Another of the main compounds found in gases was ethane, especially at significant proportions in HIPS, EPS, and PET with percentages reaching up to 30 % in some cases, and especially at the beginning of the pyrolysis reaction. Also, hydrogen, ethylene, methyl-acetylene, carbon monoxide, and propane were found in gases but in lower concentrations. Similar behavior has been reported during the pyrolysis of PE and PP (Das and Tiwari, 2018). Thus, the concentration of hydrocarbon gases varies as the pyrolysis reaction proceeds with a maximum value that subsequently decreases, which is attributed to the fact that the components with higher molecular weight produced at higher temperatures do not undergo condensation and that at the end of the process, the presence of volatile substances decreases, reporting the presence of propylene, ethane, propane, ethylene, and butane are the main components found in the gas.

It must also be taken into account that the yield of the produced gas is highly variable depending on the type of the polymer (see Table S3). Thus, in the pyrolysis of EPS, the synthetic gas yield is close to 33 %, while in the pyrolysis of PVC, this value rises to up 65 %, which has been also observed in other previous works (Maqsood et al., 2021). The generation of these fuel gases can be used to supply the energy requirements in the pyrolytic reactor if used for combustion. In that sense, the average HHV of N₂-free

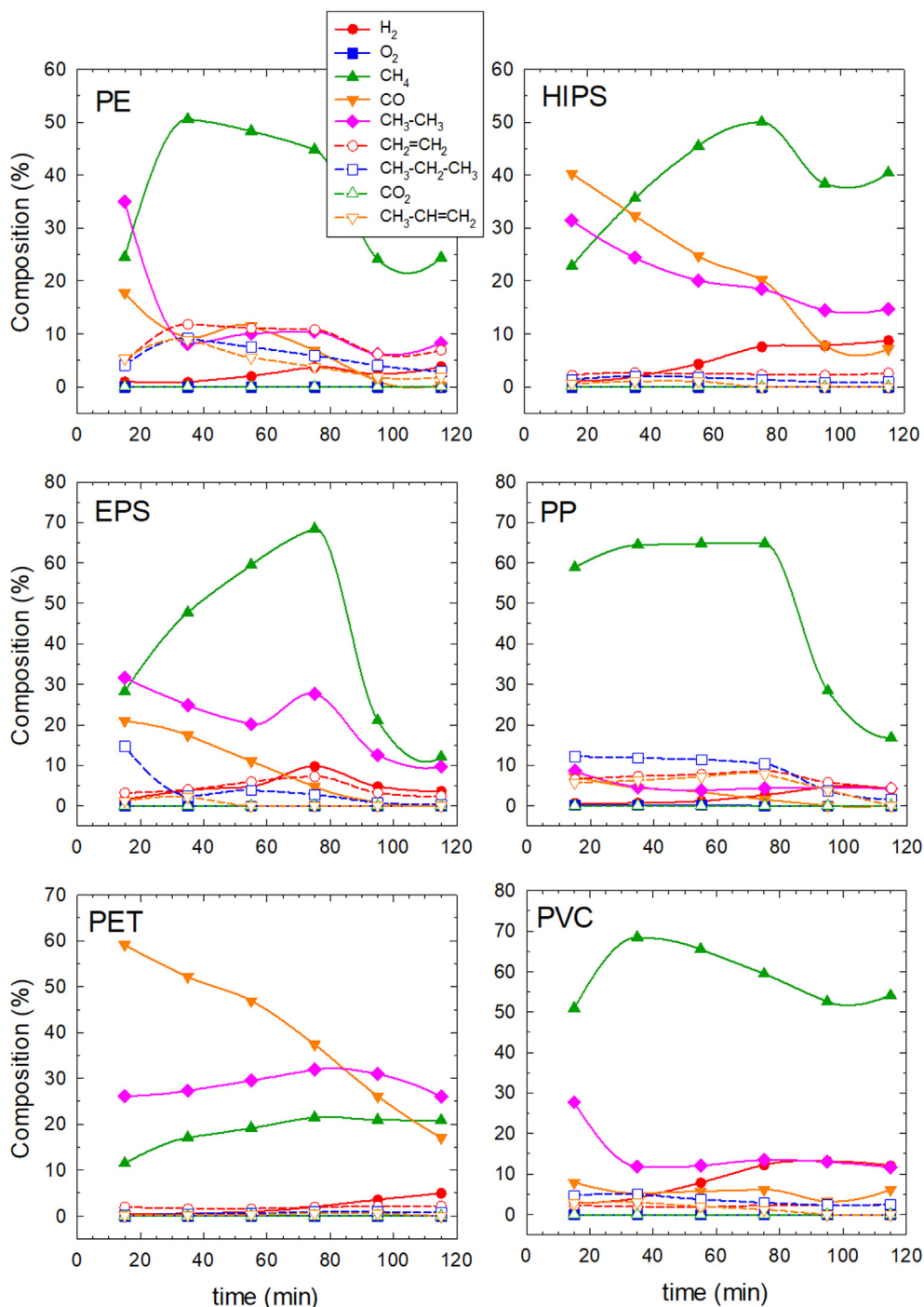


Fig. 6. Evolution of the concentration of non-condensable gases (% vol, N₂ free) found in the pyrolysis at 500 °C of the different plastics. Experimental conditions as shown in Fig. 2.

gas varies between 41.3 MJ·m⁻³ for PP and 68.1 MJ·m⁻³ for PVC, which is appropriate for use as fuel gas.

4. Conclusions

The nature of the polymer plastic used in pyrolysis highly affects not only the product yields but also the composition of the compounds produced. Temperature is important to control the oil-gas yield, with an optimum value maximizing the oil yield at 500 °C with 1 h of pyrolysis treatment. A raise of the tempera-

ture lightly decreased the oil production over 525 °C as observed in the case of PE, PP, EPS, and HIPS. PET and PVC led to very small oil yield and high char proportion due to the presence in the polymer of other elements that differ from exclusively C and H.

Regarding the composition of the oils, HIPS and EPS led to the lightest oils (C₅-C₉ fraction) in terms of carbon number aromaticity due to the high proportion of styrene. On the other hand, regarding the distribution of the heaviest hydrocarbons, PE displayed the highest proportion of compounds over C₁₃. The pyrolysis of PE led to a mix of multiple hydrocarbons, including paraffins,

isoparaffins, naphthalenes, olefins, and aromatics. The hydrocarbons detected in the oil from PP were mainly olefins. The oil from PET and PVC displayed a higher proportion of aromatics due to the presence of aromatic monomers in their structures.

The gas released during the pyrolysis was composed mainly of methane, 70 % of all the gas in the case of EPS, PP, and PVC. This value was 50 % for the pyrolysis of PE and HIPS. These maximum values were reached after 40–80 min depending on each polymer. In the case of EPS and PP, the methane considerably decreased after 80–100 min. As secondary gas, ethane was detected in all the cases. Other minority compounds were hydrogen, ethane, propane, and propane the case of PET, the gas was composed mainly of CO generated from the oxygenated monomer, which gradually decreased over time, generating methane and ethane as secondary compounds.

This work demonstrates the different nature of the oil and gases during the pyrolysis depending on the nature of the polymer. Although they end up mixed after collection in municipal wastes, the separation by families is recommendable and interesting for controlling the composition of the fuels generated.

CRedit authorship contribution statement

Mónica Calero: Investigation, Project administration, Funding acquisition, Supervision. **Rafael R. Solís:** Investigation, Data curation, Writing – original draft. **Mario J. Muñoz-Batista:** Investigation, Formal analysis, Writing – review & editing. **Antonio Pérez:** Methodology, Resources, Validation. **Gabriel Blázquez:** Investigation, Formal analysis, Resources. **M^a Ángeles Martín-Lara:** Conceptualization, Validation, Project administration, Writing – review & editing.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ces.2023.118569>.

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