

# Characterization of liquid fraction obtained from pyrolysis of post-consumer mixed plastic waste: A comparing between measured and calculated parameters



M.F. Paucar-Sánchez<sup>a</sup>, M. Calero<sup>a,\*</sup>, G. Blázquez<sup>a</sup>, M.J. Muñoz-Batista<sup>a</sup>, M.A. Martín-Lara<sup>a</sup>

<sup>a</sup> Department of Chemical Engineering University of Granada, 18071 Granada, Spain

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## ABSTRACT

In this study, thermal pyrolysis of a real mixture of plastic wastes collected from municipal solid waste of Granada (Spain) was performed to obtain a liquid oil. The goals of the present study were: 1) identify the optimal conditions to obtain maximum yields of the liquid fraction, 2) experimentally measure basic characteristic parameters of pyrolytic oils, 3) use correlations or equations used in the hydrocarbon industry to estimate the measured properties, 4) make a comparison between the measured and calculated properties by predictive mathematical expressions, 5) develop new correlations for estimating pyrolytic oil properties. As main results, the optimal temperature to obtain maximum yield of liquid fraction was 500 °C. The physical and chemical properties of pyrolytic oils changed as temperature increased due to the presence of hydrogenation and dehydrogenation reactions. Also, the approximation of the chromatography data allowed to determine, by simulated distillation, the potential fuel yields that will be obtained if processed as synthetic crude in an atmospheric tower and a vacuum tower. Finally, two novel modified equations were proposed to estimate the specific gravity and refractive index parameter for pyrolytic oils.

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## 1. Introduction

The pyrolysis or thermal cracking products of plastic wastes are somewhat unpredictable due to their nature, quantity and behavior during thermolysis, as well as the eventual influence of reaction products and mechanisms, especially when it comes to plastic wastes of unknown origin or their blend. Depending on the polymer or their mixes, and operating conditions, the gaseous and liquid products yield and composition can vary widely (Scheirs, 2006). About this, few studies have been conducted to determine interactions and synergistic effects during degradation of the polymer mix and real pool of plastic wastes. In certain cases, the results and conclusions are contradictory due to different results observed when a blend degrades, compared to the conversion of their individual polymers. On the other hand, the real and theoretical yields suggested that the primary products formed by the degradation of each polymer can react with those of the decomposition of other plastics present in the mixture modifying its structure significantly (Aguado

and Serrano, 1999). As a result, the pyrolytic oil is a complex mixture of compounds so that an individual identify of them is impossible (Scheirs, 2006), however a complete interpretation of its properties and characteristics are important to optimum design and right operation of any system built for its processing (Riazi, 2005). An assay allows to determine the products that can be produced with a given technology, difficulties and downstream processing to optimize yields and specification products, but the overriding issue when performing a comprehensive test is the cost of get a whole information (Rand, 2010).

The hydrocarbon industry has developed a technique semi-empirical that allows the calculation basic parameters to know the quality and properties of crude oils and fuels, from easily measurable laboratory data, applying standard methods, correlation of corresponding states, equations of state and others from acceptable precision. Establish the average boiling temperature from distillation data, transform various distillation curves from one type to another, estimation of molecular weight and chemical composition are the initial steps to its characterization (Riazi, 2005).

The basic laboratory data useful in the characterization methods, based on their significance and simplicity, are the boiling temperature ( $T_b$ ), specific gravity (SG), chemical composition, molecular weight ( $M$ ), refractive index ( $n$ ), elemental analysis and kinematic

\* Corresponding author.

E-mail addresses: [mfpaucars@correo.ugr.es](mailto:mfpaucars@correo.ugr.es) (M.F. Paucar-Sánchez), [mcalero@ugr.es](mailto:mcalero@ugr.es) (M. Calero), [gblazque@ugr.es](mailto:gblazque@ugr.es) (G. Blázquez), [marionunoz@ugr.es](mailto:marionunoz@ugr.es) (M.J. Muñoz-Batista), [marianml@ugr.es](mailto:marianml@ugr.es) (M.A. Martín-Lara).

viscosity ( $\nu$ ), of these at least two must be known for this purpose where the easiest and convenient to measure are  $n$  and  $SG$ , nevertheless, for light fractions the most suitable pair is the boiling temperature and specific weight, but for the heavy fractions three items are required as  $SG$  and  $\nu$  at 37.8 and 98.9 °C (Riazi, 2005).

Thus, to obtain the  $T_b$ , simulated distillation by gas chromatography is used. This is a separation method developed to reproduce the physical distillation of a mixture of hydrocarbons based on their volatilities due to the fact that these elute through of a nonpolar absorbent column according to its boiling point and with a unique retention time, yet compounds with the same volatility and different molecular structure cannot be identified (Wauquier, 2004; Riazi, 2005; Montemayor, 2008); the simulated distillation does not provide information to assess its quality, but it does give details of the products to be obtained (Rand, 2010). The  $n$  is another characterization parameter that allows estimating the composition and quality of hydrocarbons, especially molecular composition when determining the aromaticity and unsaturation by calculating the rate of paraffins and naphthenes (Riazi, 2005; Rand, 2010); unlike others this analysis is the most accurate because it allows the detection of small differences in the quality of hydrocarbons (Wauquier, 2004). On the other hand, elemental analysis provides information on the quality of petroleum products by determining the content of sulfur, nitrogen, oxygen, carbon and hydrogen (Riazi, 2005).

Various studies have been developed searching waste plastics utility alternative, such as recycling or using it as energetic sources, like fuels or chemical precursors, however, all of them focused on yields and chemical composition using specialized instruments along with measurement of basic physic properties without determining correlations that allow their calculation based on laboratory data when experimental data are not available, due to the absence of special equipments. Although some of them have employed hydrocarbon correlations to calculate certain properties, mainly from the higher heating value (HHV) (Dobó et al., 2019; Quesada et al., 2020) and other like cetane index (Quesada et al., 2019), Isoparaffin Index and RON (Das and Tiwari, 2018a and 2018b), no one has established their deviation respect from real measurement.

Since a form of evaluation and comparison of hydrocarbon correlations to estimate a certain property from the same input parameters is through a data set on used to obtain them, the objectives of this study, in addition to identifying the optimal conditions to obtain maximum yields of the liquid fraction when thermal cracking severity increases to different temperatures from 450 °C to 550 °C from real mix of plastic wastes with similar composition of the municipal waste plastics collected in Granada – Spain, were to evaluate a number of existing models for the characterization of hydrocarbons using pyrolytic oil and make a comparison between the results obtained by instrumental analytic measurements carry out on the liquid fraction of distillation, density, refractive index and elemental analysis with those predicted by the these mathematical correlations.

## 2. Materials and methods

### 2.1. Materials

Waste plastic materials were taking from the rejected fraction, unrecovered and fines from mechanical treatment of Ecocentral Plant (37° 03' 03.5" N, 3° 42' 17.8" W), compacted in bales for their end disposal at landfills; which ones were selected samples made of polypropylene (PP), polystyrene (PS), mainly high impact polystyrene with paper from tags (HIPS + P) and expanded polystyrene (EPS) and film (PE). The average composition of bales was 55.71% of polypropylene, 25.71% of film, 10% of expanded polystyrene and 8.57% of high impact polystyrene.

**Table 1**  
Correlation equations of ASTM STP 577 (ASTM, 2015).

D86 – IBP = 46.566 + 0.58289 (D2887 10%) + 0.34795 (D2887 IBP)
D86 – 10% = 33.308 + 0.61562 (D2887 10%) + 0.35110 (D2887 20%)
D86 – 20% = 22.411 + 0.48903 (D2887 30%) + 0.27528 (D2887 20%) + 0.21713 (D2887 10%)
D86 – 30% = 14.431 + 0.47035 (D2887 30%) + 0.28369 (D2887 20%) + 0.22784 (D2887 50%)
D86 – 50% = 4.876 + 0.97597 (D2887 50%)
D86 – 70% = 0.911 + 0.51975 (D2887 80%) + 0.33260 (D2887 70%) + 0.10159 (D2887 30%)
D86 – 80% = 0.279 + 0.75936 (D2887 80%) + 0.28333 (D2887 95%) – 0.09975 (D2887 FBP)
D86 – 90% = – 1.973 + 0.61459 (D2887 90%) + 0.31909 (D2887 95%)
D86 – FBP = 34.179 + 1.14826 (D2887 95%) – 0.59208 (D2887 90%) + 0.31542 (D2887 FBP)

where D86 and D2887 are ASTM methods, IBP is initial boiling point, FBP is final boiling point and temperatures are in Fahrenheit.

**Table 2**  
Constants and Restrictions of Eq. 7 (ASTM, 1999).

i	Cut Point Range	A	B	Approximate maximum allowable $X_i$ (°F)
1	100–90%	0.11798	1.6606	–
2	90–70%	3.0419	0.75497	100
3	70–50%	2.5282	0.82002	150
4	50–30%	3.0305	0.80076	250
5	30–10%	4.9004	0.71644	250
6	10–0%	7.4012	0.60244	100

**Table 3**  
Correlations equations of API procedure 3A1.1 (ASTM, 1999).

TBP (0%) = TBP (50%) – $Y_4$ – $Y_5$ – $Y_6$
TBP (10%) = TBP (50%) – $Y_4$ – $Y_5$
TBP (30%) = TBP (50%) – $Y_4$
TBP (70%) = TBP (50%) + $Y_3$
TBP (90%) = TBP (50%) + $Y_3$ + $Y_2$
TBP (100%) = TBP (50%) + $Y_3$ + $Y_2$ + $Y_1$

To facilitate the homogeneity of the samples for the different pyrolysis tests, the different polymers were separated, washed, dried and manually crushed to an approximate size of 1–3 mm. Subsequently, in the different pyrolysis experimental tests, a mixture was prepared with the same proportion of polymers than that in the bales obtained in the Ecocentral plant.

### 2.2. Methods

#### 2.2.1. Pyrolysis tests

Thermolysis experimental tests were carried out in a horizontal fixed-bed reactor (Nabertherm R 50/250/12 Model) integrated with a flow meter to regulate the inert entrainment fluid and a condensation container immersed in cold bath to separate the liquid and the gas phases.

Approximately 25 g of sample was loaded inside the reactor, then it was heated to rate of 10 °C/min from room temperature to reach different operating temperature between 450 and 550 °C, which were kept 90 min with a constant flow rate of nitrogen of 100 L/h. After the experiments, the reactor was cooled to room temperature under a constant nitrogen purge and then the solid residues were collected. Solid residue and oil were directly measured, and the yields were calculated according the following equations (gas fraction by difference to 100%):

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

**Table 4**  
Information about equations used to predict SG.

Equation number	Equation type	Needed parameters	Constants
15	$SG = a \cdot \theta_1^b \cdot \theta_2^c$	$T_{10\%}$ and $T_{50\%}$	Table 5 for choosing "a", "b" and "c" parameters.
16	$SG = a \cdot \exp(b \cdot \theta_1 + c \cdot \theta_2 + d \cdot \theta_1 \cdot \theta_2) \cdot \theta_1^e \cdot \theta_2^f$	$T_b$ and $I$	$a = 2.4381 \cdot 10^7$ $b = -4.194 \cdot 10^{-4}$ $c = -23.5535$ $d = 3.98736 \cdot 10^{-3}$ $e = -0.3418$ $f = 6.9195$
17	$SG = a \cdot \exp(b \cdot \theta_1 + c \cdot \theta_2 + d \cdot \theta_1 \cdot \theta_2) \cdot \theta_1^e \cdot \theta_2^f$	$T_b$ and CH ratio	$a = 2.86706 \cdot 10^{-3}$ $b = -1.83321 \cdot 10^{-3}$ $c = -0.081635$ $d = 6.49168 \cdot 10^{-5}$ $e = 0.890041$ $f = 0.73238$

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

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

Where  $\eta_l$ ,  $\eta_s$ ,  $\eta_g$  and  $m_l$ ,  $m_s$ ,  $m_g$  are the yields and weights of liquid, solids and gases, respectively.

The experiments have been repeated three times for each pyrolysis temperature and an average value was presented in figures and tables.

### 2.2.2. Density and specific gravity (SG)

The density's measurements were done in a handheld density meter Desnyto2Go from Mettler Toledo on 2 mL of sample according to the ASTM D7777 designation (ASTM, 2013).

In order to obtain the specific gravity, the observed density was corrected to the density at 15 °C using Table 53 A (Generalized for Crude Oil) from the Manual of Petroleum Measurement Standards and then using the relationship defined by the SI system of the following way:

$$SG = 1.001 \cdot d_4^{15} \quad (4)$$

Where  $d_4^{15}$  is the ratio of the density of hydrocarbon at 15 °C to that of water at 4 °C (API, 2003).

### 2.3. Refractive index ( $n_D$ 20) and refractive index parameter (I)

Refractive index or refractivity is a fundamental physical property that can be used in conjunction with other properties to characterize pyrolysis oils. These were evaluated on a Mettler Toledo refractometer RM40 model from 1.32 to 1.70 range. The measurement was carrying out whit 0.5 mL of oil free of impurities at 20 °C according to the ASTM D1218 and D1747 designations (ASTM, 1999 and ASTM 2000); a calibration curve was plotted using the primary referential materials from both methods to correct the observed measurements.

The Refractive Index Parameter (I) was calculated according to Eq. 5, Huang characterization parameter, (Huang, 1977; Riaz, 1980).

$$I = \frac{n_D \cdot 20^2 - 1}{n_D \cdot 20^2 + 2} \quad (5)$$

**Table 5**  
Restrictions and Constants for Eq. 15.

Distillation type	$T_{10\%}$ range, °C	$T_{50\%}$ range, °C	SG Range	A	b	c
ASTM D86	35 – 295	60 – 365	0.70 – 1.00	0.08342	0.10731	0.26288
TBP	10 – 295	55 – 320	0.67 – 0.97	0.10431	0.12550	0.20862

#### 2.3.1. Elemental analysis

The main elements present in pyrolysis oil (carbon, hydrogen, nitrogen, oxygen and sulfur) were measured using a Termo Scientific Flash 2000 CHNS/O Analyzer by rapid combustion with pure oxygen where the flue gases pass through a chromatographic separation column and a thermal conductivity detector in accordance to ASTM D5291 designation (ASTM, 2008a).

#### 2.3.2. Compositional analysis by gas chromatography

Oils samples were analyzed through of Gas Chromatography by Spectrometry Masses (GC-MS) using the Agilent 8860 Gas Chromatograph System endowed with a Phenomenex GC column and nonpolar phase ZB-1HT (30 m long, 0.25 mm internal diameter and 0.25 μm of fill thickness) coupled to a triple-quadrupole Mass Spectrometer 5977 GC/MSD model from Agilent with analysis scan speed ≤ 20000 Da/s and ionization energy by electronic impact of 70 eV.

Samples were weighted and diluted in 1 mL of chloroform, then were injected in split mode (10:1) to 250 °C together with 1.8 mL/min carry gas Helium at constant flow. The heated rate was 10 °C/min from 35 up to 350 °C. The transfer line and detector stayed at 250 °C.

#### 2.3.3. Simulated distillation (SD)

To determine the boiling range distribution of pyrolytic oil products, such as petroleum fractions with an equivalence to a 100 theoretical-plate physical distillation performed at atmospheric pressure, simulated distillation curves were constructed according to the ASTM D2887 (ASTM, 2008b) designation using the individual chromatograms of each sample analyzed. For this, the retention time of their compounds was taken to determine the boiling points by linear interpolation as follows:

$$BP_x = \left( \frac{BP_2 - BP_1}{RT_2 - RT_1} \right) \cdot (RT_x - RT_1) + BP_1 \quad (6)$$

Where  $BP_1$ ,  $BP_2$  and  $RT_1$ ,  $RT_2$  are the boiling points and retention times of referential normal paraffins, and  $BP_x$  and  $RT_x$  are the boiling points and retention times of the compounds in the sample.

The referential retention times of normal paraffins were identified from the polyethylene pyrolytic oil spectrometer using the mass spectroscopy library of the National Institute of Standards and Technology (NIST) (ASTM, 2008b).

**Table 6**  
Information about equations used to predict I.

Equation number	Equation Type	Needed parameters	Constants
18	$I = a \cdot \theta_1^b \cdot \theta_2^c$	$T_b$ and SG	a= 0.3773 b= -0.02269 c= 0.9182
19	$I = a \cdot \exp(b \cdot \theta_1 + c \cdot \theta_2 + d \cdot \theta_1 \cdot \theta_2) \cdot \theta_1^e \cdot \theta_2^f$	$T_b$ and SG	a= 0.02343 b= $7.0294 \cdot 10^{-4}$ c= 2.46832 d= $-1.0268 \cdot 10^{-3}$ e= 0.05721 f= -0.71990
20	$I = a \cdot \exp(b \cdot \theta_1 + c \cdot \theta_2 + d \cdot \theta_1 \cdot \theta_2) \cdot \theta_1^e \cdot \theta_2^f$	$T_b$ and SG	a= $3.2709 \cdot 10^{-3}$ b= $8.4377 \cdot 10^{-4}$ c= 4.59487 d= $-1.0617 \cdot 10^{-3}$ e= 0.03201 f= -2.34887
21	$I = a \cdot \exp(b \cdot \theta_1 + c \cdot \theta_2 + d \cdot \theta_1 \cdot \theta_2) \cdot \theta_1^e \cdot \theta_2^f$	$T_b$ and CH ratio	Used for heavy hydrocarbons a= $5.60121 \cdot 10^{-3}$ b= $-1.7774 \cdot 10^{-4}$ c= $-6.0737 \cdot 10^{-2}$ d= $-7.9452 \cdot 10^{-5}$ e= 0.447 f= 0.9896

2.3.4. ASTM D86 distillation

In order to reduce the conversion error between the SD to the True Boiling Point (TBP) curve by direct conversion, the SD was first transformed into ASTM distillation according with Standard Test Practice ASTM STP 577 as report in Table 1 (Riazi, 2005, ASTM, 2015).

2.4. True boiling point curve (TBP)

The distillation data available in the form of ASTM D86 can be converted to TBP according to American Petroleum Institute (API) Procedure 3A1.1 with the following equations (ASTM, 1999).

$$TBP (50\%) = 0.8718 (ASTM 50\%)^{1.0258} \tag{7}$$

where TBP (50%) is the true boiling point temperature at 50 vol percent distilled, °F, and the ASTM (50%) is the ASTM D86 temperature at 50 vol percent distilled, °F.

$$Y_i = A \cdot X_i^B \tag{8}$$

where  $Y_i$  is the true boiling point temperature difference between tow cuts points, °F,  $X_i$  is the ASTM D86 temperature difference

**Table 7**  
Information about equations used to predict CH ratio.

Equation number	Equation Type	Needed parameters	Constants
22	$CH = a \cdot \exp(b \cdot \theta_1 + c \cdot \theta_2 + d \cdot \theta_1 \cdot \theta_2) \cdot \theta_1^e \cdot \theta_2^f$	$T_b$ and SG	a= 3.47028 b= $1.4850 \cdot 10^{-2}$ c= 16.94020 d= -0.012491 e= -2.72522 f= -6.79769
23	$CH = a \cdot \exp(b \cdot \theta_1 + c \cdot \theta_2 + d \cdot \theta_1 \cdot \theta_2) \cdot \theta_1^e \cdot \theta_2^f$	$T_b$ and SG	a= $8.7743 \cdot 10^{-10}$ b= $7.176 \cdot 10^{-3}$ c= 30.06242 d= $-7.35 \cdot 10^{-3}$ e= -0.98445 f= -18.2753 This equation was developed based on data in the range of $C_{20}$ - $C_{50}$ . However, it can also be used for hydrocarbons from $C_6$ to $C_{50}$ .
24	$CH = a \cdot \exp(b \cdot \theta_1 + c \cdot \theta_2 + d \cdot \theta_1 \cdot \theta_2) \cdot \theta_1^e \cdot \theta_2^f$	$T_b$ and I	a= $8.39640 \cdot 10^{-13}$ b= $7.7171 \cdot 10^{-3}$ c= 71.6531 d= -0.02088 e= -1.3773 f= -13.6139

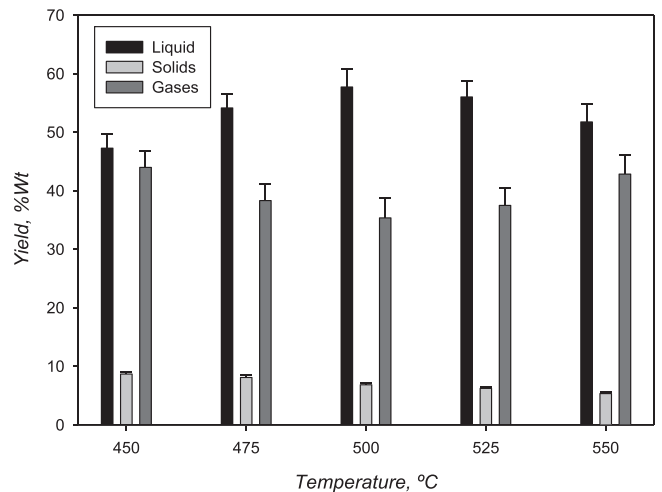


Fig. 1. Individual yields from pyrolysis of waste plastic mix.

**Table 8**  
Deviation from Measured and Calculated Data.

Estimated Parameter	Pyrolysis temperature, °C	Experimental value	Estimated value	Deviation, %
SG	450	0.8344	0.8249 –Eq. 15	-1.14
			0.8416 –Eq. 16	0.86
			0.8208 – Eq. 17	-1.62
	500	0.8349	0.8833 –Eq. 15	5.79
			0.8453 –Eq. 16	1.24
			0.8312 – Eq. 17	-0.45
	550	0.8413	0.8870 –Eq. 15	5.43
			0.8561 –Eq. 16	1.76
			0.8928 – Eq. 17	6.12
I	450	0.2786	0.2770 – Eq. 18	-0.59
			0.2761 – Eq. 19	-0.92
			0.2767 – Eq. 20	-0.69
	500	0.2781	0.2710 – Eq. 21	-2.74
			0.2764 – Eq. 18	-0.60
			0.2752 – Eq. 19	-1.03
	550	0.2846	0.2771 – Eq. 20	-0.34
			0.2738 – Eq. 21	-1.53
			0.2782 – Eq. 18	-0.97
CH ratio	450	6.05	0.2767 – Eq. 19	-1.52
			0.2792 – Eq. 20	-0.62
			0.2846 – Eq. 21	1.32
	500	6.25	6.38 – Eq. 22	3.10
			6.73 – Eq. 23	8.73
			6.79 – Eq. 24	9.61
	550	7.31	6.25 – Eq. 22	0.01
			6.45 – Eq. 23	3.11
			6.53 – Eq. 24	4.36
550	7.31	6.30 – Eq. 22	-13.93	
		6.54 – Eq. 23	-10.55	
		6.68 – Eq. 24	-8.69	

between tow cuts points, °F, and A and B are constants varying for each cut point and are given in Table 2.

Finally, to determine the true boiling point temperature at any percent distilled, the equations reported in Table 3 are applied.

### 2.5. Mean average boiling point ( $Me_{ABP}$ )

Generally, an average boiling point is defined to determine the single characterization boiling ( $T_b$ ). One of these average boiling temperature is  $Me_{ABP}$  (Mean average boiling point) that can be determined by ASTM D86 curve according the following equations (API, 1999; Wauquier, 2004):

$$V_{ABP} = \frac{T_{10\%} + T_{30\%} + T_{50\%} + T_{70\%} + T_{90\%}}{5} \quad (9)$$

$$SL = \frac{T_{90\%} - T_{10\%}}{80} \quad (10)$$

$$\ln(\Delta T_{Me}) = -1.53181 - 0.0128 * V_{ABP}^{0.6667} + 3.646064 * SL^{0.333} \quad (11)$$

$$Me_{ABP} = V_{ABP} - \Delta T_{Me} \quad (12)$$

where  $T_{i\%}$  are temperatures at “i” vol% distilled and are in K.

#### 2.5.1. Mathematical correlation for hydrocarbons

Following, several correlations for the estimation of specific gravity, refractive index parameter and carbon-hydrogen weight ratio are reported. These correlations were obtained by Raizi and Daubert (1980) and Riazi and Daubert (1987) from data on approximately 140 pure hydrocarbons in the molecular weight range of 70–300 and boiling point range between 300 and 620 K. These authors proposed correlations that can be expressed in terms of two parameters as follows:

$$\theta = a \cdot \theta_1^b \cdot \theta_2^c \quad (13)$$

$$\theta = a \cdot \exp(b \cdot \theta_1 + c \cdot \theta_2 + d \cdot \theta_1 \cdot \theta_2) \cdot \theta_1^e \cdot \theta_2^f \quad (14)$$

Values of constants in Eqs. 13 and 14 for SG, I and CH ratio and pairs of  $\theta_1$  and  $\theta_2$  listed above are given in Tables 4, 5, 6 and 7. All temperatures are in K.

## 3. Results and discussion

### 3.1. Effect of operating temperature on liquid fraction

Fig. 1 shows the yields to products when the mix of plastic waste from municipal solid waste was pyrolyzed at temperatures between 450 and 550 °C with a heating rate of 10 °C/min. Results showed that the pyrolytic oil yield was high performing pyrolysis at 500 °C, reaching a liquid product yield of 57.7%. An increase of the operating temperature to 550 °C decreased the pyrolytic oil yield to 51.8%. It can be attributed to the formation of more non-condensable gases due to the secondary cracking or reforming reactions of the heavy-molecular-weight compounds in the pyrolysis vapors (Shadangi and Mohanty, 2014). Also, a decrease of the pyrolysis temperature to 450 °C decreased the pyrolytic oil yield to 47.3%. The reason for lower liquid product yield at this low temperature can be that the temperature was not enough high for complete pyrolysis (Islam et al., 1999).

These results were also observed by others researchers. For example, Quesada et al. (2020) studied the pyrolysis of a plastic waste mixture with a composition of 50% of PE, 25% of PP and 25% of PS at 500 °C for 120 min with a heating ratio of 10 °C /min and they obtained 64% of pyrolytic oil. Also, Miandad et al. (2017) worked at 450 °C for 75 min with the same heating rate and a mixture of plastic materials (PS 50%, PE 25% and PP 25%) and they got 49% of liquid fraction. Dobó et al. (2021) prepared three blends using high density polyethylene HDPE (15%), low density polyethylene LDPE (22%), PP (49%) and PS (14%) to be pyrolyzed up to 520 °C in a batch reactor obtaining 72.85% of liquid product. Auxilio et al. (2017) collected 82%

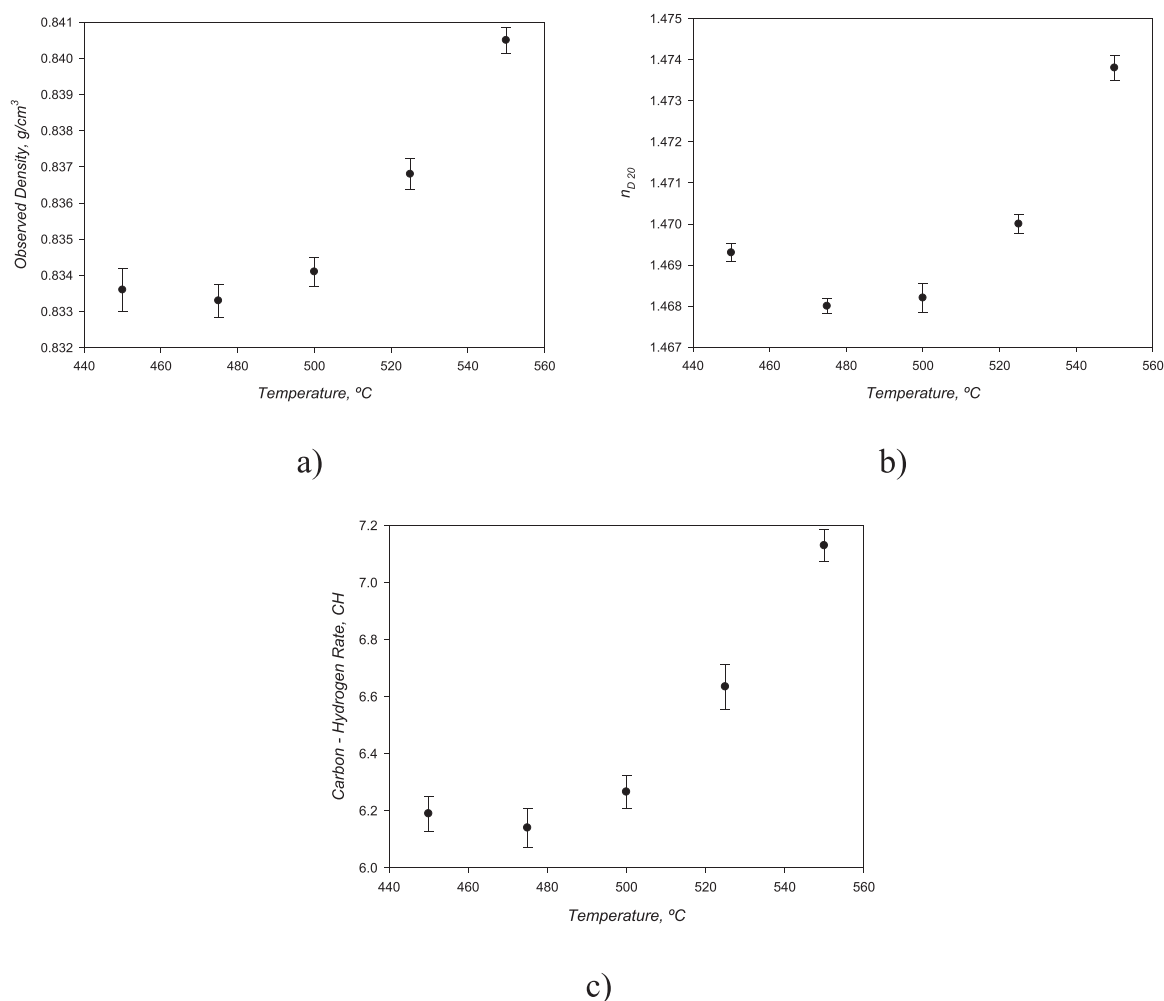


Fig. 2. Behavior of a) the specific gravity, b) the refractive index and c) the carbon-hydrogen ratio of the pyrolytic oils.

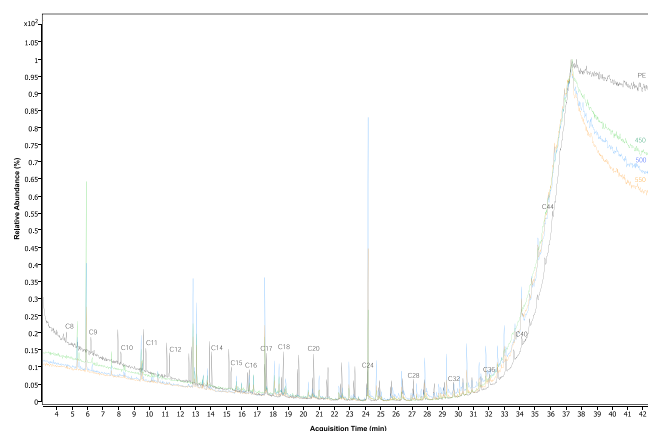


Fig. 3. Chromatograms of the pyrolytic oils obtained from the mixture of plastic waste at 450, 500 and 550 and calibration mixture.

oil from 27.5% LDPE, 27.5% HDPE, 17% PS and 28% PP at 425  $^{\circ}C$  in a continuous stirred tank reactor CSTR for 250 min. Ibrahim et al. (2018) made thermal degradation of mixed HDPE (25%), LDPE (30%), PP (30%) and PS (15%) at 400  $^{\circ}C$  and they achieved about 95% liquid oil. Costa et al. (2021) performed pyrolysis experiments with self-generated pressure, for 30 min at 440  $^{\circ}C$  and 5.5  $^{\circ}C/min$  of heating, of the mixture of LDPE (60 y 80%), PP (20 y 10%) and PS (20% and 10%) of which they drew 87% and 92.5% of liquid. A thermal decomposition

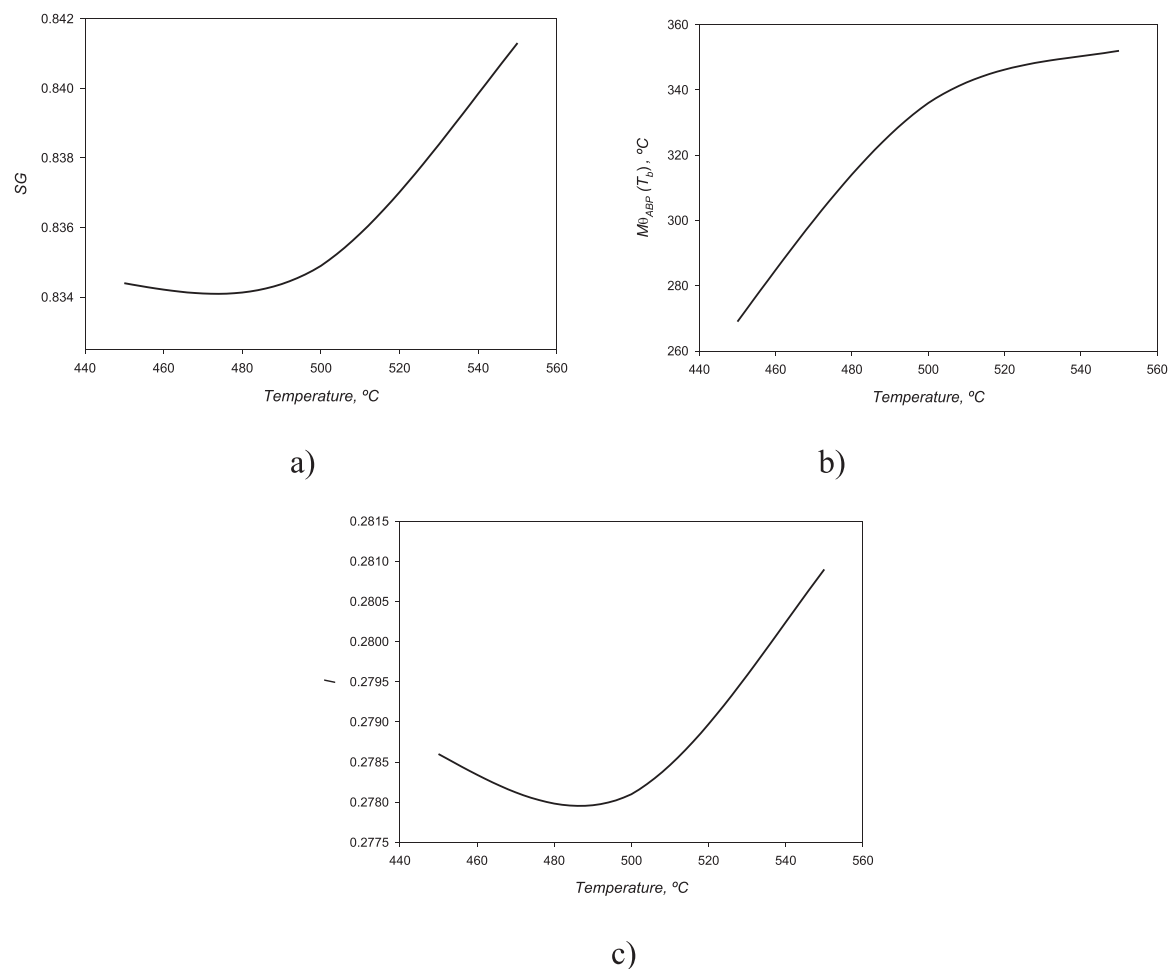
up to 430  $^{\circ}C$  for 20 min under 3.5 MPa of pressure was carried out by Pinto et al. (1999a) and they extracted 90% of liquid from 68% PP, 16% PE and 16% PS. An increase of 3.5% was gained when the composition changed at 68% PE, 16% PP and 16% PS.

The differences in the results indicate that the operating conditions, the system configuration used, the nature of the plastic waste and its composition are determining factors in obtaining better yields from the liquid fraction.

### 3.2. Experimental data on basic properties of pyrolytic oil samples

As an example, some of the numerical values measured experimentally of liquid fractions are shown in Table 8. Also the behavior of basic properties of pyrolytic oil samples with increasing the operating temperature is presented in Fig. 2. The observed density of pyrolytic oils is in the range 0.8266 – 0.8333  $g/cm^3$ . The refractive index was found in the range of 1.4682–1.4738, values that are between of those characteristic of naphthenes and aromatics (Riazi, 2005). Regarding the change of the carbon-hydrogen weight ratio from 6.19 to 7.31, as quality measurement, shows that as temperature increase, the pyrolytic oil is heavier (Riazi, 2005).

Regarding the effect of pyrolysis temperature, Fig. 2a shows as the observed density of the oils increased when the pyrolysis temperature increased, mainly between 500 and 550  $^{\circ}C$ . Fig. 2b exhibit a slight decrease of refractive index from 450 to 500  $^{\circ}C$  and an appreciable growth when the pyrolysis temperature changed from 500 to 550  $^{\circ}C$  due to hydrogenation and dehydrogenation reactions



**Fig. 4.** Trend of a) the specific gravity, b) the boiling temperature and c) the refractive index parameter of the pyrolytic oils obtained from the mixture of plastic waste at 450, 500 and 550 °C.

shown by increasing and decreasing the hydrogen weight ratio. Finally, Fig. 2c shows that as the pyrolysis temperature increases, the carbon-hydrogen ratio increases as result of presence of more unsaturated compounds due to decreasing hydrogen content and increase of carbon.

Fig. 3 shows the CG-MS results. PE chromatogram with the retention times of the normal paraffins to cover the boiling range from  $n - C_5$  to  $n - C_{44}$ , according the carbon numbers suggested by ASTM D2887 designation, to construct the simulated distillation curves of the pyrolytic oils by gases chromatography was included. Throughout the experimental chromatograms, it is evident to observe the reduction of the peak areas of some light hydrocarbons due to over cracking and the increase of the peak areas of the heavy hydrocarbons due to the greater presence of these as the pyrolysis temperatures increase.

In pyrolysis, the temperature effect is reflected in the observed or measured oil properties due to the presence of hydrogenation and dehydrogenation reactions, the first by the over cracking of the light vapors at low experimental temperature to produce hydrogen and the latter by the cracking of heavy compounds at high experimental temperature.

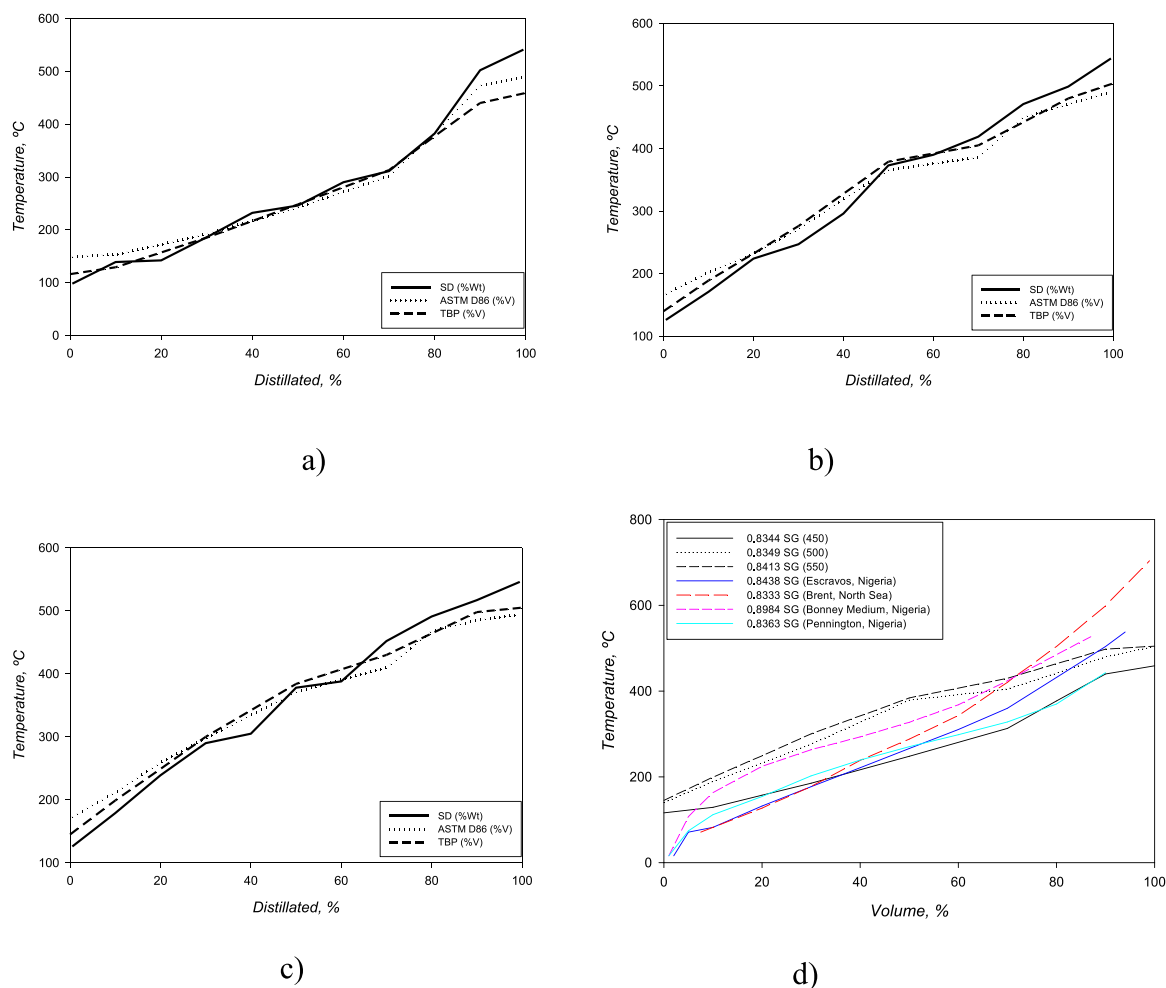
### 3.3. Conversion of measured properties into parameters for hydrocarbon characterization

Fig. 4 shows the calculated SG,  $Me_{ABP}$  and  $I$ . Specific gravity showed an appreciable rise when it reached 550 °C, changed from

0.8344 at 450 °C to 0.8413 at 550 °C. The mean average boiling point increase when was increased from 450 to 550 °C, maintain mainly constant between 500 and 550 °C. Regarding refractive index parameter, it showed a substantial increase at 550°C when the severity in pyrolysis rise, this due to minor hydrogenation reactions and intense dehydrogenation reactions. The values of refractive index indicated that the three samples are predominantly naphthenic (0.278 – 0.308) (Riazi, 2005) with increasing order for the pyrolytic oils of 500, 450 and 550 °C.

Fig. 5 shows simulated distillation (SD), ASTM D86 distillation and True Boiling Point (TBP) curves. They represent characteristic curves like those of hydrocarbons but with a lower proportion of light and heavy hydrocarbons compounds than those of crude oils. Of these, the pyrolytic oils got at 500 and 550 °C are heavier than 450 °C oil and 550 °C oil more than 500 °C oil. On the other hand, as shown the TBP curves of Escravos and Brent (Treese, 2015), typical crude oils with specific gravities near to pyrolytic oils, have marked differences in trends and composition, but those crude oils with a close tendency that the pyrolytic oils, as Pennington and Brent (Treese, 2015), have different specific gravities.

The specific gravity and the refractive index parameter reflect the changes of the chemical structure of the pyrolytic oil as experimental temperature increase. The simulated distillation curves show a lower proportion of light and heavy compounds compared as those of hydrocarbons.



**Fig. 5.** Simulated distillation, ASTM D86 curve and true boiling point at a) 450 °C, b) 500 °C, c) 550 °C and d) the three TBP curves of the pyrolytic oils obtained from the mixture of plastic waste and selected crude oils.

### 3.4. Application of mathematical correlations for hydrocarbons

In this section, a comparison between experimental and estimated parameters (Specific Gravity, Refractive Index Parameter and Carbon-Hydrogen ratio) of pyrolytic oils is presented. Fig. 6 shows the main obtained results (as an example, some of the numerical values are shown in Table 8).

Since the trends by Eqs. 14 and 16 are approximately similar to those of the experimental data, these equations have been used as a base to fitting the exponential values and obtain the following new correlations, which give  $R^2$  of 0.9963 and 0.9862 for equations 25 and 26 with average deviations of 0.14% and 0.12%, respectively.

$$SG = 2.4381 \cdot 10^7 \cdot \exp(-4.79 \cdot 10^{-4} \cdot Me_{ABP} - 23.4593 \cdot I + 3.988 \cdot 10^{-3} Me_{ABP} \cdot I) \cdot Me_{ABP}^{-0.3419} \cdot I^{6.921} \quad (25)$$

$$I = 0.3773 \cdot T_b^{-0.0217} \cdot SG^{0.92} \quad (26)$$

where  $T_b$  has been changed for  $Me_{ABP}$  in K, SG is the specific gravity at 15.5 °C and I is the refractive index parameter at 20 °C and 1 atm.

The specific gravity and the refractive index parameter calculated by Ec. 25 and Ec. 26 has a deviation of less than 0.15% from the experimentally measured data and its tendency as the temperature increases is identical from 450 to 500 °C to that formed by the experimental data.

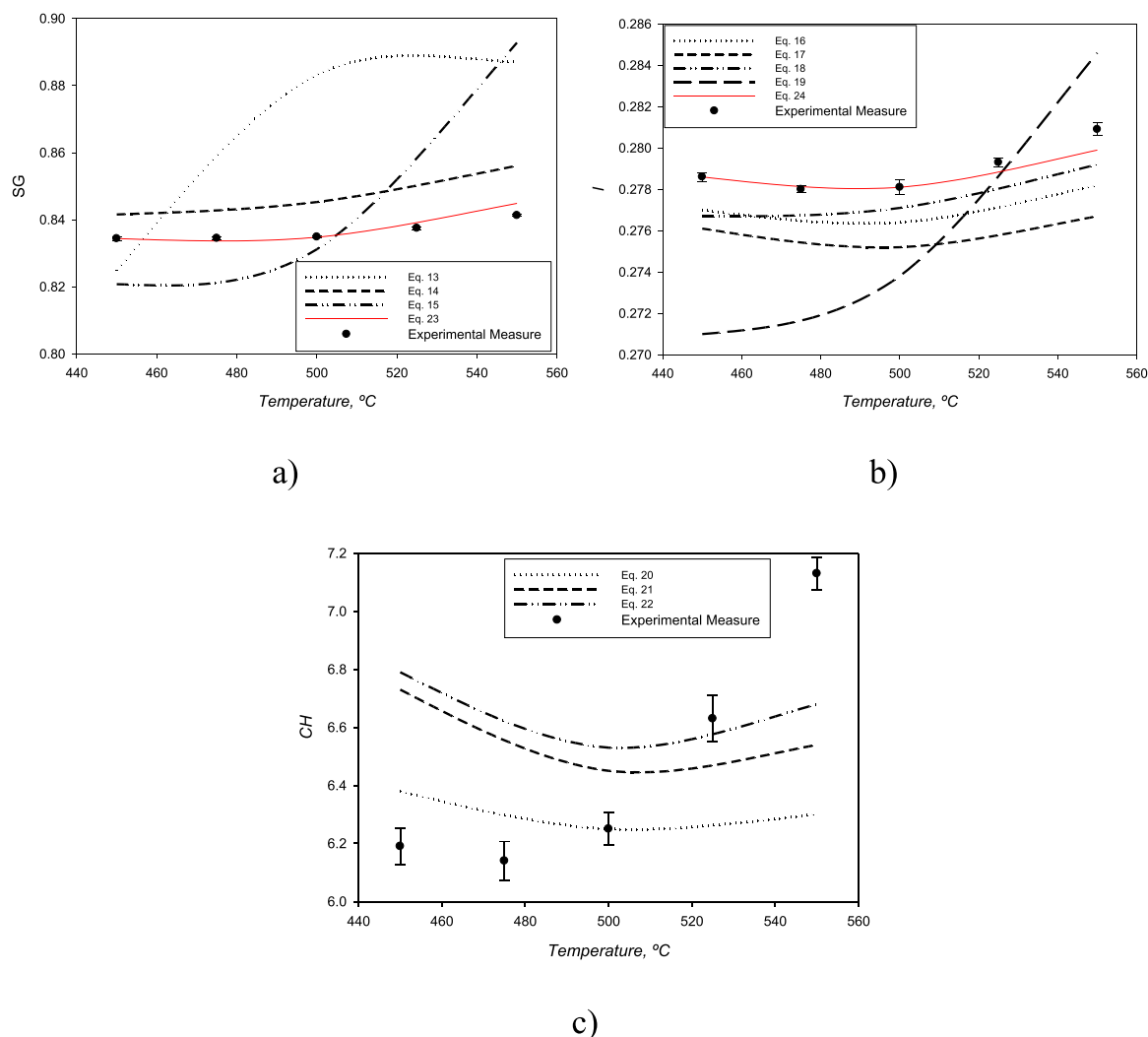
The mathematical correlations of hydrocarbons, which are based on the properties of their pure compounds, indicate that they are not suitable for the pyrolytic oil characterization obtained from plastic wastes mixtures of the investigated composition, but modified equations 25 and 26 give a better fit with less deviation for the calculation of specific gravity and refractive index parameter and seem to be appropriate to obtain these parameters when experimental data, including the boiling temperature, are not available and the molecular weights are in range of 70 – 300 or boiling point between 300 and 660 K.

To develop models for predicting the pyrolytic oil properties taking into account variables easily measured provide an economically attractive alternative to direct analysis. However, at this time, the equations proposed are limited to conditions used in our work.

### 3.5. Performance estimation of products

The yield of the possible products to be obtained by simulated distillation at atmospheric pressure, such as petroleum cuts (Montemayor, 2008) (heavy naphtha 121 – 191 °C, kerosene 191 – 277 °C, diesel 277 – 343 °C, light vacuum gas oil 343 – 455 °C, and heavy vacuum gas oil 455 – 566 °C), of the pyrolytic oils from plastic waste at operating temperatures of 450, 500 and 550 °C were calculated and results are summarized in Fig. 7. In them, it can be deduced that, in pyrolytic oil obtained at 450 °C, the naphtha cut





**Fig. 6.** Deviations of the calculated and measured properties of the pyrolytic oils obtained from the mixture of plastic waste at 450, 500 and 550 °C: a) the specific gravity b) the refractive index parameter and c) the carbon-hydrogen ratio.

predominates with 31.8% followed in a decreasing way by kerosene (27.2%), diesel (15.7%), light (17.5%) and heavy vacuum gas oils (7.7%). Increasing the heat of pyrolysis to 500 °C, the amount of naphtha (10.6%), kerosene (19.6%) and diesel (12.9%) was decreased but percentages of light (40.3%) and heavy (16.6%) vacuum gas oils were increased. An additional increase in pyrolysis temperature, up to 550 °C, changed the distribution of the products favoring the diesel recuperation yield (14.8%) and increasing the recovery of heavy vacuum gas oil (19.1%).

Other authors also reported composition of pyrolysis oils as petroleum cuts. For example, [Dobó et al. \(2021\)](#) investigated the thermal pyrolysis of HDPE, LDPE, PP and PS plastic waste mixtures with mass ratios representing the plastic demands in Hungary, European Union and the world and obtained yields between 70.3% and 74.9% of gasoline (cut from 20 to 200 °C) and between 18.8% and 21.7% of diesel (cut from 200 to 350 °C). Other authors ([Sarker and Rashid, 2013](#)) pyrolyzed a mixture of PP (50%) and PS (50%) from 200 to 420 °C for 4.5 h in a reactor with a fractionation column and obtained a 17% of kerosene, a value similar to that obtained in our work at 550 °C with different composition of the raw material (less proportion of PS and addition of other polymers). Also, thermal decomposition of a mixture with mass ratios representing the three main plastics present in municipal solid waste in Portugal was investigated in works of [Pinto et al. \(1999a\)](#)

and ([1999b](#)).<sup>1</sup> The plastic mixture was formed by a 68% of PP, a 16% of PE and a 16% of PS and pyrolysis tests were performed at a temperature of 430 °C during a reaction time of 20 min and a mean pressure of 3.5 MPa producing between 49% and 55% of gasoline (cut from 36 to 199 °C), values higher than those obtained here (34% at 450 °C). Also, [Ibrahim et al. \(2018\)](#) analyzed the thermal pyrolysis at 400 °C of a mixture of PP, LDPE, PS and HDPE with percentages of 30%, 30%, 25% and 15%, respectively at 400 °C. The authors reported a hydrocarbons composition in pyrolysis oil of 25% of naphtha (cut from 45 to 170 °C), 52% of diesel 1 (cut from 170 to 265 °C) and 21.5% of diesel 2 (cut from 265 to 370 °C). Comparing our results at the same cut-off temperatures, the value of naphtha is almost similar to that obtained in our investigation (24.6%) at 450 °C. However, the amount of diesel 1 (30.7%) was lower and the amount of diesel 2 (23.7%) was higher. Finally, [Singh et al. \(2020\)](#) analyzed the pyrolysis oil obtained at 450, 500 and 550 °C from a mixture of PE, PP, PS and PET, and determined hydrocarbon fractions in pyrolysis oil based on carbon number. Percentages of 71.60%, 70.32% and 68.75% of cut from 36 to 216 °C (C5 - C12); 16.17%, 19.64% and 24.10% of cut from 235 to 330 °C (C13 - C19) and 12.16%, 10.04% and 7.15% of cut greater than 330 °C (> C19)

<sup>1</sup> [Pinto et al. \(1999b\)](#)

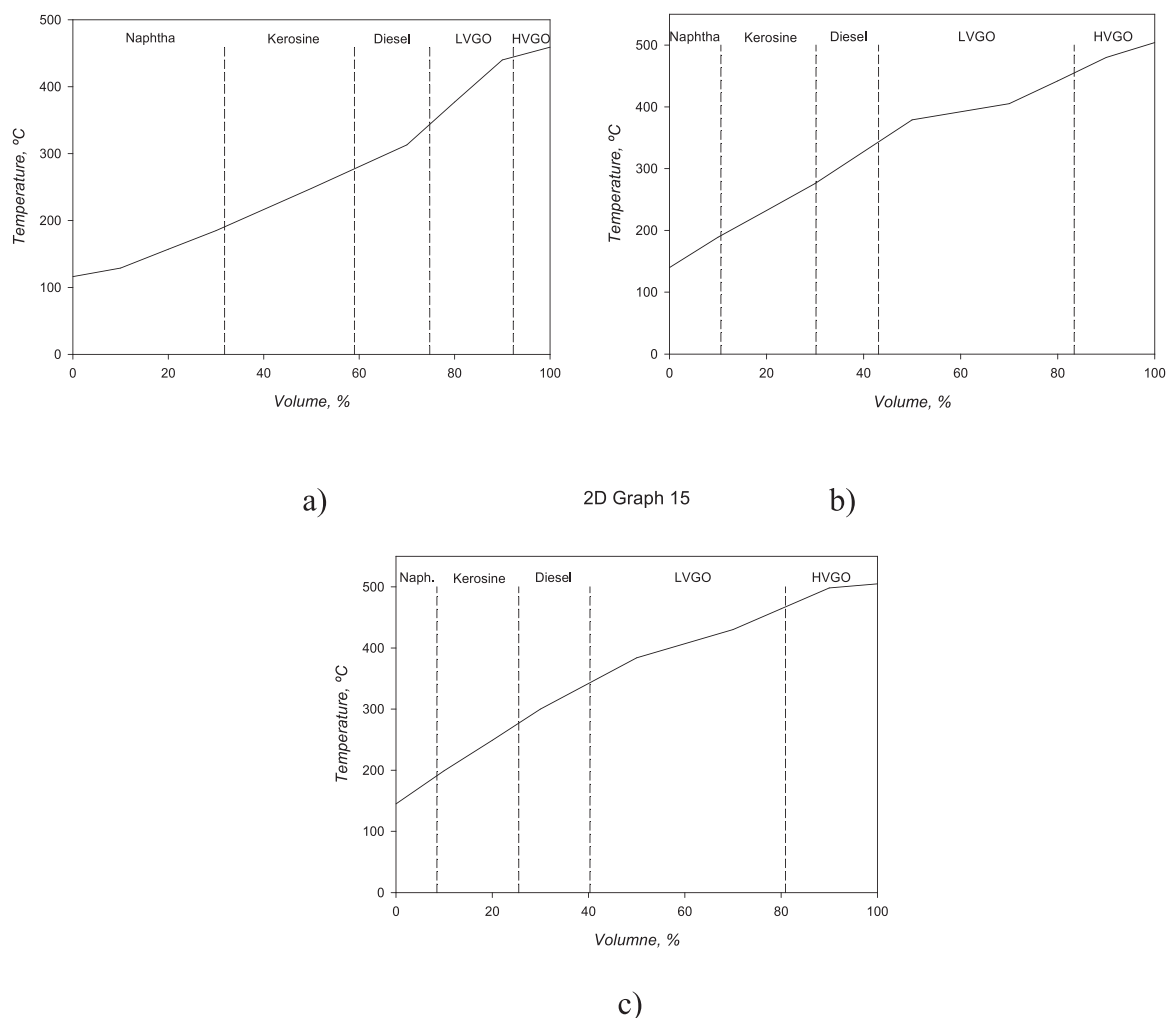


Fig. 7. Product yields of pyrolytic oils obtained from the mixture of plastic waste at a) 450 °C, b) 500 °C and c) 550 °C.

were obtained. Values differ to those obtained in our paper to identical carbon numbers.

According to the results, the differences shows that raw material, process temperature, heating rates, volatile residence time, pressure and type of reactor are significant parameters influencing the reactions that carried out during the conversion of waste plastic by pyrolysis and, consequently, the composition and characteristics of the oil samples. In this sense, [Dobó et al. \(2021\)](#) using a laboratory-scale batch reactor with a pyrolysis temperature of 520 °C, conclude that product yield and composition are highly influenced by the type of initial plastic waste. [Pinto et al. \(1999a\)](#) also found this influence of the type of plastic in the yield to product and in the composition, using a purged with nitrogen and pressurized autoclave as a pyrolysis reactor. These authors conclude that it would be possible to obtain the desired final product by controlling the mixture of plastic waste, although it is not always technically and economically possible to obtain this mixture. In addition, [Sing et al. \(2020\)<sup>2</sup>](#), as indicated above, pyrolyze three individual plastic wastes (HDPE, PP and PS), a sample of mixed plastic waste containing PE, PP, PS and PET and a simulated mixture of these polymers using a semi-batch reactor electrically heated. The authors find that the yield to products and the properties of the oil obtained depend on the type of plastic and the operating conditions such as heating rate or temperature. These authors find, for example, a higher concentration of

heavy hydrocarbons in the pyrolysis oil when the operating temperature increases.

#### 4. Conclusions

The nature of the plastic waste and its composition, along with the operating conditions and the configuration of the system to process it, are determining to obtain better yields of pyrolytic oil with a profitable distribution of valuable products. In the investigated plastic waste, from a real mix of plastic wastes with similar composition of the municipal waste plastics collected in Granada – Spain, the optimal temperature to obtain maximum yield of the liquid fraction under atmospheric pressure was 500 °C, in which a 10.6% of the naphtha cut would be achieved, 19.6% of kerosene, 12.9% of diesel, 40.3% of light vacuum gas oil and 16.6% of heavy vacuum gas oil if it is processed as synthetic crude.

The effect of the pyrolysis temperature is reflected in the oil properties due to chemical changes induced by the presence of hydrogenation reactions, by over cracking light vapors that produce hydrogen at low experimental temperatures, and dehydrogenation reactions, by cracking of heavy compounds at high experimental temperatures.

To be within the accuracy of each of the predictive mathematical correlations of hydrocarbon, which are based on the properties of pure hydrocarbons, does not necessarily indicate that these are adequate methods for pyrolytic oils characterization of the

<sup>2</sup> [Singh et al. \(2020\)](#)

investigated composition; in some cases due to restrictions, the source of data or its quantity.

However, Ec. 25 and Ec. 26 (Ec. 14 and Ec. 16 modified) seem be suitable to calculation the specific gravity and refractive index parameter of pyrolytic oils obtained from plastic wastes mixture of the same investigated composition when experimental data are not available.

### 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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