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Characterization and Distillation of Pyrolysis Liquids Coming From Polyolefins Segregated of MSW for their Use as Automotive Diesel Fuel

Alberto Gala^{a,}, Marta Guerrero^a, Beatriz Guirao^b, Marcelo E. Domine^c, José M. Serra^c*

^a Department of Innovation, Technological Waste Innovation Centre (CIAM), URBASER S.A.,
C/Azufre, 120, 50720 La Cartuja Baja (Zaragoza), Spain

^b Quality Department, Compañía Logística de Hidrocarburos – CLH, S. A., Paraje de
Vaciabotas, SN, 28830, San Fernando de Henares, Madrid, Spain

^c Instituto de Tecnología Química, Universitat Politècnica de València – Consejo Superior de
Investigaciones Científicas, Avda. de los Naranjos s/n, 46022 Valencia, Spain

Keywords

Distillation, pyrolysis, LDPE, transportation fuels, post-consumer plastic waste

Abstract

The liquids resulting from pyrolysis of industrial plastic waste (IPW) and post-consumer colour and white plastic film waste (PCPW and PWPW, respectively) at pilot scale (80 kg/h) were widely

characterized by different techniques in order to assess their potential as both petrochemical raw material and automotive diesel fuel. It was found that pyrolysis liquids mainly consisted of hydrocarbons in the diesel boiling point range (180-380 °C), amounting to approximately 50-55 % (in vol.). Therefore, the results were further contrasted with limits established by EN 590:2014 + A1:2017 standard for automotive diesel fuel. Although pyrolysis liquids showed good properties, they do not conform with some key fuel parameters for diesel engines, such as density, distillation curve, kinematic viscosity, flash point and cold filter plugging point. In order to improve these properties, PWPW pyrolysis liquids were distilled in the diesel range and the liquid fractions were characterized according to automotive diesel standards. It was found that the diesel fraction met all specifications with the exception of cold filter plugging point (-10 °C to 4 °C vs. -10 °C winter/0 °C summer) and density (800-807 kg/m³ vs. 820 kg/m³). To accomplish with standards, a blend of diesel obtained from PWPW pyrolysis liquids and commercial diesel (50/50 wt. %) was also prepared and analysed. Results revealed that the blend met the requirements of the 21 parameters demanded by the standard for a product to be marketed and used as automotive fuel in diesel engine vehicles.

1. Introduction

Plastic materials did not begin to be industrially manufactured until the 1940s [1], thus they are relatively new substances. However, nowadays plastics are used for a large and growing variety of products, applications and sectors, becoming an essential part of our lives [2-5]. In this way, those characteristics that make plastics so useful, such as durability, lightness and other intrinsic properties, also lead to a challenging sustainable waste management [6], which has become a global problem. In this sense, and taking into account that many applications are characterized by a short life [3][7], the magnitude of the problem can be estimated considering the amount of

worldwide plastic production, that was increased from 1.5 Mt in 1950 to 348 Mt in 2017, and it could be tripled in 2050 [8].

In 2016, about 27.1 Mt of plastic waste was collected through official schemes in Europe (EU 28+2), of which 27.3 % (7.4 Mt) was sent to landfill, 41.6 % (11.3 Mt) was collected for energy recovery, and 31.1 % (8.4 Mt) for recycling (mainly through mechanical recycling) [8]. As a result, approximately 70 % of European plastic waste is not recycled due to technical or economic reasons and these circumstances affect the environment negatively in terms of pollution and greenhouse gas emissions, as well as social perception regarding waste management, consumer's product industry and policy makers [9,10]. This lack of recycling contradicts the European policies directed at transforming Europe into a more circular and resourcefully efficient economy. This is the principle that has prompted the EU to adopt new directives that include a substantial reduction in landfilling of municipal solid waste to a maximum of 10 % by 2035 and a total ban on the landfill of separately collected waste [11].

At present, the main recycling route to recover the intrinsic value of plastics relies on mechanical recycling [12,13], which entails the processing of waste by physical means back into plastic products. However, there are still economical and technical barriers to mechanical recycling [14]. Therefore, it will be necessary to combine mechanical recycling methods with another valorisation options in order to manage the huge amount of plastic waste properly [9,10,15]. The combination of these technologies as complementary methods is emerging as the only way to comply with the objectives established by the EU (regarding waste disposal) in order to reduce the quantity of non-recycled plastic waste sent to landfill and to develop a circular economy strategy.

Based on URBASER's database (multinational environmental service provider), the most common polymers in municipal plastic waste are polyolefin compounds: low density polyethylene

(LDPE), high density polyethylene (HDPE), polypropylene (PP) and linear low-density polyethylene (LLDPE). In this sense it is clear the tremendous interest of a process that would allow the conversion of polyolefin into a valuable material. One of the most promising options in order to valorise this kind of plastic waste is the production of liquids by means of a thermochemical process, and pyrolysis seems to be the predominant technology used [16]. The process involves thermal decomposition of large polymeric chains into smaller molecules at moderate to high temperatures (400 - 800 °C) in absence of oxygen [13,16,17], thus obtaining very valuable products with high potential to be used as fuel or petrochemical feedstock [18-21].

Pyrolysis products can be divided into three fractions: solid residue (char), oil/wax and combustible gases [22-24]. Although the quantity and quality of these fractions strongly depend on plastic waste composition and the parameters used in the process [3,25], pyrolysis is an appropriate process to maximise the liquid yield, as proved by several studies which have reached above 75 % yield to liquids by processing polyolefins using catalytic [26-30] or non-catalytic pyrolysis [31-34].

In general, liquids coming from pyrolysis of polyolefins have similar characteristics to diesel obtained from petrochemical feedstocks [35], but some properties of these pyrolysis liquids prevent their direct use as automotive diesel. Therefore, there is need to carry out, at least, an upgrading step (i.e. distillation) [36,37] to improve some properties (i.e. density and flash point) and meet the requirements for automotive diesel established by EN 590:2014 + A1:2017 standard [38] that has been developed by the European Committee for Standardization. This European Standard specifies requirements and test methods for marketed and delivered automotive diesel fuel used in diesel engine vehicles designed to run on automotive diesel fuel that contains up to 7 % (vol.) of Fatty Acid Methyl Ester (FAME) [38].

In this context, URBASER has recently developed a Plastic to Oil (PtO) process to carry out the chemical recycling of polyolefins recovered from MSW, obtaining a high quality pyrolysis liquid product [39]. The aim of this paper is to carry out a detailed characterization of the pyrolysis liquids obtained from industrial and post-consumer plastic film waste by PtO process in order to evaluate their potential as both fuel and petrochemical raw material. Taking into account that the diesel fraction is predominant in these liquids, some distillations in the diesel range were performed and the different liquid fractions obtained were further characterized with the aim of appraising if they meet the requirements according to the EN 590:2014 + A1:2017 standard [38]. In addition, a blend of diesel from pyrolysis liquids and a commercial diesel was prepared and analysed following standards for automotive diesel.

2. Materials and Methods

2.1. Feedstocks

Three different plastic feedstocks have been used to produce three kinds of pyrolysis liquids. These materials include industrial plastic waste (IPW), provided by Granzaplast S. L. Plastics Recycling, and two post-consumer plastic film waste recovered by manual sorting from mixed MSW at the Complex for Treatment of MSW of Zaragoza (Urbaser facility) and pretreated using conventional methods (optical sorting, shredding in flakes having a size of 40 mm, wet cleaning and drying) to produce a granulated material. Then, two types of granules were obtained: 1) PCPW; granules obtained from colour plastic film recovered by ballistic separators and then manual sorting; and 2) PWPW: granules coming from white plastic film from primary sorting process, in which bulky materials are manually separated in a closed booth. Some pictures of the colour and white plastic film bales used to produce granules, as well as pictures of IPW, PCPW

and PWPW are given in [supporting information](#). Results obtained from ultimate and proximate analysis of these materials are also displayed in [supporting information](#). The polymer composition of the three different feedstocks is shown in Table 1. As it can be seen, the main component of the industrial plastic waste is LDPE, whereas LLDPE is the main polymer type in post-consumer plastic waste.

Table 1. Origin and composition of the different plastic feedstocks used for obtaining pyrolysis liquid samples.

Feedstock identification	Feedstock origin	Polyolefin composition (wt. %)			Shape
		LDPE	LLDPE	PP	
IPW	Industrial plastic waste	> 91	-	< 9	granules
PCPW	Post-consumer colour plastic waste segregated from MSW	24	69	7	granules
PWPW	Post-consumer white plastic waste segregated from MSW	26	66	8	granules

2.1. Pyrolysis process

The URBASER PtO process used for obtaining pyrolysis liquids consists of two clearly differentiated steps [39]. At the first area, plastic waste is introduced into a hopper where it is stored during each test. From there and by means of a double guillotine valve system, the polymer is fed to the melter, where it is heated in an inert atmosphere up to the necessary temperature to obtain an adequate viscosity for polymer transfer. Then, the molten polymer is continuously sent into the pyrolysis reactor. The pyrolysis reactor is a continuous flow stirred tank in which thermal degradation of polymers and volatilization of products simultaneously occur under a steady state.

The rate of feed input is gradually adjusted to that of product output in order to keep an amount of reactor contents constant. The gas leaving reactor enters a two-step condensation system, where it is cooled and separated into a gaseous product and a liquid product. The pyrolysis liquids are collected in an insulated tank, which is also heated by an electric tracing system to prevent the heavy hydrocarbons from freezing.

The installation used to carry out the process described in [39] is shown in Figure 1. The thermal cracking reactor has a production capacity of pyrolysis liquids of 80 kg/h and possesses two ceramic panels (model WATLOW VS426A14XC) for heating. The plant is also equipped with the following auxiliary services: thermal oil to heat up the melter, two chillers to carry out the condensation steps, compressed air for the automatic valves and nitrogen to inert the plant. The plant has a complete monitoring and control system that is controlled through a SCADA system (PLC: TIA-portal; Automatic logic controller: S7-1500).



Figure 1. Pilot plant facility used to produce the pyrolysis liquids.

2.2. Pyrolysis products

During the pyrolysis process, the chains of polyolefins, previously melted, crack into smaller pieces of hydrocarbons to obtain a mixture of compounds ranging from four (C₄) to forty-four (C₄₄) carbon atoms. The yield of liquid, gas and carbon solid (char) derived from thermal degradation of IPW, PCPW and PWPW through PtO technology range around 80-85 % (wt.), 10-15 % (wt.) and 5-10 % (wt.), respectively.

Pyrolysis tests were carried out under the same operating conditions for the three different feedstocks (IPW, PCPW and PWPW). Representative samples of pyrolysis liquids were collected every 30 minutes once the steady state was reached. The samples were characterized by different techniques, including PONA analysis, simulated distillation and bromine number determination. Some properties, according to the EN 590:2014 + A1:2017 standard [38], were also analysed in the CLH Central Laboratory from San Fernando de Henares (Madrid). Note that the results showed in this paper are the average values obtained from all the samples taken during a pyrolysis test.

2.2. Distillation equipment

The distillation of the PWPW pyrolysis liquids in the diesel range was made using a Pilodist PD104 HC distillation system. This equipment is characterized by a high separation efficiency for the fractionation of gasoline and diesel cuts from pyrolysis hydrocarbon mixtures. The system consists of a 35 L stirred stainless steel round-bottomed flask, which is mounted in an aluminium support frame. The filling process flows by means of a 100 mm neck (with viewing glass) and the draining by means of a drain valve at the bottom. The silvered distillation column DN80 made of borosilicate glass is equipped with a wire mesh packing to establish a high distillation rate with high separation efficiency. The fractions are distributed through an automatic fraction collector to

six final receivers of 20 L each. All distillation parameters, such as temperature, vacuum, reflux ratio and fraction collector, are controlled via the software linked to the processor control unit DCD4001.

2.3. Characterization techniques of liquids

2.3.1. Chromatographic analysis

The detailed PONA (paraffins, olefins, naphthenes and aromatics) analysis was carried out in a gas chromatograph VARIAN 3900 DHA equipped with a FID detector (Flame Ionization Detector). The conditions for this chromatographic analysis are shown in Table 2 [40].

Table 2. Conditions of the PONA chromatographic analysis.

Parameter	Condition
Capillary Column Type	TRB-Petrol (100 m x 0,25 mm x 0,5 μ m)
Injector Temperature	250 °C
Carrier gas	Ar
Flow Speed	1,5 mL/min
Detector Temperature	300 °C
Column Temperature	35 °C during 15 min 2.5 °C/min to reach 300 °C 300 °C during 79 min

Qualitative GCxGC analysis was done by using a gas chromatograph (Agilent GC system 7890A) coupled to a FID detector and a mass spectrometer (Agilent 5977A MSD). The detailed information of the analytical procedure and the attained data are provided in [supporting information](#).

2.3.2. Simulated distillation

This method is widely used to determine the boiling range distribution of petroleum products. For the selected samples, the tests have been made according to ASTM D2887 – 19 [41], using an Agilent 7890B gas chromatograph. The gas chromatographic simulation of this technique can be used for replacing conventional distillation methods and testing product specification.

2.3.3. Bromine number

Bromine number is expressed as g Br₂ per 100 g of sample and it is a proportional measurement of the olefin quantity. It is a highly demanding determination usually made by means of a standard titration of the total olefins [42]. With this analytical technique the double bonds present in the olefinic hydrocarbons are displaced by Br₂ in an acidic medium. The Br₂ excess is indirectly titrated using a sodium thiosulphate (Na₂S₂O₃) aqueous solution as titrant agent, according to ASTM D1159 – 07(2017) standard [43].

2.3.4. Other properties

The rest of properties analysed for the pyrolysis liquids, the diesel cuts obtained by distillation, the blend of diesel from pyrolysis liquids with commercial diesel, and the commercial diesel, follows official standards, according to the European Committee for Standardization (CEN) or

ASTM. The properties analysed, the related standards and the laboratory equipment used have been summarized in Table 3.

Table 3. Properties determined, related standards and laboratory equipment used.

Properties by EN 590:2014 + A1:2017 standard [38]	Standard	Equipment
Cetane number	ASTM D7668 – 17 [44]	CID (PAC)
Cetane Index	ASTM D4737 – 10 [45]	-
Density, 15 °C	ASTM D4052 – 18a [46]	Mettler Toledo Density Meter DE40 Agilent 1100 series (HPLC): Polar column G1316
Polycyclic aromatics hydrocarbons	EN 12916:2016 [47]	Quaternary pump G1311A Degasifier G1322A RI detector Agilent 1100 G1362A
Sulphur	EN 20846:2011 [48]	Thermo SN
Distillation	ASTM D86 [49]	PAC OptiDist
Kinematic viscosity, 40 °C	ASTM D445 – 19 [50]	Canon CAV – 2100
Flash point	ASTM D93 – 18 [51]	Herzog HPF360
Cold Filter Plugging Point (CFPP)	EN 116:2015 [52]	ISL V22101
Pour point	ASTM D2500 – 17a [53]	ISL CPP 5GS
Carbon residue (respect to 10 % v/v distillation residue)	ASTM D4530 – 15 [54]	ALCOR MCRT 160 PCS HFRR CAB
Wear scar, 60 °C	EN ISO 12156-1:2006 [55]	Nikon microscope at 100x magnification

Water and sediments content	ASTM D2709 – 16 [56]	STANHOPE-SETA 9000-2P
		Metrohm:
Water content	EN ISO 12937:2000 [57]	803 Ti stand module 851 titrando module
Total contamination	EN 12662:2014 [58]	Standard laboratory equipment
Ash content	ASTM D482 – 13 [59]	Standard laboratory equipment
Corrosiveness to copper (3 h, 50 °C)	ASTM D130 – 18 [60]	MC39 Julabo
Oxidative stability:		
Total insolubles	EN ISO 12205:1996 [61]	Dott Giani Scarin & C.
Accelerated method	EN 15751:2014 [62]	Dott Giani Scarin & C.
Colour	ASTM D6045 – 12 [63]	PFX 195 Lovibond
FAME content	EN 14078:2014 [64]	Perkin Elmer Spectrum One
Clear and bright	ASTM D4176 – 04 [65]	Standard laboratory equipment
<hr/>		
Other diesel properties		
<hr/>		
Simulated distillation	ASTM D2887 – 19 [66]	Agilent 7890B gas chromatograph
		Parr 6100 Compensated Calorimeter
High heating value	ASTM D240 – 19 [67]	Parr 1108 Oxygen bomb
		Metrohm:
Total acid number	ASTM D664 – 18e2 [68]	Autosampler 815 Robotic Dosino 800

Cl content	ASTM D7536 – 16 [69]	Stirrer 801 Philips MAGIX	PW-2424
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3. Results and discussion

3.1. Assessment as raw material

The results of the PONA analysis for the pyrolysis liquids obtained from the three different feedstocks, IPW, PCPW and PWPW, are shown in Table 4.

Table 4. PONA analysis results of pyrolysis liquids from IPW, PCPW and PWPW.

	IPW liquids	PCPW liquids	PWPW liquids
Paraffins (wt. %)	38.7	50.5	57.8
Olefins (wt. %)	18.4	22.5	19.3
Aromatics (wt. %)	16.5	19.0	14.2
Naphthenes (wt. %)	26.4	8.0	8.7

Results from Table 4 show that paraffins are the main compound in terms of hydrocarbon families. This is consequent with the polyolefin thermal cracking mechanism, in which the random rupture of the chains leads to aliphatic chains with different carbon atom number [70] and with the prevalence of paraffinic compounds [35,37]. The predominance of paraffinic hydrocarbons was also reported by Onwudili et al. [31]. These authors observed the presence of more than 40 % of linear alkanes in the pyrolysis liquids obtained from pure LDPE. The presence of naphthenes and aromatic compounds in pyrolysis liquids is due to the ternary gas-phase reactions of thermodynamically unstable low alkanes and alkenes at pyrolysis temperatures [70].

As can be seen in Table 4, the olefin and aromatic contents are approximately the same for the liquids obtained from the pyrolysis of IPW, PCPW and PWPW (although less aromatics are present in liquids from PWPW). However, the paraffins and naphthenes contents are ostensibly different for the IPW liquids in comparison with the PCPW and PWPW liquids. The content in paraffins is higher in pyrolysis liquids from post-consumer plastic waste (PCPW and PWPW), in which LLDPE is the main component (Table 1). In contrast, the content in naphthenes in PCPW and PWPW liquids is significantly lower than in IPW liquids. Note that LDPE is the main component of IPW (Table 1). Taking into account the composition of raw materials, it can be concluded that the observed trend in naphthenes content is consistent with the results obtained by Abbas-Abadi et al. [71] and Lee [72], who reported that the thermal degradation of LLDPE produces significantly fewer amounts of naphthenes than in the case of LDPE or PP. Table 5 shows the distribution of paraffins and olefins by carbon atom number extracted from PONA analysis.

Table 5. Distribution of paraffins and olefins by carbon atom number of pyrolysis liquids from IPW, PCPW and PWPW.*

Carbon atom number	IPW liquids		PCPW liquids		PWPW liquids	
	Paraffins (wt. %)	Olefins (wt. %)	Paraffins (wt. %)	Olefins (wt. %)	Paraffins (wt. %)	Olefins (wt. %)
5	2.4	4	1.7	2.39	3.23	4.01
6	4.4	11.8	3.1	8.76	3.91	10.81
7	6.8	11.8	4.8	9.70	5.48	9.46
8	6.8	10.2	5.5	8.56	5.58	7.86
9	6.8	9.0	5.7	8.07	5.55	7.09
10	6.8	9.0	6.3	8.61	5.82	8.25

11	7.2	7.7	5.9	7.84	6.39	7.61
12	6.6	6.8	6.0	6.92	6.34	6.96
13	6.2	6.0	6.0	6.38	5.88	5.95
14	5.8	4.9	5.8	5.38	5.63	5.20
15	5.5	3.5	5.9	4.25	5.59	4.06
16	5.1	3.1	5.6	3.83	5.33	3.87
17	4.6	2.2	5.3	2.92	4.85	3.13
18	4.0	2.2	4.8	2.33	4.36	3.01
19	3.7	1.7	4.5	2.12	3.81	2.26
20	3.2	1.4	4.1	1.98	3.47	1.98
21	2.7	1.1	3.7	1.43	3.09	1.66
22	2.3	0.9	3.3	1.17	2.71	1.42
23	1.9	0.7	2.9	1.10	2.29	1.23
24	1.6	0.7	2.5	0.67	2.00	1.11
25	1.3	0.4	2.1	0.66	1.65	0.65
26	1.1	0.4	1.9	0.36	1.43	0.63
27	0.8	0.2	1.5	0.53	1.22	0.39
28	0.7	0.2	1.3	0.36	0.95	0.55
29	0.5		1.1	0.20	0.78	0.41
30	0.3		0.9	0.19	0.63	0.21
31	0.4		0.7		0.52	0.21
32	0.3		0.6		0.46	
33	0.2		0.5		0.38	
34			0.4		0.28	
35			0.3		0.23	
36			0.2		0.18	

* Uncertainties of the values given in the Table are ± 0.5 (wt. %).

For all the pyrolysis liquids, the paraffins are concentrated between C7 and C18 carbon atom compounds, whereas the majority of compounds in the case of olefin ranges between C6 to C15 (especially between C6 to C8). C7 to C18 paraffinic compounds make up the 72.2 % of total paraffins for IPW liquids, 67.6 % for PCPW liquids, and 66.8 % for PWPW liquids, while C6 to C15 compounds entail the 80.7 % of total olefins for IPW liquids, 74.5 % for PCPW liquids, and 73.2 % for PWPW liquids.

Petroleum products are always a more or less complex mixture of hydrocarbons obtained by distillation and/or refining [73]. By considering a modern refinery scheme with many different units like hydrotreating, catalytic reforming, hydrocracking or alkylation, the pyrolysis liquids showed in Tables 4 and 5 become promising raw materials to be used downstream the petroleum crude distillation. Therefore, these liquids are clearly a higher quality feedstock than petroleum crude oil, with a high content in alkanes, as shown in Table 4, and with a carbon atom distribution considerably lighter than petroleum (Table 5). If the pyrolysis liquids from polyolefins were used as feedstock in a typical refinery, the products obtained would be similar to the products that are normally produced by distillation and/or refining of crude (e.g., gasoline, naphtha, kerosene, fuel oil and heavier).

Moving to a petrochemical point of view, it is worth noting that the pyrolysis liquids could also be used to obtain chemical compounds of interest by means of separation and purification steps. In this sense, paraffinic fractions from C12 to C18 and olefins are highly desirable raw materials in detergent industries for the manufacture of chemical products, such as alkyl-benzene sulphonic acid (ABSA) and sodium lauryl ether sulphate (SLES) [31], among others. In addition, aromatic compounds could be a source of precursors for polymerization of plastic monomers [74]. Benzene, toluene and xylenes (BTXs), which could be recovered by extractive or azeotropic distillation,

solvent extraction or adsorption, are major sources of chemicals [73]. However, the pyrolysis liquids obtained are not very rich in aromatic compounds (see Table 4), and consequently further work is necessary in order to assess if the recovery of these aromatic compounds are worthy enough to make their recovering profitable.

3.2. Quality as fuel

One of the most extended and studied uses for the pyrolysis liquids coming from plastic waste is to obtain a fuel, which could be used as automotive diesel [24,25,28,32,35,37]. A few authors have reported that this kind of product presents properties similar to diesel and therefore they could be used “as produced” for power generation [25,37]. In contrast, other authors have detected the necessity of carrying out an upgrading step of the pyrolysis liquids via distillation [24,35] or hydrotreating [36,75,76], or by blending with other petroleum products [74,77] prior to their use as fuel in automotive diesel engines.

In order to evaluate the fuel quality of the pyrolysis liquids obtained by the URBASER PtO process, an initial analysis based on compounds distribution in liquids by boiling points (simulated distillation or *simdist*) was performed. The results obtained are shown in Table 6.

Table 6. *Simdist* according to ASTM D2887 – 19 [66] of the IPW, PCPW and PWPW liquids obtained by the URBASER PtO process.

% recovered (vol. %)		Determined Values Boiling Point (°C)		
		IPW liquids	PCPW liquids	PWPW liquids
Initial point	Boiling	59.0	51.7	49.3

5	64.9	70.4	69.3
10	93.2	95.1	96.7
20	124.2	130.1	133.4
30	151.7	173.3	169.7
40	186.6	203.5	203.4
50	216.3	235.7	225.8
60	252.9	269.8	264.9
65	270.5	287.8	284.3
80	329.5	344.8	331.3
85	353.7	369.4	346.9
90	380.6	399.0	380.6
95	421.6	445.7	430.3
Final Boiling Point	506.9	641.6	567.0

The detailed results from *simdist* analysis (see [supporting information](#)) indicate that a minority fraction in the pyrolysis liquids distils at temperatures above 380 °C, thus accounting for 10, 13 and 12 % for the IPW, PCPW and PWPW liquids, respectively. The light fraction, with a boiling point lower than 180 °C, is the second one in terms of volume contribution, accounting for 38, 33 and 33 % for the IPW, PCPW and PWPW liquids, respectively. Consequently, the main fraction is in the boiling point range from 180 to 380 °C and represents a 52 % of the total for the IPW liquids, 54 % for the PCPW liquids and 57 % for the PWPW liquids. This fraction corresponds to the diesel boiling point range. Considering the results from *simdist* analysis, it can be concluded that the pyrolysis liquids mainly consist of hydrocarbons in the diesel boiling point range, and there is no significant differences for the three types of pyrolysis liquids related to the hydrocarbon

boiling point distribution by each feedstock. Therefore, properties of pyrolysis liquids could be similar to diesel fuel.

The definition of diesel fuel comprises a wide possible combination of properties (such as flash point, cetane number, viscosity, stability, volatility, etc.). To characterize diesel fuels and thereby establish a framework of definition and reference, various classifications that depend on the country are used [73]. In this study, the assessment of the potential use of pyrolysis liquids as diesel fuel, without any upgrading step (not even a simple distillation), has been carried out according to EN 590:2014 + A1:2017 standard [38]. This is the European framework reference for fuels to be used in diesel engine vehicles designed to run on automotive diesel fuel that contains up to 7 % (vol.) FAME. In addition, and according to the Spanish legislation (RD 61/2006 [78] and RD 1088/2010 [79]), the limits for the use of diesel fuel in agricultural vehicles and maritime transports (class B) and in household heating systems (class C) have been considered. Table 7 shows the basic properties obtained for the pyrolysis liquids coming from the three feedstocks (IPW, PCPW and PWPW), required by EN 590:2014 + A1:2017 [38] for automotive diesel and by RD 61/2006 [78] and RD 1088/2010 [79] for class B and C diesels, and other additional properties.

Table 7. Basic properties of the pyrolysis liquids obtained from the three feedstocks (IPW, PCPW and PWPW), limits established by EN 590:2014 + A1:2017 standard [38] (automotive diesel) and RD 61/2006 [78] and RD 1088/2010 [79] (class B and C diesel) for these properties, and other additional properties.

Properties by EN 590:2014 + A1:2017 standard, RD 61/2006 and RD 1088/2010	Units	Limits [38,78,79]			IPW liquids	PCPW liquids	PWPW liquids
		Automotive diesel	Class B diesel	Class C diesel			
Cetane index		> 46	> 46	n/a	53.7	62.3	66.1
Density, 15 °C	kg/m ³	820/845	820/880	< 900	793	799	791
Polycyclic aromatic hydrocarbons	wt. %	< 8	n/a	n/a	3.7	3.1	2.1
Sulphur	mg/kg	< 10	< 1000	< 1000	12.9	19.0	4.4
Distillation:	° C						
65 % recovered (vol. %)		> 250	> 250	> 250	262	289	311
80 % recovered (vol. %)		n/a	n/a	< 390	315	343	368
85 % recovered (vol. %)		< 350	< 350	n/a	336	366	391
95 % recovered (vol. %)		< 360	< 370	n/a	> 365	421	452
Kinematic viscosity, 40 °C	mm ² /s	2.00/4.50	2.0/4.5	< 7.0	1.29	1.81	1.89
Flash point	° C	> 55	> 60	> 60	< 25	< 25	< 25
Cold Filter Plugging Point	° C				10	25	22
Winter (October 1 st – March 31 st)		< -10	< -10	< -6			
Summer (April 1 st – September 30 th)		< 0	< 0	< -6			
Lubricity, wear scar, 60 °C	µm	< 460	n/a	n/a	377	317	362
Water content	mg/kg	< 200	< 200	n/a	130	150	130
Other basic properties	Units	Standard			IPW liquids	PCPW liquids	PWPW liquids
High Heating Value (HHV)	MJ/kg	-			46.64	46.43	48.47
Total acid number	mg KOH/g	ASTM D664 – 18e2			0.02	0.00	1.30
Cl content	mg/kg	ASTM D7536 – 16			8.0	4.0	2.5
Bromine number	g Br ₂ /100 g sample	ASTM D1159 – 07			39.6	40.0	31.0

3.2.1. Cetane index and high heating value

In many combustion diesel fuel systems and particularly in diesel engines, there is a lapse called “ignition delay” from fuel injection to the moment of autoignition. The higher tendency of a fuel to autoignition, the shorter its ignition delay is, and therefore the fuel presents better performance in the combustion process. Cetane number represents a fuel characteristic that is closely linked to autoignition [80]. However, cetane number is a property difficult to determine and with a considerably uncertain result, so the cetane index, which is a substitute for the cetane number [25], has been determined and used (Table 7). As can be seen, the results obtained for the three pyrolysis liquids are similar to the typical values for commercial diesel fuel, which presents cetane index values in the range of 45 – 70 [81,82]. As has been reported in the literature [83], paraffinic hydrocarbons have the highest cetane indexes, while aromatic compounds the lowest ones. According to the PONA analysis showed in Table 4, the PWPW liquids have a higher paraffin content and a lower aromatic content than IPW and PCPW liquids. As a result, the cetane index of the PWPW liquids is the higher one, but the other two pyrolysis liquids have also an appropriate cetane index for their use in diesel combustion engines.

Other diesel property related to the combustion process is the high heating value (HHV), which gives an idea of the thermochemical potential of a compound, representing the released energy in a complete combustion reaction with sufficient air. Although HHV is not specified in diesel fuel standards, high values of this property ensure the feasibility of using it as fuel. As shown in Table 7, pyrolysis liquids obtained from the three feedstocks (IPW, PCPW and PWPW) exhibited values of HHV very close to diesel, heavy fuel oil or other fuels (gasoline, kerosene, furnace oil, etc.) [24,35,77], thus confirming their combustion potential.

3.2.2 Polycyclic aromatic hydrocarbons, sulphur, water and Cl content

As noted earlier, a high content in aromatic compounds results in a poor cetane index in a fuel. Furthermore, particulate emission in diesel engines is directly related to PAHs content [84]. Consequently, PAHs content is limited by EN 590:2014 + A1:2017 standard [38] to 8 (wt. %), which is higher than the values obtained for the three types of pyrolysis liquids.

The presence of sulphur in diesel fuel forms SO_2 and SO_3 during the combustion process, which are then released into the atmosphere. These gases react with water to form sulphates and acid rain that is harmful to the environment [85]. Moreover, current treatment technologies for the emissions of the diesel engine exhaust gases are based on catalytic converters, whose efficacy is severely affected by sulphur level [86]. For these reasons, the sulphur level is strongly limited to 10 mg/kg for automotive diesel. This value is slightly lower than the values obtained for IPW liquids (16.5 mg/kg) and PCPW liquids (19.0 mg/kg). However, PWPW liquids with a sulphur content of 4.4 mg/kg meet this standard, so it can be concluded that PWPW would be a more suitable feedstock regarding sulphur content. These results, very close or under the requirements, indicate that the sulphur content is not expected to be a problem for the use of the liquids as diesel fuel.

All fuels have certain tendency to contain a higher or lower quantity of water, depending on their nature and room temperature. Water causes several problems in engines and other combustion devices like combustors, turbines or boilers, e.g. corrosion in the fuel feeding system or filter silting because of water crystal formation or microbiological growing in the interphase fuel/water [87]. Considering these drawbacks, fuels that do not meet water content requirement are directly considered out of specifications, and their use is automatically discarded. As can be observed in Table 7, the water content in all the pyrolysis liquids meet the value required by diesel automotive standards.

Pyrolysis liquids obtained from plastic waste often contain chlorinated compounds because of the presence of chlorine in plastic additives. This is very detrimental either to use such liquids directly as fuels [88] or supply them to the petrochemical industry [89]. In addition, inorganic chlorine could be a cause of corrosion in the engine, while organic chlorine may become a source of harmful substances [90]. The chlorine detected in the IPW, PCPW and PWPW liquids was always below 8 ppm (Table 7). Note that, this value is an ultra-low level content, even compared to other chlorine low level pyrolysis liquids, which have been previously dechlorinated [88,90], and have been identified as a suitable feedstock for refineries [91].

3.2.3. Lubricity

This property is a measurement of the fuel's own lubrication capacity necessary for different parts of the engine. This capacity is not directly related to the viscosity of the fuel, but severely influenced by some components. Oxygenated, nitrogenated and sulphurated polycyclic aromatic hydrocarbons enhance the lubricity of fuel [92]. In absence of these substances, olefinic hydrocarbons are good lubricants, whereas the lubricity of the paraffinic hydrocarbons is poor [93]. As shown in Table 4, the IPW, PCPW and PWPW liquids have relatively high olefin content, so it is expected to find a product with good lubricant properties. This fact has been confirmed by the results obtained for wear scar at 60 °C (Table 7). As can be seen, the three pyrolysis liquids exhibited lubricities that fulfil the automotive diesel requirements ($< 460 \mu\text{m}$). In particular, PCPW liquids present a better lubricity ($317 \mu\text{m}$) than the other two liquids (IPW liquids: $362 \mu\text{m}$; PWPW liquids: $377 \mu\text{m}$), probably due to the higher content in olefins of PCPW liquids. This observation allows confirming that olefins are the main lubricant compounds in the pyrolysis liquids, thus

discarding the noticeable presence of other substances, which may have a great influence in lubricity.

3.2.4. Total acid number

Acid compounds present in diesel may become salts by reaction with Ca, Na or K ions that could be found at a trace level [93]. These salts cause clogging problems in filters and injectors [94]. Therefore, and despite not being a specified parameter by legislation or standard, it is important to control the acid number in an adequate value. As can be seen in Table 7, the results obtained with respect to acid number for the three pyrolysis liquids (< 1,5 mg KOH/g) are in the range of those typical reported for commercial diesel fuel. Therefore, it is not expected to cause operational problems [95]. However, acid number must be controlled at all time in this kind of products due to a possible liquid degradation that may lead to an acidity increment. Note that an increase in TAN value would affect metal corrosion and elastomer degradation negatively [96]. Considering this, two weeks after the first analysis, additional acid number measurements were carried out for the three pyrolysis liquids, obtaining total acid number values similar to the original ones (e.g. PWPW liquids: 1.25 mg KOH/g after two weeks vs. 1.30 mg KOH/g). This fact confirms the stability of the samples regarding acidity.

3.2.5. Distillation curve

As noted earlier, a distillation curve test results in a curve that represents the percentage of recovered volume versus boiling temperature. Due to the importance of a distillation curve shape and its implication for engine performance, distillation curve is a valuable metric measurement of the overall volatility and driveability of a fuel [97]. Elevated final boiling points indicate long

combustion times, incomplete combustion of heavy hydrocarbons that leads to deposits and smoke formation increment, and poor atomization of the fuel/air mixture, which causes a diminution in the engine power and an increment in the fuel consumption [98]. On the other hand, high volatile diesel fuels may present vapour lock problems and poor atomization of the fuel/air mixture [99]. The light range of a distillation curve has little influence on engine performance, so it is not directly limited up to 65 % (in vol.), but no more than 65 % (in vol.) of diesel fuel has to be recovered at temperatures below 250 °C. As can be observed in Table 7, this requirement is fulfilled by all the samples. However, it is important to indicate that this fact does not guarantee that the liquid product meets other key diesel fuel limits, such as density and flash point specification, which are indirectly limited by the content in light hydrocarbons. In the case of diesel fuel, the most important restrictions are in the medium to high range of the boiling temperature curve (mainly temperatures involving the 65 – 95 % range of the recovered liquid volume) in order to limit the content in heavy hydrocarbons. For automotive diesel, these limits are 350 °C for the 85 % and 360 °C for the 95 % of the recovered volume of liquids. For class B diesel, the first limit is also 350 °C for the 85 % of liquid volume, but it is slightly higher for the second limit, 370 °C, for the 95 % of liquid volume. According to the results in Table 7, it can be observed that IPW liquids meet the first restriction for automotive diesel, but not the second one. As can also be seen, the final boiling point (FBP) for the IPW liquids was 365 °C, which corresponds to a value of 91.5 % (vol. %) of liquid recovered; therefore, the temperature for a theoretical 95 % recovered liquid volume would be more than 360 °C (automotive diesel limit), and probably more than 370 °C (class B diesel limit). The PCPW and PWPW liquids meet neither the first limit nor the second, presenting very high temperatures for the 95 % recovered liquid volume (> 420 °C). As conclusion from the data obtained in the distillation curve tests (Table 7), it can be extracted that there is a fraction present

in the pyrolysis liquids too heavy to use it directly in diesel engines as automotive or class B diesel. Therefore, there is need to include a separation step (i.e. distillation) in order to decrease the content in heavy hydrocarbons. Less restrictive is the limit of heavy hydrocarbons for the use of diesel as domestic heating diesel (class C), that is a product of a slightly lower quality than the other two types of diesel [100]. The pyrolysis liquids obtained from the three feedstocks fulfil the distillation curve requirements for class C diesel (Table 7).

3.2.6. Density

This parameter has a great influence on the internal combustion engine regulation since injection systems work on a volumetric basis. Variations in density lead to variations in mass of the fuel introduced to the combustion chamber, which means a variation in the air/fuel ratio. To control this complex system, the loop control in diesel engines uses density as control variable [101]. Therefore, the allowed range of density values for automotive diesel fuel is very restrictive (820-845 kg/m³ at 15 °C). As can be observed in Table 7, the density values of all the pyrolysis liquids studied are slightly lower than 820 kg/m³, resulting in slightly lighter compounds than diesel. However, it is important to note that this property could be improved by removing the lightest compounds present in the pyrolysis liquids through distillation, among other alternatives.

3.2.7. Flash point

The flash point (FP) is the lowest temperature at which the application of an ignition source causes the vapour of a sample to ignite and the flame to propagate across the surface of the liquid under specified conditions [102]. It can be used for evaluating the tendency of a compound to form flammable mixtures with air in controlled laboratory conditions. It is an important parameter for

the handling, storage and safety of fuels, as it gives an indication of fire risk in storage under ambient conditions [103]. The more number of light hydrocarbons a sample has, the lower the FP is. Regarding this parameter, the results obtained for the three pyrolysis liquids (Table 7) were found to be clearly out of diesel specifications ($< 25\text{ }^{\circ}\text{C}$ vs. $> 55\text{ }^{\circ}\text{C}$ for automotive diesel). This fact is due to the presence of very light compounds in all the samples. These considerations about the value of FP are in accordance with the results from *simdist* analysis, which revealed a considerable light fraction that distills at temperatures below $180\text{ }^{\circ}\text{C}$ (about 33 - 38 % depending on the feedstock). This observation is also in agreement with the values obtained for density (lower than automotive diesel fuel limit). To accomplish the limits required for FP, the content in the lightest compounds should be decreased by distillation.

3.2.8. Cold filter plugging point

The cold filter plugging point (CFPP) is a critical property that predicts the lowest temperature at which a fuel freely flows through filters in diesel engine systems. The CFPP data obtained for IPW, PCPW and PWPW liquids were 10, 25 and $22\text{ }^{\circ}\text{C}$, respectively (Table 7). These values are very high and totally out of specifications, probably due to the high content in long-chain paraffinic constituents with high-melting points [25]. The presence of polar/acidic structures, typical in biodiesel coming from biomass, also causes poor cold properties [102, 104], but these type of compounds are not expected to be found in pyrolysis liquids from polyolefins. Like in flash point and density cases, one option to improve this property would be by means of a distillation process, directed to remove the heaviest compounds responsible for the filter plugging. In case distillation is not enough to solve this drawback, other options could be considered, such as the blending of

the liquid product with conventional petroleum diesel [101] or the use of additives [105]. Both alternatives have also been investigated in this study.

It is also important to note that the CFPP parameter has a great influence on the diesel yield obtained by distillation of pyrolysis liquids or crude oil, since it will limit the final boiling point temperature to a greater or lesser extent depending on the heavy paraffin content.

3.2.9. Kinematic viscosity

Kinematic viscosity is a physical magnitude that provides an indication about the flowing tendency of a substance. In combustion engine systems, it is markedly important because it has a direct influence on the injection system, which has to produce fuel atomization to ensure a homogeneous mixture between fuel and air in the combustion chamber. High viscosity values lead to poor atomization performance due to excessively big drops of liquid. In contrast, low viscosity hampers distribution of fuel across the combustion chamber, causing non-homogeneous mixtures [101]. As can be observed in Table 7, none of the pyrolysis liquids obtained from URBASER PtO process is between the limits established by EN590:2014 + A1:2017 standard [38]. According to this standard, the values of kinematic viscosity are required to be in the range from 2.0 to 4.5 mm²/s. However, the kinematic viscosity values of IPW, PCPW and PWPW liquids are lower than 2.0 mm²/s (Table 7). As known, kinematic viscosity increases with chain length in aliphatic hydrocarbons [106]. This fact together with the absence of oxygen or other heteroatoms in the liquids indicate that the lighter hydrocarbons present in the samples are responsible for the low values of kinematic density observed. In the same way that other properties previously discussed, it is also necessary to carry out the distillation of the pyrolysis liquids to meet the kinematic viscosity limits required by the automotive diesel standard.

3.2.10. Bromine number

The determination of the bromine number in hydrocarbons is a common analysis made in the petrochemical industries [42] to determine the content in olefinic double bonds present in a hydrocarbon-based sample [107]. According to results in Table 7, the bromine numbers obtained for the pyrolysis liquids were 39.6, 40.0 and 31.0 g Br₂/100 g for IPW, PCPW and PWPW liquids, respectively. These values can be considered as moderate compared to the bromine numbers of similar liquid products, higher than 50 [76]. The presence of high contents in olefins causes oxidative instability, leading to the formation of gums [76]. Therefore, the olefin content in pyrolysis liquids should probably be reduced to use as diesel fuel. In this sense, catalytic hydrogenation would be an alternative. However, it also has to be taken into account that while more olefins are converted into paraffins, the product becomes more stable but also less lubricant. Therefore, a balance should be reached. With the contents in olefins above-mentioned, the addition of an antioxidant, like butylated hydroxyl-toluene (BHT), may be a cost-efficient alternative to improve the oxidative stability without losing lubricant properties [108].

In view of a whole assessment of the pyrolysis liquids as fuel and considering the limits shown in Table 7 for EN 590:2014 + A1:2017 standard [38], as well as RD 61/2006 [78] and RD 1088/2010 [79], it can be concluded that none of the three feedstocks (IPW, PCPW and PWPW) allows obtaining pyrolysis liquids that can be used directly as diesel fuel. Despite the fact that all pyrolysis liquids exhibited good fuel properties, there is a lack of consistency to reach automotive diesel, class B diesel or class C diesel status because some specifications are not fulfilled. The values of density, distillation curve, kinematic viscosity, flash point and CFPP did not meet the limits required for automotive and class B diesel. Regarding class C diesel, with not so rigorous

limits, it was found that the pyrolysis liquids met density, distillation curve and kinematic viscosity specifications, but the value of flash point was too low and CFPP was too high. It is important to note that all the properties that must be improved to meet diesel standards have a common factor: their enhancement can be attained by means of an optimized distillation process. The results of the distillation experiments are discussed in the next section.

3.3. Diesel distillation cuts

Commercial diesel has a typical distillation cut between 160 – 360 °C [81]. As it has been discussed earlier, the main fraction of hydrocarbons in the pyrolysis liquids obtained from IPW, PCPW and PWPW is in the range from 180 to 380 °C, representing more than 50 % of the liquid volume. This range of boiling temperatures corresponds to typical diesel fuel. In addition, the removal of the lightest and heaviest fractions from the pyrolysis liquids may improve density, distillation curve, kinematic viscosity, flash point and CFPP. This fact is a key point to meet automotive diesel standards. In this sense, the distillation conditions should be optimized because the values of these properties are strongly influenced by the boiling point of the compounds present in the resulting hydrocarbon mixture, so small changes in the lower or higher boiling points may produce great variations on them. Taking this into account, several distillation tests were carried out varying the initial and final boiling points in order to comply with the maximum parameters according to automotive diesel standards. PWPW liquids were used to carry out these tests, because this feedstock seems to produce the better product in terms of sulphur content, and no other substantial differences were observed compared to the liquids obtained from IPW and PCPW. The properties, more clearly influenced by boiling points, were analysed for the different

diesel range cuts obtained from the distillation of PWPW liquids. The results obtained are summarized in Table 8.

Table 8. Properties obtained from different diesel range cuts of distilled PWPW pyrolysis liquids, according to EN 590:2013 + A1:2017 standard [38] (automotive diesel) and RD 61/2006 [78] and RD 1088/2010 [79].

		Theoretical cut temperatures (°C)							
Properties by EN 590:2013 + A1:2017 standard, RD 61/2006 and RD 1088/2010		160	160	180	180	190	190	210	
	RD Units	360 UPD1	390 UPD2	390 UPD3	395 UPD4	390 UPD5	395 UPD6	395 UPD7	
Density, 15 °C	kg/m ³	799	802	806	807	807	807	804	
Flash point	°C	62	63	80	78	73	83	88	
Cold Filter Plugging Point	°C	- 10	1	2	4	2	3	2	
Distillation	°C								
65 % recovered (vol. %)		272	290	297	300	303	301	262	
80 % recovered (vol. %)		295	316	321	324	318	326	297	
85 % recovered (vol. %)		304	326	339	333	335	334	318	
95 % recovered (%)		325	350	353	355	347	360	356	

As can be seen in Table 8, a liquid product similar to automotive diesel was obtained by distillation of the PWPW pyrolysis liquids. This product has been referenced as Urbaser PtO Diesel (UPD). Note that all the diesel cuts obtained (UPD1 to UPD7) meet the requirements concerning distillation curve according to EN 590:2014 + A1:2017 standard [38]. In addition, it can be observed that the 95 % recovered liquid volume for the diesel cuts with theoretical final boiling points of 390 and 395 °C (UPD2 to UPD7) is very close to the limit established by the standard (< 360 °C). This observation indicates that the final boiling point has reached the limit, and then the maximum content in heavy compounds. Therefore, an increase of the upper distillation cut temperature would lead to non-compliance with this parameter. On the other hand, it can be observed that the removal of heavy compounds from PWPW pyrolysis liquids also improves the CFPP. This value was decreased from 22 °C for the PWPW pyrolysis liquids to 1 - 4 °C for the diesel cuts with final boiling points of 390 and 395 °C (UPD2 to UPD7). However, it is important to indicate that these values do not meet the RD 61/2006 regulation [78], neither for winter (CFPP < -10) nor for summer (CFPP < 0). Only UPD1 presented a CFPP value in agreement with the legal requirements, but it was necessary to decrease the final boiling point to 360 °C, with the subsequent liquid yield reduction.

Regarding the light part of the distillation curve, it is important to note that the flash point has been improved for all diesel cuts. As can be observed in Table 8, the FP values were increased from < 25 °C for the pyrolysis liquids to temperatures higher than 55 °C (automotive diesel specification). This increase was due to the removal of the lightest compounds. Although this fact also had a positive impact on density, none of the diesel range cuts reached the lower limit required by the automotive standard for diesel (820 kg/m³). The inclusion of heavy compounds would be

required to reach this value. However, there is no option to increase the content in heavy compounds by distillation due to the final boiling point limit. This value is restricted to 390 or 395 °C in order to meet the temperature requirement of 95 % recovered liquid volume established by automotive diesel standards.

3.4. Diesel mixture

The distillation of the PWPW pyrolysis liquids in the diesel range allowed to improve some properties, but density and CFPP were still out of specifications for automotive and class B diesel. As it has been mentioned previously, the blending of the pyrolysis liquids with conventional petroleum diesel or the use of additives are potential options to meet the required value of CFPP. In this sense, an additive to improve CFPP, a key property for engine performance, was added to UPD4 in a concentration of 1000 ppm (UPD4A). Table 9 shows the results obtained for UPD4A according to EN 590:2014 + A1:2017 standard [38]. As expected, the density did not improve with the use of additives. The value of density could only be enhanced by mixing the UPD with other heavier products, thus the blending solution seemed to be the best alternative to improve both properties simultaneously. In order to assess this alternative, UPD4 was blended with a commercial automotive diesel (CD) as this diesel cut presents the wider theoretical cut temperature range and the highest density value. UPD1 also seemed to be a good option to blend with commercial diesel because of its low CFPP, but it was discarded due to the low theoretical cut temperature range (low diesel fraction yield from pyrolysis liquids distillation).

As density is an additive property, to reach a value of 823 kg/m³ (above the limit value of 820 kg/m³ established for automotive diesel), UPD4 and commercial diesel (CD) were blended in a ratio of 50/50 (wt. %). The blend was also improved with a CFPP additive (1000 ppm). The

properties of the blend with additives (CDUPD4A) were analysed using EN 590:2014 + A1:2017 standard [38] as a reference. Table 9 shows the results obtained for the UPD4/commercial diesel blend with additives (CDUPD4A) and the commercial diesel (CD) used for the blend.

Table 9. Properties of the UPD4 with additives (UPD4A), the UPD4/commercial diesel blend with additives (CDUPD4A) and the pristine commercial diesel (CD) and the properties limits by EN 590:2014 + A1:2017 standard [38], RD 61/2006 [78] and RD 1088/2010 [79].

Properties by EN 590:2014 + A1:2017 standard, RD 61/2006 and RD 1088/2010	Units	Limits [38,78,79]			Commercial diesel/		
		Automotive diesel	Class diesel	C	UPD4 blend with additives		Commercial diesel
					UPD4A	CDUPD4A	
Cetane number		≥ 51	n/a	66.1	62.1	51.5	
Cetane index		≥ 46	n/a	67.2	58.9	51.6	
Density, 15 °C	kg/m ³	820/845	< 900	807	823	839	
Polycyclic aromatics hydrocarbons	wt. %	≤ 8	n/a	2.6	3.1	3.5	
Sulphur	mg/kg	≤ 10	≤ 1000	7.0	6.9	6.0	
Distillation (vol.):	° C						
65 % recovered		≥ 250	≥ 250	297	299	299	
80 % recovered		n/a	≤ 390	321	324	323	
85 % recovered		≤ 350	n/a	329	332	331	
95 % recovered		≤ 360	n/a	353	356	357	
Kinematic viscosity, 40 °C	mm ² /s	2.00/4.50	≤ 7.0	2.65	2.77	2.80	
Flash point	° C	> 55	≥ 60	77	68	57	
Cold Filter Plugging Point	° C			0	- 12	- 19	

Winter (October 1 st – March 31 st)		≤ -10	≤ -6			
Summer (April 1 st – September 30 th)		≤ 0	≤ -6			
Pour point	° C		≤ 4	4	1	- 5
Carbon residue (in respect to 10 % v/v distillation residue)	(wt. %)	≤ 0.30	≤ 0.35	0.07	0.06	0.03
Wear scar, 60 °C	µm	≤ 460	n/a	418	322	224
Water and sediment content	(vol. %)	n/a	≤ 0.1	< 0.01	< 0.01	< 0.01
Water content	mg/kg	≤ 200	n/a	40	40	40
Total contamination	mg/kg	≤ 24	n/a	31.1	16.5	< 12
Ash content	(wt. %)	≤ 0,01	n/a	< 0.001	< 0.001	0.001
Corrosiveness to copper (3 h, 50 °C)	scale	≤ class 1	≤ class 2	1A	1A	1A
Oxidative stability:						
Total insolubles	g/m ³	≤ 25	n/a	8*	6*	2
Accelerated method	hour	≥ 20 ¹	n/a	41	> 20	-
Colour	scale	≤ 2	blue ²	L2.0	L2.0	L1.5
FAME content	(vol. %)	≤ 7	n/a	0.07	2.42	5.2
Clear and bright		pass	n/a	Meet	Meet	Meet

1 This method is only applicable for diesel fuel containing more than 2 % (vol.) FAME

2 Additivated with a dye for fiscal purposes

*Additivated with 1500 ppm BHT

As can be observed in Table 9, UPD4A meets all the parameter requirements established by the EN 590:2014 + A1:2017 standard [38], RD 61/2006 [78] and RD 1088/2010 [79] for Class C diesel, with the exception of density, winter CFPP and total contamination. It is important to notice that CFPP additives contain heavy compounds that lead to high results in total contamination test, and then the product could be considered free from solids or particles. Moreover, UPD4A is

expected to be a good product for diesel engines considering that its cetane index is not excessively high [109]. It is also worth noting that automotive engines are designed to work with standardized fuels to fulfil environmental regulations, among others [110], but this does not mean that a non-standard fuel cannot be used. A diesel fuel with good properties, like UPD4A, could be admitted by an engine manufacturer without modifications in the engine or with some minor adjustments.

As expected, CDUPD4A can be considered a fully commercial product, meeting CFPP specification for winter and summer, but not with a margin as wide as CD (- 19 °C for CD vs. - 12 °C for CDUPD4). Other key properties for engine performance and emissions, like cetane index, PAH content, sulphur content or kinematic viscosity, among others, are quite similar between CDUPD4A and CD. Therefore, it can be concluded that the blend of UPD4 and commercial diesel with additives (CDUPD4A) is a high quality product that meets all the diesel fuel specifications, and thus it can be used in automotive diesel engines.

4. Conclusions

Pyrolysis liquids obtained from industrial plastic waste (IPW) and two-post consumer plastic film waste (PCPW and PWPW) have been characterized by different techniques, including PONA analysis, simulated distillation and bromine number. In addition, parameters established by the EN 590:2014 + A1:2017 standard, RD 61/2006 and RD 1088/2010 were also analysed to assess their potential use as automotive diesel fuel. In order to improve some key diesel properties, pyrolysis liquids were distilled in the diesel range and the liquid fractions were characterized according to automotive diesel standards. A blend of diesel obtained from pyrolysis liquids and commercial diesel (50/50 wt. %) was also prepared and analysed.

The main conclusions obtained in this study are summarized as follows:

- Pyrolysis liquids mainly consist of hydrocarbons in the diesel boiling point range (about 50 % in vol. in the range of 180-380 °C).
- Paraffins are the main components of the pyrolysis liquids. For IPW liquids, 72.2 wt. % of total paraffinic compounds are in the range of C7-C18, while these values were 67.6 and 66.8 wt. % for PCPW and PWPW, respectively.
- The content in paraffins turned out to be higher in liquids obtained from pyrolysis of post-consumer plastic film waste (PCPW: 50.5 wt. %; PWPW: 57.8 wt. %), in which LLDPE is the main component. Paraffins in pyrolysis liquids from IPW (LPDE: > 91 wt. %) were 38.7 wt. %.
- The relatively high content in paraffins and the low molecular weight of the pyrolysis liquids make this product highly desirable for petrochemical industry to be used in different points of the crude refining process.
- There are no significant differences in olefin and aromatic contents of the IPW, PCPW and PWPW liquids. These values are in the range of 18-23 wt. % and 14-19 wt. %, respectively. For IPW liquids, 80.7 wt. % of total olefins are in the range of C6-C15, while these values were 74.5 and 73.2 wt. % for PCPW and PWPW, respectively.
- Thermal degradation of PCPW and PWPW resulted in liquids with a lower content in naphthenes than IPW (~ 8-9 wt. % vs. 26.4 wt. %), mainly due to differences in polymer composition of the raw materials.
- The origin of plastic film waste (industrial or post-consumer from mixed MSW) had a negligible influence on the hydrocarbon distribution according to the boiling point ranges.
- Cetane index was higher in PWPW liquids than PCPW and IPW, mainly due to the higher content in paraffins. The values obtained for all the pyrolysis liquids (56-66) were observed

to be very close to commercial diesel. The energy content values of IPW, PCPW and PWPW liquids (HHV: 46-48 MJ/kg) were also similar to diesel fuel.

- IPW, PCPW and PWPW liquids exhibited ultra-low level content in chlorine. The sulphur content in PWPW liquids was lower than the limit established by diesel automotive standard (4.4 mg/kg vs. 10 mg/kg). These values for PCPW and IPW were slightly higher (19.0 and 16.5 mg/kg, respectively).
- Diesel specifications for PAHs content, water content and lubricity properties were met by IPW, PCPW and PWPW liquids. The values of TAN were also in the range of commercial automotive diesel.
- Density, distillation curve, kinematic viscosity, flash point and cold filter plugging point of the pyrolysis liquids were found to be out of diesel specifications. This prevents their direct use as automotive diesel fuel.
- Distillation of the pyrolysis liquids in the diesel range allowed obtaining a liquid product that met the standard requirements for automotive diesel, with the exception of density and CFPP.
- The blending of Urbaser PtO diesel (UPD) with commercial diesel in a 50/50 (wt. %) ratio meets the 21 parameters required by the standard for a product to be marketed and used as automotive fuel in diesel engine vehicles. This strategy becomes a successful option for converting the pyrolysis liquids into a high quality product that allows contributing to the circular economy.

AUTHOR INFORMATION

Corresponding Author

* E-mail address: ajgala@urbaser.com

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SUPPORTING INFORMATION

Supporting information file1: This document includes pictures and properties of the feedstock used to obtain the pyrolysis liquids.

Supporting information file2: This document includes simulated distillation curves of the three pyrolysis liquids and detailed information of 2D-GC measurements.

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