Title: Production and Droplet Combustion Characteristics of Waste Tire Pyrolysis Oil

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ABSTRACT

Pyrolysis of scrap tires has been found in several recent studies to be an attractive alternative to cope with the waste tire disposal problem while, at the same time, allowing for energy recovery. This work aims to contribute to the understanding and feasibility of this alternative by studying it as an end to end process, encompassing the pyrolysis oil production procedure, a subsequent physicochemical characterization of the obtained oil, and finally its single droplet combustion characteristics. The tire pyrolysis liquid (TPL) was produced in a continuous auger reactor on pilot scale (150 kWth of nominal capacity) and its combustion characteristics were acquired by means of a drop tube facility, where the TPL burning behavior was compared to that of conventional Spanish heating oil (FO). The evaluated combustion characteristics included droplet size evolution, burning rates, flame and soot shell morphology, microexplosion occurrence and soot analysis. When compared to FO, TPL displayed considerably lower burning rates, although the consistent occurrence of microexplosions effectively shortened the TPL droplets lifetimes below those of FO. TPL also presented smaller flame standoff ratios and a higher propensity to soot. A TPL-FO blend of interest for heating applications (with only 5 % of TPL due to its high sulfur content), was also tested, showing identical results to those of neat FO for all the studied combustion characteristics. The reported results are thought to provide valuable data regarding the combustion behavior of a well characterized tire pyrolysis oil. Due to the strictly controlled experimental conditions, which are also representative of those found in real flames, these experimental results could also be used as the fuel-specific input data required for the simulation of realistic spray flames.

KEYWORDS

Waste Tire, Pyrolysis Oil, Tire Pyrolysis Liquid, Droplet Combustion, Microexplosion

1. INTRODUCTION

The continuous growth in the amount of waste tires disposed worldwide is currently a major environmental problem, as a sustainable recovery and recycling of this residue presents significant technical difficulties, primarily due to the complex structure and composition of tire materials [1]. On the other hand, its disposal in landfills is not an option, as it can be a source of uncontrollable toxic fires and pollution. In fact, the disposal of waste tires in landfills is currently banned in the EU, according to the Council Directive 1999/31/EC. The dimensions of this environmental issue are substantial, as the number of end-of-life tires in the current decade has been estimated to be in the range of 1 billion units disposed per year worldwide [2-4].

One of the most promising alternatives to cope with this problem is to pyrolyze the scrap tires, as it has been highlighted in several works (e.g., [2, 5, 6]). Pyrolysis is a thermochemical process where a certain feedstock is heated at moderate temperatures (generally, between 400 °C and 800 °C) under inert environment at atmospheric pressure. Under these conditions, the raw material is converted into light gas, liquid and a carbonaceous solid or char [7]. Thus, this process transforms waste tires into new products with added value. In the case of rubber obtained from waste tires, a remarkable part of the material is transformed into carbon black (about 40%) that can be reused in the production of new tires. As carbon black is usually synthesized through the incomplete combustion of oil heavy fractions, its recuperation by means of this process would significantly reduce the environmental impact of its production. Another main product of pyrolysis is the tire pyrolysis oil, corresponding to the liquid fraction. This oil contains a substantial amount of bio-oil, as around 50% of the rubber used in tire manufacturing originates from natural sources (hevea tree). Tire Pyrolysis Liquid (TPL) is mainly used for heat and power production, reducing therefore the needs of fossil

fuels. In light of the huge amounts of waste tires disposed every year and the high calorific value of TPL (~40-44 MJ/kg, according to [2]), the potential for fossil fuel reduction is substantial. Finally, the non-condensable gas is typically used in situ to provide the energy needed for the pyrolysis process. Usually, all the plants incorporate a gas cleaning system to avoid sulfur compounds and particulate matter emissions, making the pyrolysis process globally clean. Despite the fact that commercial facilities and technology suppliers can be found all around the world, the practical applicability of the products obtained from waste tire pyrolysis, and namely of TPL, remains nowadays with prospects of growth, with diverse studies addressing the production and combustion characterization of different oils obtained through the pyrolysis of waste tires, as it will be detailed down below.

Several works have examined the performance of TPL-diesel mixtures in both automotive [8, 9] and non-automotive diesel engines [5, 10, 11]. Regarding the automotive application of TPL, an alternative fuel for diesel engines was produced from waste vehicle tires by the method of pyrolysis after the reduction of sulfur content with Ca(OH)_2 [12, 13]. Different blends were tested in a diesel engine obtaining good performance in the case of low sulfur tire fuels as alternative fuel in diesel engine. Also, the addition of an ignition improver, diethyl ether (DEE), to a tire derived fuel-diesel blend was evaluated on a direct injection diesel engine [14]. The investigation results indicated that the ignition delay was found to decrease with a blend of 40 % light fraction pyrolysis oil as the percentage of DEE increased. Frigo et al. [13] proved that engine tests with mixtures of TPL up to 20 % can be used in diesel engines without engine modifications, whereas mixtures with TPL from 20 % to 40 % need modifications of the injection to compensate the longer ignition delay.

As typical TPLs usually present substantially high sulfur contents, their use in internal combustion engines is seriously limited by fuel regulations. In fact, environmental restrictions associated with SO₂, NO₂ and CO emission levels higher than the acceptable limits prescribed by the European Air quality standard (EU2015/2193), restrict the use of TPL in automotive engines. As stated above, a possible alternative is their desulfurization by means of processes as those presented in [6, 15]. A more straightforward approach is its use for heat generation in boilers, large stationary engines for heating and other energy-demanding industrial processes [1], as the sulfur limits regarding this application are considerably more permissive than those set for automotive purposes (1000 ppm instead of 10 ppm, according to the Spanish Royal Decree 61/2006).

Concerning the application of TPL-diesel mixtures as a fuel in burners/boiler units, García-Contreras et al. [16] studied the replacement of diesel fuel by a blend (50 %/50 % by volume) of TPL-diesel in a residential boiler, obtaining the same performance as that achieved with diesel although with higher particulate matter emissions. However, all these studies have been mainly focused on the environmental impact without taking into account the combustion behavior.

The already cited studies on final applications provide insight into relevant fuel combustion characteristics from a realistic and applied point of view, and therefore are a usual method for determining the combustion features of a novel fuel such as TPL. However, the complexity of those combustion configurations makes it impossible to strictly control all the relevant parameters, and the obtained results might depend on slight changes in non-controlled variables such as the atomization characteristics or the fuel-air mixing within the combustion chamber. A dependency on the experimental setup used for the tests is thus inevitably introduced, being difficult to precisely

determine whether certain combustion behavior is entirely attributable to the tested fuel or, on the contrary, is an indirect result of changes in another related process. By contrast, in the single droplet configuration, all the relevant variables influencing results can be well characterized, and the extracted combustion features are thus inherently ascribable to the studied fuels. This approach has been used in several works in order to characterize the combustion behavior of alternative fuels, with a special focus on biofuels and their blends with conventional, well-known petro-fuels (e.g. [17] for butanol-gasoline or [18] for biodiesel-diesel mixtures) and also on different residual fuels (e.g. oil-water emulsions and coal-water slurries containing petrochemicals in [19, 20]).

Single droplet combustion results are less common for pyrolysis oils than for other alternative fuels, although tire-derived oils have received very little attention and the currently available studies are mostly referred to bio-oils produced from lignocellulosic biomass. Yang and Wu [21] examined the droplet combustion characteristics of a pinewood bio-oil obtained from slow pyrolysis blended with butanol. They found that bio-oil addition consistently decreased butanol burning rates, while enhancing the formation of a solid residue and promoting the occurrence of microexplosions. Chen et al. [22] also registered microexplosions for a pyrolytic oil produced from castor seeds, which in turn underwent almost complete evaporation, leaving a negligible amount of solid residue. Hou et al. [23] investigated the droplet combustion characteristics of a bio-oil produced from fast pyrolysis of lauan wood, both pure and blended with diesel and heavy fuel oil. They concluded that ambient temperatures and the mixing ratios were decisive factors regarding the droplet combustion characteristics. For low percentages of bio-oil, their distinctive features (such as microexplosion occurrence) were difficult to find. The works cited so far relied on the suspended droplet technique,

where roughly ~ 1 mm sized droplets were suspended on ceramic fibers and burned. Garcia-Perez et al. [24] studied the combustion behavior of two different biomass vacuum pyrolysis oils under more realistic conditions, namely with ~ 60 μm sized droplets ignited in free fall (and therefore, without the possible interaction of the suspending fibers). Surprisingly, no microexplosions were registered for any of the studied bio-oils under such experimental conditions. Shaddix and Hardesty [25, 26] also used a drop-tube facility with droplets in the range of ~ 350 μm , performing a thorough study on the combustion characteristics of flash pyrolysis oils produced from a variety of bio-feedstocks. They found quite low burning rates for all of them, with values closer to those of heavy fuel oils than to heating oil. However, the consistent occurrence of microexplosions effectively shortened the bio-oil droplet lifespans, and consequently the overall lifetimes of the studied pyrolysis oils were quite similar to those of conventional heating oil.

As stated above, the cited studies evaluated the single droplet combustion characteristics of different pyrolysis oils produced from bio-feedstocks. To the best of the authors' knowledge, this kind of study has not been addressed so far for TPL, even though its chemical composition and properties are entirely different to those of bio-oils. This work aims therefore to fill this gap by studying the single droplet combustion behavior of a well-characterized TPL, both neat and blended with conventional heating oil. The experimental conditions used are intended to be as close to those found in real applications as possible, with free-falling, small-sized droplets (150 μm) immersed in a gaseous coflow which simulates the temperature and coflow compositions found in real flames. Relative velocities between the free-falling droplets and the coflow were also minimized, so that droplets were only minimally disturbed by convective effects and

burnt in a practically 1-D configuration, facilitating therefore comparison with theoretical one dimensional droplet combustion models.

2. MATERIAL AND METHODS

2.1. Pyrolysis oil preparation and characterization

The TPL used in this research is the result of more than 500 kg of granulated waste tires pyrolyzed in a continuous auger reactor plant of 150 kWth of nominal capacity and corresponding to technology readiness level 5 (TRL 5) described in detail elsewhere [8, 27]. This experimental campaign was conducted in 13 experiments that gave as the result 100 h of continuous operation without any significant technical problem. The reaction temperature and pressure were 550°C and 1 bar, respectively. N₂ was used as carrier gas at 5 Nl/min. The waste tire mass flow rate was 6.7 ± 0.1 kg/h, and the residence time of the feedstock inside the reactor was 3 min. These conditions were selected as those maximizing both the liquid yield and the tire rubber conversion. As a consequence, yields to liquid, solid, and gas were 42.6 ± 0.1 , 40.5 ± 0.3 , and 16.9 ± 0.3 wt % respectively. Before characterization, TPL was subjected to decantation (30 days) in order to deposit possible fine char particles that could have been carried over from the reactor. The properties of the TPL have been previously reported [8, 28] and are shown in Table 1.

Table 1. Properties of the obtained TPL.

Property	Method	TPL
HHV (MJ/kg)	ASTM 240-09	42.70
LHV (MJ/kg)		40.49
C (wt.% ^a)		86.19
H (wt.% ^a)		10.33
O (wt.% ^a)		0.00
N (wt.% ^a)		0.79
S (wt.% ^a)		0.83
H/C atomic ratio		1.44
AFR _{st} (kg/kg)	From elem. composition	13.46
Molar mass (kg/kmol)	From AspenTech HYSYS	142.5
Density at 15° C (kg/m ³)	EN 12185	917
Kinematic viscosity at 40°C (cSt)	EN 3104	2.39
Initial boiling point (°C)	EN 3405	82.2
T50 (°C)	EN 3405	231.1
Final boiling point (°C)	EN 3405	302.5
Final percent of distillate		80
Calculated cetane index (CCI)	ASTM D4737-04	17.6
Saturates (wt.%)	From TLC	5.5
Aromatics (wt.%)	ASTM 6379/04 for diesel	65.2
Polars (wt.%)		29.3
Cold filter plugging point (°C)	EN 116	9
Lubricity (lm WS 1.4)	EN 12156	162.59
Water content (ppms ^b)	EN 12937	689.9
Total acid number (mg/KOH)	From Mettler Toledo T50	5.0
Flash point (°C)	EN 3679	23.0
Smoke point (mm)	ASTM D1322	9
Oxidation stability (h)	EN 15751	16

TLC: Thin layer chromatography.

^a As received.

^b On mass basis.

The chemical composition of the TPL was also analyzed by GC-MS using a Varian CP-3800 gas chromatograph connected to a Saturn 2200 ion trap mass spectrometer. A capillary column, Agilent CP-Sil 8 CB, low bleed, 5 % phenyl, 95 % dimethylpolysiloxane, (60 m × 0.25 mm i.d. × 0.25 µm film thickness) was used. An initial oven temperature of 40 °C was maintained for 4 min. Then, a ramp rate of 4 °C/min was implemented to reach a final column temperature of 300 °C. This temperature was maintained for 21 min. The carrier gas was He (BIP quality) at a constant column flow of 1 mL/min. The injector, detector, and transfer line temperatures were 280, 200, and 300 °C, respectively. Samples volumes of 1 µL (50 µL diluted to a final volume of 500 µL in a mixture of 1:1 CH₂Cl₂:C₂H₆O) were injected applying a 25:1 split mode, with a solvent delay of 7.5 min. The MS was operated in electron ionization mode within a 35–550 m/z range. Each peak was assigned to selected compounds according to the corresponding m/z values, which were previously defined in the automatic library search NIST 2011. Each sample was analyzed by duplicate, and results were computed as an average. A total of 101 compounds identified in the liquid were divided in the following chemical families: aromatics (40 compounds) cyclic hydrocarbons (21 compounds), linear paraffins (18 compounds), n-alkenes (20 compounds) and esters (2 compounds) (Table 2). Some simplifications of the GC/MS analysis were assumed to determine the semi-quantitative composition of the different groups since, first, a unique response factor was used for all the identified compounds, and second, it was supposed that the whole sample was eluted and analyzed in the GC-MS chromatogram.

Table 2. Chemical composition by families of tire pyrolysis oil determined by GC–MS.

Normalized	RSD (%) ^a

	peak area (%)	
Aromatics	75.37	0.33
Cyclic Hydrocarbons	14.09	0.82
Linear Paraffins	3.40	3.39
n-Alkenes	5.76	1.17
Esters	1.39	3.81

^a RSD = relative standard deviation for samples injected by duplicated in the GC-MS

Each one of the main organic compounds present in the TPL were identified according to GC-MS. Regarding repeatability, good results were obtained for the different chemical families indicating a wide variety in its composition. The major compounds were associated with aromatic compounds (75.37 %), mainly constituted by a single aromatic ring with alkyls substituents where toluene and the mixture of xylenes showed the highest remarkable percentages (14.65 and 17.45 % respectively). Other heavier aromatic compounds were mainly associated with substituted naphthalene as well as indene. In addition to the aromatic compounds, D-limonene, a natural terpene included in the cycloalkanes family, represented 4.48 % of the total in the TPL followed by o-cymene (3.96 %), also aromatic compound. This predominant aromatic composition and the relevant presence of limonene and cymene has already been reported in the literature [29] although in this case, these last compounds were not the major compounds in the TPL. Also, linear hydrocarbons both alkanes and alkenes were obtained, with percentages between 3-6 % (Table 2) and with predominance of alkenes versus alkanes. The identified alkanes were hexadecane, heptadecane, octadecane, nonadecane, eicosane and tetracosane and some other high molecular weight alkanes. In addition to the main hydrocarbons, sulfur-containing compounds and nitrogen-containing compounds were also identified, with a low percentage of some oxygenated compounds in the form of esters.

2.2 Droplet combustion facility

The evaporation and combustion processes of the isolated droplets were characterized using LIFTEC's Droplet Combustion Facility (DCF). The main elements of the setup are shown in Fig. 1; **Error! No se encuentra el origen de la referencia..** A more detailed description can be found in previous works [30-32].

Droplets with an initial diameter (D_0) of 150 micrometers ($150.1 \pm 0.5 \mu\text{m}$) were formed at a piezoelectric apparatus at a 25 Hz rate, providing an interdroplet spacing long enough ($> 100 D_0$) to effectively avoid any significant interaction among droplets [18]. The free-falling droplets were introduced into a flat-flame burner's exhaust gases, providing thereby a controllable environment to study the evaporation and combustion processes of fuel droplets under temperature and gas compositions representative of those found in real flames. Since in actual applications oxygen concentration can significantly vary among regions within the flame, three different conditions were chosen, namely with a 0, 3 and 5 % O_2 volumetric fraction (dry basis) in the gaseous coflow. These levels are thought to be representative of the oxygen range observed by droplets during their evaporation in boilers, where most of the liquid droplet evaporation occurs in a central, low-oxygen and fuel-rich core (e.g., see oxygen maps in [33, 34]).

Fig. 1. Scheme displaying the main elements of the DCF.

The droplet combustion characteristics were completely determined by means of optical techniques. The droplet diameter and velocity were obtained from pictures recorded with a CCD camera (QImaging Retiga SRV, 12-bit) equipped with a telemicroscope and backlighting by means of a LED stroboscope. This optical system was synchronized to record two consecutive shots of the same free-falling droplet 500 μ s apart. A second camera (Hamamatsu C11440-36U, 12-bit) recorded the light emitted from the envelope flames and soot particles. In order to highlight the droplet shadow, making it distinguishable from the flame, a weak backlight was included, capturing therefore in the same frame the droplet and its envelope flame. Images were post-processed in order to extract different droplet combustion characteristics in the most repeatable way. This post-processing was performed in Matlab, using background subtraction, contrast enhancement and automatic edge detection algorithms.

Additionally to this close-up optical setup, the macroscopically visible flame traces were obtained through a third camera (Teledyne DALSA Genie Nano C4060) fitted with a DSLR lens. As such traces provide visual information regarding the amount of

soot present in the combustion chamber, these pictures were also processed to extract information concerning the sooting tendency of each fuel.

3. RESULTS AND DISCUSSION

Since the intended application of the obtained TPL is its combustion in boilers, information regarding its combustion characteristics seems most desirable. Due to its high sulfur content (0.83 wt.% as received, Table 1), the pyrolysis oil must be diluted in order to fulfil the Spanish regulations, which establishes a limit of 1000 ppm for heating applications . A realistic blend would be 5 % TPL in 95 % (by weight) conventional heating oil. This mixture, named TPL5, was compared with pure tire pyrolysis oil (TPL) and with neat Spanish heating oil (FO). A pure and well-known compound such as n-Hexadecane (99% purity) was also included as a reference, since it has been used as a baseline for comparison in different works addressing diesel and heating oil combustion tests (e.g., in [18, 30, 35]) . The main physicochemical properties of heating oil and hexadecane are summarized in Table 3 (for a more detailed description, the reader is referred to [30]).

Table 3. Selected properties of heating oil (FO) and hexadecane.

Fuel	Molecular formula	C (wt.%)	H (wt.%)	Boiling point (°C)	LHV (MJ/kg)	AFR (kg/kg)	Density at 20 °C (kg/m ³)
FO	C _{13.21} H _{24.63}	86.5	13.5	271–352 ^b	41.92	14.5	861
Hexadecane ^a	C ₁₆ H ₃₄	84.9	15.1	286	44.20	14.9	773

^a Extracted from [36]

^b Distillation curve (20-80% mass distilled).

3.1 Droplet, soot shell and flame images

The combustion process of the studied fuels for the 5 % O₂ condition is illustrated in Fig. 2. The depicted pictures are obtained from the backlighted Camera 1 (Fig. 1; **Error! No se encuentra el origen de la referencia.**), and display the liquid fuel droplet surrounded by nearly-spherical soot shells for certain cases. Similar soot shells are reported in convection-free environments achieved through microgravity such as [17, 35]. In these works, the soot particles produced inside the envelope flame remain trapped at a certain radial location, where viscous drag and thermophoresis forces balance. The onset of soot shells is, however, a quite infrequent event for droplet combustion tests at normal gravity, as any small relative velocity droplet-coflow (either caused by natural or by forced convection) would drag the small soot particles away. Slip velocities between droplets and the surrounding coflow were experimentally minimized in this work (Reynolds number <0.4), enabling the onset of quite spherical soot shells for high soot-yield conditions. In the authors' opinion, the occurrence of these spherical soot shells implies that even if test were conducted at normal gravity, droplets evaporate and burn under conditions close to spherical symmetry, especially in the droplet's vicinity, facilitating thus the comparison with theoretical 1-D droplet combustion models.

When comparing among fuels, the first significant difference is the occurrence of microexplosions for the pure pyrolysis oil (at 2.00 and 2.20 s/mm²) whereas the other fuels, including TPL5, evaporated smoothly until droplet extinction. In spite of the obvious differences between TPL and pyrolysis oils derived from bio-feedstocks, this disruptive behavior was also noted by several authors when studying the single droplet combustion characteristics of different bio-oils (for instance, in [21-23, 25, 26]). The fact that TPL droplets also underwent this shattering events is a novel result, which

nonetheless concurs with most of the previous characterizations performed on bio-oil droplets. The experimental setup used here, with non-suspended droplets is thought to provide reliable results in this regard, as the potential influence of the solid filament (which can act as a heterogeneous nucleation site) is avoided. The wide differences in volatility between TPL compounds (as it can be observed in Table 1), in addition to the high temperature coflow used in this work, could cause the bursting characteristics of TPL. The recorded microexplosions were quite violent and, in most cases, shattered the droplets in secondary disintegrations. TPL droplets consistently bursted after a first period of smooth evaporation. However, the onset of microexplosion slightly varied within a short interval, typically not broader than 0.2 s/mm^2 . The quantitative data extracted from these images, including droplet size measurements and microexplosion occurrence instants for each condition, shall be presented in the following section.

Fig. 2. Droplet and soot shell evolution for the examined fuels at the 5 % O_2 condition. Images are organized in accordance with their normalized time after injection: t/D_0^2 (s/mm^2).

Regarding the already mentioned soot shells, further differences can be noted among fuels. Whereas FO, TPL5 and TPL display clearly visible soot shells, none was found

for hexadecane, pointing to a much less sooty behavior of this fuel. The addition of a 5 % TPL to conventional heating oil does not appear to significantly change its behavior, with nascent soot shells emerging by approximately the same normalized time as for neat FO (1.20 s/mm^2), and maintaining similar thickness throughout all the droplet combustion lifespan. Pure TPL, on the other hand, already displays a distinguishable soot shell by 1.00 s/mm^2 , pointing to a higher sooting tendency, at least in the earlier stages of droplet combustion. This higher soot yield can be ascribed to the aromatic-rich nature of TPL, which displays a much higher aromatic composition than heating oil (according to Table 2, 75.37% of TPL consists on aromatics, whereas this figure is reduced to 29.16% in the studied heating oil [30]). For the 3 % O_2 condition, the registered soot shells were much fainter, and the evaporation case (0 % O_2) did not feature any soot shells. These differences can be primarily attributed to the temperature increase caused by the envelope flame as oxygen availability in the coflow rises [30].

Even though the majority of microexplosions effectively shattered the TPL droplets in a secondary atomization process (as those presented in Fig. 2), there were cases where these events displayed a lower intensity, with droplet puffing and swelling. The three main observed typologies are presented in **Fig. 3**, where the non-cropped double-shot images acquired with Camera 1 (Fig. 1) display the droplet just before the microexplosion (upper droplet), and the resulting smaller fragments after it. The time interval between shots is $500 \mu\text{s}$, and therefore the characteristic time for the shattering event can be considered to be in the order of tens of microseconds. The LED pulse duration is of only $1 \mu\text{s}$,

effectively freezing such high-speed process. While Fig. 3; **Error! No se encuentra el origen de la referencia.**a shows an efficient microexplosion, where the original droplet is shattered into much smaller fragments, the event displayed in Fig. 3; **Error! No se encuentra el origen de la referencia.**b is rather a swelling and puffing phenomenon than a proper disintegration. In this case, the vapor accumulation inside the droplet does not lead to a sudden breakup, but causes a much slower droplet swelling coupled with puffing of small liquid fragments and a significant deviation from the original droplet's free-falling path. Fig. 3; **Error! No se encuentra el origen de la referencia.**c, on the other hand, displays a complete breakup of the initial droplet, as happened in Fig. 3; **Error! No se encuentra el origen de la referencia.**a, but without a trace of any especially relevantly sized sub-droplet. As, according to the well-known d^2 -law, droplet lifetime approximately scales with its diameter squared, the occurrence of microexplosions such as those displayed in Fig. 3; **Error! No se encuentra el origen de la referencia.**a or Fig. 3; **Error! No se encuentra el origen de la referencia.**c would effectively shorten the droplet combustion lifetime to practically a few instants after the disintegration event. Much less straightforward to predict is the combustion history of swelling droplets (Fig. 3; **Error! No se encuentra el origen de la referencia.**b), as their random deviation made it extremely difficult to keep them in focus. Even though the images presented in ; **Error! No se encuentra el origen de la referencia.** correspond to different oxygen conditions, no correlation was found between oxygen availability and mode of microexplosion. The occurrence of a complete fragmentation or a swelling process seemed to respond to apparently random patterns, as TPL droplets subjected to exactly the same conditions alternatively displayed both phenomena.

Fig. 3. Different microexplosion typologies registered with Camera 1: a) TPL droplet, $L=27$ mm, 5 % O_2 ; b) TPL droplet, $L=31$ mm, 0 % O_2 ; c) TPL droplet, $L=29$ mm, 3 % O_2 .

In addition to the droplet and soot shell data obtained by means of the backlighting camera, Camera 2 (Fig. 1; **Error! No se encuentra el origen de la referencia.**) recorded the envelope flames around the droplets. A representative selection of these flame images for neat TPL tested with the three oxygen conditions is presented in Fig. 4.

Fig. 4. TPL flame evolution at the three studied oxygen conditions. Images are organized in accordance with their normalized time after injection: t/D_0^2 (s/mm^2).

Differences among oxygen conditions can be clearly observed, with smaller and brighter flames as oxygen availability increases. The studied pyrolysis oil displays a strong soot yield for all the studied oxygen conditions, and thus its flame characteristics are extracted from the soot continuous-spectrum emission. It is well known that soot is created in the inner side of the shell flame, and therefore the actual chemiluminescence flame would be located slightly farther from the droplet, although in these tests it remained eclipsed by the much stronger soot emission. Note that for the 0% O₂ case no combustion can take place, and the sooty emission presented in Fig. 4 is entirely ascribed to the thermal emission of the soot clouds when exposed to the high-temperature coflow. Analogous behaviors were found for FO and TPL5, although with slightly wider flames (flame sizes will be quantified in the following section). Hexadecane, on the other hand, displayed a much less pronounced sooty emission and, for the 5 % O₂ condition, the actual chemiluminescence bluish flame was visible within the first stages of droplet combustion. It is noteworthy that, for higher oxygen availabilities than those used in this study (namely 10 % O₂), the absence of any soot emission for hexadecane allowed the visualization of a considerably spherical blue envelope flame throughout all the droplet lifetime, supporting therefore the already discussed 1-D configuration of the combustion process (in spite of the obvious buoyancy effects displayed by soot clouds in Fig. 4).

The different typologies of registered microexplosions can also be clearly observed in Fig. 4, where the combustion process can either finish abruptly with a complete droplet shattering or proceed after an abrupt deviation of the droplet trajectory caused by the swelling and puffing event. This second situation can be clearly observed in two pictures of the 5 % O₂ case, where the droplets appear to be violently propelled away from their original position.

3.2 Quantitative data

As stated above, the droplet combustion process was entirely characterized from the images presented in the previous section. These pictures were processed in order to extract their main combustion characteristics, namely their burning rates and their droplet and flame size evolutions with time, which shall be quantified and presented here. Since the droplet combustion process is intended to be studied under experimental conditions as representative of real flames as possible, tests were performed at 0, 3 and 5 % O₂, covering therefore a typical range of oxygen availabilities around droplets in real flames, where the initial 21 % practically only exists at the injection plane, before fresh air gets mixed with hot flame gases. The heating oil test at the 0% O₂ condition was performed twice to check the repeatability of the experimental procedure. Only a 0.5% relative difference was found for droplet burnout time, while a 0.7% difference was observed for the evaporation rate.

The extracted droplet size and burning rate evolution curves for the three selected oxygen conditions are presented in Fig. 5 . The droplet size results are shown in the left column in terms of normalized diameter squared against normalized time.

Normalization is applied with the initial droplet diameter (D_0). At a first glance, the curves are in accordance with the d^2 -law and, after a significant heat-up transient period, the normalized size decreases linearly with time with a seemingly quite constant slope named burning rate (K). In order to gain insight into this relevant parameter, the D^2 - t curves were fitted to a polynomial function (4th order), whose derivative provides the burning rate dependence with time: $K = -d(D^2)/dt$. These results are displayed in the right column of Fig. 5, where it can be seen that, contrary to the notion of a nearly constant, time-independent burning rate which could be initially drawn from the D^2 - t curves, all the calculated K - t curves display a gradual increase in K which spans for a substantial

part of the droplets lifetimes before reaching a quasi-steady value. This progressive burning rate increase is primarily ascribed to the initial heating transient of the liquid phase .

Fig. 5. Normalized droplet size and burning rate evolution for FO, TPL5, TPL and hexadecane at the three studied oxygen conditions.

The evaporation characteristics reported in Fig. 5 for FO and TPL5 are virtually identical over the course of the whole droplet lifespan. The small addition of TPL to

heating oil does not appear to drive any significant change in the evaporative behavior (0 % O₂), nor in combustion (3 and 5 % O₂). Neat pyrolysis oil on the other hand, shows an earlier onset of vaporization, which can be clearly noted by the absence of initial droplet volumetric expansion. This is ascribed to the lower boiling point of the lightest fractions of the pyrolysis oil (Table 1) in comparison with those of heating oil (Table 3) or with the boiling point of hexadecane. Even though the TPL droplets start their vaporization earlier, their burning rates are soon surpassed by those of FO, TPL5 and hexadecane, fuels which also display clearly higher quasi-steady burning rates. These considerably lower K would induce longer droplet lifetimes for TPL in comparison with heating oil if it were not altered by microexplosion occurrence. In spite of the obvious differences among fuels, this behavior was also noted for several bio-oils in [25, 26], where the onset of bursting events for the different pyrolysis oil substantially reduced their overall burnout times even below of those of a light fuel oil with a considerably higher (by a factor of 2-3) burning rate. Even though TPL also shows a lower K compared to FO (Fig. 5), this difference is much smaller than that noted in the referred works. This would point to considerably higher K values for tire-derived pyrolysis oils than for bio-oils, as it could be ascertained from a comparison of TPL and typical bio-oil composition and main thermophysical properties. For instance, TPL contains no water (bio-oils studied in [25] ranged 16-30% in water content), it has a substantially higher LHV (40.49 MJ/kg according to Table 1, whereas bio-oils in [25] displayed 16-19 MJ/kg) and also a significantly lower density (917 kg/m³ in contrast to 1210-1230 kg/m³ in [25]).

As it can be noted in Fig. 5, the TPL curves suddenly terminate at values in the range of $(D/D_0)^2 \approx 0.40$, precisely due to the apparition of the already described microexplosion events which, for a considerable fraction of the observed cases, shattered the droplets.

This behavior was registered for the three oxygen conditions, although with slight differences regarding the instant at which the droplets disintegrated. As stated above, microexplosions consistently occurred for TPL droplets, although this phenomenon could usually appear randomly within an interval of roughly 0.2 s/mm^2 . Table 4 summarizes these intervals for the three studied oxygen conditions.

Table 4. Observed intervals of microexplosion occurrence for TPL droplets.

	First microexplosion		Last microexplosion	
	$(D/D_0)^2$	t/D_0^2 (s/mm ²)	$(D/D_0)^2$	t/D_0^2 (s/mm ²)
0 % O ₂	0.40	2.3	0.33	2.4
3 % O ₂	0.44	2.1	0.34	2.3
5 % O ₂	0.51	1.8	0.41	2.0

In addition to the presented results on droplet size and burning rates, the sooty flames captured by Camera 2 (Fig. 4) were also post-processed and analyzed to quantify their size evolution with time. The flame standoff ratio ($\text{FSR} = D_f/D$) is a widely used parameter in droplet combustion studies as a metric describing flame behavior. The measured FSR for both combustion conditions (3 and 5 % O₂) are displayed in Fig. 6, showing a practically coincident behavior between heating oil and TPL5 for both oxygen conditions, whereas the pure pyrolysis oil displays a closer relative position of the flame to the droplet. The classical theory of droplet combustion dictates that the FSR is expected to be constant along the whole droplet combustion lifespan. Fig. 6, however, displays a steady increase of FSR with time. This experimental behavior is attributed to the accumulation of fuel vapor in the droplet's vicinity, effect which is enhanced when the oxygen fraction in the coflow is low [37]. When comparing both oxygen conditions, it is also worth noting that the first appearance of a measurable

flame is delayed as the oxygen availability decreases, as it can be visually confirmed in Fig. 4.

Fig. 6. Flame standoff ratio (D_f/D) evolution for all the studied fuels at the 3 and 5 % O_2 condition.

3.3 Visual aspect and luminosity of flame traces

Besides the already presented droplet and flame pictures, long exposure images of the macroscopically visible flame streaks were captured with a color camera. These flame streaks are created by the combustion of the free-falling droplet stream, and they provide insight into the soot yielded for each fuel and condition, as incandescent soot radiates a characteristic luminosity. Fig. 7 compares the flame streaks recorded for FO, TPL5, TPL and hexadecane (3 % O_2 coflow condition), along with their extracted luminosity profiles.

Fig. 7. Flame traces pictures and luminosity profiles for the 3 % O_2 condition. The exposure time used in the displayed images is 200 ms (5 droplets injected during the exposure interval).

For each long-exposure photograph, all pixels' values were added across a given cross section, providing thereby an axial evolution of luminosity for all the studied fuels' traces. Even if the quantitative value of these results is not clear, the obtained profiles can be used to estimate relative differences in the soot yielded for various fuels at certain fixed and well know experimental conditions. It is important to note that the traces images displayed in Fig. 7 are significantly overexposed for a better visualization, and therefore the luminosity profiles were extracted from a different set of pictures, with much lower exposure values (namely, with higher f-stop numbers). The overexposure of the displayed images artificially enhances regions with very low signals, as it can be noted when comparing pictures and luminosity profiles. Whereas the images show noticeable luminosities throughout the displayed 100 mm, the signals recorded after 35 mm for TPL and after 50 mm for FO and TPL5 are negligible when compared with the upstream luminosity values, as demonstrated by the non-saturated profiles shown in Fig. 7.

The displayed pictures highlight clear differences among fuels, with hexadecane practically not showing any soot emission and FO, TPL5 and TPL presenting clear yellowish flame traces, as it was expected due to their sooty behavior. Heating oil and TPL5 profiles can be considered to be alike, taking into account the qualitative kind of results that this optical method can provide. This similarity in luminosity profiles between FO and TPL5 is consistent with the already discussed identical behavior regarding soot shell appearance and thickness. Pure pyrolysis oil on the other hand, displays much higher luminosity values within the first millimetres after injection, in accordance with the earlier onset of soot shell illustrated in Fig. 2. This could point to a higher soot yield, particularly during the first stages of droplet combustion.

Another fundamental difference between the pure pyrolysis oil and the other fuels is microexplosion occurrence, as already stated. This difference can also be macroscopically observed in Fig. 7. Whereas FO and TPL5 profiles display a bell-shaped luminosity profile with a turning point in the region of droplet extinction, pure pyrolysis oil shows a bimodal, more abrupt profile, with the microexplosion location clearly marked by an increase in the registered soot emission.

4. CONCLUSIONS

This study used a continuous auger reactor on pilot scale (150 kWth of nominal capacity) in order to produce a tire pyrolysis liquid (TPL), which was later exhaustively characterized, including GC-MS analysis. As the intended use of the prepared TPL is its use in burners, its combustion characteristics were subsequently extracted by means of a droplet combustion facility. Single droplet combustion tests were performed to TPL, both pure and blended with conventional heating oil (5 % TPL by weight). Neat heating oil and hexadecane were also studied.

All the examined droplet combustion characteristics (droplet size evolution, burning rates, flame standoff ratios, soot shells and flame luminosity profiles) were found to be practically identical for pure heating oil and TPL5, pointing to virtually indistinguishable combustion behaviors between both fuels. On the contrary, pure TPL showed an earlier onset of vaporization, ascribed to the lower boiling point of its lightest fractions as compared to those of heating oil. TPL also displayed significantly lower burning rates and flames located slightly closer to the droplet surface. Droplet microexplosions occurred consistently for droplet sizes in the order of $(D/D_0)^2 \approx 0.40$, effectively shortening the lifetimes of TPL droplets even below of those of conventional heating oil. Although most of the recorded microexplosions effectively shattered the TPL droplets into small fragments, swelling and puffing events were alternatively

observed in some cases. As droplets subjected to exactly the same conditions displayed both phenomena, this behavior is thought to respond to apparently random patterns. No correlation was found between microexplosion mode and oxygen availability, although it was determined that ambiances richer in oxygen promoted an earlier occurrence of these events. Neat TPL exhibited higher values of flame luminosity, pointing to a higher soot emission (and therefore a higher soot yield). This behavior is in accordance to the earlier onset of a distinguishable soot shell for TPL in comparison with heating oil and TPL5. No solid residue was found for any of the studied fuels or blends, although the occurrence of microexplosions for TPL hindered droplet tracking downstream the disintegration location.

The reported results are thought to contribute to the scarce available data regarding the combustion behavior of a well characterized tire pyrolysis oil. As the single droplet tests were performed under strictly controlled experimental conditions, which also intend to be representative of those found in real applications, the provided data could be used for the simulation of realistic spray flames as well as for the design of adapted combustion equipment.

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REFERENCES

- [1] Sienkiewicz M, Janik H, Borzędowska-Labuda K, Kucińska-Lipka J. Environmentally friendly polymer-rubber composites obtained from waste tyres: A review. *Journal of cleaner production* 2017;147:560-71.
- [2] Martínez JD, Puy N, Murillo R, García T, Navarro MV, Mastral AM. Waste tyre pyrolysis—A review. *Renewable and Sustainable Energy Reviews* 2013;23:179-213.
- [3] Machin EB, Pedroso DT, de Carvalho Jr JA. Energetic valorization of waste tires. *Renewable and Sustainable Energy Reviews* 2017;68:306-15.
- [4] Singh R, Mondal S, Ruj B, Sadhukhan A, Gupta P. Interaction of three categories of tyre waste during co-pyrolysis: Effect on product yield and quality. *Journal of Analytical and Applied Pyrolysis* 2019.
- [5] İlkılıç C, Aydın H. Fuel production from waste vehicle tires by catalytic pyrolysis and its application in a diesel engine. *Fuel Processing Technology* 2011;92(5):1129-35.
- [6] Chen T-C, Shen Y-H, Lee W-J, Lin C-C, Wan M-W. An economic analysis of the continuous ultrasound-assisted oxidative desulfurization process applied to oil recovered from waste tires. *Journal of cleaner production* 2013;39:129-36.
- [7] Enagi II, Al-Attar K, Zainal Z. Liquid biofuels utilization for gas turbines: A review. *Renewable and Sustainable Energy Reviews* 2018;90:43-55.
- [8] Martínez JD, Rodríguez-Fernández J, Sánchez-Valdepeñas J, Murillo R, García T. Performance and emissions of an automotive diesel engine using a tire pyrolysis liquid blend. *Fuel* 2014;115:490-9.
- [9] Wang W-C, Bai C-J, Lin C-T, Prakash S. Alternative fuel produced from thermal pyrolysis of waste tires and its use in a DI diesel engine. *Applied Thermal Engineering* 2016;93:330-8.
- [10] Doğan O, Çelik MB, Özdalyan B. The effect of tire derived fuel/diesel fuel blends utilization on diesel engine performance and emissions. *Fuel* 2012;95:340-6.
- [11] Murugan S, Ramaswamy M, Nagarajan G. Assessment of pyrolysis oil as an energy source for diesel engines. *Fuel processing technology* 2009;90(1):67-74.
- [12] Aydın H, İlkılıç C. Analysis of combustion, performance and emission characteristics of a diesel engine using low sulfur tire fuel. *Fuel* 2015;143:373-82.
- [13] Frigo S, Seggiani M, Puccini M, Vitolo S. Liquid fuel production from waste tyre pyrolysis and its utilisation in a Diesel engine. *Fuel* 2014;116:399-408.
- [14] Tudu K, Murugan S, Patel S. Effect of diethyl ether in a DI diesel engine run on a tyre derived fuel-diesel blend. *Journal of the energy institute* 2016;89(4):525-35.
- [15] Chen T-C, Shen Y-H, Lee W-J, Lin C-C, Wan M-W. The study of ultrasound-assisted oxidative desulfurization process applied to the utilization of pyrolysis oil from waste tires. *Journal of Cleaner Production* 2010;18(18):1850-8.
- [16] García-Contreras R, Martínez JD, Armas O, Murillo R, García T. Study of a residential boiler under start-transient conditions using a tire pyrolysis liquid (TPL)/diesel fuel blend. *Fuel* 2015;158:744-52.
- [17] Xu Y, Avedisian CT. Combustion of n-butanol, gasoline, and n-butanol/gasoline mixture droplets. *Energy & Fuels* 2015;29(5):3467-75.

- [18] Li T, Zhu D, Akafuah N, Saito K, Law C. Synthesis, droplet combustion, and sooting characteristics of biodiesel produced from waste vegetable oils. *Proceedings of the Combustion Institute* 2011;33(2):2039-46.
- [19] Kuznetsov G, Vershinina KY, Valiullin T, Strizhak P. Differences in ignition and combustion characteristics of waste-derived oil-water emulsions and coal-water slurries containing petrochemicals. *Fuel processing technology* 2018;179:407-21.
- [20] Vershinina KY, Shlegel NE, Strizhak PA. Influence of the initial temperature of coal water slurries containing petrochemicals on their ignition characteristics. *Applied Thermal Engineering* 2018;138:591-602.
- [21] Yang S, Wu M. The droplet combustion and thermal characteristics of pinewood bio-oil from slow pyrolysis. *Energy* 2017;141:2377-86.
- [22] Chen G-B, Li Y-H, Lan C-H, Lin H-T, Chao Y-C. Micro-explosion and burning characteristics of a single droplet of pyrolytic oil from castor seeds. *Applied Thermal Engineering* 2017;114:1053-63.
- [23] Hou S-S, Rizal FM, Lin T-H, Yang T-Y, Wan H-P. Microexplosion and ignition of droplets of fuel oil/bio-oil (derived from lauan wood) blends. *Fuel* 2013;113:31-42.
- [24] Garcia-Perez M, Lappas P, Hughes P, Dell L, Chaala A, Kretschmer D, et al. Evaporation and combustion characteristics of biomass vacuum pyrolysis oils. *IFRF Combustion Journal* 2006;200601:1-27.
- [25] Shaddix CR, Hardesty DR. Combustion properties of biomass flash pyrolysis oils: final project report. Sandia National Labs., Albuquerque, NM (US); Sandia National Labs., Livermore, CA (US); 1999.
- [26] Shaddix CR, Tennison PJ. Effects of char content and simple additives on biomass pyrolysis oil droplet combustion. *Symposium (International) on Combustion*. 27. Elsevier; 1998:1907-14.
- [27] Aylón E, Fernández-Colino A, Murillo R, Navarro M, García T, Mastral A. Valorisation of waste tyre by pyrolysis in a moving bed reactor. *Waste Management* 2010;30(7):1220-4.
- [28] Martínez JD, Lapuerta M, García-Contreras R, Murillo Rn, García T. Fuel properties of tire pyrolysis liquid and its blends with diesel fuel. *Energy & Fuels* 2013;27(6):3296-305.
- [29] Umeki ER, de Oliveira CF, Torres RB, dos Santos RG. Physico-chemistry properties of fuel blends composed of diesel and tire pyrolysis oil. *Fuel* 2016;185:236-42.
- [30] Muelas Á, Remacha P, Ballester J. Droplet combustion and sooting characteristics of UCO biodiesel, heating oil and their mixtures under realistic conditions. *Combustion and Flame* 2019;203:190-203.
- [31] Angeloni M, Remacha P, Martínez A, Ballester J. Experimental investigation of the combustion of crude glycerol droplets. *Fuel* 2016;184:889-95.
- [32] Muelas Á, Remacha P, Martínez A, Ballester J. Combustion Behavior of Jet A Droplets and its Blends With Butanol. *ASME Turbo Expo 2017: Turbomachinery Technical Conference and Exposition*. American Society of Mechanical Engineers; 2017:V04ATA073-V04AT04A.
- [33] Ballester J, Dopazo C. Experimental study of the influence of atomization characteristics on the combustion of heavy oil. *Combustion science and technology* 1994;103(1-6):235-63.
- [34] Ballester JM, Fueyo N, Dopazo C. Combustion characteristics of heavy oil-water emulsions. *Fuel* 1996;75(6):695-705.

- [35] Pan K-L, Li J-W, Chen C-P, Wang C-H. On droplet combustion of biodiesel fuel mixed with diesel/alkanes in microgravity condition. *Combustion and Flame* 2009;156(10):1926-36.
- [36] National Center for Biotechnology Information. PubChem Compound Database; Available from: <https://pubchem.ncbi.nlm.nih.gov/compound/11006>. [Accessed May 29 2019].
- [37] Law C, Chung S, Srinivasan N. Gas-phase quasi-steadiness and fuel vapor accumulation effects in droplet burning. *Combustion and Flame* 1980;38:173-98.