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Co-pyrolysis of biomass with waste tyres: upgrading of the liquid bio-fuel

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Abstract

Co-pyrolysis of forestry wastes and waste tyres is carried out using different facilities: a fixed bed reactor and a continuous auger reactor. Remarkably, only one phase is found in the liquid fraction, which is not achieved by mixture of the pure liquids. In addition, positive effects between waste tyre and biomass are evidenced, being more notable even synergetic in the auger reactor. It is found that whilst acidity, density and oxygen content decrease, pH and calorific value increase with respect to the merely biomass pyrolysis liquid, leading to upgraded bio-oil. Upgrading process is linked to the presence of radical interactions between waste tyres and biomass pyrolysis products. In addition, it is observed that the addition of waste tyres to the feedstock blend is significantly decreasing the amount of aldehydes and phenolic compounds, which is beneficial for improving the stability of the new bio-oils.

Keywords: pyrolysis, biomass, waste tyre, bio-oil, upgrading

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1. Introduction

The use of renewable sources and waste valorisation is increasing because of several factors, which include global warming, negative environmental impact due to the use of fossil fuels and the increase of energy demand and availability of waste materials. Therefore, it is necessary to study how to improve current processes to obtain an energy benefit with a minimum environmental impact. Pyrolysis valorisation process shows some advantages (environmental and technical) with respect to other valorisation processes. The most important one is the production of a liquid fuel that can be easily stored and transported. In addition to this liquid fraction, solid and gas fractions are produced, which can also be used as fuels (solid and gas fractions) or be valorised for the production of activated carbon (solid fraction). Thus, the study of pyrolysis processes to find the best operational conditions is of great interest.

There are several reviews focused on biomass pyrolysis for liquid fuel production [1-4]. Generally speaking, it can be stated that characteristics of the liquid fraction, such as appearance, miscibility, density, viscosity, distillation, and aging for liquids, markedly depend on the feedstock, the type of reactor, the process conditions and the efficiency of the condensation system [2]. Nonetheless, the pyrolysis liquid product, also called bio-oil, has chemical and physical properties well documented in the literature [5], see Table 1. As fuel, bio-oil has several environmental advantages over fossil fuels since it is renewable, locally produced and has lower environmental impact (close to CO₂/GHG neutral, no SO_x emissions, 50% lower NO_x emissions) [3]. However, it presents some disadvantages for its application as fuel such as high water content, high viscosity, poor ignition characteristics and corrosiveness [1], as well as high oxygen content, high solids content and chemical instability [4]. Pyrolysis liquids are unstable due to their high amount of reactive oxygen-containing compounds [6].

The instability is seen as a viscosity increase during storage, which, connected with the formation of water, finally leads to the separation of a lignin-rich bottom sludge [7].

Due to their structural water, bio-oil has been shown to be immiscible with diesel oil or other hydrocarbon fuels [8, 9]. Hence, an increasing number of methods for bio-oil upgrading are being investigated and developed for improving the quality of bio-oil.

The processes to get improved bio-oils mainly include hydroprocessing and catalytic cracking, although other processes such as esterification and reactive distillation have been also evaluated [4].

On the other hand, scrap tyres are a non-destructible and non-biodegradable waste through time making difficult their post-treatment and/or their recycling [10]. After their life cycle, tyres become wastes and only a few can be re-used. As the disposal of scrap tyres in landfills is prohibited in Europe, it is necessary to find an alternative route to take advantage of their high potential as energetic and raw material source. There are many different manufacturers and countless different formulations available all over the world; being the composition of the tyres influenced by both the tyre grade and manufacture processes. Consequently, the tyre pyrolysis, as a process to recover tyre energy, offers products that may also vary in terms of yield, chemical composition and characteristics. These properties depend not only on the source and grade of the tyres, but also, on the reactor configuration, efficiency in heat transfer and experimental conditions [10]. Even so, tyre pyrolysis liquids (a mixture of paraffins, olefins and aromatic compounds) have been found to have almost coincidental results regarding the marginal moisture and oxygen content. In addition, it is worth highlighting that some physico-chemical properties of the tyre pyrolysis liquids are fairly comparable to those found in commercial automotive diesel fuels, as shown in Table 1. These facts, together with their miscibility with diesel fuel [11] have encouraged their use as a replacement

for conventional liquid fuels in compression ignition engines as showed in [12-14]. However, further studies are necessary to utilize tyre derived oils as a liquid fuel or feedstock, since higher sulphur content and wider distillation range than commercial fuels can be problematic.

Related to biomass and waste tyres co-pyrolysis, Cao et al. [15] concluded that co-pyrolysis of sawdust and waste tyre using a fixed bed reactor can inhibit the unsuitable formation of PAHs produced by pyrolysis of tyre alone. The authors also showed a synergetic effect between both feedstock, which was reflected in an improvement of the pyrolytic liquid quality in terms of density, viscosity and elemental composition when compared to the liquid obtained from only biomass pyrolysis. Thus, it would be very interesting to study the co-pyrolysis of both feedstock in a continuous facility such as an auger reactor, since it is well-known that the type of reactor and process conditions could lead to different properties of the liquid fuel. In fact, co-pyrolysis of wood biomass and polymers such as polyethylene and polypropylene showed that the composition and the nature of both, biomass and synthetic polymers, as well as pyrolysis conditions have a great influence on the yield, the chemical structure and the physical properties of products [16].

This study aims to evaluate the co-pyrolysis of forestry waste woodchips containing bark and waste tyre scraps (using blends up to 20% of waste tyre) as a way for upgrading the physico-chemical properties of the bio-oil obtained from merely biomass. Co-pyrolysis of biomass with a feedstock of different composition could offer a simple route for upgrading the bio-oil in one step avoiding or minimizing the need for additional catalytic stages. In the first place, a thermogravimetric study was carried out to determine the temperature interval where simultaneous devolatilization of both feedstock takes place. Secondly, co-pyrolysis process was evaluated both in a fixed bed

reactor and in a continuous auger reactor, in which pyrolysis of scrap tyres [17, 18] and forestry wastes [19] have been run successfully before. Finally, chemical and physical properties of the different pyrolysis fractions obtained were determined for both reactors.

2. Experimental

2.1 Feedstock

Pine woodchips (15 mm of nominal size) and waste-tyre scraps (5 mm of nominal size) were used for the experiments. The biomass consisted of Aleppo pine (*Pinus halepensis*) containing bark from forestry wastes and it was dried prior to the experiments (moisture content of 4.0 wt.%). The waste-tyre scraps were composed of rubber without the steel thread and the textile netting (moisture content of 0.9 wt.%). The ultimate analysis of both materials was carried out in a Carlo Erba EA1108 instrument, the moisture content was determined according to ISO-589-1981; the ash content was measured according to ISO-1171-1976 and the volatile matter was determined according to ISO-5263-1974. The heating value was measured experimentally with a calorimetric bomb IKA C-2000 and determined according to UNE164001EX for the biomass and according to ISO-1929-76 for the waste-tyres. Table 2 shows the feedstock characterisation.

2.2 Thermogravimetric analysis

Three experiments from room temperature to 700 °C at 10 °C/min were performed for each feedstock and for a mixture of 80 wt.% biomass and 20 wt.% waste tyre (80/20). This 80/20 mixture is the maximum blend of waste tyre present in the feedstock since the aim of this paper is to upgrade the properties of the liquid fraction

obtained from solely biomass. The solid weight loss and temperature was recorded in a thermobalance SETARAM Setsys. The sample weight used in all experiments was 20 mg and the carrier gas was nitrogen at 150 l_N/min.

2.3 Fixed bed reactor

Pyrolysis was carried out in a kanthal fixed bed reactor (74 cm length and 1.6 cm internal diameter) in order to study feedstock devolatilisation in a small scale, see Figure 1. Samples of 20 g were pyrolysed using nitrogen as carrier gas (0.8 l_N/min) previously preheated. The reactor was heated externally with an electrical heater at 80 °C/min to the final pyrolysis temperature of 500 °C. The reaction time was set to 15 minutes. An ice-cooled trap was used to collect the liquids. Liquid and solid yields were obtained by weight, while the gas yield was calculated by the gas composition sampled in a gas bag. Each run was performed three times and the value reported for each yield is the average value with its absolute error. Different feedstock mixtures on mass basis were studied in the fixed bed reactor: 100% of biomass (100/0); 90% of biomass and 10% of waste tyres (90/10); 80% of biomass and 20% of waste tyres (80/20) and 100% waste tyres (0/100).

2.4 Auger reactor

In order to test the scalability of the process, an auger reactor pilot plant described in detail in previous publications [17-19] was used. The experimental setup presents an excellent reproducibility and stability and is able to process up to 15 kg/h of wastes tyres. This supposed a thermal inlet power of around 150 kW_{th} when merely waste tyres are used as a feedstock. This type of reactor not only promotes the

continuity of the process, but also it controls key variables of the pyrolysis process such as the mass flow rate and the residence time of the feedstock inside the reactor.

Experiments were set at 500°C using nitrogen as carrier gas at 5 l_N/min and a mass flow rate of 5 kg/h. The residence time of the feedstock inside the reactor was fixed in 5 min. Liquid and solid yields were obtained directly by weight, while the gas yield was calculated by the gas composition sampled in the gas bags. Both liquid and non-condensable gas samples were collected once the steady state was reached, approximately after 45 minutes from the beginning of the experiment. As done for the experiments carried out in the fixed bed reactor, the pyrolysis yields are the average value of three repetitions. Liquid samples were sealed in bottles and kept refrigerated prior to analysis. Co-pyrolysis of different feedstock mixtures was carried out using the same proportion mixtures used in the fixed bed reactor and described above.

2.5 Product characterisation

Complete characterisation of the liquid fuel was carried out by ultimate composition (Carlo Erba EA1108), calorific value (IKA C-2000), water content by Karl-Fischer titration (Crison Titromatic) according to ASTM E203-96; total acid number (TAN) and pH (Mettler Toledo T50), density (Anton-Paar DMA35N) and viscosity (Brookfield LVDV-E). Qualitative Gas Chromatography/Mass Spectrometry (GC/MS) analysis was performed in a THERMO Trace GC Ultra with MS DSQII to identify the main compounds in the liquid fuel. Prior to analysis, the liquid samples were filtered and diluted with methanol (1:10) in the case of the biomass samples and with dichloromethane for the waste tyre samples. 200 ppm of 1-octanol were added as internal standard. The capillary column was a DB-Petro (100 m x 0.25 mm ID x 0.50 µm film thickness) with helium as carrier gas with an initial flow of 2.3 ml/min during

the first 84 minutes, an increasing flow rate from 0.2 to 1.8 ml/min and kept at a constant flow rate of 1.8 ml/min during the rest of the analysis. The oven temperature was initially programmed at 40 °C (4 min), after that a first heating rate was set at 1°C/min up to 55 °C, a second heating rate of 2 °C/min to 185 °C, a third heating rate of 10°C/min to 250 °C and finally held at 250 °C for 60 min. The injector, the ion source and the transfer line temperatures were kept constant at 300, 230 and 280°C respectively. A sample volume of 1 µl was injected applying 1:7 split mode. After a solvent delay of 8 min for the biomass samples and 10.4 min for the waste tyre sample, a full mass spectrum was acquired. The MS was operated in positive electron ionisation mode and an m/z range from 30 to 500 was scanned. The voltage applied to the multiplier detector was 1275 V in order to obtain the total ion chromatograms (TICs) in a full-scan acquisition method. The identification of peaks is based on computer matching of the mass spectra with the NIST library. Once the identification is carried out, a Selective Ion Monitoring (SIM) chromatogram of the principal ion of each compound is extracted from the full-scan spectra.

Furthermore, the solid fraction (char) was characterized by measuring its calorific value (IKA C-2000). In addition, the non-condensable gases were determined by gas chromatography using a Varian's 490-GC PRO coupled to a TCD detector and equipped with a Molsieve 5 Å column to analyse H₂, O₂, N₂ and CO and with a HayeSep column to analyse CO₂, H₂S and hydrocarbons. The oven programs used were isothermal at 60 and 90 °C for the Molsieve and Hayesep column respectively.

2.6 Synergetic effect

The occurrence of synergetic interactions for both the product yields and properties was observed based on a comparison between the experimental pyrolysis

results and the theoretical pyrolysis data. Theoretical values were calculated from each individual feedstock and their respective mass ratio, assuming that there are no interactions among the pyrolytic vapour molecules (see equation 1). Herein, α_1 and α_2 represent the product yield or physico-chemical property from biomass and tyre, respectively; while w_1 and w_2 are the mass proportion, from the aforementioned feedstock, respectively. Thus, if the experimental co-pyrolysis is leading to a bio-oil property value better than the y value, it can be concluded that a vapour interaction is likely taking place and, consequently, a synergetic effect occurs.

$$y = w_1\alpha_1 + w_2\alpha_2 \quad (1)$$

It is worth highlighting that, in a strict sense, theoretical values of the different liquid properties cannot be calculated since biomass bio-oils and tyre pyrolytic oils are not miscible.

3 Results and discussion

3.1 Thermogravimetric analysis

Wood decomposition takes place mainly in three steps [21]: first lignin decomposition, which lasts until 500 °C, followed by hemicellulose decomposition and, finally, cellulose decomposition. Tyre pyrolysis has been also described elsewhere [20, 22, 23] and three main steps of devolatilisation are also found: a first step of low reaction rates linked to pyrolysis of tyre rubber additives; a second step with a sharp peak related to natural rubber decomposition and finally, a third step assigned to the decomposition of synthetic rubber (styrene-butadiene rubber and butyl rubber).

The aim of the thermogravimetric analysis is to assess the thermal behaviour under pyrolysis conditions of each feedstock and the biomass/waste tyre blend. The work is focused on blends lower than 20 wt.% of waste tyres since the main objective is

to upgrade the liquid obtained from merely biomass pyrolysis. Figure 2 shows the TG as well as the DTG plots for the three biomass/waste tyres samples used (100/0, 80/20 and 0/100). The theoretical values calculated for the blend as an additive reaction are also included as showed by Zhou et al. [24]. As expected, biomass devolatilisation starts at slightly lower temperature, approximately 200 °C, than waste tyre devolatilisation. Figure 2 also points out that the peak decomposition temperature (temperature of the maximum rate of weight loss) of the blend is similar to that obtained for biomass (around 361 °C) but lower than that found for waste tyre (372 °C).

From the thermograms, it can be established the devolatilisation temperature window for possible interactions between both feedstock. The temperature ranges for pyrolysis of biomass and tyre overlap at temperatures from 250 to 500 °C. Thus, radicals released during the pyrolysis process could coexist in this temperature range and interactions between them are likely to occur. These interactions could produce variations among the characteristics of the pyrolysis products, such as leading to a single phase liquid fuel with improved properties. In fact, some differences can be observed when comparing the experimental and the theoretical curves. The experimental and theoretical weight loss curves are similar until 300 °C, whereas mostly biomass pyrolysis takes place. From this temperature the experimental curve of weight loss lays over the theoretical one, increasing the difference up to 400 °C and slightly decreasing at higher temperatures. Secondary reactions produced from interactions among radicals seem to increase the fraction of solid remaining for the blend sample likely due to the adsorption of these volatile compounds on its porosity as showed elsewhere [20].

The facts described above are more accurately observed in the rate of weight loss. The experimental curve is lower than the theoretical one from 250 to 375 °C, when

the rate of weight loss of tyre is lower than the biomass one. At temperatures from 375 to 500 °C the experimental rate of weight loss is higher than the theoretical one, as well as the rate of weight loss of tyre increases over the biomass curve. The complete devolatilisation of the blend finishes at approximately 500 °C, which is similar to the pure feedstock. Thus, lignin from biomass and natural rubber from waste tyre seem to start the degradation process. Subsequently, lignin, hemicellulose and cellulose decomposition products probably interact with pyrolysis products of both the natural rubber and the synthetic rubber from tyre. As commented above, these interactions could lead to the formation of deposits on the porosity of the solid fraction that consequently decrease the rate of weight loss compared to the pure components. Finally, the remaining lignin, the deposits and the residual components of waste tyre, styrene-butadiene and butyl rubber (synthetic rubber) decompose up to 500 °C, increasing the rate of weight loss. Therefore, 500 °C seems to be an adequate temperature both to ensure the interaction between the biomass and the waste tyre pyrolytic radicals and to achieve a complete conversion of both feedstock. This value is in agreement with results reported by Cao et al. [15].

3.2 Product yields from fixed bed reactor

Product yields from co-pyrolysis of biomass and waste tyres conducted in the fixed bed reactor are shown in Figure 3. The pyrolysis product yields are the average of three repetitions with a relative error lower than 2%. Liquid yields of 50.0 ± 0.9 wt.% and 47.6 ± 0.7 wt.% are obtained for feedstock consisting of merely biomass and waste tyres, respectively. In-between values of liquid yields are obtained when co-pyrolysis of biomass and waste tyres is performed, 48.5 ± 0.7 wt.% and 48.0 ± 0.8 wt.%, for 90/10 and 80/20, respectively. It is noteworthy that a single liquid phase is obtained for all the

biomass/waste tyre blends. In addition, liquid yields marginally lower than the theoretical values are obtained. By comparing the theoretical and experimental values for both the liquid and gas yields (see Figure 3), it can be highlighted that the formation of non-condensable gas is favoured versus liquids during the co-pyrolysis process, leading to gas yields slightly higher than the theoretical ones. Regarding the char yield, total conversion is obtained for biomass (100/0) and waste tyre (0/100) pyrolysis since char yield values closely resemble the sum of the fixed carbon and the ash content. In addition, there is a clear tendency showing an increase of the amount of char when the tyre proportion of the feedstock increases. This is due to the lower proportion of volatile matter and the higher percentage of fixed carbon (by the carbon black added in the tyre manufacture) present in the waste tyres compared to the forestry biomass. Moreover, it can be concluded that total conversion is also reached for the biomass and waste tyre blends since no differences are obtained between the experimental and theoretical values.

3.3 Product yields from auger reactor

Figure 4 shows the results obtained from the auger reactor pilot plant. As mentioned earlier, the pyrolysis product yields are the average of three repetitions leading to a relative error lower than 3%. Again, a single liquid phase is obtained, which is a very remarkable result. The same tendency observed in the fixed bed reactor regarding the char yield occurs in the auger reactor, although higher char yields are obtained overall. In pyrolysis, the highest feedstock conversion is achieved when the char yield match the non-volatile matter of the feedstock (fixed carbon plus the ash content). For the merely biomass pyrolysis, a difference of only 4.4 points between the char yield and the sum of the fixed carbon and the ash content is attained, indicating

almost total conversion of the forestry biomass. In addition, a liquid yield (52.0 ± 1.3 wt.%) comparable to other studies previously reported in the literature is obtained [19]. However, it can be observed for merely waste tyre pyrolysis that the char yield (48.3 ± 1.0 wt.%) is significantly higher than that reported in other works (around 40.0 wt.%) where total waste tyre conversion is reached [10, 17]. In addition, this char yield is considerably higher than the sum of the fixed carbon and the ash content (35.8 wt.%, see Table 2). Thus, it can be stated that the waste tyre conversion is not totally achieved under these experimental conditions. Accordingly, lower liquid yield ($38.3 \text{ wt.}\% \pm 0.8$ wt.%) compared with former studies carried out in the same plant using waste tyre [18] is achieved. Although these experimental conditions are not optima for merely waste tyre pyrolysis, it is worth commenting that the use of a higher reaction temperature for biomass/waste tyre blends processing is ruled out since these experimental conditions would favour the occurrence of undesired secondary reactions as thermal cracking, increasing the water content and decreasing the liquid yield, as showed elsewhere for merely biomass pyrolysis in this type of reactors [19]. Therefore, the reaction temperature is fixed at 500 °C. Unfortunately, longer residence times as those above used in the fixed bed, which could lead to higher feedstock conversion, could not be implemented due to the intrinsic system characteristics.

For the biomass/waste tyre blends, it can be observed that the higher the tyre proportion, the higher the char yield. In addition, unlike the results obtained in the fixed bed reactor, there are some differences between the experimental and the theoretical values. Whilst the theoretical char yield for the blend 90/10 ($27.6 \text{ wt.}\% \pm 0.6 \text{ wt.}\%$) is comparable to the experimental one ($26.7 \pm 0.7 \text{ wt.}\%$), the theoretical value for the blend 80/20 ($29.9 \text{ wt.}\% \pm 0.6 \text{ wt.}\%$) is lower than the experimental one ($33.3 \pm 0.8 \text{ wt.}\%$). This fact could be related to the promotion of secondary reactions between the

waste tyre and biomass radicals, leading to char formation. Moreover, it can be observed that the liquid yield decreases with the tyre proportion in the blend. The highest liquid yield is found for the 90/10 blend (56.0 ± 1.6 wt.%), which is remarkably higher than both the yield obtained in the fixed bed reactor (48.5 ± 0.7 wt.%) and the theoretical value (50.6 wt.% ± 1.3 wt.%). In addition, this value is higher than that obtained for the pyrolysis of merely biomass. This result suggests a synergetic effect towards the production of bio-oils between both feedstock at those experimental conditions, which could be again related to the promotion of interactions between biomass and waste tyre radicals leading to the formation of bio-oil. A different behaviour is observed for the 80/20 blend. In this case, the liquid yield is comparable to that obtained for the fixed bed (48.0 ± 0.8 wt.%) and to the theoretical value (49.2 wt.% ± 1.2 wt.%). As the char yield obtained is remarkably higher than the theoretical value, it can be again stated that the presence of higher proportion of waste tyre in the blend is likely increasing the probability of radical interactions, promoting the formation of char instead of bio-oil. In agreement with these results, it is obtained that gas yields decrease with increasing waste tyre proportion in the blend, being this effect more apparent for the 80/20 blend. In addition, it is also observed that the theoretical values are higher than the experimental ones, which is again showing that the addition of waste tyres to the pyrolysis process is promoting the occurrence of radical interactions. It can be concluded that although the presence of waste tyre in the blend is promoting the interaction of pyrolysis radicals towards bio-oil production, the proportion of waste tyre in the blend should be kept low since char formation could be increased, as it is observed for the 80/20 blend.

3.4 Product characterisation

3.4.1 Liquid characterisation

As mentioned previously, no phase separation is evidenced in the liquid fraction for all the blends considered in both reactors. According to Chiaramonti et al. [25] water contents higher than 30 wt.% lead to phase separation, forming two phases with different properties. Multi-phase liquids can be due to high moisture content in the feedstock as well as to the chemical composition of the original biomass feedstock [5]. The water present in bio-oils, when is lower than 30 wt.%, is usually miscible with the oligomeric lignin-derived components because of the solubilizing effect of other polar hydrophilic compounds [1]. As it is shown in Figs. 5 and 6, the water content in the liquid fractions for both reactors is lower than 30 wt.%, which explains the formation of a single phase bio-oil for the merely biomass pyrolysis experiment. Additionally, it should be highlighted that since biomass bio-oils and tyre pyrolytic oils are not miscible even at low waste tyre bio-oil ratios, it can be assumed that radical interaction during the pyrolysis reaction leads to a new bio-oil that avoids phase separation.

Generally speaking, the properties of the liquid produced in the fixed bed reactor (Figure 5) show a slight decrease on both the water content and TAN, compared to those obtained with merely biomass. In addition, pH and calorific value increase whilst the O content decreases (Table 3). This suggests a positive effect on these properties when the waste tyre content increases in the blend. However, the improvement obtained for all these properties is lower than that expected from the pure feedstock pyrolysis. As shown in Figure 5, the experimental values for these properties are poorer than the hypothetical theoretical ones. This fact could be related to the intrinsic characteristics of the fixed bed reactor. Reaction radicals are slowly released and quickly evacuated from the reactor, which is decreasing the probability of interactions between biomass and waste tyre radicals. It is worth commenting that some radical interactions are still taking

place since a single phase is obtained whilst biomass bio-oils and tyre pyrolytic oils are not miscible even at low waste tyre bio-oil ratios.

On the other hand, experimental results from the auger reactor reveal a remarkable upgrading for some liquid properties. Thus, a positive interaction between both feedstock seems to take place resulting in upgraded properties such as lower TAN, lower density, higher pH, higher calorific value and lower oxygen content (see Fig. 6 and Table 4). In addition, the experimental values for these properties (except for pH and oxygen content), are better than the theoretical ones, showing a synergetic effect.

As showed in Fig. 6, after waste tyre addition TAN decreases from 97.0 to 75.1 and to 71.1 mg KOH/g for the 90/10 and 80/20 blends, respectively. Accordingly, pH values slightly increase from 2.3 to 2.5. As pointed out by Bhattacharya et al. [26], pH values mainly reflect the presence of carboxylic acids, such as formic, acetic and propanoic acids, generated due to cellulose and hemicellulose pyrolytic degradation, whilst TAN gives a better tendency about the amount of acidic compounds present in the liquid. It is worth commenting that although a 80/20 blend leads to lower TAN values, the synergic effect is more apparent for the 90/10 blend. In agreement with these results, it can be observed in Table 5 that the area ratios of acidic compounds identified by GC/MS is always reduced after the addition of waste tyres and that the positive effect is relatively higher for the 90/10 blend. Against this background, it should be pointed out that even though acidity is improved and the concentration of these compounds is reduced, a further bio-oil upgrading should be performed for its application as fuel in standard engines, where a value lower than 10 is accepted in order to avoid corrosiveness problems and deposits formation [27].

Remarkably, LHV is the property with the major upgrading since it changes from 14.9 to 19.0 and to 25.0 MJ/kg for the 90/10 and 80/20 blends, respectively. Thus,

it shows an increase up to 27 % and to 70 %, respectively. Albeit a synergetic effect is observed for both blends, this effect is more significant for the 80/20 blend. A noteworthy fact is that a remarkably higher LHV is achieved despite of this bio-oil has a higher water content than that theoretically expected. Higher LHV could lead to substantial higher thermal efficiencies than bio-oil from merely biomass, when is used as fuel in modified internal combustion engines. According to Yang et al. [28], the heating value has the major effect on engine thermal efficiency and power output. An increase in the heating value of a fuel will increase the engine power output for the same fuel consumption rate given the increase of both thermal input and efficiency.

Moreover, it is found that the C and H contents in the liquid gradually increase with the proportion of waste tyres in the feedstock, whilst the O content decreases (Table 4), supporting the data obtained for the calorific value. Table 4 also shows that the experimental C and H contents are poorer than those theoretically expected. A higher water content than that theoretically expected in the bio-oil could explain this fact. The water in the bio-oil comes mainly from water in the biomass and dehydration during pyrolysis. Since water in the biomass is comparable for all the experiments, it can be assumed that the addition of waste tyre to the feedstock blend also promotes dehydration reactions, being this effect more apparent at higher waste tyre ratios. It can be assumed that the presence of some additives in the waste tyres, such as CaO [29], is favouring dehydration reactions. Density also decreases from 1.2 to 1.1 g/cm³ as the waste tyre increases in the blend. However, these values are still higher than those found in standard fuels such as distillate marine fuels (0.89-0.90 g/cm³) and residual fuels (around 1.0 g/cm³) as found in standard ISO 8217.

Regarding viscosity, results disagree with the behaviour theoretically expected. The viscosity increases as the tyre ratio increases in the blend, since for merely waste

tyre the lowest value is found. Again, this result suggests that waste tyre radicals released in the auger reactor favour radical interactions, leading to the formation of higher molecular weight organic compounds, which, in turn, increase the viscosity of the liquid fraction. Unfortunately, this assumption could not be confirmed by GC/MS analysis since heavier compounds than methyl-phenanthrene could not be analysed.

Representative bio-oil samples of the four feeding blends obtained in the auger reactor (100/0, 90/10, 80/20 and 0/100 of biomass/waste tyre blends) are also analysed by means of qualitative GC/MS using 1-octanol as internal standard. A total of 180 compounds are identified, of which 75 belonged to the 100% biomass samples and 115 to the 100% waste tyre sample. Table A1 in the supplementary data shows the identified compounds with their area ratio (average of the compound area divided by the area of the internal standard) for all the blends. It can be observed that new compounds are not formed during the co-pyrolysis process of biomass/waste tyre blends compared to the pyrolysis of the pure feedstock. In addition, all the compounds detected in the pyrolysis of merely biomass are present in the blend samples whilst only ten compounds detected during the pyrolysis of merely waste tyre are also identified in the blend samples. These ten compounds (from highest to lowest abundance) are limonene; p-xylene; toluene; 1,2,3-trimethylbenzene; 1-ethyl-4-methylbenzene; 1,3,5,5-Tetramethyl-1,3-cyclohexadiene; 1,3-dimethylbenzene; benzene; 1,3-cyclopentadiene; and 1-methyl-1,4-cyclohexadiene. Therefore, it can be concluded that the addition of low amounts of waste tyre to the feedstock blend only slightly alters the nature of the bio-oil although an upgraded bio-oil is obtained. Thus, the main compounds present in the biomass and waste tyre blends (above 3 of the area ratio) are mainly levoglucosan, furfural, phenols, acids, esters, aldehydes, ketones and limonene (see Table 5). During pyrolysis of holocellulose (hemicellulose and cellulose), two competing pyrolytic pathways are

mainly responsible for its primary decomposition, depolymerisation and pyrolytic ring scission. Depolymerisation process forms various anhydrosugars (mainly levoglucosan), furans and other products [30]. As shown in Table 5, the levoglucosan area ratio is only slightly reduced with increasing waste tyre in the feedstock blend. Thus, although it cannot completely rule out, it seems that secondary reactions between primary holocellulose decomposition products and waste tyre radicals are unlikely to take place. In agreement with this, aldehydes and ketones, which are the main products formed from the pyrolytic ring scission of holocellulose, are reduced according to the proportion of waste tyre added to the blend. Area ratios of both, aldehydes and ketones, are reduced around 10 % and around 20 % for the 90/10 and 80/20 blends, respectively. Particular attention should be paid to the aldehydes since they pose a big threat to the stability of the crude bio-oil [31]. Secondary degradation reactions may occur, since phenolic compounds tend to polymerize with aldehydes under acidic conditions [32]. Therefore, it can be highlighted that the relative content of the aldehydes is decreased after waste tyre addition, which is beneficial for improving the stability of bio-oils. On the other hand, phenolic compounds are originated from the decomposition of lignin [30, 33, 34]. In addition to their influence on the bio-oil instability, it is well-known that the lignin-derived products are mainly responsible for the high molecular weight and viscosity of bio-oils and thus, one of the aims of any upgrading process is to remove these compounds. It can be observed in Table 5 that the area ratio of these compounds is significantly decreased for the biomass/waste tyre blends, being this reduction about 20 % and about 40 % for the 90/10 and 80/20 blends, respectively. Thus, a synergic effect towards phenolic compounds removal is taking place. Since experimental gas yields are lower than the theoretical values for the biomass/waste tyre blends and the concentration of aromatic compounds is not affected by the amount of waste tyre in the

feedstock, it can be assumed that phenol precursors are likely interacting with waste tyre radicals to form heavier liquid compounds or char, depending on the amount of waste tyre added to the biomass feedstock. Therefore, it can be observed that the addition of waste tyres to the feedstock blend is significantly decreasing the amount of aldehydes and phenolic compounds, which is beneficial for improving the stability of the new bio-oils. Indeed, the viscosity of the biomass/waste tyre blends was measured after six months and no significant changes were appreciated. Therefore, it can be concluded that the addition of waste tyres to the biomass feedstock in an auger reactor is a potential way for upgrading the quality of bio-oils. However, reactor size and process conditions should be optimised so that interactions between waste tyre and biomass radicals could be tuned to promote bio-oil production even at high waste tyre contents in the feedstock.

3.4.2 Char characterisation

No major differences are found regarding the reactor effect on the calorific value of the char. The LHV of char obtained from both reactors is around 30 MJ/kg. This high energy content could be very attractive for combustion processes since LHV is higher than that found in some coals used for power generation and/or thermal applications [35].

3.4.3 Non-condensable gas characterisation

Generally speaking, a similar trend can be noticed in both facilities. As expected, the concentration of heavier hydrocarbons and hydrogen of the gas fraction produced in both reactors increases as the amount of waste tyres increases in the feed (Table 6).

Similarly, H₂S concentration increases with the waste tyre ratio in the blend, given its higher concentration of S (Table 2). In contrast, CO and CO₂ decrease proportionally as the proportion of waste tyre increases. It is worth pointing out that the incorporation of waste tyre to the feeding blend leads to the formation of heavier hydrocarbons, such as

C_3H_6 and C_4H_{10} . As a consequence, the LHV increases with the waste tyre ratio in the blend. For the 80/20 blend, this value is 20.5 MJ/Nm^3 when the process is conducted in the fixed bed reactor and 17.5 MJ/Nm^3 when the process is performed using the auger reactor. This value is remarkably higher than that found for merely biomass pyrolysis ($12 - 13 \text{ MJ/Nm}^3$), and hence, can likely contribute with the energy demand for driving the co-pyrolysis process.

Conclusions

Pyrolysis process has been performed in a fixed bed reactor and in an auger reactor pilot plant. In both systems it has been observed that the addition of waste tyres to the biomass feedstock is improving the bio-oil properties and, remarkably, one phase is obtained. It has been found that bio-oils with improved properties are attained for the auger reactor and even a synergetic effect is observed for some of them. Radical interactions between waste tyres and biomass pyrolysis products can promote the formation of a stable bio-oil with upgraded properties.

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Figure Captions

Figure 1. Kanthal fixed bed reactor diagram.

Figure 2. TG and DTG for biomass, waste tyre and 80/20 blend. Black solid line for merely waste tyre. Gray solid line for merely biomass. Green dotted line for theoretical behavior of the 80/20 blend and purple dashed line for experimental behavior of the 80/20 blend.

Figure 3. Product yields produced in the fixed bed reactor. Solid lines for experimental results and dashed lines for theoretical values; ■ in blue for experimental liquid yield, □ in blue for theoretical liquid yield; ♦ in red for experimental gas yield, ◇ in red for theoretical gas yield; ● in black for experimental char yield, ○ in black for theoretical char yield.

Figure 4. Product yields produced in the auger reactor. Solid lines for experimental results and dashed lines for theoretical values; ■ in blue for experimental liquid yield, □ in blue for theoretical liquid yield; ♦ in red for experimental gas yield, ◇ in red for theoretical gas yield; ● in black for experimental char yield, ○ in black for theoretical char yield.

Figure 5. Some properties of the liquid fraction produced in the fixed bed reactor. Black colour for experimental values; gray colour for theoretical values.

Figure 6. Some properties of the liquid fraction produced in the auger reactor. Black colour for experimental values; gray colour for theoretical values.

Table 1. Typical properties of wood pyrolysis bio-oil, tyre pyrolysis liquid and diesel fuel

Property	Bio-oil	Tyre-oil	Commercial diesel N°2
Moisture (wt.%)	15-30	0-4	0-0.02
pH	2-3	4-7	5-6
TAN (mg KOH/g)	90-110	5-10	0-0.5
Density at 15 (kg/m ³)	1100-1200	900-950	820-845
Viscosity at 40°C (cSt)	15-30	3-6	2-4.5
Elemental composition (wt.%)			
C	54-58	80-90	84-87
H	5-7	8-12	11-15
O	35-50	0-2	0.0
N	0-0.2	0.4-1.0	0.01-0.3
S	0-0.1	0.8-1.5	0-0.01
Ash (wt.%)	0-0.2	0-0.2	0.0
HHV (MJ/kg)	16-19	40-44	42-46

Table 2. Proximate and ultimate analyses and calorific value of forestry waste and waste tyres

Proximate analysis on dry basis (wt.%)	Forestry waste	Waste tyres
Ash	1.1	3.8
Volatiles	81.8	64.2
Fixed carbon	17.1	32.0
Ultimate analysis on dry basis (wt.%)		
Carbon	49.6	87.9
Hydrogen	6.4	7.4
Nitrogen	0.2	0.3
Sulphur	0.0	1.1
Oxygen ^a	43.8	0.0
HHV as received (MJ/kg)	19.5	38.6
LHV as received (MJ/kg)	18.0	37.0

^a by difference

Table 3. Ultimate analysis of the liquid fraction produced in the fixed bed reactor

Element	100/0	90/10		80/20		0/100
	E.V	E.V	T.V	E.V	T.V	E.V
C (wt %) ^a	36.3	36.6	41.4	40.2	46.5	87.1
H (wt %) ^{a,b}	8.1	8.1	8.4	8.2	8.6	10.8
N (wt %) ^a	0.3	0.3	0.3	0.3	0.3	0.5
S (wt %) ^a	0.0	0.0	0.1	0.1	0.2	0.8
O (wt %) ^c	55.3	54.9	49.9	51.3	44.4	0.8

^a as received; ^b includes the hydrogen from water, ^c by difference; E.V: experimental values; T.V: theoretical values

Table 4. Ultimate analysis of the liquid fraction produced in the auger reactor

Element	100/0	90/10		80/20		0/100
	E.V	E.V	T.V	E.V	T.V	E.V
C (wt %) ^a	38.8	41.2	43.6	44.5	48.4	86.9
H (wt %) ^{a,b}	6.5	6.9	7.0	7.8	7.4	11.1
N (wt %) ^a	0.4	0.5	0.4	0.5	0.5	0.8
S (wt %) ^a	0.0	0.2	0.1	0.4	0.1	0.7
O (wt %) ^c	54.3	51.2	48.9	46.8	43.5	0.5

^a as received; ^b includes the hydrogen from water, ^c by difference; E.V: experimental values; T.V: theoretical values

Table 5. Composition of the bio-oil produced in the auger reactor

Compound	100/0	90/10	80/20	0/100
Furfural	3.30	2.71	2.08	-
Levoglucosan	25.58	24.57	22.96	-
Ketones	44.91	40.8	36.31	-
Aldehydes	12.20	11.18	10.18	-
Alcohols	0.46	0.45	0.45	-
Acids	26.79	23.39	22.66	-
Esters	4.30	4.15	3.69	-
Phenols	37.36	30.49	24.12	-
Limonene	-	3.95	4.01	19.89
BTX	-	1.74	1.48	16.90
Paraffins	-	-	-	4.49
Olefins	-	0.35	0.23	17.69
Aromatics	-	3.23	3.23	47.90
Naphthenics	-	0.60	0.50	64.90

Proportion of the compound families are calculated as the sum of the area ratios shown in Table A1 (supplementary data)

Table 6. Gas composition produced in both fixed bed and auger reactor in free basis of N₂ and O₂

Gas (vol.%)	Fixed bed reactor				Auger reactor			
	100/0	90/10	80/20	0/100	100/0	90/10	80/20	0/100
H ₂	2.3	2.4	3.4	13.4	1.9	2.4	3.6	12.0
CO	43.9	40.9	36.2	12.0	42.6	40.6	37.1	20.0
CO ₂	41.8	41.3	35.8	8.2	42.1	42.3	40.0	8.0
CH ₄	9.6	9.9	14.7	7.6	10.6	9.6	10.7	7.4
C ₂ H ₄	0.9	1.4	1.7	10.7	0.8	1.1	2.0	10.7
C ₂ H ₆	0.9	1.4	1.9	7.8	0.9	1.2	1.8	2.4
C ₃ H ₈	0.6	1.4	2.0	9.6	0.9	1.3	1.8	3.4
C ₃ H ₆	0.0	0.1	0.4	1.6	0.1	0.2	0.3	9.1
C ₄ H ₁₀	0.0	1.0	3.7	28.9	0.0	1.1	2.7	24.9
H ₂ S	0.0	0.2	0.3	1.2	0.0	0.2	0.3	1.4
LHV (MJ/Nm ³)	11.4	15.3	20.5	66.0	12.1	13.8	17.5	59.4

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.