Physico-chemical properties of chars obtained in the co-pyrolysis of waste mixtures

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ABSTRACT

The present work aims to perform a multistep upgrading of chars obtained in the co-pyrolysis of PE, PP and PS plastic wastes, pine biomass and used tires. The quality of the upgraded chars was evaluated by measuring some of their physico-chemical properties in order to assess their valorisation as adsorbents' precursors. The crude chars were submitted to a sequential solvent extraction with organic solvents of increasing polarity (hexane, mixture 1:1 v/v hexane:acetone and acetone) followed by an acidic demineralization procedure with 1 M HCl solution. The results obtained showed that the upgrading treatment allow the recovery of 63–81% of the pyrolysis oils trapped in the crude chars and a reduction in the char's ash content in the range of 64–86%. The textural and adsorption properties of the upgraded chars were evaluated and the results indicate that the chars are mainly mesoporous and macroporous materials, with adsorption capacities in the range of 3.59–22.2 mg/g for the methylene blue dye. The upgrading treatment allowed to obtain carbonaceous materials with quality to be reused as adsorbents or as precursors for activated carbon.

1. Introduction

Human activity, in its many aspects, is reflected in an increasing diversity and continued production of wastes being necessary to ensure their appropriate destination to minimize the negative impacts on human health and on environment.

Only in the European Union (EU-27) the waste generated in 2008 amounted to a total of 2.62 billion tonnes [1].

Landfill disposal together with incineration are the most used and implemented options in what concerns waste management [1,2]. To improve its image and public acceptability, incineration is increasingly presented as an energy production process instead of a process of waste mass-burn [3]. Incineration completely destroys the organic content of wastes while other thermochemical alternatives allow the conversion of wastes into new organic products that can be used as raw materials for chemical industries or as substitutes for traditional fuels.

One of those alternatives is pyrolysis that consists in the thermal degradation of waste in an oxygen-free environment or with low oxygen content so that the formation of harmful substances such as dioxins can be controlled.

Nowadays wastes such as plastics, used tires and lignocellulosic biomass are, presently, generated in huge amounts [4–6] and considered suitable raw materials for pyrolytic processes since natural and synthetic polymers are broken down into smaller hydrocarbon chains. The products formed include fuel gas and pyrolysis oil that have industrial and energetic interesting applications [7–9].

Although pyrolysis conditions are usually optimized in order to maximize the gas and liquid products, non-volatilization of raw materials, recondensation and/or recombination of thermal cracking products may occur leading to a solid fraction named as pyrolytic char.

This solid char is mainly composed by a carbon-rich matrix that contains almost all the inorganic compounds present in the raw wastes and a significant amount of condensed by-products formed during the pyrolysis process dispersed throughout the solid porous structure.

To minimize the cost and increase the sustainability of the pyrolysis process, the pyrolytic char should be valorized as are the gaseous and liquid products instead of being directed to landfill disposal. Combustion of char is a possibility, since it provides process energy for pyrolysis. An interesting alternative is the valorisation of the char as adsorbent of pollutants [10]. Usually, the pyrolysis chars have porous structures compatible with adsorption purposes [11–18], moreover, due to their potential adsorptive properties, the solid chars are good precursors for manufacturing activated carbons by means of physicochemical activation [12,14,19,20].

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Table 1
Composition of the three waste mixtures submitted to pyrolysis and yields of products obtained in the co-pyrolysis experiments.

Waste mixture	Composition (w/w)	Co-pyrolysis reaction products (w/w)
1	30% pine + 30% tires + 40% plastics	10% gases + 60% liquids + 25% chars + 5% losses
2	50% pine + 50% plastics	12% gases + 54% liquids + 22% chars + 12% losses
3	50% tires + 50% plastics	2% gases + 97% chars + 1% losses

The co-pyrolysis of waste mixtures containing plastics, lignocellulosic biomass and used tires has been previously studied [21,22] in order to obtain high-quality liquid products; a reasonable amount of chars was obtained in these experiments. Bernardo et al. studied the chemical and ecotoxicological characterization of those chars [23–26] in order to provide some information about the composition and risk assessment of these materials. The main conclusion of the studies was that these chars have to be submitted to appropriate treatments in order to improve their quality if a valorisation/reuse is to be considered.

The main aims of the present study are to perform an efficient upgrading of the chars obtained during the co-pyrolysis of different mixtures of plastics, pine biomass and tire wastes and to perform a characterization of the physico-chemical properties of the upgraded chars in order to validate their valorisation as precursors of adsorbents.

2. Materials and methods

2.1. Char samples

The char samples were obtained from the pyrolysis of three different waste mixtures, as indicated in Table 1. The waste mixtures were selected in order to improve the liquid yields as well as the quality of the liquid fraction as fuel through H-donor effect of plastics. This was the main goal of previous studies [21,22]. Based on these studies, it was decided to include the plastic wastes in the three waste mixtures. Plastics wastes were a mixture of 56% (w/w) polyethylene, 27% (w/w) polypropylene and 17% (w/w) polystyrene, simulating the composition of the plastic fraction present in Portuguese Municipal Solid Wastes (MSW). Pyrolysis experiments were carried out in stirred batch autoclaves of 1 and 5 L, built in Hastelloy C276 (Parr Instruments) using an initial nitrogen pressure of 0.41 MPa, a reaction time of 15 min and a temperature of 420 °C. In these pyrolysis reactors the heat transfer from the furnace to the autoclave is a slow process with heating rates of around 5 °C/min until the desired temperature of 420 °C is reached. Therefore, the residence time of the materials inside the autoclave is significantly higher than the reaction time at the temperature chosen.

More information about the pyrolysis installation and experiments can be found in previous papers [21,22,27].

The chars obtained from the co-pyrolysis of waste mixtures 1, 2 and 3 were named as chars 1, 2 and 3, respectively.

2.2. Upgrading of the pyrolysis chars

2.2.1. Sequential solvent extraction (SSE)

The chars obtained in the pyrolysis experiments were carbonized particulate residues impregnated with the pyrolysis oil. In order to remove and recover these pyrolysis liquid products trapped in the raw chars, a sequential solvent extraction (SSE) was performed: extraction with hexane followed by extraction with a mixture of 1:1 (v:v) hexane:acetone and a final extraction with acetone. The solvent extractions were performed using the Soxhlet method adapted from EPA 3540C Method [28] for 16 h at a rate of 4 cycles/h. The char to solvent ratio was around 33 g/L. The solvents were eliminated from the crude extract solutions using a vacuum rotary evaporator. All extracts were equilibrated to room temperature and weighed to determine the extraction yields.

2.2.2. Demineralization procedure

After SSE has been performed, the extracted chars were heated at a temperature of 350 °C, for 2 h, in order to eliminate solvent residues, and some condensed organic products that were not removed by the solvents and that can obstruct the char pores.

The last step of the upgrading treatment was a demineralization procedure in order to decrease the ash content of the char: the samples were treated with 1 M HCl, at 60 °C, for 60 min, with continuous stirring in two successive washing stages. The acid to char ratio was of 100 ml/g. At the end of the acidic washing steps, the mixtures were allowed to settle and then filtrated to separate the pyrolytic char which was further washed several times with deionized water to remove residual acid and solubilize salts. Finally, the washed char samples were oven-dried at 110 °C, for 24 h.

The amount of metals leached in each of the acidic washing steps was monitored by using a Thermo Elemental Solaar atomic absorption spectrometry (AAS) equipment.

2.3. Physico-chemical characterization of chars

The ash content in the crude char samples and in the chars after the SSE was determined by the combustion of the char samples at 650 °C in a muffle furnace. The residue non-combusted at this temperature that presents a stable residual weight was considered to be mainly composed of inorganic matter and was designated by ashes.

The upgraded chars were submitted to a thermal analysis that consists in measuring the progressive weight loss associated with the combustion of samples in a muffle furnace under an air atmosphere from room temperature up to 750 °C with increments of 50 °C, remaining 10 min at each temperature stage. This thermal analysis allow to define the composition of the upgraded chars in terms of the volatility of their components: volatile organic compounds were those volatilized up to 250 °C [29]; the weight loss registered between 250 °C and 350 °C was attributed to semi-volatile compounds [30], while the weight decrease observed from 350 °C to 600 °C was assigned to the volatilization and combustion of heavy organic compounds denominated fixed carbon [31]; the residue non-combusted above 600 °C that presented a stable weight was considered to be ashes [31].

Elemental analysis was performed with a LECO elemental analyser. Carbon, hydrogen and nitrogen were determined according the ASTM D5373 standard [32]. Sulphur determination followed the ASTM D4239 standard [33].

The apparent density was estimated as the weight obtained from the char occupying a given volume.

The mineral content of the chars was determined according to the following procedure: the chars were submitted to a previous digestion performed with hydrogen peroxide 30% (v/v) in a heated bath at a temperature of 95 °C followed by *aqua regia* (HCl:HNO$_3$, 3:1, v/v) at the same temperature. Finally, a microwave acidic digestion with *aqua regia* in closed PTFE vessels was used to complete the solubilization of the inorganic components of the samples. The metals were quantified in the digested samples using AAS.

2.3.1. Textural and adsorption properties of the upgraded chars

The textural properties of the upgraded chars were evaluated by the adsorption of N$_2$ at 77 K using an ASAP 2010 Micromeritics apparatus. Adsorption measurements were made after outgassing the samples under vacuum for at least 3 h at 300 °C.
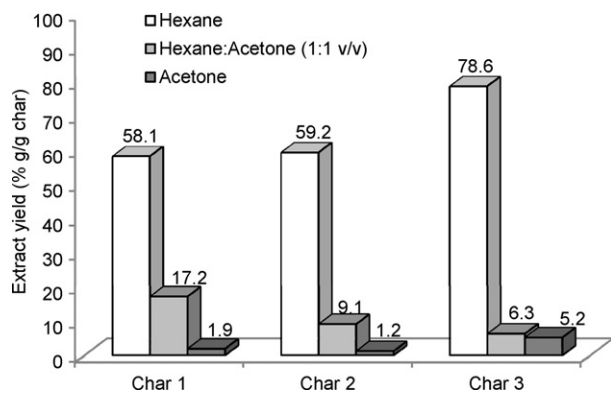
Fig. 1. Extract yields of the chars obtained in each extraction step.

The isotherms were used to calculate the apparent surface area (S_{BET}) through the BET equation and the total pore volume (V_{TOTAL}), mesopore volume (V_{MESO}) and pore size distribution through the Barrett, Joyner, and Halenda (BJH) method (ASAP 2010 Micromeritics software version 4.0).

The volume and pore size distribution for meso and macropores were determined with a mercury porosimeter Micromeritics AutoPore IV 9500 with the software version 1.07. The combination of gas adsorption and mercury intrusion data enables the complete pore volume distribution of the samples to be evaluated.

To assess the adsorption capacity of moderate size pollutant molecules by the upgraded pyrolysis char, the methylene blue test was performed [34]. It involves the addition of successive millilitre portions of a standard methylene blue solution with a concentration of 120 mg/L to a sample of pyrolytic char (0.1 g) until no further colour reduction occurs by stirring the mixture for 5 min.

3. Results and discussion

3.1. Pyrolysis chars

The yields of products obtained in each of the co-pyrolysis experiment are presented in Table 1. The yield of liquids corresponds to the free liquid decanted from the autoclave.

Comparing the results, it can be concluded that the addition of tires to the waste mixture increased the char yield. The pyrolysis of waste mixture 3 did not produce any free liquid products since they were all soaked in the char. Taking into account that a relatively slow pyrolysis was carried out, it was expected a significant yield of chars in the waste mixtures with pine biomass and tires, since when these materials are individually pyrolysed, char contents between 30 and 50% are obtained [21,22]. The pyrolysis of plastics in these conditions usually does not lead to a significant char yield [35].

3.2. Upgrading of the pyrolysis chars

3.2.1. Sequential solvent extraction (SSE)

Bernardo et al. [23,25,36] have previously demonstrated that the chars obtained in the co-pyrolysis of plastics, biomass and tire wastes have to be submitted to an organic decontamination in order to reduce their toxicity. The authors concluded that a sequential extraction with solvents of increasing polarity can provide a better removal of the pyrolysis liquid-phase products from the char than an individual extraction with any of those solvents. In this work, the same approach was applied to the three chars obtained and the results concerning the sequential solvent extractions are presented in Fig. 1.

The extraction yields obtained in the different extraction steps show that most of the organic products present in the three

Table 2
Ash content of the char samples before and after the SSE.

	Char 1		Char 2		Char 3	
	Before SSE	After SSE	Before SSE	After SSE	Before SSE	After SSE
Ashes (% w/w)	2.35	3.66	0.64	1.39	2.73	8.68

SSE – sequential solvent extraction.

chars are non-polar and therefore soluble in pure hexane. Only residual amounts are polar enough to resist the extraction with hexane:acetone (1:1, v/v), being recovered with pure acetone.

The total extraction yields (ratio between the total mass of extracts obtained in the three extraction steps and the mass of char sample) of the sequential extractions were of 66% for char 1, 63% for char 2 and 81% for char 3. The highest extraction yield, obtained for char 3, corresponds to the complete impregnation of the liquid phase in the char.

These results show that this procedure not only ensures an efficient decontamination of the chars but also allows the recovery of a significant fraction of the pyrolysis oil and/or condensed by-products, improving the yield of the liquid products.

3.2.2. Demineralization of chars

Table 2 presents the ash content of the chars, before and after the SSE. As expected, an increase in the ash content was observed as a consequence of the concentration effect resulting from the removal of organic matter from the chars in the solvent extractions.

In order to know which are the metals present in higher amounts in the ashes of the three chars, the inorganic content of the chars after the SSE was determined. Fig. 2 shows the metal distribution in each of the chars representing only the metals with concentrations above 0.5% w/w.

From the results shown in Fig. 2, it is clear that the metal present in higher amount in the chars from the waste mixtures 1 and 3 is zinc (Zn). These waste mixtures included used tires in their composition (Table 1) and this material is the source of Zn, as previously demonstrated by the authors [30]. In char 1, calcium (Ca) is the element more abundant after zinc, presenting a relatively high concentration (25.9%) for an individual element.

In the case of char 2, obtained from the co-pyrolysis of the waste mixture with plastics and biomass, the metal prevalent is magnesium (Mg). The principal source of Mg was the pine biomass [36]. Also, calcium (Ca), potassium (K) and iron (Fe) are significant elements in this char.

The high ash contents and their composition, particularly in chars 1 and 3, are not compatible with a safe reutilization or valorisation of these materials as adsorbents for liquid-phase applications since there is the possibility of heavy metal leaching, which restricts the applications of the chars.

Taking this into account, a demineralization procedure was applied to the chars in order to decrease the ash content. The main inorganic components of the chars where used as control elements of the demineralization process. Thus for char 1, the leaching of Zn and Ca was monitored; Mg, Ca and K were the control elements used for char 2, while for char 3 only Zn leaching was studied.

Fig. 3 presents the concentrations of the metals in the chars before and after the demineralization procedure.

Zinc is effectively removed by hydrochloric acid from chars 1 and 3 presenting removal efficiencies of respectively 88.3% and of 69.1%. Char 3 presented huge amounts of Zn (around 60 g/kg) and the removal efficiency of 69.1% could probably be improved by an extra acidic washing step or a higher acid to char ratio.

Calcium was better removed from Char 1 (74.5%) than from Char 2 (68.0%) although the concentration of this metal was higher than 5 g/kg for Char 1 and lower than 2 g/kg for Char 2. These results
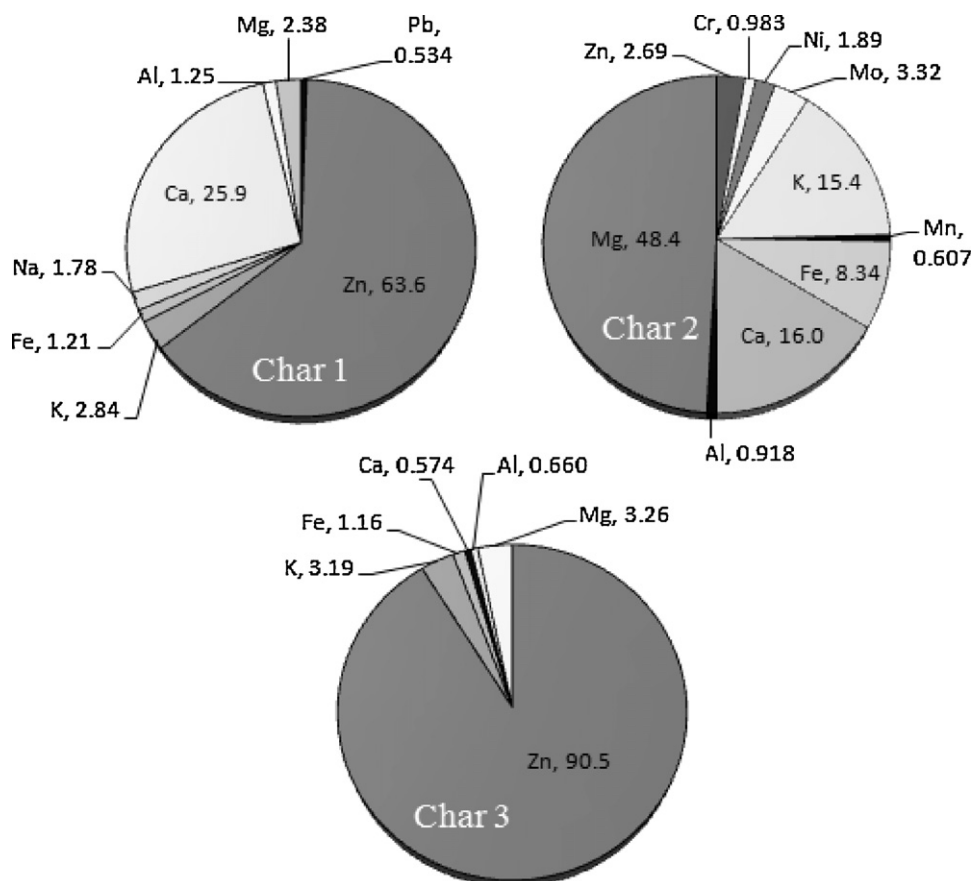
Fig. 2. Metal distribution (in % w/w) in the chars after the SSE.

indicate that char overall composition and structure may also affect the removal efficiency of individual components regardless of their initial concentrations.

Char 2 presented significant removal efficiencies, particularly for Ca and K, but not so much for Mg, which was the metal present in higher amount in this char. Less than a half (44.4%) of the total content of Mg in char 2 was removed, what may indicate that Mg is in a form more resistant to acidic lixiviation. The leaching resistance of magnesium in pyrolysis chars from different residues was also noted by Hwang et al. [37,38]. According to these authors, textural parameters of the char such as the specific surface area and pore structure can also be a reason to restrain metal leaching.

Also, Wang et al. [39,40] assume that in carbonaceous materials some metals might be strongly associated with the organically matrix and they are not easily solubilized with acids and/or they are matrix-encapsulated as fine mineral particles to which an acid solution has hardly access.

The results given by the thermal analysis of the upgraded chars are presented in Table 3 and comparing the ash contents before and after the demineralization treatment, chars 1, 2 and 3 present a reduction in the ash content of around 70%, 86% and 64%, respectively. These results show that the demineralization procedure was efficient in the removal of most of the inorganic contaminants.

The availability of the remaining inorganic components in the chars after the acidic washing may be evaluated with different leaching tests and this will be object of study in a future work. However, the metal of concern that is Zn, is usually resistant to leaching [23,25] in these type of chars indicating that they might be safely used in water treatment applications.

Chars 1 and 2 still contain relatively amounts of volatile and semi-volatile matter which is consistent with the higher values of apparent density presented by these chars.

Concerning the elemental analysis, whose results are also presented in Table 3, the three chars present a high carbon content and together with the low ash content, making them suitable percursors to high quality activated carbons.

Chars 1 and 3, from the co-pyrolysis of waste mixtures with tires, presented higher sulphur content. Sulphur comes from the tire waste as a result of the vulcanisation process and the presence of this element in the char indicates that some of the metals might

Table 3
Characterization of the chars after the upgrading treatment (SSE followed by demineralization treatment).

	Char 1 upgraded	Char 2 upgraded	Char 3 upgraded
Volatiles (% w/w)	2.23	5.61	1.78
Semi-volatiles (% w/w)	4.82	3.01	0.40
Fixed carbon (% w/w)	91.8	91.2	94.7
Ashes (% w/w)	1.11	0.20	3.16
C (% w/w) ar	79.0	67.2	87.7
H (% w/w) ar	1.8	2.2	0.6
N (% w/w) ar	1.0	1.2	0.6
S (% w/w) ar	0.44	0.10	0.74
O (% w/w)[a] ar	16.7	29.1	7.2
HHV (kJ/g)	28.0	23.0	30.6
Apparent density (g/cm^3)	0.474	0.499	0.358

ar – as-received basis; HHV – high heating value – calculated according to Eq. (1).
[a] by difference (include the oxygen in the free moisture associated with the sample and errors).
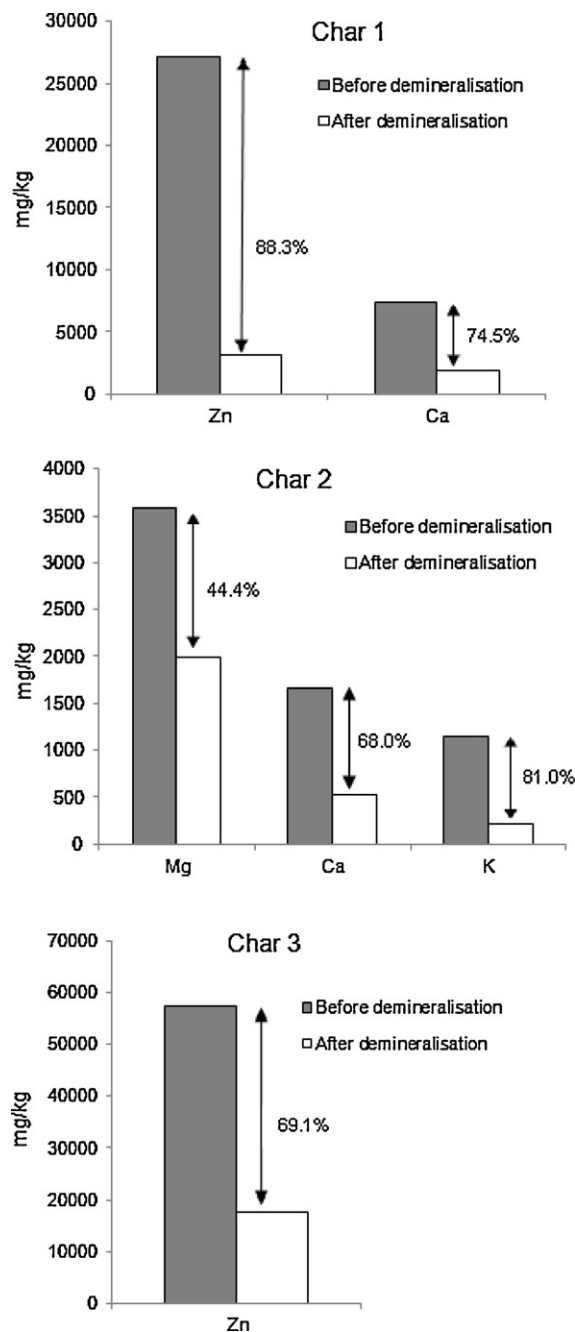
Fig. 3. Concentrations of metals (in mg/kg) used as control elements in the demineralization procedure for each of the chars and removal efficiencies (in %).
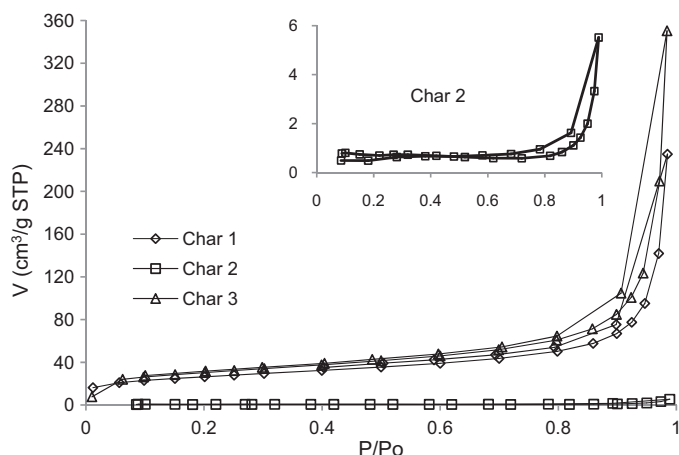

Fig. 4. N_2 adsorption–desorption isotherms of the upgraded chars at 77 K.

Char 2 presents the lowest HHV because of the higher content of oxygen. The calculated HHV for chars 1 and 3 indicate that these materials have calorific values comparable to other fuels such as coal, ethanol, among others [44] making their combustion for energy recovery also a possible valorisation alternative.

3.3. Textural and adsorption properties of the upgraded chars

Fig. 4 presents the N_2 adsorption–desorption isotherms of the chars at 77 K and it can be seen that for char 2 the amount adsorbed of N_2 is very small in the entire relative pressure (P/P_0) range, which indicates that this char is almost a non-porous material. According to the IUPAC classification, chars 1 and 3 exhibit isotherms of type II [45], typical of non-porous or macroporous adsorbents. However, the hysteresis loop present in the isotherms of those chars is usually associated with capillary condensation in mesopore structures. This type of hysteresis loop is characteristic of aggregates of plate-like particles giving rise to slit-shaped pores.

The textural parameters given by the N_2 isotherms are presented in Table 4. The mesoporosity of Chars 1 and 3 can be confirmed with the average pore diameter (mesopores are in the range 0.002–0.05 μm) and the mesopore volume. The low values of BET surface areas of these chars are in agreement with the fact that these samples are resulting from a pyrolysis process with no further activation step, therefore it is expected that some residual volatile matter may block the incipient porosity of the chars [11].

Low values of BET surfaces areas were also reported for non-activated chars obtained in the individual pyrolysis of pine biomass (0.65–112.4 m^2/g) [46–49] and tires (10–95 m^2/g) [9,12,15,50–54].

Given the fact that Char 2 does not present micro- and mesopores, it is not possible its characterization by N_2 adsorption. Thus, mercury porosimetry was used as a complementary technique.

Fig. 5 presents the results obtained with mercury porosimetry and shows that char 2 presents porosity in the macropore range, more specifically it is an interparticle porosity due to the high pore size diameter at which occurs the mercury intrusion. This char was also the one that presented the highest apparent density and higher content of volatile matter (Table 3) which is indicative that this char still contains a significant amount of condensed volatiles obstructing the pores. Further treatment by devolatilization/activation might lead to pore widening.

For chars 1 and 3, the results from mercury porosimetry are in good agreement with those obtained by N_2 isotherms since peaks of mercury intrusion in the mesopore and macropore range are observed. The pore volume distribution for these chars (Table 4) shows that macropores prevail over mesopores: 75% and 65.1% of

have formed sulphides that were then incorporated into the char [41].

Chars 1 and 2 that resulted from pyrolysis of mixtures containing pine biomass presented higher amounts of oxygen and nitrogen, which can be indicative of the presence of polar functional groups on the char surface [42].

The high heating value of the upgraded chars, presented in Table 3, can be estimated using the results from the ash content and the elemental analysis according to Eq. (1) proposed by Channiwala [43]:

$$HHV \text{ (in kJ/g)} = 0.3491\,C + 1.1783\,H - 0.1034\,O - 0.0211\,Ashes$$
$$+ 0.1005\,S - 0.0151\,N \qquad (1)$$

Table 4
Textural characterization and methylene blue number of the upgraded chars.

Sample	From N$_2$ adsorption–desorption isotherms				From Hg porosimetry			Methylene blue number (mg/g)
	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	Mesopore volume (cm^3/g)	Average pore diameter (μm)	Total pore volume (ml/g)	Mesopore volume (ml/g)	Macropore volume (ml/g)	
Char 1	91.4	0.363	0.354	0.018	2.04	0.510	1.53	13.8
Char 2	2.03	0.009	n.c.	n.c.	1.51	0.040	1.47	3.59
Char 3	105	0.542	0.544	0.019	2.09	0.730	1.36	22.2

n.c. – not calculated.
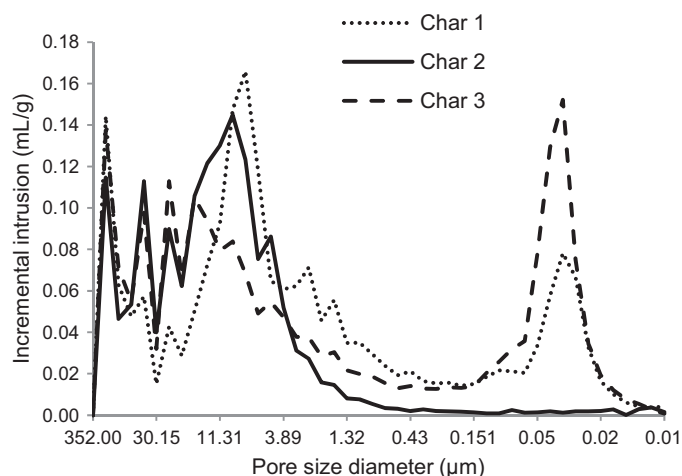
Fig. 5. Incremental intrusion *vs* pore size for mercury porosimetry.

macropores for chars 1 and 3, respectively. The macroporosity are probable due to the aggregates of plate like particles as indicated by the N$_2$ adsorption–desorption studies.

It is clear that the chars resulting from the co-pyrolysis of waste mixtures with tires present better textural properties; chars from the individual pyrolysis of tires are mostly constituted of carbon black and this carbonaceous material presents, typically, porous surfaces [12,50,55].

The methylene blue numbers obtained for the three upgraded chars are also presented in Table 4. The methylene blue adsorption test reveals the adsorptive properties of a carbon towards a larger molecule and this dye often serves as a model compound for removing large organic contaminants from aqueous solutions. Since these chars were found to be mesoporous and macroporous materials, they should have good adsorption properties towards bulky molecules.

The methylene blue numbers obtained, in particular for chars 1 and 3, are comparable or even higher than those obtained for various adsorbents prepared from different precursors [56], namely, a commercial activated carbon (9.81–13.4 mg/g), activated carbons derived from agricultural and industrial wastes such as fruit stones, nutshells, and corncob (0.84–22.1 mg/g), natural materials such as kaolin, clay and glass wool (2.24–22.66 mg/g), some bioadsorbents such as fungi and algae biomass (1.17–18.54 mg/g), several agricultural solid wastes (2.23–22.47 mg/g) and industrial solid wastes such as fly ashes (0.51–16.6 mg/g).

As expected, Char 2 presented the lowest methylene blue number given its lower surface area.

4. Conclusions

In this work an upgrading treatment was carried out in crude chars from the co-pyrolysis of different mixtures of plastics, biomass and tire wastes in order to produce value-added carbonaceous materials.

The chars were submitted to sequential organic solvent extractions with high yields of removal/recovery of the pyrolysis liquid-phase products.

In order to decrease the ash content of the chars, a demineralization procedure was successfully applied and high efficiency removals of the major metallic elements were achieved.

Heteroatoms such as oxygen, sulphur and nitrogen are present in the upgraded chars, which can be indicative of the presence of polar functional groups on chars' surface.

The upgraded chars are mainly mesoporous and macroporous with significant adsorption capacity for the bulky molecule methylene blue.

Since no activation treatment was performed in the chars they present relatively low surface areas.

The upgrading treatments performed over the chars allowed to obtain carbonaceous materials having sufficient quality to be reused as precursors for adsorbents.

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