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# Study of the organic extraction and acidic leaching of chars obtained in the pyrolysis of plastics, tire rubber and forestry biomass wastes

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**Abstract**

The present work aims to perform a characterization of chars obtained in the co-pyrolysis of waste mixtures composed by plastics, tires and pine biomass, to provide knowledge about the composition, leaching behavior and risk assessment of these materials in order to define strategies for their possible valorization or safe disposal. The chars were submitted to sequential solvent extractions with organic solvents of increasing polarity that allow the recovery of significant amounts of the pyrolysis oils trapped in the crude chars improving the yield of the pyrolysis liquids. An acidic demineralization procedure was successfully applied to the chars and high efficiency removals of the majority of the heavy metals were achieved. The demineralization study also demonstrated that hazardous heavy metals such as chromium, nickel and cadmium are significantly immobilized in the char matrix, and other heavy metals of concern such as zinc and lead will not represent a leaching problem if acidic conditions were not used. The obtained chars present sufficient quality and characteristics to be used as fuel or alternatively, to be used as adsorbents or precursors of activated carbon.



*Keywords:* Chars; pyrolysis; extraction; leaching

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## 1. Introduction

Incineration is the most used and implemented thermochemical treatment of wastes. However, with incineration the organic content of wastes is completely destroyed, making more attractive the thermochemical treatment alternatives, such as pyrolysis, that allow the conversion of wastes into new organic products that can be used as raw materials for chemical industries in addition to energy production as substitutes of traditional fuels. Although pyrolysis is relatively insensitive to the input material, some wastes such as plastics, tires and lignocellulosic biomass are considered to be suitable raw materials to pyrolytic processes due to their chemical composition (mainly carbon and hydrogen as in crude oil) combustible properties and high volatile matter content, in addition to the fact that they are natural and synthetic polymers easily cracked down by pyrolysis into smaller polymeric chains of hydrocarbon gas and pyrolysis oil that have industrial and energetic interesting applications [1-3].

Generally, pyrolysis conditions are optimized in order to maximize the lighter fractions, but the production of a significant fraction of solid by-product (char) may occur. This solid char is mainly composed by a carbon-rich matrix that contains almost all the mineral matter present in the raw wastes and a significant amount of extractable organic compounds formed during the pyrolysis process dispersed throughout a porous structure.

As the pyrolysis of wastes to produce valuable gaseous and liquid products is growing in importance, it is anticipated that large amounts of char pyrolysis will be available as by-products. To minimize the cost and increase the sustainability of the pyrolysis process, the pyrolytic char has to be upgraded and valorized similarly to what is done to the gaseous and liquid products or, ultimately, a safe disposal has to be considered.

With this background, the main aim of this work was to perform a characterization of chars obtained in the co-pyrolysis of waste mixtures composed by plastics, tires and pine biomass, to provide knowledge about the composition, leaching behavior and risk assessment of these materials in order to define strategies for their possible valorization or safe disposal.

## 2. Materials and Methods

### *2.1 Pyrolysis experiments and char samples*

Pyrolysis experiments were carried out in stirred batch autoclaves of 1 and 5 litres, built in Hastelloy C276 (Parr Instruments) using an initial nitrogen pressure of 0.41 MPa, reaction time of 15 min, temperatures of 400-420 ºC and heating rates of around 5ºC/min. More details of the pyrolysis installation and experiments can be found in previous works [4-7].

The char samples were obtained from the pyrolysis of three different waste mixtures as indicated in Table 1. Plastics wastes were a mixture of PE, PP and PS, simulating the composition of the plastic fraction present in the Portuguese MSW. The chars obtained from mixtures 1, 2 and 3 were named as chars 1, 2 and 3, respectively.

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

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

### *2.2 Sequential Solvent Extractions (SSE)*

The chars obtained in the pyrolysis experiments were a carbonized and viscous residue impregnated with pyrolysis tars, thus very smelly. In order to remove and recover these tars trapped in the raw chars, a sequential solvent extraction (SSE) was performed as follows: 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 [8] during 16h at a rate of 4 cycles/h. 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.

### *2.3 Thermal analysis*

The 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 750ºC with increments of 50ºC, remaining 10 min at each temperature stage. This thermal analysis allow to define the composition of the chars in terms of the volatility of their components: volatile organic compounds were those volatilized up to 250ºC ; the weight loss registered between 250ºC and 350ºC was attributed to semivolatile compounds, while the weight decrease observed from 350ºC to 600ºC was assigned to the volatilization and combustion of heavy organic compounds denominated fixed carbon; the residue non-combusted above 600ºC that presented a stable weight was considered to be ashes.

### *2.4 Mineral content of the chars*

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 95ºC 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. A broad group of heavy metals were quantified in the digested samples using atomic absorption spectrometry (AAS).

### *2.5 Acidic demineralization*

After SSE has been performed, the extracted chars were heated at a temperature of 350ºC, during 2 hours in a muffle furnace, in order to eliminate solvent residues, and some condensed volatiles that were not removed by the solvents and that can obstruct the char pores.
An acidic leaching procedure was conducted in the char samples with 1M hydrochloric acid (HCl) solution, at 60ºC, during 60 min, with continuous stirring in two successive leaching stages. The acid to char ratio was of 100 ml/g. At the end of each leaching step, 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 110ºC, for 24h. The amount of metals leached in each of the acidic leaching steps was monitored by using AAS.

## 3. Results and discussion

The yields of products obtained in each of the pyrolysis experiment are presented in Table 1. Comparing the results presented in Table 1, it can be seen that pyrolysis yields depend on the type of feedstock, with an increasing of char's production from waste mixtures with tires. The pyrolysis of waste mixture 3 did not produce any free liquid products since they were all soaked in the char.

The pyrolysis of plastics in these conditions usually does not lead to a significant char yield, therefore the resulting chars are originate from the pyrolysis of lignocellulosic biomass and tires, which are known to give significant char's yields (30-40%) when individually pyrolyzed [5-7].

The char obtained in the individual pyrolysis of tires is mainly constituted by the carbon black powder used as filler in tire production and a mixture of carbonized rubber polymer and nonvolatile hydrocarbons, plus other tire rubber additives such as zinc, sulfur, silicates, among others [9].

Lignocellulosic chars are considered to be constituted by the decomposition products of hemicellulose, cellulose and lignin, which is known to contribute significantly to the overall char yield [10], and also with degradation products of the extractives components as well as the mineral matter initially present in the biomass.

### *3.1 Sequential Solvent Extractions (SSE)*

Fig. 1 presents the results concerning the sequential solvent extractions of the three chars.

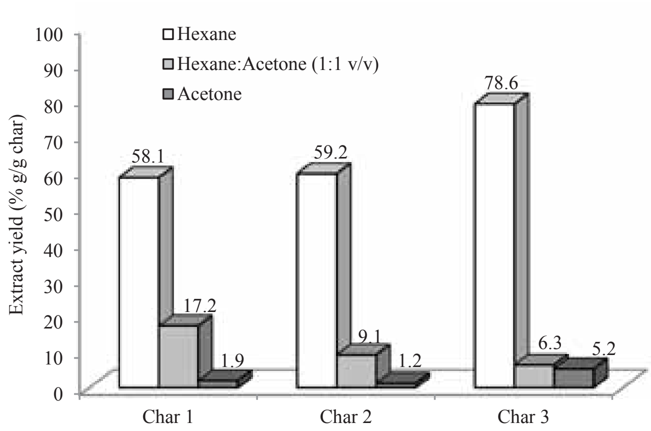


Fig. 1. Extraction yields of the chars obtained in each extraction step

The extraction yields obtained in the different extraction steps show that most of the extractable organic compounds present in the three chars have low polarity being soluble in pure hexane. Bernardo et al. [11-13] have previously demonstrated that the tars extracted from chars obtained in the co-pyrolysis of plastics, biomass and tire wastes are very complex mixtures with condensable hydrocarbons such as aliphatics, aromatics like PAH and phenyl derivatives, several benzene derivatives along with other oxygen-containing hydrocarbons.

The global extraction yields (ratio between the total mass of extracts obtained in the three extraction steps and the mass of char sample) were of 66% for char 1, 63% for char 2 and 81% for char 3. The highest extraction yield obtained for char 3 confirms that the pyrolysis liquid oils of mixture 3 were completely retained in the char.

These results show the importance of developing strategies to recover the tars that remained in pyrolysis chars since they are sources of high-valuable chemicals in addition to fuel properties [14].

The results from the thermal analysis of the crude and extracted chars are presented in Table 2 and it can be concluded that the sequential solvent extractions allow to remove mainly the volatile matter from the crude chars and, consequently, the heavier components correspond to higher relative mass fractions in the extracted chars. It seems that the semi-volatile content of the chars were not significantly affected by the organic extractions.

Table 2. Composition of crude and extracted chars in terms of the volatility of their components

| | Char 1 | | Char 2 | | Char 3 | |
|---|---|---|---|---|---|---|
| | Before SSE | After SSE | Before SSE | After SSE | Before SSE | After SSE |
| Volatiles (% w/w) | 36.4 | 2.62 | 43.7 | 5.36 | 25.5 | 1.18 |
| Semi-volatiles (% w/w) | 14.9 | 12.4 | 15.7 | 9.92 | 9.3 | 14.2 |
| Fixed carbon (% w/w) | 46.4 | 81.3 | 40.0 | 83.3 | 62.5 | 75.9 |
| Ashes (% w/w) | 2.35 | 3.66 | 0.64 | 1.39 | 2.73 | 8.68 |

### *3.2 Mineral content of the chars*

Table 3 shows the heavy metal content of the chars after the sequential solvent extractions. A wide range of heavy metals was chosen to be quantified in the chars to give complete information about the metal content. The mean and standard deviation of duplicates are shown.

Table 3. Heavy metal content of the chars after the SSE

| (mg/kg) | Char 1 | Char 2 | Char 3 |
|---|---|---|---|
| Cd | <0.6 | <4.78 | 13.7±0.6 |
| Pb | 76.6±5.9 | 15.8±4.3 | 88.1±16.0 |
| Zn | 9128±183 | 99.6±1.9 | 28685±1022 |
| Cu | 4.5±2.5 | <4.3 | <4.3 |
| Cr | <4.5 | 36.4±5.4 | 14.0±0.3 |
| Ni | <1.8 | 70.0±47.2 | <6.5 |
| Mo | <33.5 | 123±37 | <8.8 |
| Ba | <11.3 | <16.8 | <16.8 |
| Hg | 0.25±0.05 | <0.13 | <0.13 |
| As | 0.29±0.01 | 0.32±0.03 | 0.51±0.05 |
| Se | 0.16±0.11 | 1.10±0.7 | 0.100±0.004 |
| Sb | 0.76±0.34 | <0.07 | 0.21±0.02 |

From the results presented, it is clear that the metal present in higher amount in the chars from the waste mixtures 1 and 3 is Zn. These waste mixtures included used tires in their composition (Table 1) and this material is the source of Zn. Zinc oxide, sometimes along with magnesium oxide, is added as an activator during the vulcanizing process [15].

Lead was quantified in both chars 1 and 3 with significant amounts since the tires were the waste with major amounts of this metal [12].

Char 2 presented significant amounts of Cr, Ni and Mo which were not detected in raw wastes [12]. The autoclaves where pyrolysis experiments were performed are built in Hastelloy C276 which is a nickel-molybdenum-chromium wrought alloy. A possible explanation for the presence of these metals is the contamination of the pyrolysis products by some release of heavy metals from the pyrolysis autoclaves.

### *3.2 Acidic demineralization*

The chars presented high ash contents, particularly those resulting from the waste mixtures with tires that may not be compatible within a safe valorisation or disposal.

The chars were submitted to an acidic demineralization procedure with the aim of decreasing their ash content and also to give information about the speciation of the metals in char's matrix and their mobility. The main metallic elements present in the chars where used as control elements of the demineralization study. Thus for char 1, the leaching of Zn and Pb was monitored; Zn, Cr, Ni and Mo were the control elements used for char 2, while for char 3 the leaching of Zn, Pb and Cd was studied.

Table 4 shows the removal efficiencies of the metals studied as well as the ash reduction in the chars.

Table 4. Removal efficiencies (in % w/w) of the metals studied in the acidic demineralization

| Char | Removal efficiencies (% w/w) | | | | | | Ash removal (% w/w) |
|---|---|---|---|---|---|---|---|
| | Zn | Pb | Cr | Ni | Mo | Cd | |
| 1 | 88.3 | 73.6 | - | - | - | - | 70 |
| 2 | 62.1 | - | 15.7 | 38.8 | 87.9 | - | 86 |
| 3 | 69.1 | 89.4 | 0 | - | - | 13.2 | 64 |

Zn was effectively removed from chars 1, 2 and 3, indicating that this metal was in a chemical form that is acid-extractable. In chars 1 and 3 it is possible that some Zn is in the form of sulphide, since ZnS has its origin in the sulfidation of ZnO added to control the rubber vulcanization process in tires manufacturing [15]. Both forms ZnO and ZnS are readily soluble in acidic conditions.

Pb was also significantly removed from chars1 and 3 showing that Pb is in a form soluble in hot HCl such as PbS [16].

If chars 1 and 3 would be considered for water treatment application, the pH range should be taken into account since ZnS and PbS are quite leachable for $pH<6$ [17].

Char 2 presented high removal efficiency for Mo, but not so much for Cr and Ni what may indicate that these elements are in a form resistant to acidic lixiviation. Riley et al. [16] and Wang et al. [18-19] assumed that in carbonaceous materials some metals such as Ni and Cr might be strongly associated with the organically matrix and they are not easily solubilised with acids and/or they are matrix-encapsulated as fine mineral particles to which an acid solution has hardly access.

Char 3 presented low removal efficiency for Cd. The leaching resistance of Cd in pyrolysis chars from different residues was also noted by Hwang et al. [20-21]. 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.

Chars 1, 2 and 3 presented a significant reduction in the ash content which show that the demineralization procedure was efficient in the removal of most inorganic contaminants.

## 4. Conclusions

Chars obtained in the co-pyrolysis of waste mixtures composed by plastics, tires and pine biomass were submitted to a characterization in order to provide knowledge about the composition, leaching behavior and risk assessment of these materials in order to define strategies for their possible valorization or safe disposal.

Submitting the chars to sequential solvent extractions with solvents of increasing polarity resulted in the removal/recovery of significant amounts of the pyrolysis tars.

The chars present high ash contents, particularly those resulting from the waste mixtures with tires that are not compatible within a safe valorisation or disposal. In order to decrease the ash content of the chars, a demineralization procedure was successfully applied and high efficiency removals of the majority of the metallic elements were achieved.

The demineralization study also demonstrated that hazardous heavy metals such as chromium, nickel and cadmium are significantly immobilized in the char matrix, and other heavy metals of concern such as zinc and lead will not represent a leaching problem if acidic conditions were not used.

The pyrolysis chars studied are solid carbonaceous residues with high fixed carbon making their combustion for energy recovery a possible valorisation alternative.

Other interesting alternative is the valorisation as adsorbent since the adsorption properties of pyrolysis chars are well known [3, 22]. Moreover, due to its porous characteristics and high carbon content, the solid char constitutes a good precursor for the manufacture of activated carbons.

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