EVALUATION OF THE ENVIRONMENTAL HAZARD OF CHAR RESIDUES PRODUCED IN THE CO-PYROLYSIS OF DIFFERENT WASTES: CHEMICAL AND ECOTOXICOLOGICAL CHARACTERIZATION

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SUMMARY: Char residues produced in co-pyrolysis of different wastes were characterized through chemical and toxicity tests. A fraction of the solid chars was treated by extraction with dichloromethane. Different volatility fractions present in the extracted and non extracted char were evaluated. A selected group of heavy metals was determined in both chars.
Chars were subjected to the leaching test ISO/TS 21268 – 2 and the resulting eluates were further characterized by determining a group of inorganic parameters and the concentrations of several organic contaminants.
An ecotoxicological characterization was performed by using the bio-indicator *Vibrio fischeri*.
The chemical and ecotoxicological characterization led to a classification of the chars as ecotoxic materials.

1. INTRODUCTION

Thermal treatment of wastes is an alternative to the deposition in landfills and also allows their valorisation as energy resources and raw materials for chemical processes. The thermal treatments often used are combustion, gasification and pyrolysis. Incineration leads to the release of toxic and greenhouse gases and completely destroys the organic matter content of the wastes. Gasification and pyrolysis enable the production of gaseous and/or liquid fuels from the waste, thus recovering the energetic and organic value of these wastes (Malkow, 2004). In the pyrolysis processes, wastes are subjected to medium to high temperatures in the absence of air or in an oxygen-deficient atmosphere, producing a hydrocarbon mixture (gaseous and liquid

Proceedings Sardinia 2009, Twelfth International Waste Management and Landfill Symposium
S. Margherita di Pula, Cagliari, Italy; 5 - 9 October 2009

fractions) that can be used as fuel or as feedstock in chemistry industries, and a carbon-rich solid residue (the solid fraction). The carbonaceous residue is mostly constituted of black carbon but also contains the mineral matter initially present in the wastes and a significant amount of the liquid by-products formed during the pyrolysis process. The carbonaceous residue produced in the pyrolysis process is not normally considered economically interesting, and is usually disposed of in landfills. Therefore, it is important to evaluate the short, medium and long-term stability of these residues, namely to evaluate the possible leaching of toxic compounds and the ecotoxicity of the eluates.

The European legislation establishes criteria for the acceptance of wastes in landfills (CEC, 2003) through the leaching standard EN 12457 (EN 12457, 2002). These criteria are mainly based on the leaching of inorganic compounds and DOC, despite the fact that many of contaminants of concern are organic compounds. Only the classification as inert residues includes the leaching of a restrigent group of organic compounds. However, the EN 12457 specifies a scope which excludes the leaching of organic contaminants.

Recently, an ISO leaching standard, ISO/TS 21268, dealing with the release of organic compounds in contaminated soils has been proposed (ISO/TS 21268, 2007). This standard includes a series of procedures designed to prevent the loss of non volatile organic contaminants but excludes the application to volatile organics from its scope.

The aim of this study was the chemical and ecotoxicological characterization of chars produced by the co-pyrolysis of different mixtures of plastics, biomass and tyres. A evaluation of their hazard potential was performed.

2. MATERIALS AND METHODS

2.1 Pyrolysis assays and chars

Two type of wastes mixtures were submitted to pyrolysis:

1) 70% (w/w) pine biomass and 30% (w/w) plastics; the chars obtained from the pyrolysis of this mixture were defined as chars 1;

2) 30% (w/w) pine biomass, 40% (w/w) plastics and 30% (w/w) used tyres; the chars obtained from the pyrolysis of this mixture were defined as chars 2.

The plastics were a mixture of 56% (w/w) Polyethylene, 27% (w/w) Polypropylene and 17% (w/w) Polystyrene. Pyrolysis experiments were conducted in a 1L autoclave, during 15 min at a temperature of 420ºC with an initial pressure of 0.41 MPa. More detailed information relative to the pyrolysis procedure was already described in a previous work (Paradela et al., 2009).

One part of the solid chars obtained in the pyrolysis assays were submitted to a Soxhlet extraction with dichloromethane (DCM) with the aim of reduce the organic load of the chars.

2.1.1 Determination of the organic matter content in the char residues

The organic content in the char residues was determined by measuring the weight loss associated with the combustion of the solid samples in a microwave muffle furnace (Bernardo et al., 2009a).

2.1.2 Determination of the content in heavy metals in the chars

The char residues were submitted to a previous digestion with hydrogen peroxide 30% (v/v) in a heated bath at a temperature of 95ºC and then with *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.

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A selected group of heavy metals (chromium, nickel, cadmium, lead, zinc and copper) were quantified in the digested samples using atomic absorption spectrometry (AAS) (APHA, 1996).

2.2 Leaching tests

The leaching methodology followed the standard leaching test ISO/TS 21268 – 2 (ISO/TS 21268-2, 2007). This standard has been developed to measure the release of inorganic and non-volatile organic constituents from soil and soil materials and the ecotoxicological effects of the eluates. In this work, an adaptation of this standard was made taking into account the physical similarities between solids of pyrolysis and soil materials (they are both granular materials) and because there are no standards specific for the determination of organic compounds in char residues. Although the scope of this leaching standard does not include volatile organics, since the contact between the residues and the leaching solution is performed in closed vessels, it should also allow the representative sampling of volatile organic compounds.

The eluates used in heavy metals determinations were preserved according to the international standard ISO 5667-3 (ISO 5667-3, 1985). For the ecotoxicological tests and the determination of organic contaminants, the eluates were preserved at a temperature of 4±1ºC.

2.2.1 Chemical characterization of the eluates

The eluates were analyzed for the following inorganic parameters: pH (ISO 10523, 1994) and heavy metals content (chromium, nickel, cadmium, lead, zinc and copper) by AAS (APHA, 1996).

In the present study, the determination of organic contaminants was focused on the volatile group because these are also commonly the compounds with lower molecular weight and higher water solubility. The volatile aromatic hydrocarbons are usually benzene derivatives with different alkyl groups in the different positions of the aromatic ring and have in common the properties of being highly toxic, with a high to medium volatility and a low to medium water solubility. The lighter members of this group are benzene, toluene, ethylbenzene and xylene (usually referred as the BTEX group), and they have a particularly high environmental mobility.

Therefore, the organic compounds chosen to be monitored and quantified were a group of 15 aromatic hydrocarbons: Benzene, toluene, ethylbenzene, o/*m/p/*-xylenes, cumene, propylbenzene, 4-ethyltoluene, *tert*-butylbenzene, 1,2,4-trimethylbenzene, 1-methylpropylbenzene, butylbenzene, 1,4-diethylbenzene and 1,2,4,5-tetramethylbenzene.

The concentrations of the 15 volatile benzene derivatives in the eluates were determined by headspace static sampling and gas chromatography with mass spectrometry (Bernardo et al., 2009b).

The 15 aromatic hydrocarbons were selected taking into account results from a previous work (Bernardo et al., 2009a). Moreover, these compounds are typical components of the liquid fractions obtained from the individual pyrolysis of plastics, biomass and tyres or their mixtures (Paradela et al., 2009; Marin et al., 2002; Islam et al., 2008;) so it is expectable that they should be present as contaminants of the solid residue resulting from the pyrolysis process.

2.2.2 Ecotoxicological characterization of the eluates

The ecotoxicological parameter analyzed in the eluates was the luminescence inhibition of the bacterium *Vibrio fischeri* ("Azur Environmental Microtox® system") according to ISO 11348-3 (ISO 11348-3, 2003).

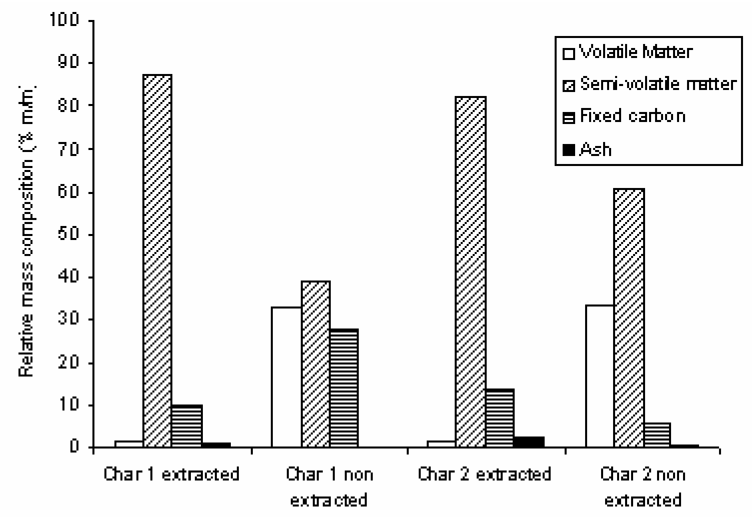

Figure 1. Relative mass composition (% m/m relatively to the initial weight of each char).

3. RESULTS AND DISCUSSION

3.1 Organic matter content in the char residues

The relative mass composition of chars 1 (produced in the co-pyrolysis of pine and plastics wastes) and chars 2 (produced in the co-pyrolysis of pine, plastic and tyres wastes) is shown in Fig. 1. This relative mass composition is based on the volatility of the chars components (volatile, semi-volatile, non-volatile organic matter and ashes). It was considered that volatile organic compounds were those that were lost at temperatures up to 200ºC. The weight loss registered between 200ºC and 350ºC was attributed to semi-volatile compounds, while the weight decrease observed from 350ºC to 550ºC was assigned to losses of heavy organic compounds (fixed residue). The residue non-combusted above 550ºC is considered to be mainly composed of inorganic matter and is designated as ashes.

The DCM extraction removed most of the volatile contaminants from the chars and consequently the heavier components corresponded to higher relative mass fractions than those of the non extracted chars. The relative mass composition profile of the chars submitted to extraction is very similar. Comparing the chars non treated, some differences are observed, namely, char 2 presented a higher relative mass fraction of semi-volatile matter and a lower relative mass fraction of fixed carbon when compared to char 1. It seems that the introduction of tyres in the pyrolysis process raised the semi-volatile fraction in the resulting char.

3.2 Inorganic characterization of the raw wastes, char residues and eluates

Table 1 shows the content of heavy metals in the chars and eluates. For the eluates, the result is presented in leached substance mass per mass unit of char.

The chars showed detectable amounts of Cr, Ni and Zn, while the concentrations of Cd, Cu and Pb were below the respective detection limits. The higher concentrations of the metals in the treated chars could be attributed to a concentration effect, due to the extraction of the light organic fraction during the DCM treatment. Comparing the chars from the different pirolysis mixtures, it can be observed that the chars produced in the co-pyrolysis of the ternary waste mixture presented higher amounts of the detected metals. The introduction of tyres wastes in the mixture can be the source of this higher contamination.

Table 1. Inorganic characterization of the chars and eluates

	Char 1 extracted	Char 1 non extracted	Char 2 extracted	Char 2 non extracted	Eluate 1 extr	Eluate 1 non extr	Eluate 2 extr	Eluate 2 non extr
pH					6.0	6.2	4.8	4.9
Cd (mg/kg)	<5.0	<5.0	<5.0	<5.0	<0.12	<0.12	<0.12	<0.12
Cr (mg/kg)	102	4.98	353	171	<1.15	<1.15	<1.15	1.46
Cu (mg/kg)	<7.5	<7.5	<7.5	<7.5	<1.9	<1.9	<1.9	<1.9
Ni (mg/kg)	91.1	44.1	144	8.9	30.6	<1.03	<1.03	<1.03
Pb (mg/kg)	<55.0	<55.0	<55.0	<55.0	<5.00	<5.00	<5.00	<5.00
Zn (mg/kg)	57.0	47.2	31117	3615	5.45	1.76	181.0	222.0

Eluate 1 extr – eluate resulting from char 1 extracted; eluate 1 non extr - eluate resulting from char 1 non-extracted; eluate 2 extr – eluate resulting from char 2 extracted; eluate 2 non extr - eluate resulting from char 2 non-extracted

In particular, the heavy metal Zn was quantified in the extracted char with major amounts.

In the eluates, all the metals analyzed were below the detection limits, except for Ni, Cr and Zn, which also appeared in significant quantities in the solid residues. However, and in particular for Cr, its mobility was significantly reduced since it was only detected in a very lower amount in the eluate 2 from the non-treated char 2. Ni was detected only in eluate 1 obtained from the extracted char and altough the treated char 2 presented the highest amount of Ni, its release was supressed. As expected from its concentration in the chars, Zn is the heavy metal present in higher amounts in the eluates. However, its mobility was reduced, particularly from char 2 extracted. Previous studies (Hwang et al., 2007; Kistler et al., 1987) have shown that pyrolysis may have a positive effect on the immobilization of heavy metals in solid residues. The adsorptive capacity of the char by its specific surface area and the pore structure might be also considered as a reason for restraining metal leaching. Nevertheless, the amount of Zn leached from the chars is still significant.

Eluates pH values are also presented in Table 1. Eluates 1 and 2 present significant differences in pH values, since eluates 1 showed slightly neutral pH values (from 5.7 to 6.2) and similar to the pH of the leaching solution (7.4), which means that there was not a significant leaching of acidic or basic components of the char residues. Eluates 2 have considerably lower pH values than those of eluates 1, which means that there was a significant leaching of acidic components from chars 2.

3.3 Organic characterization of the eluates

Table 2 shows the concentrations of the 15 aromatic hydrocarbons in eluates. None of the 15 aromatic hydrocarbons were detected in eluate 1 from the extracted char and only toluene, ethylbenzene, m/p-xylene and butylbenzene/1,4-diethylbenzene were detected in eluate 2 from the extracted char, although in minor concentrations (1-1.4 µg/L), which confirms that the extraction of the chars with DCM was an efficient method for the removal of volatile organic contaminants. On the other hand, the eluates obtained from the non treated chars showed a strong contamination with relevance for BTEX compounds and cumene that were quantified in the high ppb range. These compounds were found in high concentrations in the liquid fraction of the corresponding pyrolysis process (Paradela et al., 2008; Paradela et al., 2009).

The results obtained indicate that this leaching procedure allows the discrimination between chars with high and low organic contamination producing completely different organic loads of the eluates. Moreover, this procedure is also useful for the determination of volatile organic compounds, when performed with some adaptations to prevent volatilization of the lighter contaminants.

Table 2. Concentrations of the organic compounds in eluates.

Analytes	Concentrations (μg/L)			
	Eluate 1 extr	Eluate 1 non extr	Eluate 2 extr	Eluate 2 non extr
Benzene	<0.8	3.8	<0.8	72.3
Toluene	<0.04	511	1.0	508
Ethylbenzene	<0.03	277	1.0	297
m/p-xylene	<0.01	1.71	1.1	116
o-xylene	<1.0	49.3	<1.0	7.4
Cumene	<1.0	9.0	<1.0	127
Propylbenzene	<1.2	1.59	<1.2	5.5
4-ethyltoluene	<1.0	1.03	<1.0	10.8
Tert-butylbenzene	<1.4	<1.4	<1.4	<1.4
1,2,4-trimethylbenzene	<1.1	<1.1	<1.1	4.1
1-methylpropylbenzene	<1.3	<1.3	<1.3	<1.3
Butylbenzene/1,4-diethylbenzene	<0.02	0.20	1.4	1.6
1,2,4,5-tetramethylbenzene	<0.6	<0.6	<0.6	1.3

3.4 Ecotoxicity Tests

The ecotoxicological data obtained in the eluates are shown in Table 3. The luminescence inhibition of *Vibrio fischeri* was evaluated for an exposure period of 5, 15, and 30 min, with and without pH adjustment to the optimum pH value for *Vibrio fischeri*.

No significant toxicity was detected in eluate 1 from the extracted char. Only for an exposure period of 30 min was it observed that there was a 50% luminescence inhibition for concentrations of approx. 70% (v/v). However, eluate 2 from the extracted char 2 showed toxicity to *Vibrio fischeri* for concentrations of 2.4-17.4%. In this eluate, a significant decrease in the ecotoxicity was observed after the pH correction, in particular for an exposure period of 5 min. However, for the longer exposure period, no significant differences in the ecotoxicity are observed with and without pH correction

Eluates obtained from the non treated chars presented the highest toxicity with concentrations of 0.6-1.27% inducing a 50% of luminescence inhibition. For eluate 2, the pH correction didn't cause a decrease in the ecotoxicity. Probably, the inhibition effect of contaminants is very high and independent of other variables. The high toxicity levels of the eluates obtained from the non extracted chars seemed to be mainly associated with the high concentrations of organic contaminants such as BTEX. However, also the eluates resulting from the extracted chars still present a significant toxicity, in paricular, eluate 2. This toxicity should result from contaminants that are not soluble in DCM and are fairly soluble in the leaching solution, like the inorganic contaminants, namely Zn, which was found in significant amounts in this eluate. Polar organic contaminants with the same solubility characteristics could also be present and contribute to the ecotoxicity.

Table 3. Ecotoxicity of eluates to *Vibrio fischeri* bacterium, for exposure periods of 5, 15, and 30 minutes

Eluate	Effective concentration, EC_{50} (%) (v/v)					
	5 min		15 min		30 min	
	Without pH_{corr}	pH_{corr} (pH = 7.4)	Without pH_{corr}	pH_{corr} (pH = 7.4)	Without pH_{corr}	pH_{corr} (pH = 7.4)
Eluate 1 extr	>99		>99		70.4	
Eluate 1 non extr	1.0		1.3		1.1	
Eluate 2 extr	17.4	27.4	7.8	10.9	2.4	3.6
Eluate 2 non extr	0.9	0.7	0.9	0.6	0.6	0.6

3.5 Assessment of the hazard and ecotoxic potential of the char residues

The assesment of the hazard and ecotoxic potential of the pyrolysis chars were performed using the Council Decision 2003/33/CE (CEC, 2003) and the Criteria and Evaluation of Waste Ecotoxicity (CEMWE) (CEMWE, 1998) by comparing the results presented in Tables 1, 2 and 3 with the limit-values defined in the 2003/33/CE and CEMWE. The classification of the chars is presented in Table 4.

Table 4. Classification of the chars according the limit-values defined in the EC legislation and in the CEMWE proposal.

Char	Hazardous potential	Ecotoxicity potential
Char 1 treated	Hazardous	Ecotoxic
Char 1 non treated	Non-inert and non-hazardous	Ecotoxic
Char 2 treated	Hazardous	Ecotoxic
Char 2 non treated	Hazardous	Ecotoxic

4. CONCLUSIONS

The results obtained in this work indicate that the extraction with DCM is an effective method for the removal of organic contaminants of high to medium volatility from pyrolysis chars and, therefore, represents a potential reduction on their ecotoxicity.

The non volatile organic fraction and the inorganic fraction remain in the chars after the DCM extraction. The non volatile organic fraction is hardly soluble in water or aqueous solutions, so is virtually immobilized in the solid residue during leaching procedures. The inorganic fraction, that includes compounds like heavy metals, can be leached from the chars and be responsible for the ecotoxicity of the eluates from treated chars.

Regarding the release of heavy metals, Zn and Ni were the heavy metals that exceeded the limit-values of the legislation and criteria used and whose presence was associated with a significant hazardous and ecotoxic potential; heavy metals decontamination treatments of the chars should be evaluated.

The results of this study underline the need for relating ecotoxicological and chemical parameters, including inorganic and organic compounds, in the hazard assessment of solid residues and the need of harmonization of the different procedures and criteria in the legislation.

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