Evaluation of the Toxicity of Char Residues Produced in the Co-Pyrolysis of Different Wastes

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EXECUTIVE SUMMARY

The high amounts of solid waste produced in industrial installations and in urban centers is a complex problem of today's society. The traditional strategies for solid waste transformation and disposal include landfilling or incineration. Other approaches are being exploited namely waste selective collection and recycling or the energetic valorization of solid wastes through pyrolysis.

In the pyrolytic process, the wastes are converted into a gaseous and liquid phase that can be used in energy production or as feedstock in chemistry industries. A solid residue (char) is also produced in a proportion that depends on the pyrolysis conditions. Even when the operating conditions are optimized in order to minimize the solid fraction, a reasonable amount of chars are obtained.

These chars are mainly composed of a carbon-rich matrix that contains the mineral matter initially present in the wastes as well as components of the liquid fraction. Therefore, these solid residues have a toxicity potential due to the presence of heavy metals or organic compounds that must be assessed in order to define their safe reutilization or disposal.

In the present study, the chars produced in the co-pyrolysis of plastics, pine biomass and tyres were characterized through chemical and ecotoxicological tests. A fraction of the solid chars was treated by extraction with dichloromethane. Different volatility groups of compounds 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 and organic parameters. An ecotoxicological characterization was performed by using the bio-indicator *Vibrio fischeri*.

The chemical and ecotoxicological results were compared and analysed according to the Council Decision 2003/33/CE and the Criteria on the Evaluation Methods of Waste Ecotoxicity (CEMWE).

The results of the chemical characterization indicate that the extraction of the char residues with an appropriate organic solvent allows the efficient elimination of the volatile organic contaminants thus decreasing the potential toxicity of these chars. The semi-volatile and non-volatile fractions were not, apparently, affected by this pre-treatment.

Regarding the release of heavy metals from extracted and non-extracted chars during the leaching tests, a strong contamination with Zn was found in both eluates, which contribute to a classification of the corresponding chars as hazardous and ecotoxic materials.

Also the results of the ecotoxicological characterization of the eluates led to a classification of these chars as ecotoxic materials.

INTRODUCTION

The accumulation of enormous amounts of municipal and industrial solid wastes has become a serious environmental issue in many countries. The limitations and impacts of the existing waste treatment procedures, namely, landfilling and incineration, has led to the increasing development of thermal treatment technologies that allow the energetic and chemical valorization of these wastes and minimize the discharge of pollutants into the environment.

One of those thermal technologies is pyrolysis that consists in the treatment of wastes at relatively high temperatures in the absence of air or in an oxygen-deficient atmosphere. This technology produces a hydrocarbon mixture (vapour and liquid fractions) that can be used as fuel or as feedstock in chemistry industries, and a carbon-rich solid residue (the solid fraction).

Although the pyrolysis experiments are usually optimized in order to maximize the liquid and gaseous fractions, it is expected that a relatively high fraction of solids will be produced. It is, therefore, necessary to study the material composition and properties of these solid chars in order to define strategies for their possible reutilization or safe disposal.

Generally, the pyrolytic char does not possess properties of sufficiently high quality to be reused as raw material and, unless an upgrade step is performed, its final destination is landfilling. The assessment of the toxicity and ecotoxic potential of this kind of residues and their leachates requires an in-depth knowledge of the material composition and leaching behaviour.

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 concerning contaminants are organic compounds. Only the classification as inert residues includes the leaching of a restrict group of organic compounds. However, the EN 12457 specifies a scope which excludes the leaching of organic contaminants.

The standardization of the leaching techniques dealing with the extraction of organic compounds is still just beginning and, recently, an ISO leaching standard 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. There is no standard leaching techniques applicable to residues with a high load in organic compounds, specially the volatile ones.

The organic contaminants leached from a given material or residue depend, obviously, on its composition and may include classes of compounds such as aromatic and polyaromatic hydrocarbons, aliphatic hydrocarbons, polychlorinated biphenyls and dioxins, among others.

The 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 (BTEX), and they have a particularly high environmental mobility.

In the present study, the determination of organic contaminants was focused on the BTEX group because these are also commonly the compounds with lower molecular weight and higher water solubility.

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

Experimental Part

The waste mixture subjected to pyrolysis was composed of 30% (w/w) pine biomass, 40% (w/w) plastics (mixture of polyethylene, polypropylene and polystyrene) and 30% (w/w) used tyres. 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 reducing the organic load of the chars. The char residue submitted to the extraction with DCM was defined as char residue A and the non extracted char residue was defined as char residue B.

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).

A selected group of heavy metals (cadmium, lead, zinc, copper, mercury and arsenic) were quantified in the chars, submitted to a previous acidic digestion, using atomic absorption spectrometry (AAS) (APHA, 1996).

The chars were submitted to the leaching standard ISO/TS 21268 – 2 (ISO/TS 21268-2, 2007) and the eluates were analyzed for the following inorganic parameters: pH (ISO 10523, 1994) and heavy metals content (cadmium, lead, zinc, copper, mercury and arsenic) by AAS (APHA, 1996).

The concentrations of the BTEX compounds in the eluates were determined by headspace static sampling and gas chromatography with mass spectrometry (HS-GC-MS) (Bernardo et al., 2009b). Other volatile aromatic compounds present in the eluates were tentatively identified by the comparison of their mass spectra with references from the Wiley and NIST spectra libraries.

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).

Results and Discussion

The organic content of chars A and B is shown in Figure 1, expressed as relative mass composition, based on the volatility of their components (volatile, semi-volatile, non-volatile organic matter and ashes). According to these results, a previous extraction of the char residues with an appropriate organic solvent allowed an efficient removal of the volatile organic fraction but, apparently, didn't affect the semi-volatile and non-volatile fractions. The high content of semi-volatile compounds in residue A is mostly due to a concentration effect resulting from the removal of light organic compounds.

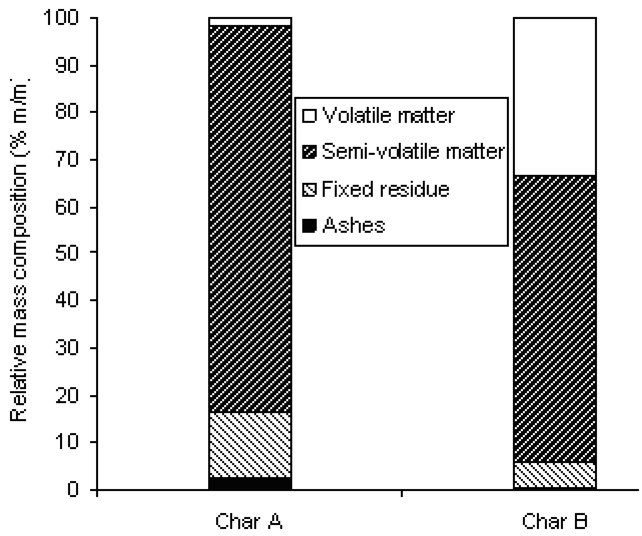

Figure. 1. Relative mass composition (% w/w relatively to the initial weight of each residue). (Char A – extracted with DCM, Char B – non extracted).

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. Eluate A was produced through the leaching of char A (previously extracted with DCM) and eluate B resulted from char B (not extracted).

Table 1. Inorganic characterization of the chars and eluates

	Char A	Char B	Eluate A	Eluate B
pH			4.81	4.94
Cd (mg/kg)	<5.0	<5.0	<0.11	<0.11
Pb (mg/kg)	<55.0	<55.0	<0.50	0.76
Zn (mg/kg)	31 117	3 615	181.0	222.0
Cu (mg/kg)	<7.5	<7.5	<1.9	<1.9
Hg (mg/kg)	<0.3	<0.3	0.08	<0.01
As (mg/kg)	<0.1	<0.1	<0.004	<0.004

Zn was detected in both char residues, while the other metals were below the respective detection limits. The concentration of Zn in char A is about ten times higher than the concentration of this metal in char B; this difference probably results from the concentration effect associated with the extraction of the light organic fraction during the DCM treatment. As expected from its concentration in the chars, Zn is also the heavy metal present in higher amounts in the eluates. In what concerns the other heavy metals analyzed, they were practically absent from the eluates as they were from the chars: a residual amount of Pb was found in eluate B, a minor amount of Hg was found in eluate A and all other metals were bellow their detection limits.

The pH of the eluates is also shown in Table 1. Both eluates have similar pH values and considerably lower than the pH of the leaching solution (7.42) which means that there was a significant leaching of acidic components from both chars.

Concerning the results from the organic characterization, only toluene, ethylbenzene and m/p-xylene were detected in eluate A (Table 2), although in low concentrations. This means that the

DCM extraction step was efficient in removing these organic contaminants from the pyrolysis chars. On the other hand, Eluate B showed a significant contamination with BTEX compounds, with predominance of toluene (Figure 2). These compounds were found in high concentrations in the liquid fraction of the corresponding pyrolysis process (Paradela et al., 2009).

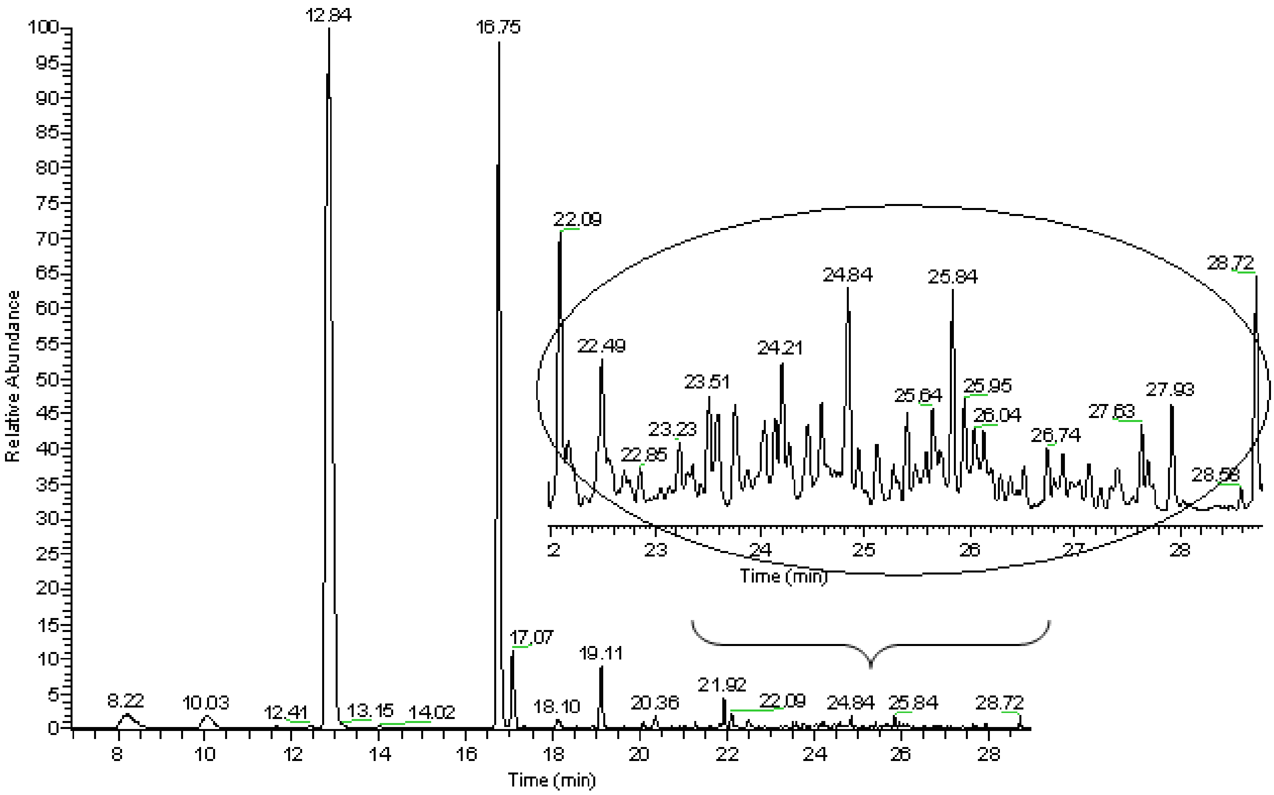

Figure 2. HS-GC-MS chromatogram of eluate B.

Other volatile organic contaminants were also tentatively identified in the eluates. Besides for the confirmation of the presence of BTEX, several other aromatic hydrocarbons (PAHs, furans and other benzene derivatives) and other organic compounds such as phenolics were also detected in eluate B (Table 3). These organic compounds are typical components of the liquid fraction obtained from the individual pyrolysis of plastics, biomass and tyres or their mixtures (Paradela et al., 2008; Paradela et al., 2009; Marin et al., 2002; Islam et al., 2008; Fassinou et al., 2009) so it is expectable that they should be present as contaminants of the solid residue resulting from the pyrolysis process.

The alkyl substituted phenols detected result, typically, from the thermochemical interaction between the biomass and aromatic-derived products. The compounds detected in higher relative concentration were BTEX. It was possible to detect other aromatic compounds in eluate A, namely, methylcumene, an isomer of trimethylbenzene, butylbenzene and 1,4-diethylbenzene, although in very low relative concentration (relative chromatographic peak area).

Table 2. BTEX concentrations in the eluates (μg/L)

Analytes	R.T. (min)	Concentrations (μg/L)	
		Eluate A	Eluate B
Benzene	8.22	<0.8	72.3
Toluene	12.86	1.0	507.7
Ethylbenzene	16.75	1.0	297.0
m/p-xylene	17.08	1.1	116.4
o-xylene	18.10	<1.0	7.4

Table 3. List of the organic compounds detected in the eluates.

Name	R.T. (min)	Relative concentration (%)	
		Eluate 1	Eluate 2
Benzene[1]	8.23		2.61
Dimethylfuran (isomer)[2]	10.07		1.47
Hydrocarbon[2]	11.64		0.17
Toluene[1]	12.85	56.08	58.69
Ethylmethylfuran (isomer)[2]	14.02		0.15
Ethylbenzene[1]	16.75	26.4	27.4
m/p-Xylene[1]	17.08	6.22	3.03
o-Xylene[1]	18.09		0.46
Cumene[1]	19.10		1.83
Propylbenzene[1]	20.09		0.21
4-Ethyltoluene[1]	20.36		0.54
Methylstyrene (isomer)[2]	21.01		0.08
1,2,4-Trimethylbenzene[1]	21.28		0.15
Methylcumene (isomer)[2]	21.93	3.8	0.63
Trimethylbenzene (isomer)[2]	22.10	0.91	0.36
Methylstyrene (isomer)[2]	22.45		0.14
Butylbenzene/1,4-Diethylbenzene[1]	22.68	6.59	
Methylcumene (isomer)[2]	23.23		0.05
1,2,4,5-Tetramethylbenzene[1]	24.05		0.09
Methylcumene (isomer)[2]	24.14		0.07
Methoxyphenol/Methylphenol (isomer)[2]	24.20		0.16
Dimethylcumene (isomer)[2]	24.45		0.11
Dimethylstyrene (isomer)[2]	24.58		0.24
Ethylstyrene (isomer)[2]	24.84		0.33
Trimethylstyrene (isomer)[2]	25.40		0.09
Naphthalene[2]	25.84		0.21
Ethylbenzonitrile[2]	25.94		0.11
Methoxymethylphenol (isomer)[2]	26.04		0.11
Benzothiazole[2]	26.74		0.07
Trimethylphenol (isomer)[2]	26.89		0.04
Methylnaphtalene (isomer)[2]	27.93		0.12
Benzenebutanenitrile[2]	28.73		0.22

1 – Compound identified by co-injection of standards; 2 – compound tentatively identified by comparison with the spectra of NIST and Wiley libraries and by comparison between isomer molecular structures; R.T. – Retention time

The ecotoxicological data obtained in the eluates are shown in Table 4. The luminescence inhibition of *Vibrio fischeri* was evaluated for an exposure period of 5, 15, and 30 min.

Eluate B presented the highest toxicity with concentrations of 0.4-0.8% inducing a 50% of luminescence inhibition. Eluate A showed EC_{50} values to *Vibrio fischeri* of 2.0-9.7%, a value significantly lower than the one obtained for eluate B, which could be attributed to its lower organic content resulting from the extraction of char A with DCM. The toxicity of eluate A should result from contaminants that are not soluble in DCM and are soluble in the leaching solution like the inorganic contaminants, namely Zn, which was found in significant amounts in this eluate. Also, the pH values of the eluates, in the range of 4-5, were not in the optimum range for *Vibrio fischeri,* which could contribute to the toxicity exhibited by the eluates.

Table 4. Ecotoxicity of eluates to *Vibrio fischeri* bacterium, for exposure periods of 5, 15, and 30 minutes.

Eluate	Efective concentration, EC_{50} (%) (v/v)		
	5 min	15 min	30 min
A	9.7	3.9	2.0
B	0.8	0.6	0.4

CONCLUSION

A previous extraction of these char residues with an appropriate organic solvent allowed to remove efficiently the volatile organic fraction thus decreasing the potential of toxicity of the char. The semi-volatile and non-volatile fractions were not, apparently, affected by this pre-treatment.

The assessment 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 4 with the limit-values defined in the 2003/33/CE and CEMWE.

Both chars, treated and non-treated were classified as hazardous and ecotoxic material. Zn was the only heavy metal that exceeded the limit-value of the legislation and whose presence was associated with significant ecotoxicity. Considering the final destination for these residues, namely, the deposition in a landfill or a possible valorisation, it should be considered the treatment of the chars with a Zn decontamination procedure.

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