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Ecotoxicological Assessment of Ashes and Particulate Matter from Fluidized Bed Combustion of Coal

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Toxicity of ash and particulate matter from the gases generated in coal fluidized bed combustion (FBC) has been determined by the Microtox assay according to the standard leachate procedure. Results are compared with the polycylic aromatic hydrocarbon (PAH) content of the particulate matter, which was determined by fluorescence spectroscopy. Although PAHs are considered highly toxic compounds, the low ecotoxicity values obtained could be explained by the low solubility of the compounds in water. The Microtox assay may underestimate the toxicity of water-insoluble compounds unless they are previously extracted with an organic solvent. Nevertheless, this type of assay can be very useful for measuring the potential toxicity of residues when exposed to water sources such as rain water and the risk of the components being dissolved and transported by runoff water. © 1998 Academic Press

INTRODUCTION

The organic matter of coal is composed of two complementary structures, the dominant one being a macromolecular insoluble fraction containing condensed aromatic and hydroaromatic units connected by ether and thioether linkages and short alkyl bridges. The other contains various aliphatic and aromatic hydrocarbons of low to medium molecular mass, mostly soluble in organic solvents.

When coal undergoes combustion, important physical and chemical changes (contraction–swelling, devolatilization, decarboxylation, changes in fluidity and plasticity) occur and some of the resulting compounds are released into the atmosphere. In addition, cyclization reactions caused by the thermal process may occur, and, as a consequence, further aromatic clusters may develop. Both the inherent aromatic hydrocarbons and those formed during the process are significant atmospheric pollutants (Smith, 1984). Depending on their molecular mass, polycylic aromatic hydrocarbon molecules can exist in the gas phase ($<$ six-ring PAHs), in the solid phase ($>$ six-ring PAHs), or in both phases (four- and five-ring PAHs) in the air. Distribution is placed in favor of the particulate phase at cooler temperatures and toward the gas phase in the summer. These organic compounds are considered highly toxic, are generated throughout the combustion process, and may form adducts with proteins. It has been proven that some PAHs have a carcinogenic effect.

The toxicity of synthetic, xenobiotic organic chemicals to aquatic life forms and microorganisms has been the subject of considerable research in the past few decades. Even though considerable toxicity research has been done on various aquatic species, only a few studies have focused on the effects on microorganisms. Recently, new assays have been developed for assessing ecotoxicity employing microorganisms, the Microtox assay (Microbics Corp., 1991) being widely used because of its simplicity, consistency, and reproducibility. This assay employs a marine bacterium (*Photobacterium phosphoreum*) as test organism and experimentally measures the effective concentration of the toxic agent that produces 50% inhibition of a standardized culture.

This paper reports a study of the ecotoxicity of ash and particulate matter generated in the fluidized bed combustion (FBC) of two types of coal. The levels of PAHs in the particulate matter from the combustion gas were compared with ecotoxicity values. The ecotoxicity of samples was determined by the Microtox assay.

EXPERIMENTAL

A high-rank coal and a low-rank coal from different mining areas in Spain (Table 1) were burned in a laboratory-scale fluidized bed combustor (up to 200 g/h) at 750, 850, and 950°C, with a 40% excess of O_2 and sand as fluidizer. The gas flow was twice the minimum fluidization velocity (Mastral *et al*., 1995). Combustion efficiencies are listed in Table 2.

Two cyclons downstream of the combustor retained particulate matter. Part of the contents of the cyclons was extracted with dimethyl formamide (DMF) by ultrasonication for 15 min. The extract was analyzed by synchronous

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TABLE 1
Characteristics of the Coals

Composition	Low-rank coal	High-rank coal
%C (daf)	69.40	87.44
%H (daf)	5.80	6.05
%N (daf)	1.11	1.90
%S (db)	6.12	0.26
% Ash (as received)	22.52	50.47

TABLE 3
Amounts (g) Collected in Cyclons and Ash Pit from Coal FBC (476 g of Coal Burned)

Type of coal	Low-rank coal			High-rank coal		
T (°C)	750°C	850°C	950°C	750°C	850°C	950°C
First cyclon	14.2	18.2	17.0	24.2	25.1	25.8
Second cyclon	1.4	1.3	1.4	—	—	—
Ash pit	48.5	58.0	62.0	50.0	100.4	84.2

fluorescence in a spectrofluorometric apparatus provided with a xenon lamp and quartz cells of 10-mm path length. The slit width of excitation and emission used to obtain the spectra was 2.5 nm and the sweep speed was 240 nm min^{-1}. The remainder of the contents of the cyclons and the ash pit was leached with distilled water for 24 h, in a light acid medium (pH 5.2), with the aim of imitating the process as it occurs in nature. The extract was subsequently filtrated through a 0.45-μm cellulose filter and stored at 8°C until the Microtox assay.

The Microtox assay, used to determine the toxicity of samples from coal combustion ash, as previously mentioned, exposes microorganisms (a marine bacterium, *P. phosphoreum*) to test samples and measures the toxic effect of the sample on the organisms by measuring the light output of the luminiscent bacteria after they have been exposed to the sample and comparing the result with light output of a control (reagent blank) that contains no sample. The degree of light loss indicates the degree of toxicity of the sample. Results are normally expressed in effective concentration, EC_{50}, the concentration of a sample at which the light output is reduced by 50% under defined conditions of exposure time (5–15 min) and temperature (15°C). The results reported were obtained using the Microtox data analysis software and an exposure time of 15 min.

RESULTS AND DISCUSSION

The amounts of solids collected in cyclons and the ash pit are listed in Table 3. As can be seen, most of the particulate matter in the gas from the combustion of coals was retained in the first cyclon; hence, the analysis of PAHs and ecotoxicity could be carried out only on the contents of this cyclon and the ash pit.

The quantities of total polycyclic aromatic hydrocarbons collected in the first cyclon are provided in Table 4. The following PAHs were detected: fluorene, benzo[a]pyrene, pyrene, chrysene, anthracene, acenathrene, benzo[a]anthracene, dibenzo [9h] anthracene, coronene, perylene, and benzo[k]fluoranthene.

The results of the Microtox assay carried out in the leachates obtained from the particulate matter resulting from the combustion of coal, expressed as EC_{50} values in milligrams per liter, are presented in Table 5. The results indicate that the ash collected in the ash pit is less toxic than the particulate matter collected in the cyclons, both in the residue obtained from combustion of low-rank coal (LRC) and in the residue from combustion of high-rank coal (HRC). This might be due, on the one hand, to the diluting effect of the sand used as fluidizer and collected in the ash pit together with the combustion ash and, on the other hand, to the very high combustion efficiencies resulting in an insignificant PAH content in the ash.

Toxicity values of particulate matter collected in the cyclons are higher for the LRC than for the HRC. This may be due to the lower pH values of the leachate obtained from LRC residue (3.8–4.2), which did not require addition of acetic acid for the Microtox assay, probably because of its higher sulfur content, compared with the pH values of the leachates obtained from HRC residue. The acidity of the samples appears to have a higher toxic effect than the total content of PAHs.

Variations of toxicity with temperature were not significant in the ash collected in the ash pit from HRC (EC_{50} values on the order of 100,000 mg/liter), whereas in the other cases an increment in toxicity was observed at the highest temperature (950°C), which is more significant in the case of the ash from the ash pit obtained with LRC (EC_{50} =

TABLE 2
Efficiences (%) Reached at Fluidized Bed Combustion of Coals

	750°C	850°C	950°C
Low-rank coal	98.8	99.1	99.4
High-rank coal	88.6	96.4	97.1

TABLE 4
Total Amount (ng/kg) of PAHs Collected in the First Cyclon

	Low-rank coal	High-rank coal
750°C	695.9	98.8
850°C	161.1	315.0
950°C	153.2	162.0

TABLE 5
Ecotoxicity [EC_{50}] Values of the Particulate Matter from FBC of Coals

	Low-rank coal		High-rank coal	
	First cyclon	Ash pit	First cyclon	Ash pit
750°C	10,400	360,700	27,960	107,490
850°C	13,300	311,500	30,100	108,680
950°C	8,500	10,000	65,670	97,810

10,000 mg/liter). This variation in ecotoxicity with temperature is not consistent with the variation in total amount of PAHs since the maximum was obtained, in the case of particulate matter, at a temperature of 850°C (Mastral *et al.*, 1996). An explanation for this fact could be that not only the total amount of PAHs is important but also the concentrations of the different types of PAHs which might have different toxic effects. In addition, the Microtox assay is performed in an aqueous medium and not all PAHs demonstrate the same water solubility (Nirmalakhandan, 1994a, b; Boxall and Maltby, 1995).

CONCLUSIONS

European legislation on toxic and dangerous residues established that a residue is classified as toxic when its $EC_{50} \leq 3000$ mg/liter. Hence, the residues generated in the fluidized combustion of coal (ash and particulate matter) studied in this work can be classified as "nonecotoxic," according to the Microtox assay.

Although there is evidence that some PAHs are toxic and carcinogenic, if the Microtox test is carried out with leachates according to standard procedure, low toxicity values are obtained due to the low solubility in water of PAHs. Different results would be obtained if the PAHs were extracted with an organic solvent and the test were carried out with the extracts or if the test were carried out directly with the solid matrix. These latter procedures are adequate for measuring the toxicity of PAHs but should not be used when the aim is to determine the potential toxicity of residues to ascertain their behavior when dumped in a waste deposit or when they are going to be recycled. In these cases, the leachate standard procedure should be used.

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