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Quality of Ashes Produced in the Co-Combustion of Coal and MBM in a Fluidized Bed Reactor

R. Barbosa[1], N. Lapa[1], H. Lopes[2], I. Gulyurtlu[2], B. Mendes[1]

[1] UBiA, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal, e-mail: rfb@fct.unl.pt
[2] LNEG, UEZ, Ed. J., Estrada do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal

Abstract. Since the 90's decade there are severe restrictions to the use of MBM, due to BSE. The co-combustion of Meat and Bone Meal (MBM) and coal is a possible energetic valorization route for MBM. However, the chemical and ecotoxicological properties of the ashes produced in this co-combustion process need to be more characterized. In order to evaluate the chemical and ecotoxicological properties of this type of ashes, three combustion tests were performed in a fluidized bed reactor (FBR): 1) combustion of coal; 2) co-combustion of coal and MBM; 3) combustion of MBM. The characterization of the ashes was focused on the following aspects: (1) the bulk content of metals; and (2) the chemical and ecotoxicological characterization of eluates. The ashes were classified according to their ecotoxicity levels based on the French regulation CEMWE. According to Council Decision (CD) 2003/33/EC, all fly ashes need stabilization prior to landfilling, except the 1st cyclone ash produced in the co-combustion test that could be landfilled in a hazardous waste landfill. The bottom ashes were classified as non-hazardous residues. The novelty of this paper is related with two aspects: 1) the use of MBM as co-fuel; and 2) both chemical and ecotoxicological characterization of the ashes produced during the combustion of coal and MBM.

Key words

Combustion, coal, meat and bone meal, ecotoxicity

1. Introduction

The replacement of fossil fuels by renewable sources of energy can contribute to improve the environmental performance of the power production and to move forward in the sustainability way [1]. The experience has shown that the availability of alternative fuels can be a serious obstacle for its extensive use for energy production. The use of non-hazardous wastes may be an alternative to biomass, if they are economically unattractive for recycling or if they have a high cost for land filling [2]. Co-firing non-hazardous wastes with coal is, therefore, a subject of great interest for the sustainability of energy production and the reduction of the emissions of fossil greenhouse gases [3]. The use of these wastes for energy is promising if they combine well with other fuels during the conversion process for energy and don't have negative effect on the combustion system, on the ash quality and on the gaseous emissions [4]. The utilization of MBM as animal feedstock was forbidden in 1994, by the European Union, since it was in the origin of the spreading of Bovine Spongiform Encephalopathy (BSE) which can promote the equivalent human disease (Creutzfeldt-Jakob disease). One possible way for the valorization of MBM is its incineration ([5], [6]).

2. Materials and Methods

2.1. FBC, fuels and combustion conditions

The combustion and co-combustion tests were performed in a bubbling FBR of LNEG/UEZ. Further details of this FBR are shown in Gulyurtlu and Monteiro (1991) [7] and Lapa et al. [8]. Three combustion tests were performed: 1) combustion of coal; 2) co-combustion of coal and MBM (85% Coal+15% MBM); 3) combustion of MBM. Each combustion test produced three types of ashes: bottom ashes and two cyclone ashes (1st cyclone and 2nd cyclone ashes). The bottom ashes were collected at the bottom of the FBR and the fly ashes were collected by two containers located at the bottom of each cyclone. The bed material used was cleaned river sand. The fossil fuel used was a bituminous coal from the Colombian mine of El Cerrejón. MBM was produced in slaughter houses of Germany.

2.2. Bulk characterization of fuels and ashes

The digestion of the samples was performed according with the USEPA Method 3051A. The following chemical elements were analyzed in the acidic digested samples: As (EN ISO 11969, 1996), Hg (ISO 5666/1, 1983), Cd, Cu, Ni, Pb and Zn (ISO 8288, 1996), Sb, Se, Mo, Ca, Na, K and Ba (AAS flame quantification – APHA et al., 1996), Cr (AAS flame quantification/Method A – ISO 9174, 1990).

2.3. Leaching test, chemical and ecotoxicological characterization of eluates

The ashes were submitted to the leaching test described in the European leaching standard EN 12457-2. The eluates were submitted to same chemical parameters described above for digested samples, plus the following parameters: pH, DOC, CN^-, SO_4^{2-}, F^-, TDS (APHA/AWWA/WPCF, 1996), Cl^- (ISO 9297, 1989), Cr (ISO 9174, 1990), Cr (VI) (NF T90-043, 1988), phenol compounds (ISO 6439, 1990). The eluates were also characterized for the following ecotoxic parameters: a) Luminescence inhibition of the bacteria *Vibrio fischeri* (ISO 11348-3, 2003); b) Mobility inhibition of the crustacean *Daphnia magna* (ISO 6341); and c) growing inhibition of the algae *Pseudokirchneriella subcapitata* (ISO 8692).

3. Results and discussion

3.1. Bulk characterization of fuels

Table 1 shows the metals bulk composition of the fuels for a set of metals.

Table 1 – Bulk composition of the fuels used in the combustion tests (mg/kg db)

Parameter	Coal	MBM
Ba	<3.7	452
Sb	<0.07	0.1
Mo	<22.4	117
Se	<0.2	0.3
Cu	<9.4	9.9
Zn	36.8	94.3
Cr	33.5	<10.2

MBM has shown the highest concentrations of the set of heavy metals analyzed. The major differences in the concentration were observed for the parameters Ba, Mo and Zn. The high concentration of Ba, Mo and Zn, in MBM, can be explained by the fact that, when consumed by the cattle, they are rapidly transported in blood plasma and accumulated in the bones ([9], [10], [11]). The concentration of Cr was higher in coal than in MBM. The concentration of As, Hg, Cd, Pb and Ni were below the quantification limit (QL) in both fuels.

3.2. Bulk characterization of ashes

Table 2 shows the bulk composition of the ashes.

Table 2 – Bulk composition of the bottom, 1st and 2nd cyclone ashes (mg/kg db)

Parameter	Bottom ashes		
	Coal	Coal+MBM	MBM
K	4,016	8,070	5,705
Na	3,129	7,731	8,121
Ca	48,056	18,078	129,617
Cr	172	162	133
Zn	18.3	28.6	128
Ni	69.6	30.3	43.5
Cu	<8.4	<10.4	<9.3
Pb	<17.4	<18.9	<17.6
Cd	19.5	22.5	<0.70
Ba	<10.4	133	3,110
Mo	<34.8	<37.7	<35.2
Sb	<0.10	<0.11	<0.11
Se	<0.70	<0.75	<0.70
Hg	<0.42	<0.45	<0.42
As	1.4	0.89	<0.70
Parameter	1st cyclone ashes		
	Coal	Coal+MBM	MBM
K	14,082	14,442	9,583
Na	6,778	8,585	15,544
Ca	15,880	51,336	238,378
Cr	313	308	572
Zn	148	178	233
Ni	298	173	202
Cu	47.8	49.9	81.1
Pb	<26.2	<22.5	81.1
Cd	<9.1	<18.6	177
Ba	1,238	1,608	485
Mo	<37.8	73.3	140
Sb	<0.11	<0.11	<0.11
Se	32	1.9	<0.73
Hg	<0.45	<0.61	<0.44
As	3.5	3.4	<0.73
Parameter	2nd cyclone ashes		
	Coal	Coal+MBM	MBM
K	14,735	17,890	27,016
Na	6,733	9,300	23,236
Ca	9,185	16,463	210,427
Cr	59	292	4,800
Zn	167	234	1,495
Ni	156	158	3,828
Cu	68.7	73.4	470
Pb	44.7	35.6	470
Cd	19.8	19.7	5,7
Ba	1,086	1,428	1,782
Mo	90.3	102	508
Sb	<0.11	<0.11	<0.11
Se	9.7	12.9	<0.73
Hg	<0.44	<0.75	0.9
As	6	6.2	4.8

Coal: Combustion of coal; Coal+MBM: Co-combustion of coal and MBM; MBM: Combustion of MBM

Generally, the content of metals is higher in the fly ashes. The substitution of coal by MBM has promoted, generally, a higher concentration of metals in the ashes. The concentrations of Cr, Ni and As were similar in the bottom ashes. The 2nd cyclone ashes, especially those produced in the combustion of MBM, have presented the highest concentration of Cr, Zn, Ni, Cu and Pb, which can be attributed to the lower particle size of the ashes that usually present enrichment in heavy metals due to volatilization/condensation phenomena, especially in presence of high levels of Cl ([12], [13], [14]). Ba and Mo were also found in high concentrations in the ashes from the combustion tests were MBM was used as fuel. The 1st and 2nd cyclone ashes, produced in the combustion of coal and co-combustion test, have retained As and Se in higher levels than those observed in same type of ashes produced in the combustion of MBM, although the levels were insignificant in the fuels. The same behavior was observed for Cr and Cd.

3.3. Leaching behavior of ashes

3.3.1. Chemical characterization of the eluates

Table 3 shows the release of chemical species from the ashes under the leaching test conditions. The concentrations of Sb, Zn, Ni, Cu, Pb, Cd and Phenolic Compounds were below QL. The pH values of the eluates produced by the bottom ashes were between 8.00 and 11.51, which can be attributed to the high level of alkaline oxides in the bottom ashes. The pH values of the eluates produced by 1st cyclone ashes were slightly lower (7.44 and 10.50) than those from the bottom ashes. The pH levels of the eluates from the 2nd cyclone ashes were similar to those from 1st cyclone ashes (7.34 to 11.27). The decrease of pH levels from the bottom to fly ashes are, probably, associated with the presence of acidic condensates from the flue gases. The concentration of Cr(VI) was below the QL, except in the eluates produced by the ashes from the combustion of MBM. The concentration of Cl^- was, generally, higher in the eluates produced by ashes of co-combustion test and in the combustion of MBM, which can be due to the high concentration of this element in MBM [15]. The concentrations of F^- and SO_4^{2-} were higher in the ashes resulting from the combustion tests in which coal was used as fuel. Generally, Cl^-, F^-, SO_4^{2-} were found in higher concentration in fly ashes, which may be associated with the accumulation of particles with high content of these species and more soluble forms [14]. The combustion tests in which MBM was used as fuel have produced ashes with higher concentration of TDS, specially the fly ashes retained in the 2nd cyclone. This fact may be associated with higher contents of soluble species in these particles [14].

Table 3 – Chemical characterization of the eluates produced by the ashes (pH: Sorensen; other species: mg/kg db)

Parameter	Bottom ashes		
	Coal	Coal+MBM	MBM
pH	11.51	9.69	8
SO_4^{-2}	1,580	2,897	1,863
DOC	54.2	77.4	<0.99
TDS	4,652	4,775	11,685
CN^-	<0.13	<0.13	<0.13
Cl^-	98.5	<25.0	993
F^-	95.7	1.5	79
K	52	153	2986
Na	127	244	2,310
Ca	757	799	113
Cr	<0.49	<0.50	2
CrVI	<0.49	<0.50	1.6
Ni	<0.20	<0.20	<0.20
Ba	<1.6	6	<1.6
Mo	6.9	6.1	<0.97
Se	0.19	<0.009	0.5
Hg	<0.01	<0.01	<0.01
As	<0.03	<0.03	<0.03
	1st cyclone ashes		
	Coal	Coal+MBM	MBM
pH	10.5	9.61	7.44
SO_4^{-2}	18,925	18,734	1,786
DOC	4.2	129	12.8
TDS	26,401	31,519	23,056
CN^-	0.3	0.47	0.21
Cl^-	179	206	1,559
F^-	135	108	52.3
K	650	610	3,852
Na	781	958	3,782
Ca	1,939	2,880	1,610
Cr	<0.51	<0.51	4.6
CrVI	<0.51	<0.51	1.8
Ni	<0.20	<0.20	<0.20
Ba	4.5	<1.6	6.5
Mo	33.3	18.2	46.1
Se	29.7	0.1	0.09
Hg	<0.01	<0.01	<0.01
As	<0.03	<0.03	<0.03
	2nd cyclone ashes		
	Coal	Coal+MBM	MBM
pH	11.27	10.81	7.34
SO_4^{-2}	13,531	10,320	1,338
DOC	<1.0	98.9	72.3
TDS	23,955	35,098	120,056
CN^-	<0.13	<0.13	0.25
Cl^-	103	156	302
F^-	110	95.4	641
K	341	1,033	2,430
Na	658	2,302	22,739
Ca	2,953	1,234	6,621
Cr	<0.51	<0.52	3.3
CrVI	<0.51	<0.52	1.7
Ni	<0.20	<0.20	17.2
Ba	<1.6	2.7	4.1
Mo	71.3	79.7	35.5
Se	0.82	9.6	0.28
Hg	0.05	<0.01	<0.01
As	0.12	<0.03	0.17

According to CEMWE, the chemical characterization of the eluates has led to the following classification: 1) the ashes from the combustion of coal and co-combustion test were classified as non-ecotoxic; 2) the ashes produced in the combustion of MBM were classified as ecotoxic due to Cr(VI) (bed ashes), Cr (1st cyclone ashes) and Ni and Cr(VI) (2nd cyclone ashes).

3.3.2. Ecotoxicological characterization of the eluates

Table 4 shows the Toxicity Units (TU) obtained of the eluates of ashes (TU = 100%/EC, where EC is the Effective Concentration, in %).

Table 4 – TU limits defined in CEMWE and TU of the eluates

Material/Assay		*D. magna*	*V. fischeri*	*P.*
CEMWE limit		**10**	**10**	**1000**
Bottom ashes	Coal	1.95	4.59	4.63
	Coal+MBM	<1.05	<1.01	1.91
	MBM	<1.05	2.58	<1.05
1st cyclone ashes	Coal	<1.05	<1.01	<1.05
	Coal+MBM	<1.05	<1.01	<1.05
	MBM	1.57	2.35	<1.05
2nd cyclone ashes	Coal	<1.05	<1.01	28.6
	Coal+MBM	<1.05	<1.01	1.31
	MBM	3.39	<1.01	2.53

The eluates produced by the ashes have presented low ecotoxicological levels and below the CEMWE limit values. According to CEMWE, the ecotoxicological characterization has led to the classification of all ashes as non-ecotoxic. The bottom ashes produced by combustion of coal have promoted higher ecotoxicity levels probably due to the high pH levels ([16], [14], [17]) or the synergic effect of the factors pH and solubility of heavy metals. The 2nd cyclone ashes have produced eluates with the highest ecotoxicological levels, especially those produced in the combustion of coal. The *P. subcapitata* was particular sensitive to the eluate produced by the 2nd cyclone ashes from the combustion of coal. Further studies are needed to justify this behavior.

3.4. Overall ecotoxicological classification of the ashes according to CEMWE

The ashes produced during the combustion of coal and during the co-combustion test have not shown evidences of ecotoxicity. All ashes produced during the combustion of MBM are ecotoxic, due to the chemical composition of the eluates.

3.5. Classification of ashes according with the Council Decision 2003/33/EC

Table 5 shows the classification of the ashes according the CD 2003/33/EC. All fly ashes require stabilization prior to landfilling, except the 1st cyclone ash produced in the co-combustion test that can be landfilled in a hazardous waste landfill. The bottom ashes produced during the combustion tests were classified as non-hazardous.

Table 5 – Classification of the ashes according to CD 2003/33/EC

Material/Assay		*Classif.*	*Due to…*
Bottom ashes	Coal	N-H	Mo, Se, F^-, SO_4^{2-}, TDS
	Coal+MBM	N-H	Mo, SO_4^{2-}, TDS
	MBM	N-H	Cr, Ni, Cl^-, F^-, SO_4^{2-}, TDS
1st cyclone ashes	Coal	DnA	Mo Se
	Coal+MBM	H	Mo, F^-
	MBM	DnA	Mo
2nd cyclone ashes	Coal	DnA	Mo
	Coal+MBM	DnA	Mo, Se
	MBM	DnA	Mo, Ni, F^-, TDS

N-H: Non Hazardous; H: Hazardous; DnA: Deposition not Allowed

4. Conclusions

The substitution of coal by MBM produced ashes with higher content of heavy metals but with similar leaching rates. According to CEMWE the ashes produced during the combustion of coal and co-combustion test didn't show evidences of ecotoxicity. All ashes produced during the combustion of MBM are ecotoxic due to the chemical composition of the eluates. According to the CD 2003/33/EC, all fly ashes need stabilization prior to landfilling, except the 1st cyclone ash produced in the co-combustion test that was classified as hazardous residues. The bottom ashes were classified as non-hazardous residues. Further studies related with the possible valorization of the ashes are needed.

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