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The synergistic effect in coal/biomass blend briquettes combustion on elements behavior in bottom ash using ICP-OES

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This paper focuses on the study of the synergistic effect in coal/biomass blend briquettes combustion on behavior of Al, As, Ba, Cd, Co, Cr, Cu, Fe, Ga, K, Mn, Mo, Ni, P, Pb, Si, V, W, Zn, Zr and characterization of raw materials and bottom ashes. The manufacturing of coal/biomass briquettes although not commonly used is an attractive approach, as briquettes combustion is more technologically advantageous than the fluidized bed combustion. In the same time this technology is a way to render valuable materials of low calorific power and results in diminishing polluting emission. Raw materials and briquettes from different blends of pitcoal/sawdust were subjected to combustion in a 55 kW-boiler. The total content of elements after digestion in the HNO_3 – HF mixture and the content in water leachate at a solid/liquid ratio of 1:2 were determined both in raw materials and bottom ash by ICP-OES. The total content of elements was higher in pitcoal than in sawdust. The synergistic effect depends both on coal/biomass ratio in blend and element nature. The water leachable fraction of elements from ash decreased along with the increase of sawdust weight excepting macronutrients (K, P) and Si.

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Keywords: Coal/biomass briquettes, Bottom ash, ash leaching, Optical emission spectrometry

1. Introduction

Coal/biomass blends are increasingly important in meeting targets for renewable energy utilization [1-5]. In connection with the EU regulations stipulating the utilization of renewable sources for energy production, Romania will have to triple in the next years its energy production capacities from renewable sources. A promising way is the employment of by-products from wood processing industry as energy source. Although having lower calorific power than coal, biomass is considered an environmentally safe way of providing energy, especially for process heat and district-heating purposes. The use of biomass for industrial purposes is small but is a strategic resource in the effort to fulfill the Kyoto agreement to replace fossil fuels and to mitigate greenhouse gas emissions. The most widespread use of biomass in energy industry is co-combustion with coal by various technologies like cofiring, fluidized bed or in form of briquettes of coal and biomass [5, 6]. Although not commonly used the combustion of coal/biomass briquettes represents an attractive approach to provide energy for industrial and domestic purposes. The advantages are related to similar rate of combustion to that of coal, a uniform combustion, reduced particulate emission. Moreover the same coal combustion facilities can be used without major modifications [7]. The process of briquetting consists of coal and biomass mixing together with a binding substance of residual origin (molasses, oily organic wastes, starch, etc.) than pressing [2, 8]. The ash resulted from coal combustion alone or in mixture with biomass should not be regarded only as waste, since it could be used in industrial and agricultural purposes [5]. Ashes contain heavy metals, which could be released by leaching when residues are disposed on municipal landfill and represent a matter of concern for the environment [9-11]. The concentration of the heavy metals in ash depends on the fuel nature, ash type, namely bottom or fly ash as well as technology of firing [7].

Co-combustion raises the question of combustion products, their influence on environment and the synergistic effects that may change the composition of burning emission and bottom ash. The biomass favors the release of hydrogen sulphide during the thermal treatment. This fact can be explained in terms of the hydrogen-donor character of the biomass [12]. The synergistic effect is also important in relation with both organics and heavy metals. Devolatilization characteristics of coal and biomass blends show synergistic effects regarding the behavior of aromatics and phenols during burning. The amplitude of effects depends on type of coals and biomass in the fuel blend and pyrolysis technique, respectively [13]. The organic compounds of interest in the study of co-combustion effects are: polycyclic aromatic hydrocarbons (PAH), alkyl PAH, phenols, aldehydes, ketones, oxygenated and nitrogenated polycyclic aromatic compounds (*O*-PAC, *N*-PAC), dioxins, polycyclic aromatic sulphur hydrocarbons (PASH), common volatile organic compounds (VOC), inorganic gases (CO, CO_2, SO_x and NO_x) [14, 15]. The synergistic behavior of heavy metals in coal/biomass co-combustion processes is not studied.

Main objective of this study is finding a clean coal utilization combined with biomass (sawdust) as briquettes for energy generation. For this purpose the synergistic effect in pitcoal/sawdust blend briquettes combustion on several elements behavior (Al, As, Ba, Cd, Co, Cr, Cu, Fe, Ga, K, Mn, Mo, Ni, P, Pb, Si, V, W, Zn and Zr) was studied by their monitoring in raw materials and bottom ash using inductively coupled plasma optical emission spectrometry (ICP-OES). The influence of the combustion process was evaluated by determining the total element content and that extracted in water leachates of raw materials and bottom ash. The mass balance of elements allowed the assessment of the elements enrichment in bottom ash.

2. Experimental

2.1 Materials and briquettes manufacturing

The block diagram of the technological process of bio-briquettes manufacturing is presented in Fig. 1. The materials used were granulated pitcoal coming from the Jiului Valley (Roamania) and wastes from wood industry (sawdust of resinous, walnut, oak, etc.). The pitcoal powder and sawdust were dried at 65º C than mixed in different ratios (w/w) in the range of 10-75 % sawdust, molasses and lime as binding additives and the mixture was shaped into briquettes under a pressure of 10 – 30 kN/m^2. The presence of sawdust provided an improved mechanical strength and allowed a higher pressure to be applied in order to lessen the volume of briquettes.

2.2 Burning system

The combustion of pitcoal, sawdust of resinous, beech and oak and briquettes containing pitcoal and resinous sawdust was conducted in a 55 kW-boiler (PIFATI-SA) located within the Laboratory of Boilers and Combustion Installations of the Department of Classic Thermo-mechanic and Nuclear Equipment, University Politehnica Bucharest. Combustion was conducted under natural convection conditions with air in excess. The boiler volume is 0.25 m^3 (750 mm lenghtx550 mm widthx600 mm height). It has a cast iron grid for combustion with a slight slope towards the supply door, [4]. The energy delivered by the boiler provides the warm-up of a space volume of 500 m^3, the equivalent of an individual housing. The amount of the bottom ash decreased along with the increase of the sawdust fraction in the blend subjected to combustion and was in the range of 2.0 – 13.5 % of the combusted weight.

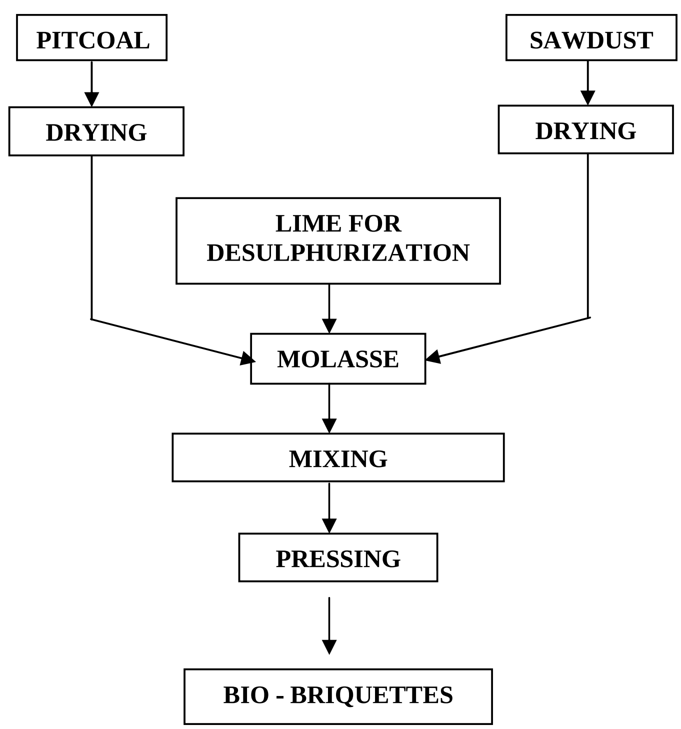

Fig. 1. Block diagram of the technological process of bio-briquettes manufacturing.

2.3 Instrumentation

The determinations were carried out using the ICP multichannel spectrometer SPECTRO CIROS^{CCD} (Spectro Analytical Instruments Kleve, Germany). Details about operating conditions are given in Table 1. The wavelengths and the limits of detection for the ICP - OES are presented in Table 2.

Table 1. Operating parameters for the ICP – OES SPECTRO CIROS^{CCD}.

Equipment	SPECRO CIROS^{CCD}
Generator	Free – runing 27.12 MHz operated at 1400 W.
Plasma torch	Inductively coupled plasma, axial viewing; torch positioning (mm): X = - 3.9; Y = + 3.6; Z = + 2.6. Argon flow rates: Outer gas 12 L min^{-1} Intermediate gas 0.6 L min^{-1} Nebulizer gas 1 L min^{-1}
Sample introduction system	4 channel peristaltic pump, K2 cross – flow nebulizer, double pass Scott type spray chamber. Sample uptake rate: 2 mL min^{-1} Flushing time: 40 s Delay time: 20 s
Optics	160 – 800 nm double grating Paschen – Runge multichannel spectrometer. Chamber filled with Ar.
Detector	22 Charge Coupled Detectors (CCDs)
Data processing	Smart Analyzer Software. Background correction: linear and square two points models, best SNR strategy, integration time 45 s and 3 successive measurements for each parallel sample.

Table 2. Wavelengths and limits of detection (3σ criteria) in ICP - OES.

Element	λ / nm	LOD/ ng ml^{-1}	Element	λ / nm	LOD/ ng ml^{-1}
Al	396.152	4	Mn	257.610	0.4
As	189.042	6	Mo	379.825	10
Ba	455.404	0.2	Ni	341.476	7
Cd	214.438	1	P	213.618	3.5
Co	238.892	1.5	Pb	220.351	35
Cr	283.563	14	Si	212.412	7
Cu	324.754	1.5	V	292.402	4
Fe	261.187	5	W	239.709	20
Ga	403.299	12	Zn	213.856	0.4
K	766.490	11	Zr	343.823	0.1

A mortar grinder Restch RM 100 and a sieve shaker Restch AS 200 (Haan, Germany), an overhead shaker REAX20/8 Heidolph (Kelheim, Germany), a Memmert UFE 500 oven (Schwabach, Germany) and a closed – vessel microwave system Berghof MWS-3+ with temperature control mode (Eningen, Germany) were used during preparation of the analytical samples.

2.4 Reagents and standard solutions

A stock solution of 1000 μg mL^{-1} of Al, Ba, Cd, Co, Cr, Cu, Fe, Ga, K, Mn, Ni, Pb, and Zn and another of 1000 μg mL^{-1} of As, Mo, Si, P, V, W and Zr purchased from Merck (Darmstadt, Germany) were used in this study for preparation of calibration standards. Standard solutions in the range of 0 – 5 μg mL^{-1} element were prepared by serial dilution of the stock standard solutions with 5 % HNO_3 (v/v) and high purity water (18.2 MΩ . cm^{-1}) from a Milli Q system (Millipore, Milford, MA, USA). Ultrapure nitric acid 65 %, Suprapure hydrofluoric acid 40 % purchased from Merck (Darmstadt, Germany), and boric acid 99.9 % purchased from Carlo Erba Reagenti (Milano, Italy) were used for digestion of samples. Argon (5.0 quality) from Linde Gas SRL Cluj – Napoca, Romania was used as working gas for ICP generation.

2.5 Analytical sample preparation

The ash, coal, sawdust and minced briquettes samples were dried in an oven at 105 ± 5^0 C for 2 h. After cooling the samples were sieved through a 4 mm sieve and the remaining fraction was grinded down until more than 95 % of the sample was sieved through. Three replicates of 175 g of sample prepared in such way were leached with high purity water at solid-to-liquid ratio of 1:2. The leaching was performed in a Heidolph shaker at 16 rpm, for 24 ± 0.5 h at 20 ± 2^0 C (SR EN 12457/1:2003). The total content of elements was determined based on 3 replicates of sample (< 250 μm) subjected to the acid digestion using the reagents volumes mentioned in Table 3.

Elements were determined in solutions by ICP-OES.

Table 3. Scheme for sample preparation by microwave digestion for total element content.

Sample	Mass (g)	1st Stage		2nd Stage
		V_{HNO3} 65% (mL)	V_{HF} 40% (mL)	V_{H3BO3} saturated (mL)
Pitcoal	0.2000	9	4	30
Sawdust and briquettes	0.3000	10	3	30
Ash	0.4000	9	4	30

The digestion program in closed PTFE containers of the microwave system is presented in Table 4.

Table 4. Operating conditions for the microwave digestion system.

Ash						
1st Stage					2nd Stage	
	Steps					
Parameter	1	2	3	4	1	2
Temperature / ^{0}C	180	230	230	100	200	100
Ramp time / min	2	2	1	1	5	1
Hold time / min	7	19	19	5	15	15
Power / %*	90	90	90	10	90	10
Coal, sawdust, briquettes						
Temperature / ^{0}C	150	180	180	100	200	100
Ramp time / min	2	2	1	1	5	1
Hold time / min	7	19	19	5	15	15
Power / %*	90	90	90	10	90	10

*100 % power corresponds to 1450 W

3. Results and discussion

3.1 Characterization of raw materials and bottom ashes

The range and average values of major, minor and trace elements in pitcoal, sawdust and bottom ash are summarized in Tables 4-6. The contents of As, Ba, Cd, Co, Cr, Ga, Ni, Pb and W in pitcoal were over the average values for most world coals, while those of Cu, Mo, P, V, Zn and Zr were similar [16]. Among major elements, Al and K occurred in higher concentrations than reported for feed coals used in a power plant in Turkey but Fe fall in the same range [17].

Higher concentrations of both major and trace elements were found in pitcoal than in sawdust used as raw materials in the briquettes manufacturing. The contents of heavy metals found in bottom ash are comparable to those reported in the literature [7]. The major elements (Al, Fe, Si) and some traces (As, Co, Cu, Ni, V, W and Zr) were found in higher concentration in ash resulted from pitcoal, while in sawdust ash elements considered as macronutrients (K, P) as well as Ba, Cd, Cr, Ga, Mn, Mo, Pb and Zn were present in higher concentrations.

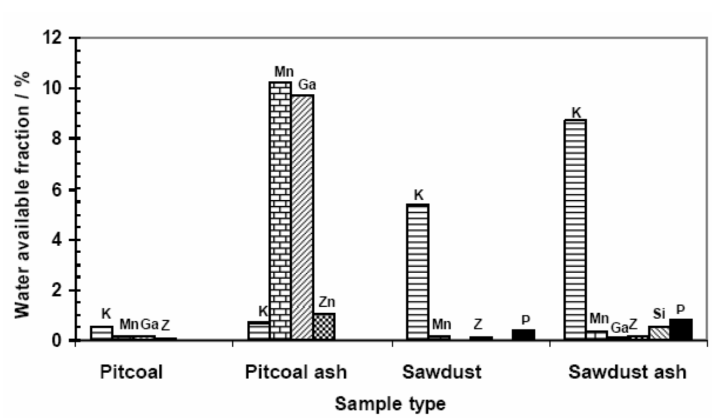

Fig. 2. Comparative extraction degrees in water of several elements from pitcoal, pitcoal ash, sawdust and sawdust ash at a solid/liquid ratio of 1:2.

Table 5. Total content of elements in pitcoal and pitcoal ash samples after acidic digestion (mg/Kg unless indicated otherwise).

	Pitcoal				Pitcoal ash			
Element	Average	Median	Min	Max	Average	Median	Min	Max
% Al	7.4	7.5	6.9	8.0	7.3	7.5	6.6	7.8
% Fe	2.3	2.3	2.2	2.4	2.7	2.7	2.4	3.0
% K	1.7	1.8	1.5	1.9	1.6	1.9	1.0	2.1
% Si	14.1	13.9	12.6	16.0	8.3	9.3	5.9	9.6
As	328	324	309	355	314	323	293	324
Ba	2000	1690	1020	3585	2106	2089	2040	2190
Cd	19	18	18	22	37	36	36	39
Co	240	237	233	252	304	308	273	329
Cr	118	117	105	132	177	173	162	195
Cu	50	51	44	53	411	388	311	534
Ga	272	269	242	307	262	269	232	283
Mn	281	277	248	319	224	228	201	242
Mo	32	33	25	37	35	36	28	41
Ni	110	108	93	129	225	228	204	242
P	476	478	426	521	477	485	438	507
Pb	416	402	383	477	1169	1196	1100	1210
V	87	89	76	96	109	107	96	123
Zn	126	122	98	163	12910	12850	12490	13390
Zr	92	89	77	115	94	94	86	102
W	167	167	158	175	202	209	184	213

Table 6. Total content of elements in sawdust and sawdust ash samples after acidic digestion (mg/Kg unless indicated otherwise).

	Sawdust				Sawdust ash			
Element	Average	Median	Min	Max	Average	Median	Min	Max
% Al	0.25	0.11	0.07	8.8	2.0	5.1	2.4	5.5
% Fe	0.11	0.06	0.04	0.28	1.7	1.6	1.4	2.2
% K	0.28	0.14	0.13	0.80	3.9	4.4	2.1	5.2
% Si	5.6	2.2	1.8	19.8	7.2	6.8	4.0	10.7
As	161	150	145	211	157	152	114	203
Ba	707	403	378	1790	6900	6900	5670	8135
Cd	6	5	4	10	41	46	22	55
Co	3	3	1	5	224	233	200	240
Cr	5	6	1	7	352	403	185	470
Cu	3	3	2	5	170	178	127	205
Ga	22	21	3	48	1290	1290	782	1805
Mn	41	15	1	150	1080	1030	610	1605
Mo	12	11	11	19	42	39	28	57
Ni	11	7	3	22	39	45	3	114
P	98	65	51	183	2380	1900	1850	3400
Pb	157	152	128	207	4210	4090	3390	5155
V	3	4	1	5	52	48	44	62
Zn	41	32	15	80	21400	19870	19495	24850
Zr	56	19	14	212	71	67	50	95
W	18	6	6	64	137	156	86	170

The supraunitary ratio of elements concentrations in ash/raw material, higher for sawdust than pitcoal, shows a grater enrichment of elements in sawdust ash.

The analysis of raw materials and corresponding bottom ash leachates revealed an increase of water mobility following combustion for most of elements. Element release was higher from pitcoal ash compared to sawdust ash excepting K, P and Si (Fig. 2). In relation with OM 95/2005 regarding waste classification, bottom ashes comply with requirements for non-dangerous waste and could be used as amendments on agricultural land.

Table 7. Total content of elements in briquettes and briquettes ash after acidic digestion (mg/Kg unless indicated otherwise).

	Briquettes				Briquettes ash			
Element	Average	Median	Min	Max	Average	Median	Min	Max
% Al	6.7	7.0	6.0	7.2	6.3	6.3	5.0	7.4
% Fe	1.7	1.8	1.4	1.9	1.7	1.5	1.4	2.4
% K	1.4	1.3	1.2	1.6	1.9	2.2	1.0	2.6
% Si	8.5	8.5	7.7	9.4	11.8	11.6	11.1	12.8
As	224	237	187	246	200	195	167	233
Ba	855	840	820	905	2890	2730	1960	4150
Cd	12	17	4	17	26	29	20	30
Co	170	200	114	201	200	175	170	283
Cr	83	94	58	98	114	62	59	275
Cu	45	51	30	55	91	93	80	99
Ga	147	175	80	186	1950	2380	367	2670
Mn	146	160	115	166	1550	1880	355	2080
Mo	24	27	13	31	28	17	24	35
Ni	93	134	3	141	104	78	75	184
P	265	272	236	290	2140	2390	1205	2575
Pb	263	390	9	395	960	754	715	1630
V	66	69	57	73	61	43	41	116
Zn	247	305	93	345	6960	4750	4135	14200
Zr	60	61	55	62	63	53	51	97
W	105	112	78	126	190	184	183	200

3.2 Synergistic effect in pitcoal-sawdust blend combustion

In order to study the fate of elements during combustion of pitcoal/sawdust blends, their concentrations were determined in the bottom ashes resulted from briquettes containing 0; 10; 25; 50; 75 and 100% sawdust. Results are plotted in Fig. 3. According to [18], when the content of an individual component in the combusted product is linearly proportional to the blending ratio there is no synergistic effect between coal and biomass over the selected range of experimental conditions

As shown in Fig. 3, the synergistic effect on elements behavior during combustion of pitcoal/sawdust blend was complex depending on the composition of the mixture subjected to burn and element type. For a group of nine elements (Al, As, Cd, Co, Cr, Fe, K, Ni and V) the synergistic effect was the highest. For this group of elements it was observed a maximum content in the bottom ash for briquettes containing 25-50% sawdust. For the rest of elements (Ba, Cu, Ga, Mn, Mo, P, Pb, Si, W, Zn and Zr) the synergistic effect was less evident since their concentration in bottom ash increased almost continuously with the increase of the sawdust weight in the blend. Generally, the synergistic effect decreased with the increase of sawdust fraction in the briquettes. The range of recovery degrees of elements in bottom ash calculated based on amounts corresponding to parent material and ash is presented in Table 8.Elements can be divided into two groups considering their recovery degrees in bottom ash. To the first group belong elements of high recovery degree (Fe, Ba, Cd, Co, Cr, Cu, Ga, K, P, Pb, V, Zn), generally retained on Fe compounds. The second group comprises elements with lower recovery degree bound mainly to Al and Si (Al, Si, As, Mo, Mn, Ni, W, Zr) suggesting that high amounts of them are volatilized during combustion and evacuated along with the gaseous products. The development of volatile compounds of As during combustion is responsible for its low recovery degree in bottom ash. Although considered as refractory elements Al, Mo, W, Si and Zr sublimate probably during combustion in a significant extent. From the point of view of elements enrichment in bottom ash, the manufacturing of briquettes containing 75% pitcoal and 25% resinous sawdust seems advantageous. The recovery degrees of elements in ash from the combustion of a briquettes charge with this composition are shown in Fig. 4.

According to Fig. 4, recovery degrees over 20% were found for Ba, Cd, Cu, Ga, K, P, Pb and Zn in bottom ash of briquettes and were within the range of those obtained for the bottom ashes of different mixtures of parent materials.

The synergistic effect on elements availability from bottom ash resulted from briquettes combustion was investigated based on the extraction degrees in water related to total contents. The extraction degrees for several elements from bottom ash in water for a solid/liquid ratio 1:2 are presented in Fig. 5.

The synergistic effect is observable through the non-linear change in the extraction degree of elements from ash in water along with the composition of the blend subjected to burn. The leachability of elements seen as essential plant nutrients (K, P) increased up to 8 and 0.8% respectively as the biomass fraction in the blend increased. The reason is that these elements are absorbed from soil by plants as water soluble species and are found further in ash also in soluble form. The extraction degree of Si from sawdust bottom ash in water was appreciable and could seem anomalous at first sight, however it agrees with literature data. The soil water contains Si as silicic acid in concentration on the order of major plant nutrients and is readily absorbed together with macronutrients. Consequently Si concentration in plants is appreciable ranging from 1 to 10 % or even higher [19]. The water availability of other elements from pitcoal ash was (%): 10 (Ga, Mn), 1 (Zn), 0.5 (Co), 0.2 (Cd), 0.1 (Cu) and decreased as the sawdust in the mixture increased. The same tendency was found for elements with possible toxic effect (As, Cd, Pb) but with water extraction degrees below 0.01 %.

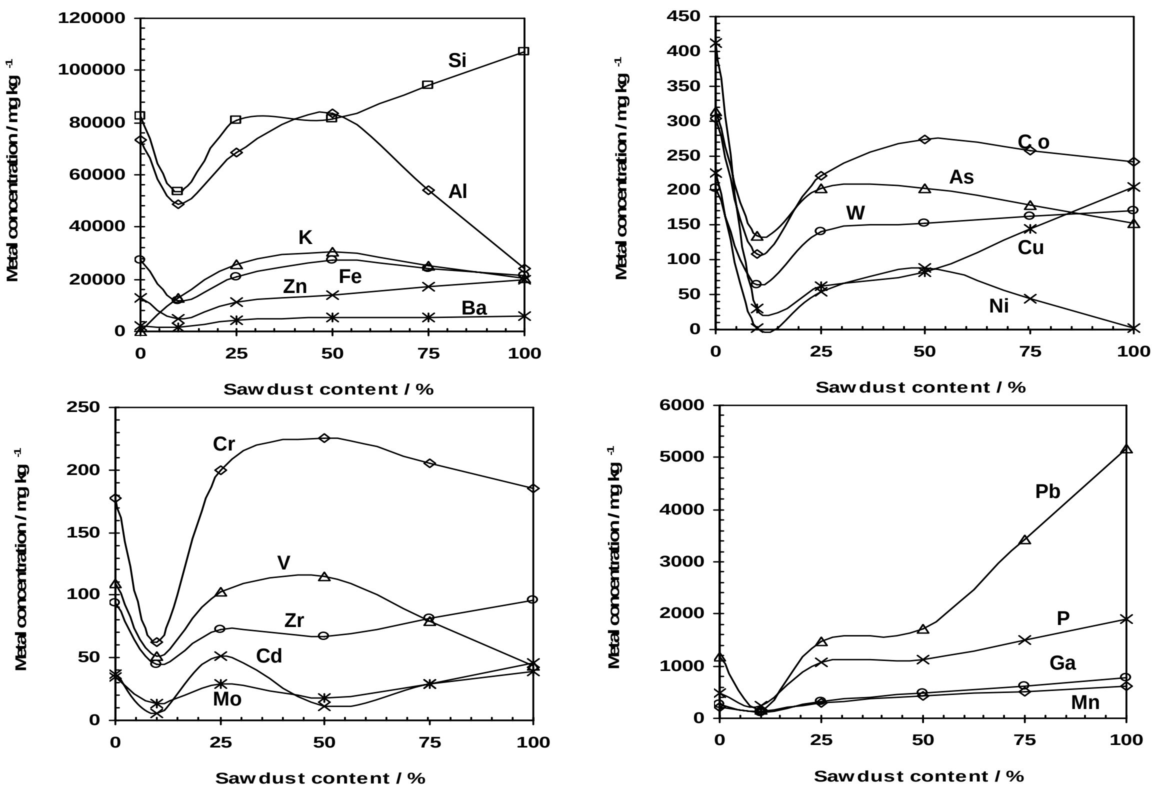

Fig. 3. Total element contents in bottom ash from combustion of briquettes of different compositions.

Table 8. Range of recovery degrees (%) of elements in bottom ash from combustion of briquettes.

Element	Average	Median	Minimum	Maximum	Element	Average	Median	Minimum	Maximum
Al	31.9	23.3	14.9	62.4	Cd	55.7	65.8	17.9	93.1
K	50.7	58.7	5.2	93.1	Ba	42.9	28.8	16.0	86.4
Cr	47.8	43.5	17.8	85.5	Pb	71.1	74.8	37.3	91.6
Mn	31.0	27.7	12.1	62.4	Si	23.6	23.5	11.2	38.7
Fe	48.5	38.8	18.2	92.7	P	50.2	41.5	15.2	94.1
Co	42.9	38.1	15.3	72.4	V	48.7	48.6	18.9	80.4
Ni	33.0	31.2	18.5	48.1	As	15.5	15.2	2.9	24.1
Cu	67.4	75.9	20.2	95.5	Zr	18.5	15.4	6.8	27.9
Zn	40.9	39.5	19.8	71.3	Mo	24.2	16.4	13.8	42.3
Ga	42.3	44.9	13.7	91.8	W	36.2	34.5	18.4	54.8

The element fractions extracted in water from bottom ash of briquettes containing 75% pitcoal and 25% resinous sawdust are plotted in Fig. 6. The extraction degrees in water of elements from bottom ash of briquettes containing 75% pitcoal and 25% resinous sawdust (Fig.6) were similar to those obtained in the analysis of the ashes presented above (Fig.3). The extraction degrees of toxic elements such as As, Cd and Pb were very low as a result of their presence as water insoluble species in ash.

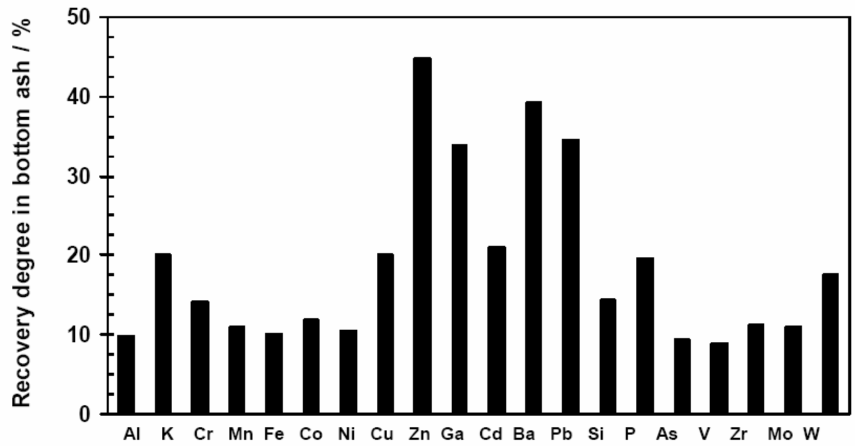

Fig. 4. Recovery degrees of elements in bottom ash from combustion of briquettes containing 75 % picoal and 25 % resinous sawdust.

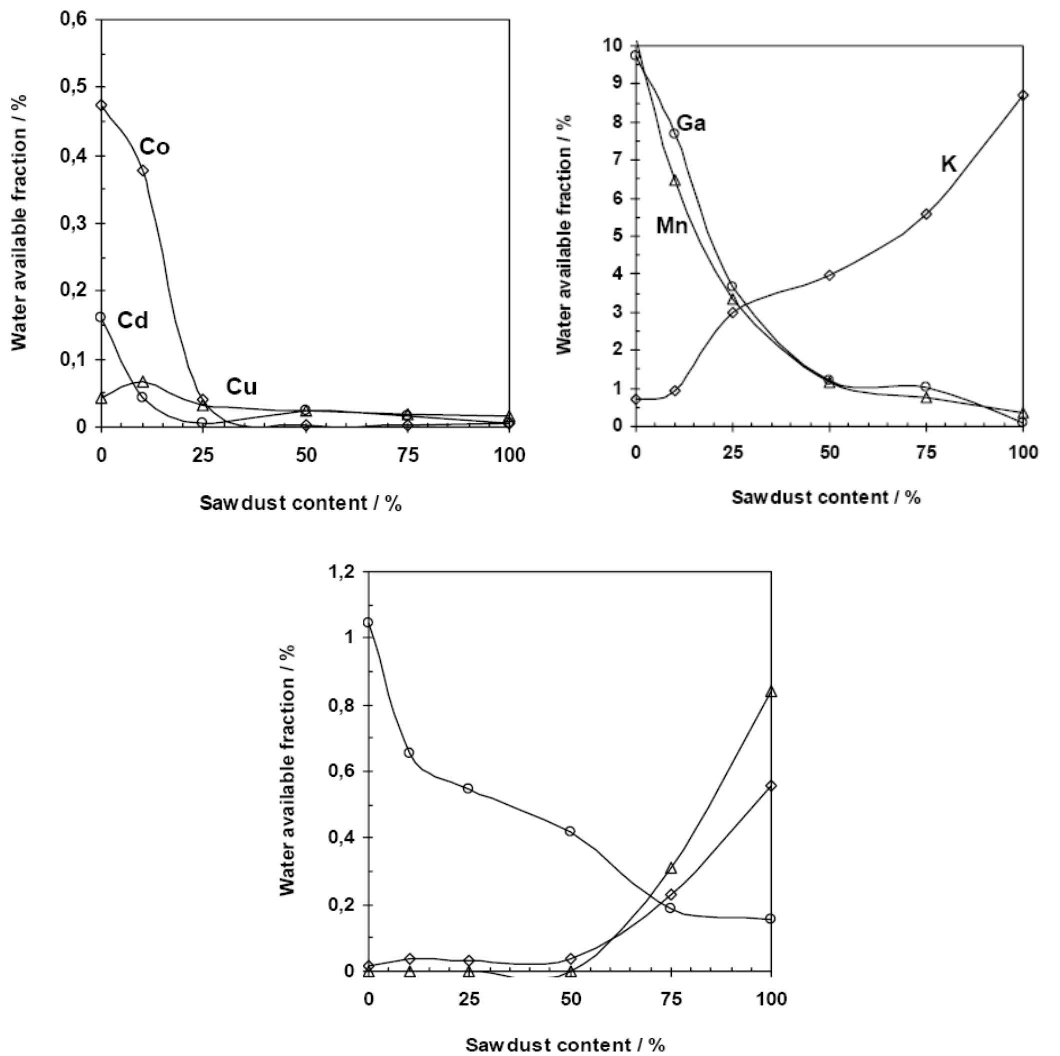

Fig. 5. Extraction degrees of elements from bottom ash by water leaching for a solid/liquid ratio 1:2

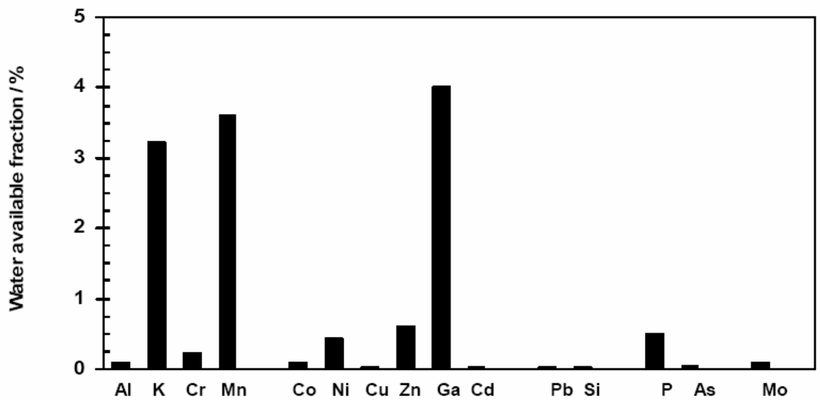

Fig. 6. Extraction degrees of elements by water leaching of ash resulted from briquettes containing 75% pitcoal and 25% resinous sawdust for a solid/liquid ratio 1:2

4. Conclusions

The study demonstrates that the synergistic effect in coal/biomass briquettes combustion on the total content and water leachable fraction of elements in bottom ash depends on the combusted blend and element type. The synergistic effect was higher for Al, As, Cd, Co, Cr, Fe, K, Ni, V and lower for Ba, Cu, Ga, Mn, Mo, P, Pb, Si, W, Zn and Zr. Characterization of parent materials emphasized a total content of elements in pitcoal higher than in sawdust. The enrichment of elements was higher in sawdust bottom ash compared to pitcoal. The mass balance revealed recovery degrees in bottom ash up to 70-95 % for Ba, Cd, Co, Cr, Cu, Fe, Ga, K, Pb, V and Zn and lower, up to 30-50% for As, Al, Mn, Mo, Ni, Si, W, Zr. The leachability study emphasized higher extraction degrees for Cd, Co, Cu, Ga, Mn and Zn in pitcoal bottom ash and their decrease along with the increase of the biomass fraction in the combusted blend. The extraction degrees of macronutrients (K, P) and Si were maximum for sawdust ash. For the rest of elements under study, of which some toxic (As, Cd, Pb), extractions were below 0.01%, corresponding to concentrations below those stipulated by the legislation covering the transport, storage and disposal of wastes. The manufacturing of coal/biomass blend briquettes provides a promising approach to render valuable materials of low calorific power ensuring in the same time environment protection against pollution with toxic elements as easily water leachable species.

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