Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Trace elements partitioning during co-firing biomass with lignite in a pilot-scale fluidized bed combustor

Zuhal Gogebakan¹, Nevin Selçuk*

Department of Chemical Engineering, Middle East Technical University, 06531 Ankara, Turkey

ARTICLE INFO

Article history: Received 25 January 2008 Received in revised form 30 May 2008 Accepted 30 May 2008 Available online 7 June 2008

Keywords: Lignite Biomass Co-firing Trace element Partitioning

ABSTRACT

This study describes the partitioning of 18 trace elements (As, Ba, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, Tl, V, Zn) and 9 major and minor elements (Al, Ca, Fe, K, Mg, Na, S, Si, Ti) during co-firing of olive residue, hazelnut shell and cotton residue with high sulfur and ash content lignite in 0.3 MWt Middle East Technical University (METU) Atmospheric Bubbling Fluidized Bed Combustor (ABFBC) test rig with limestone addition. Concentrations of trace elements in coal, biomass, limestone, bottom ash, cyclone ash and filter ash were determined by inductively coupled plasma optical emission and mass spectroscopy (ICP-OES and ICP-MS). Partitioning of major and minor elements are influenced by the ash split between the bottom ash and fly ash and that the major proportion of most of the trace elements (As, Ba, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Tl, V and Zn) are recovered in fly ash when firing lignite only. Co-firing lignite with biomass enhances partitioning of these elements to fly ash. Co-firing also shifts the partitioning of Cd, P, Sb and Sn from bottom to fly ash.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Co-firing applications of biomass with coal in fluidized bed combustors have been steadily increasing in both capacity and number over the past decade for reducing pollutant emissions. However, gradual introduction of increasingly restrictive legislations on emissions from combustion sources and increasing public concern relating to the emissions of trace elements has been keeping the topic attractive for further research.

There are a few studies on the trace elements and their partitioning behavior in fluidized bed combustion systems co-firing coals with different sustainable fuels, mainly wastes, carried out in beds of sand [1–7]. However, trace elements behavior in systems co-firing coals with biomasses such as olive residue, hazelnut shell and cotton residue has not been carried out to date.

There exist 9.3 billion tons of indigenous lignite reserves characterized by low calorific value and high ash and sulfur contents. Moreover, Turkey is the leading producer of hazelnut and one of the lead producers of cotton and olive in the world. Availability of significant amounts of olive residues, hazelnut shells and cotton residues and indigenous lignite reserves make the co-firing option attractive. Olive residue is a specific type of biomass from olive oil production process. It is the remaining part of olives after pressing and extraction of olive oil. Hazelnut shells are the residues of hazelnut crushing plants. Cotton residues are produced from cotton oil production process. Cotton is grown mainly for the fibers or lint, but cotton seeds having high amount of oil content are also very important. Lint and fiber of the cotton are removed firstly by hand and then mechanically by ginning process. The remaining part, cotton seed, is then extracted for cotton oil.

Absence of data on trace element behavior of fluidized bed combustion systems co-firing indigenous lignite with olive residue/hazelnut shell/cotton residue blends, on one hand, and the recent trend in utilization of biomass with local reserves in industry and utility boilers, on the other, necessitate investigation of fluidized bed combustion characteristics of these fuel blends with respect to trace element partitioning.

In an attempt to achieve this objective, a typical Turkish lignite with high ash and sulfur contents was co-fired with different types of biomass in the 0.3 MW_t Middle East Technical University (METU) Atmospheric Bubbling Fluidized Bed Combustor (ABFBC) test rig with limestone addition and partitioning behavior of major and minor ash components and trace elements was investigated.

2. Experimental

This study is based on experimental data collected as part of a research project for the investigation of combustion and gaseous





^{*} Corresponding author. Tel.: +90 312 210 2603; fax: +90 312 210 2600. *E-mail addresses*: zuhalgogebakan@hotmail.com (Z. Gogebakan), selcuk@metu.edu.tr (N. Selçuk).

¹ Tel: +90 312 210 4387, Fax: +90 312 210 2600.

^{0304-3894/\$ -} see front matter © 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2008.05.149



Fig. 1. METU 0.3 MWt ABFBC test rig.

emission characteristics of biomass co-fired with low quality lignite having high ash and sulfur contents. Tests were carried out on the 0.3 MWt ABFBC test rig located in the Chemical Engineering Department of Middle East Technical University.

2.1. Combustor

Fig. 1 shows the flow sheet of the 0.3 MW_t ABFBC test rig. As can be seen from the figure, the test rig basically consists of a forced draft (FD) fan, a windbox with an ash removal system, a modu-

Table 1

Characteristics of fuels

lar combustor, a cyclone with a recycle leg, a baghouse filter, an induced draft (ID) fan and a coal and limestone feeding system. The main body of the test rig is the modular combustor formed by five modules of internal cross-section of $0.45 \text{ m} \times 0.45 \text{ m}$ and 1 m height. Inner walls of the modules are refractory lined and insulated. The first and fifth modules from the bottom refer to bed and cooler, respectively, and the ones in between are the freeboard modules. There exist two cooling surfaces in the modular combustor, one in the bed and the other in the cooler providing 0.35 and 4.3 m^2 of cooling surfaces, respectively. There are 14 ports for

	Lignite				Olive residue	Hazelnut shell	Cotton residue	
	Test 1	Test 2	Test 3	Test 4				
Proximate analysis (as	received basis, % by	wt)						
Moisture	16.48	16.75	17.14	17.47	6.07	7.62	6.93	
Ash	26.74	23.89	27.46	24.29	4.24	1.46	5.38	
Volatile matter	31.05	32.04	30.36	31.44	75.69	73.04	75.57	
Fixed carbon	25.74	27.33	25.04	26.80	14.00	17.89	12.13	
LHV (MJ/kg)	13.3	14.0	12.5	13.4	18.1	17.5	17.4	
d_{32} (mm)	0.58	0.59	0.47	0.48	0.36	5.88	1.85	
$\rho_{\rm p} ({\rm kg}/{\rm m}^3)$	1508	1508	1508	1508	985	533	607	
Ultimate analysis (dry	basis, % by wt)							
Carbon	44.93	44.83	41.92	40.04	50.22	49.77	46.79	
Hydrogen	4.09	4.00	4.01	3.84	6.38	5.86	6.48	
Nitrogen	1.14	1.20	0.96	0.98	1.72	0.56	4.40	
Oxygen	13.96	17.66	15.64	21.42	37.03	42.15	36.23	
Sulfur	3.86	3.61	4.33	4.29	0.14	0.08	0.32	
Ash	32.02	28.70	33.14	29.43	4.51	1.58	5.78	

Tal

 Table 2

 Ash analyses of fuels. % by wt

	Lignite			Olive	Hazelnut	Cotton	
	Test 1	Test 2	Test 3	Test 4	residue	shell	residue
SiO ₂	56.56	52.70	51.91	50.11	31.19	2.28	0.00
Al_2O_3	17.49	19.14	21.83	22.57	5.29	2.59	0.81
Fe ₂ O ₃	10.99	11.26	12.15	11.46	5.17	7.11	4.95
CaO	9.21	7.78	7.92	7.79	17.52	38.84	10.83
MgO	0.57	0.52	0.58	0.55	2.51	6.60	14.77
SO₃	2.05	5.23	2.31	4.24	2.64	5.50	0.00
Na ₂ O	1.45	1.62	1.60	1.51	5.21	7.40	10.29
K ₂ O	0.31	0.21	0.33	0.18	27.95	27.86	57.51
TiO ₂	1.38	1.54	1.37	1.58	2.52	1.81	0.85

thermocouples and 10 ports for gas sampling probes along the combustor. Two ports for feeding coal/biomass/limestone mixture are provided in the bed module, one 0.22 m, the other 0.85 m above the distributor plate.

In order to measure the concentrations of O_2 , CO, CO_2 , SO_2 , NOand N_2O along the combustor and also downstream of cyclone at steady state, combustion gas is sampled by gas sampling probes and transferred to gas conditioning system through a heated line, where the sample is filtered, dried and cooled. Sampled gas then passes through two analyzers in series, ABB Advanced Optima 2000 and Siemens Ultramat 6, respectively. In ABB Advanced Optima 2000, O_2 concentration is measured by a magneto-mechanical analyzer module Magnos 106 whereas CO, CO_2 , NO and N_2O concentrations are measured by an infrared analyzer module Uras 14. In Siemens Ultramat 6, SO_2 concentration is measured by nondispersive infrared module.

The output signals from analyzers and process values such as temperatures, air and water flow rates, pressures and speed of screw conveyors are logged to a PC by means of a data acquisition and control system, Bailey INFI 90. Further details of the test rig are given in elsewhere [8].

2.2. Co-firing tests

In order to investigate partitioning behavior of trace elements during co-firing of a typical low calorific value and high ash content lignite with various biomass types in fluidized bed combustor, four tests were carried out. In the first test lignite was fired with limestone addition only in order to form a base case for co-firing runs. In following tests, lignite was co-fired with olive residue, hazelnut shell and cotton residue. Characteristics of the lignite and biomasses burned in the tests are summarized in Tables 1 and 2. In all tests, the lignite was burned in its own ash due to its high ash content (\sim 25%). Inert bed material utilized in all tests was bed ash obtained previously from combustion of the same lignite in the same test rig. Characteristics of limestone added are given in elsewhere [9]. Trace element concentrations in coal, biomasses and limestone were determined by a microwave-assisted acid digestion followed by inductively coupled plasma optical emission spectrometry and mass spectrometry (ICP-OES and ICP-MS, respectively). A combination of nitric, hydrochloric and hydrofluoric acid was employed in microwave oven followed by boric acid addition for removal of the hydrofluoric acid from the reaction mixture [10].

The microwave digestion was carried out by using Anton Paar Multiwave 3000 oven. ICP-OES and ICP-MS measurements were performed using PerkinElmer Optima 4300 DV and PerkinElmer DRC II, respectively. Trace element concentrations of lignite, biomasses and limestone used in the tests are given in Tables 3–5, respectively.

Table 6 lists the operating conditions of the tests. Lignite was firstly burned with limestone addition, and then co-fired with olive

ole	3
-----	---

	Test 1	Test 2	Test 3	Test 4	Detection limit
ICP-MS					
As	46.1 ± 0.9	41.6 ± 0.5	52.7 ± 0.3	65.7 ± 0.5	0.01
Ba	89.5 ± 2.7	98.0 ± 1.1	94.8 ± 0.8	108.4 ± 0.9	0.008
Cd	0.108 ± 0.002	0.106 ± 0.004	0.114 ± 0.002	0.185 ± 0.008	0.002
Со	5.03 ± 0.08	5.48 ± 0.08	5.57 ± 0.16	5.93 ± 0.08	0.002
Li	23.9 ± 1.0	23.1 ± 0.7	$\textbf{28.8} \pm \textbf{0.7}$	27.0 ± 0.9	0.008
Mo	3.70 ± 0.01	4.02 ± 0.08	4.39 ± 0.08	4.09 ± 0.08	0.002
Pb	16.26 ± 0.54	16.59 ± 0.08	12.29 ± 0.16	21.38 ± 0.16	0.017
Sb	0.48 ± 0.04	0.58 ± 0.02	0.414 ± 0.002	0.49 ± 0.02	0.02
Se	< 0.18	<0.18	<0.18	<0.18	0.18
Sn	2.41 ± 0.04	4.22 ± 0.12	1.98 ± 0.04	3.60 ± 0.32	0.008
Tl	0.777 ± 0.004	$\textbf{0.832} \pm \textbf{0.004}$	0.581 ± 0.004	0.604 ± 0.080	0.003
ICP-OE	S				
Cr	6.6 ± 0.1	13.2 ± 0.1	6.4 ± 0.1	6.6 ± 0.3	0.007
Cu	54.0 ± 0.3	57.1 ± 0.2	49.0 ± 1.0	52.7 ± 1.7	0.01
Mn	110.0 ± 1.0	114.0 ± 0.5	96.0 ± 1.0	106.2 ± 0.3	0.0014
Ni	<0.015	5.3 ± 0.3	<0.015	<0.015	0.015
Р	75.9 ± 2.1	50.3 ± 1.3	47.1 ± 1.5	58.5 ± 3.0	0.08
V	112.1 ± 0.5	121.9 ± 2.0	114.0 ± 1.0	111.4 ± 1.1	0.009
Zn	$\textbf{39.3} \pm \textbf{1.3}$	39.9 ± 0.3	34.7 ± 0.1	34.7 ± 0.7	0.006

residue, hazelnut shell and cotton residue at 49, 42 and 41 wt% shares in their own ashes. The operating parameters other than biomass type were tried to be maintained constant from one test to another. Feed point location was 0.22 m above the distributor plate for all tests.

3. Results And discussion

3.1. Recovery rates

Ash recovery rates for Tests 1, 2, 3 and 4 were found to be 92, 93, 94 and 103%, respectively. Compared to the ash recovery rates reported in the literature [2,7,9] and considering the difficulty in closing the total solid mass balances over the fluidized bed combustors, the closure of the total ash balances is acceptable in all tests. However, deviation in the total mass balance from 100% was taken into account in order not to reflect the imbalance in the total mass balance to the species mass balances [2,7,9].

Table 4

Trace element concentrations in biomasses, mg/kg, on dry basis

	Olive residue Hazelnut shell		Cotton residue	Detection limit
ICP-MS				
As	0.72 ± 0.02	0.29 ± 0.02	0.12 ± 0.01	0.01
Ba	14.7 ± 0.1	18.2 ± 0.2	2.27 ± 0.02	0.008
Cd	0.017 ± 0.001	0.040 ± 0.001	0.022 ± 0.001	0.002
Со	0.527 ± 0.005	0.380 ± 0.005	0.472 ± 0.004	0.002
Li	0.776 ± 0.005	0.118 ± 0.005	0.136 ± 0.004	0.008
Mo	0.25 ± 0.01	0.13 ± 0.01	1.61 ± 0.01	0.002
Pb	3.24 ± 0.01	3.53 ± 0.04	1.22 ± 0.02	0.017
Sb	0.144 ± 0.001	0.066 ± 0.001	0.028 ± 0.001	0.02
Se	<0.18	<0.18	<0.18	0.18
Sn	0.616 ± 0.006	0.110 ± 0.005	1.455 ± 0.014	0.008
Tl	0.016 ± 0.001	<0.003	<0.003	0.003
ICP-OES				
Cr	8.98 ± 0.11	1.82 ± 0.03	2.23 ± 0.01	0.007
Cu	15.3 ± 0.2	7.9 ± 0.2	11.3 ± 0.1	0.01
Mn	26.2 ± 0.2	106.3 ± 0.4	17.1 ± 0.1	0.0014
Ni	5.1 ± 0.1	1.97 ± 0.02	2.8 ± 0.1	0.015
Р	907 ± 10	146 ± 3	7361 ± 97	0.08
V	2.91 ± 0.02	1.05 ± 0.03	5.3 ± 0.4	0.009
Zn	14.8 ± 0.1	22.7 ± 0.2	32.2 ± 0.1	0.006

Table 5

Trace element concentrations in limestone, mg/kg, on dry basis

			L	imest	one					Detection limi
ICP-MS										
As		10.4 ± 0.4						0.01		
Ba		97.7 ± 1.6						0.008		
Cd		0.062 ± 0.001						0.002		
Со			1	$.08\pm0$	0.02					0.002
Li			1	7.1 ± 0).2					0.008
Mo			0	$.97 \pm 0$	0.01					0.002
Pb			5	.20±	0.05					0.017
Sb			0	.302 ±	0.014	ŀ				0.02
Se			<	0.18						0.18
Sn			2	.22±	0.04					0.008
Tl			0	.168 ±	0.009)				0.003
ICP-OES										
Cr		9.2 ± 0.1							0.007	
Cu			1	1.1 ± 0).1					0.01
Mn			4	7.6 ± 0	0.1					0.0014
Ni			5	$.9 \pm 0.1$.1					0.015
Р			5	9 ± 1						0.08
V		9.3 ± 0.1						0.009		
Zn			8	$.3 \pm 0.$.3					0.006
	~									
15	0									
			i i	ш	п				al I	
12	5-	ſ	N	ш				1	ш	
				н					١.	
° 10	0-			н						
<u>S</u>	1	nl		ш						
9 7	5-			ш				n N		
8				ш						
age 25	0-			n	IIIn					
2	5 -									Test 1
2										Test 2
										Test 3
	A	Ca	Fe	K	Ma	Na	S	Si	Ti	rest 4



Fig. 2 shows the recovery rates of major and minor ash components for all tests. As can be seen from the figure, the closure is fairly good for most of the components except for Na, K, Mg and S. Recovery rates of trace elements are given in Figs. 3 and 4. The imbalances are observed in the species mass flow rates. These imbalances could result from analyzing very small quantity of sample from large quantities of highly heterogeneous matter, very low concentrations of elements under investigation, analytical errors

Table 6

Operating conditions



Fig. 3. Trace elements recovery rates (from left to right, first bar: Test 1, second bar: Test 2, third bar: Test 3, fourth bar: Test 4).



Fig. 4. Trace elements recovery rates (from left to right, first bar: Test 1, second bar: Test 2, third bar: Test 3, fourth bar: Test 4).

and experimental errors in preparing the samples for ICP-OES and ICP-MS analyses or a combination of all [11].

3.2. Partitioning of major and minor elements

Major and minor element concentrations of bottom, cyclone and filter ashes during the fluidized bed combustion of lignites with and without biomass addition are given in Tables 7 and 8. As can be seen from the tables, order of magnitudes of all ash component concentrations remain the same with addition of olive residue, hazelnut shell and cotton residue.

Fig. 5 displays the partitioning of major and minor ash components in bed, cyclone and filter ashes for the runs under consideration. As can be depicted from the figure, the partitioning

Parameter	Test 1 Lignite	Test 2 Lignite + olive residue	Test 3 Lignite + hazelnut Shell	Test 4 Lignite + cotton residue
Coal flow rate (kg/h)	69	30	32	36
Biomass flow rate (kg/h)	0	29	23	25
Limestone flow rate (kg/h)	22	11	14	13
Ca/S molar ratio (added)	3	3	3	3
Bed drain flow rate (kg/h)	8	1.5	2.2	0.0
Cyclone ash flow rate (kg/h)	19	11	12	18
Baghouse ash flow rate (kg/h)	1.2	1.7	1.9	0.0
Air flow rate (kmol/h)	14	14	14	15
Excess air (%)	21	28	22	21
Superficial velocity (m/s)	1.9	1.9	1.9	2.0
Average bed temperature (°C)	848	852	854	857
Average freeboard temperature (°C)	817	849	835	843
Bed height (m)	1.1	1.1	1.1	1.2
Bed pressure drop (cm H_2O)	63	61	60	63

Table 7	
Major and minor element concentrations in Tests 1 and 2, % by wt, on dry bas	is

	Test 1			Test 2			
	Bottom ash	Cyclone ash	Filter ash	Bottom ash	Cyclone ash	Filter ash	
SiO ₂	32.74	23.27	32.19	28.75	19.58	22.21	
Al_2O_3	16.09	8.04	9.69	13.28	7.51	8.49	
Fe_2O_3	5.68	7.40	12.61	5.49	6.67	14.29	
CaO	28.30	39.96	22.95	31.25	45.10	27.80	
MgO	1.60	4.61	1.40	1.80	4.63	3.11	
SO ₃	11.99	13.47	17.80	15.61	12.65	18.79	
Na ₂ O	1.23	1.36	1.14	1.19	1.60	2.37	
K ₂ O	1.17	0.97	0.51	1.27	1.43	1.19	
TiO ₂	1.20	0.91	1.72	1.37	0.83	1.76	

of major and minor ash components follow the ash split between the bottom ash and fly ash. For the experiments and the test rig under consideration ash splits to fly ash were found as 71, 89 and 87% for Tests 1, 2 and 3, respectively. Comparison between ash split to fly ash values for lignite only and lignite co-fired with biomasses shows that ash split to fly ash increases by about 20 percentage points when lignite is co-fired with biomasses. This is considered to be the reason behind enhancement of major and minor elements partitioning to fly ash.

3.3. Partitioning of trace elements

Concentration of Se (<0.18 mg/kg) could not be measured as its concentration was below the detection limits of the instrument. Hg concentration could not be quantified by ICP techniques because it is volatilized during the sample preparation procedure [12]. To compare the trace element concentrations in bottom, cyclone and filter ashes, relative enrichment factors (REs) were calculated.

Table 8

Major and minor element concentrations in Tests 3 and 4, % by wt, on dry basis

	Test 3			Test 4			
	Bottom ash	Cyclone ash	Filter ash	Bottom ash	Cyclone ash	Filter ash	
SiO ₂	27.52	31.51	27.60	24.62	17.52	32.16	
Al_2O_3	12.42	7.96	8.42	7.94	2.45	5.98	
Fe ₂ O ₃	4.88	6.98	14.68	4.30	6.89	17.52	
CaO	37.93	31.48	27.46	39.95	53.10	22.91	
MgO	1.34	2.06	1.95	1.93	1.89	1.54	
SO₃	12.58	15.94	15.27	18.08	15.93	15.81	
Na ₂ O	1.01	1.46	1.55	1.15	0.36	1.97	
K ₂ O	1.10	1.31	1.02	0.89	1.10	1.07	
TiO ₂	1.22	1.30	2.04	1.13	0.76	1.05	

Table	9
-------	---

Relative enrichment factors of trace elements in bottom and fly ashes



Fig. 5. Partitioning of major and minor elements (from left to right, first bar: Test 1, second bar: Test 2, third bar: Test 3).

Relative enrichment factor is defined as the ratio of element concentrations in ash to coal multiplied by the ash content in coal [13].

The enrichment factors of trace elements in bottom and filter ashes are given in Table 9. As can be seen from the table, volatile elements As, Ba, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Tl, V and Zn are mostly enriched in fly ash. These findings are in accordance with the previous studies on coal firing [7,9,14] and biomass mixture and coal co-firing [15]. The relative enrichment factors of As, Co, Cu, Mn, Mo, Tl, V and Zn are found to be lower than 0.7 in all bottom ashes and hence fall into Class II elements which are enriched in fly ash [13]. During cotton residue co-firing run, relative enrichment factors were found to be only slightly lower due to low trace element concentrations within the ash streams.

Li which is a non-volatile element due to its high boiling point $(1342 \,^{\circ}C)$, was found to enrich in fly ash in all tests. This may be due to the fact that Li melts and coalesces with the alumina silicates to become a part of fly ash [11].

Although, species mass balances over the fluidized bed combustor could not be closed, some light could be shed to the fate of trace elements in fluidized bed combustion of high ash content low quality lignites with biomasses by investigating their partitioning behavior.

Figs. 6 and 7 illustrate the partitioning of trace elements in bed, cyclone and filter ashes. For each ash component first, second and third columns refer to Tests 1, 2 and 3, respectively. The major proportions of As, Cr, Mn, Ni, Pb, V and Zn were recovered in the cyclone ash for all runs. This finding complies with the data for coal com-

	Test 1		Test 2		Test 3		Test 4	
	Bottom ash	Fly ash						
As	0.32	3.83	0.40	3.36	0.28	2.92	0.29	2.56
Ba	1.64	1.92	1.20	1.84	1.24	1.84	0.87	1.54
Cd	1.94	1.46	1.55	1.62	1.44	1.37	0.62	1.00
Со	0.68	2.26	0.63	2.23	0.74	2.45	0.58	2.11
Cr	1.52	2.23	0.58	0.95	1.46	2.51	1.04	2.42
Cu	0.08	0.75	0.07	0.72	0.10	0.88	0.07	0.78
Li	0.80	2.46	0.62	3.59	0.46	2.73	0.41	2.62
Mn	0.78	1.57	0.65	1.46	0.52	1.43	0.73	1.78
Мо	0.27	2.52	0.39	1.98	0.35	1.98	0.29	1.77
Ni	0.00	0.00	0.48	1.44	3.17	8.82	1.65	6.05
Р	4.01	0.91	0.30	0.86	1.52	1.97	0.05	0.44
Pb	0.88	0.99	0.70	0.76	1.04	1.03	0.42	0.61
Sb	1.69	2.04	0.96	1.62	1.34	2.21	0.79	1.67
Sn	0.65	0.51	0.34	0.36	0.63	0.66	0.18	0.23
Tl	0.42	0.89	0.37	1.06	0.63	1.67	0.38	1.33
V	0.18	1.61	0.20	1.50	0.25	1.73	0.22	1.67
Zn	0.31	0.73	0.23	0.63	0.24	0.70	0.16	0.72



Fig. 6. Partitioning of trace elements (from left to right, first bar: Test 1, second bar: Test 2, third bar: Test 3).



Fig. 7. Partitioning of trace elements (from left to right, first bar: Test 1, second bar: Test 2, third bar: Test 3).

bustion given in [7,9]. As can also be seen from the figure Ba, Co, Cu, Li, Mo and Tl were mostly recovered in fly ash. The capture of As in fly ash could be attributed to partial condensation of these high volatile species due to the low operating temperatures (\sim 350 °C) both at the exit of the combustor due to presence of cooler and in the cyclone [5].

As the ash content of biomasses are much lower compared to that of lignite, the partitioning behavior of trace elements are expected to be similar to those of lignite firing test [15], however, comparisons between the trace element partitioning of the tests with and without biomass addition reveal that addition of olive residue and hazelnut shell enhances the partitioning of As, Ba, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Tl, V and Zn to fly ash. In addition, cofiring shifts the partitioning of Cd, P, Sb and Sn from bottom to fly ash. The reason behind the shift is explained by porous char of biomass [16,17] leading to increase in surface area of ash particles over which condensation of vaporized elements can take place.

4. Conclusions

Partitioning of major and minor ash components and trace elements of a typical low calorific value and high ash content Turkish lignite co-fired with olive residue, hazelnut shell and cotton residue during the fluidized bed combustion was investigated by performing four experiments in 0.3 MW_t METU ABFBC test rig. The following conclusions were reached under the observations of this study:

- Ash split between the bottom and fly ashes is the major parameter determining the distribution of major and minor ash components.
- Co-firing enhances the partitioning of As, Ba, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Tl, V and Zn to fly ash.
- Co-firing shifts the partitioning of Cd, P, Sb and Sn from bottom to fly ash.

Acknowledgements

Financial supports provided by The Scientific and Technical Research Council of Turkey (TUBITAK) through a research project MAG 104M200 in aid of this research are gratefully acknowledged.

References

- H. Lopes, T. Trindade, I. Gulyurtlu, I. Cabrita, Characterisation of FBC ashes from co-combustion of coal with oily residues, Fuel 80 (2001) 785–793.
- [2] L.E. Åmand, H.M. Westberg, M. Karlsson, B. Leckner, B. Coda, M. Hocquel, R. Berger, K.R.G. Hein, X. Feng, M. Abul Milh, Co-combustion of dried sewage sludge and coal—the fate of heavy metals, Proceedings of 16th International Conference on Fluidized Bed Combustion (Ed. D.W. Geiling), FBC01-108 in CD-ROM, ASME, Reno, Nevada, USA, May 13–16 (2001).
- [3] B. Coda, K. Sandelin, R. Backman, R. Berger, K.R.G. Hein, Trace element behavior when co-firing coal, straw, paper sludge under bubbling fluidized bed conditions, Proceedings of 16th International Conference on Fluidized Bed Combustion (Ed. D.W. Geiling), FBC01-122 in CD-ROM, ASME, Reno, Nevada, USA, May 13-16 (2001).
- [4] M.Y. Tsai, K.T. Wu, C.C. Huang, H.T. Lee, Co-firing of paper mill sludge and coal in circulating fluidized bed boiler, Waste Manage. 22 (2002) 439– 442.
- [5] I. Gulyurtlu, M.H. Lopes, P. Abelha, I. Cabrita, J.F.S. Oliveira, The study of partitioning of heavy metals during fluidized bed combustion of sewage sludge and coal, Proceedings of 17th International Conference on Fluidized Bed Combustion (Ed. S. Pisupati), FBC2003-079 in CD-ROM, ASME, Jacksonville, Florida, USA, May 18–21 (2003).
- [6] N. Wolski, R. Berger, J. Maier, K.R.G. Hein, Bubbling fluidized bed co-combustion of different sustainable fuels--trace element behavior, Proceedings of 17th International Conference on Fluidized Bed Combustion (Ed. S. Pisupati), FBC2003-131 in CD-ROM, ASME, Jacksonville, Florida, USA, May 18-21 (2003).
 [7] L.E. Åmand, B. Leckner, Metal emissions from co-combustion of sewage sludge
- and coal/wood in fluidized bed, Fuel 83 (2004) 1803–1821.
- [8] E. Degirmenci, N. Selçuk, Dynamic behavior of an AFBC test rig: an experimental study, Proceedings of 15th International Conference on Fluidized Bed Combustion (Ed. R.B. Reuther), FBC99-0100 in CD-ROM, ASME, Savannah, USA May 16–19 (1999).
- [9] N. Selçuk, Y. Gogebakan, Z. Gogebakan, Partitioning behavior of trace elements during pilot-scale fluidized bed combustion of high ash content lignite, J. Hazard. Mater. B137 (2006) 1698–1703.
- [10] N. Koukouzas, J. Hämäläinen, D. Papanikolaou, A. Tourunen, T. Jäntti, Mineralogical and elemental composition of fly ash from pilot scale fluidised bed combustion of lignite, bituminous coal, wood chips and their blends, Fuel 86 (2007) 2186–2193.
- [11] J.A.R. Brown, Overview of trace element partitioning in flames and furnaces of utility coal-fired boilers, Fuel Process. Technol. 39 (1994) 139–157.
- [12] B.B. Miller, D.R. Dugwell, R. Kandiyoti, Partitioning of trace elements during the combustion of coal and biomass in a suspension-firing reactor, Fuel 81 (2002) 159–171.
- [13] R. Meij, Trace element behavior in coal-fired power plants, Fuel Process. Technol. 39 (1994) 199–217.
- [14] I. Demir, R.E. Hughes, P.J. DeMaris, Formation and use of coal combustion residues from three types of power plants burning Illinois coals, Fuel 80 (2001) 1659–1673.
- [15] P. Grammelis, G. Skodras, E. Kakaras, Effects of biomass co-firing with coal on ash properties. Part 1: characterization and PSD, Fuel 85 (2006) 2310–2315.
- [16] M. Sami, K. Annamalai, M. Wooldridge, Co-firing of coal and biomass fuel blends, Prog. Energy Combust. Sci. 27 (2001) 171–214.
- [17] O. Senneca, Kinetics of pyrolysis combustion and gasification of three biomass fuels, Fuel Process. Technol. 88 (2007) 87–97.

