

TRACE ELEMENTS EMISSIONS DURING FLUIDIZED BED COMBUSTION OF BIOMASS AND COAL 17TH EUROPEAN BIOMASS CONFERENCE – HAMBURG 2009

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ABSTRACT: Trace elements content in different biomass fuels shows high degrees of variability. The fate of trace elements in combustion processes is influenced by its volatility, the concentration in the fuel, the combustion facility, the flue gas cleaning system, the operating conditions and the presence of sorbents in the combustion zone.

The behavior of trace elements during the co-combustion tests at two facilities of 75 kWth and 3.5 MWth was evaluated. The biomass selected was olive oil waste (OOW) for being a representative agricultural residue from Spain. As most of the biomass, it shows high reactivity due to their high volatile content (77%) and medium heating value (19.6 MJ/kg). In relation to the trace elements content, the higher concentrations were found for arsenic and cadmium. One subbituminous Spanish coal was selected to mix with OOW.

Heavy metals were collected and analyzed from three different locations of the facility: bottom ash, before the particle retention system and the stack. Gas sampling and analysis were done according to the EPA Method 29. The results showed that the volatility of metals was rather low, resulting in emissions below the legal limits. Most of trace elements were retained in the ash collected at the ceramic filter.

Keywords: cocombustión, fluidized bed, pilot plant, emissions

1 INTRODUCTION

The declining energy supplies and severe environmental constraints, compel us to sharply focus our attention on the need of additional amounts of clean sources. Among the different alternatives to replace fossil fuels, biomass and biomass waste materials have become an increasingly important option. Co-firing is the addition of biomass as a complementary energy source in fossil-fuel fired boilers. Waste-to-energy is gaining increasing attention as landfill costs and environmental concerns rise in many developed countries.

Nowadays, biomass is seen as the most promising energy source to mitigate greenhouse gas emissions. Large scale utilization of biomass energy could contribute to the sustainable development of different environmental, social and economical aspects. Biomass offers a number of advantages in comparison with fossil fuels. Biomass is regarded as a renewable energy source with zero to low CO₂ emissions if produced in a sustainable manner [1].

Among the various types of biomass fuels suitable for energy production, one of the most promising agricultural residues is a dry solid olive oil waste (OOW) called "orujillo" obtained by oil extraction from olive foot cake. Olive oil waste is generated in abundance in rural Mediterranean regions. The EU generates about 80% of the world production, being Spain, Greece and Italy the three main producers. Approximately, 2.2 million t/yr of orujillo are generated in Spain, which means 30% of total world production [2].

The content of trace elements in the fuels is of crucial importance both for gaseous emissions and for the deposition of ashes as well as national and international legislation has lately become increasingly severe. Trace elements (As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, V, Zn) present in some biomass fuels play an important role in the various practices of this renewable feedstock. The presence of the trace elements in the fuel depends upon the source of biomass. The mechanisms influencing trace elements in combustion process are complex.

The present work aims at investigating heavy metals

partitioning between different fractions in FB combustors using different percentages of biomass as a fuel, and at comparing the results from two different scales of fluidised bed technology: pilot and demonstration scale. This research is being subsidized under a Spanish Science and Innovation Ministry Project (COCOTRA).

2 EXPERIMENTAL SECTION

2.1 Materials

The fuels used on the combustion tests were olive oil waste, subbituminous coal from Puertollano (Spain) and mixtures of both fuels. **Table I** shows proximate, ultimate, ash analyses and the heating values of these fuels. All value is given on a dry basis (d.b.). Fixed carbon and oxygen content were calculated by difference.

Table I. OOW and subbituminous coal analysis

	OOW	Sub. coal
Proximate analysis (wt%, db)		
Moisture	6.8	5.0
Volatile matter	74.8	25.7
Ash	8.3	40.2
Fixed carbon	16.9	34.0
Ultimate analysis (wt%, db)		
Carbon	49.3	50.8
Hydrogen	5.7	3.5
Nitrogen	1.5	1.2
Sulfur	0.01	0.8
Oxygen	35.0	3.4
Chlorine	0.2	0.1
Ash analysis; %		
Al	0.15	3.6
Ca	1.0	0.19
Fe	0.9	1.7
K	0.22	0.62
Mg	0.25	0.15
Na	0.002	0.14
Ti	0.01	0.11
HHV, MJ/kg	19.6	20.2

The main characteristics of the OOW are a high volatile matter content, which makes the ignition easy, and a very low sulfur content. Although chlorine concentration is relatively low, this element plays a very important role in terms of the formation of alkali silicates. It increases the volatility of the alkali metals, releasing them as alkali chlorides and hydroxides in the gas phase. In the absence of sulfur, chlorides often reside on the surface [3].

Olive oil wastes contain an important presence of problematic elements as Se, Cd and Hg, (e.g. **table II**).

Table II. Trace elements content in OOW and Subbituminous coal samples.

Trace elements, ppb	OOW	Sub. coal
Hg	17	258
As	462	31
Cd	192	399

The chemical analysis of the fuels, bottom ash, fly ash and filter ash from the stack was carried out after digestion in a microwave oven employing strong acids (HF, HNO₃ and H₃BO₃) and its subsequent analysis by inductively coupled plasma-mass spectroscopy (ICP-MS).

2.2 Test facilities

Two atmospheric bubbling fluidised bed facilities, pilot scale and demonstration scale, have been used for the experimentation.

Figure 1 shows the layout of the experimental fluidised bed unit. The 75 kWth atmospheric bubbling fluidised bed pilot scale facility has a main column (riser) of 0.3 m i.d. and 3 m height, two high efficiency cyclones in series, fuel feeding and ash discharging system and a flue gas analysis system. Bed material consists of sand with a particle size between 0.5 and 1 mm. and 95% silica content.

The temperature within the BFB was continuously monitored at several points within the BFB. The combustor system takes around 3 hours to stabilize. At heights ≤ 0.6 m from the distribution plate the bed temperature remained at around 850°C. Lower temperatures were measured at freeboard zone.

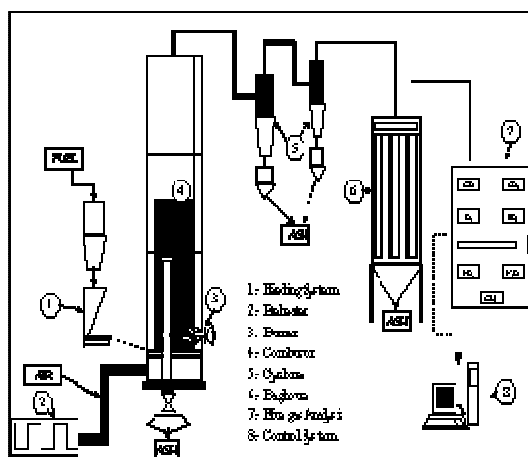


Figure 1. CIEMAT 75 kWth atmospheric bubbling fluidised bed test rig

The 3.5 MWth BFB demonstration plant is mainly composed by boiler, heat recovery zone, pressure reducing valve, condenser degasifying, air blower, induced draft fan, propane gas burner, feeding system, bag filter, flue gas analyzer, water treatment system and controlling and monitoring system, **Figure 2**.

The fluidizing air enters to the boiler through a constant speed fan blower supplying 5000 kg/h of combustion air. The boiler has rectangular section 3 m *1.5 m. The fuel is fed at the lower part of the boiler pneumatically. There are two fuel feeding points. The capacity of the feeding system is about 700 kg/h according to the fuels density. The heat released in the combustion process heat up the water inside the wall piping. The combustion temperature is 850°C. The freeboard ensures the adequate residence time of gases inside the furnace. Hot gases leaving the boiler heat up the water and vapor inside of these. Subsequently, the flue gases are cleaned in a bag filter. The ashes generated in the process of combustion are collected in hoppers.



Figure 2. CIEMAT 3.5 MWth atmospheric bubbling fluidised bed facility

2.3 Characterization of flue gases and fly ashes

The flue gas sampling system consists of the sample probe, heated sample line and sampling unit. The sample probe is used for continuous dust extraction from gases and to avoid high temperature or humid processes.

The sampling line features a replaceable smooth PTFE core carried in a flexible corrugated stainless steel tube. The sampling line was cooled in order to maintain the inlet gas temperature within the working range of the analyzer: 160-200°C.

The Temet sampling unit is especially designed for emission monitoring measurements, for on site measurements. It is an ideal tool for measuring trace concentrations of pollutants in wet, corrosive gas streams. The composition of the raw gas was analyzed before the bag filter. CIEMAT uses a Fourier transformed infrared, FTIR that is able to discern the following species: CO, CO₂, H₂O, NO_x, N₂O, SO₂, HCl and NH₃.

Flue gas sampling was conducted at flue gas duct located at the entrance of the stack after ceramic filter. Isokinetic conditions were maintained and sample was collected for 20 min at each point. Laboratory glassware for solution preparation and the field impingers were thoroughly cleaned using hot soap water wash and overnight soaking in dilute nitric acid. Demineralised water was used for rinsing after hot soap water wash. All reagents and chemicals used were of analytical grade and

milli-Q water was used for final washing of the glassware, impingers and during solution preparation. Solution blanks were also analyzed to check contamination of mercury.

The recovered samples are digested and appropriate fractions are analyzed by inductively coupled plasma-mass spectroscopy (ICP-MS).

3 RESULTS AND DISCUSSION

3.1 Thermodynamic equilibrium calculations

Recent studies in relation to the behaviour of trace elements in combustion processes have been focussed on co-firing of coal and biomass. These studies show, how the fate of trace elements during combustion processes, is highly dependent on the presence of different compounds in fuel as Cl, Ca and S [4].

Thermodynamic equilibrium calculations were performed to evaluate the influence of different compounds in the distribution and mode of occurrence of heavy metals in co-combustion processes.

The theoretical calculations have showed that, in absence of interactions with ashes, trace metals tend to be released to the atmosphere in gas phase. However, there are different factors that may alter the volatility of these elements:

- In case of mercury, the presence SO_2 favours the formation of the condensed sulphate to lower temperatures than $300\text{ }^\circ\text{C}$, increasing the retention in the ashes.

- In presence of calcium, antimony tends to react to form new compounds: $Ca_2Sb_2O_7$, $Ca(SbO_3)_2$, $Ca_3(SbO_4)_2$.

- Arsenates are the most probable resultant forms from the interaction of the arsenic with the components of the flying ashes. $FeAsO_4$ is relatively stable; it vaporizes over $1000\text{ }^\circ\text{C}$. $AlAsO_4$ can be formed even at very high temperatures ($T < 1400\text{ }^\circ\text{C}$), whereas $NaAs_3O_8$, KAs_3O_8 and K_3AsO_4 are stable at lower temperatures, below $900\text{ }^\circ\text{C}$. The presence of calcium and magnesium originates new compounds: $Mg_3(AsO_4)_2$, stable between 400 and $1100\text{ }^\circ\text{C}$ and $Ca(AsO_2)_2$ stable between 650 and $750\text{ }^\circ\text{C}$. On the contrary, silicon tends to increase arsenic volatility. [5]

- The interaction of Cadmium with fly ash components also increases the formation of condensed species ($CdSO_4$, CdO). New compounds, $CdO \cdot Al_2O_3$ and $CdSiO_3$, are observed between 600 and $1100\text{ }^\circ\text{C}$.

3.2 Experimental results

Trace metals partitioning to different ash fractions, is influenced by many factors including temperatures in different zones, combustion air distribution and the physical and chemical form of compounds containing the metals. Besides the temperature, the particle size of the fly ash and the gaseous atmosphere in the precipitation zone also play an important role.

The non-volatile compounds remaining in the charcoal, form ash particles with a wide range of compositions, shapes and sizes related to the characteristics of the parent material. A substantial part of this ash remained in the bed and formed the bottom ash and the ash collected at the economizer while the rest were present in the flue gases forming the coarse part of fly ash, with particles sizes between a few μm to hundreds of μm , **figure 3**. It is observed that the metals are collected principally in the economizer and in the bag

filter.

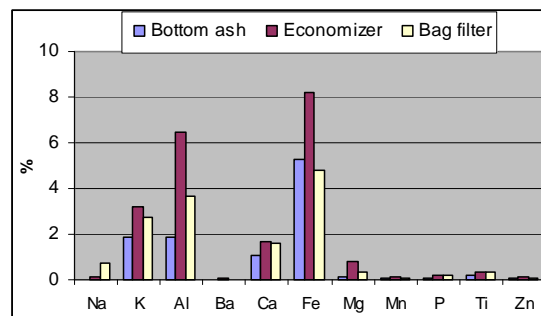


Figure 3. Different species partitioning in ash streams at demonstration plant using coal/olive oil wastes mixture (60/40) as fuel.

The quantity of ash produced during each trial test at the bottom ashes, economizer and the bag filter were measured. The concentration of particles emitted through the stack was less than 0.1% of the total ash produced, which confirms the high efficiency of the bag filter.

The sum of fly ashes and bottom ashes is higher than the content of ashes of the fuel. The high quantity of ash produced is due to the silica employed as bed material, which makes increase the production of ashes, mainly in the bottom ashes and, in a minor extent, in the fly ashes, as result of the leaching of some bed material to upper zones of the combustor and at this case, to the significant level of unburned carbon in the ash.

The experimental results have shown that trace elements are more volatile than the rest of metals, **Figure 4**. In relation to mercury, a small enrichment is observed in the ashes of the bag filter and of the economizer, between $150\text{--}400\text{ }^\circ\text{C}$ which, according to the thermodynamic balances, corresponds to the range of temperature of $HgSO_4$ formation. Mercury enrichment in the bed material has not been found. Mass balance results shows how mercury is liberated in gaseous form during the combustion process, which is consistent with the thermodynamic predictions.

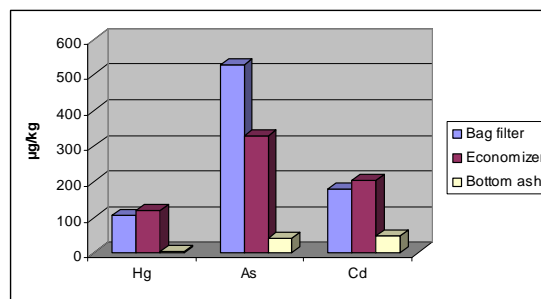


Figure 4. Trace elements partitioning in different ash streams, at the demonstration plant using coal/olive oil wastes mixture (60/40) as fuel.

In arsenic case, a partial volatilization is observed, showing a major retention in the ashes that mercury, with similar values for RE in the different samples of ashes (slightly higher in the filter), as it was predicted by the thermodynamic equilibrium calculations, where a total

retention of arsenic is observed over 800 °C, as FeAsO_4 , $[\text{Ca}_3(\text{AsO}_4)_2]$ and $[\text{Mg}_3(\text{AsO}_4)_2]$.

A high retention is observed for cadmium at top temperatures of 400°C (economizer), which corresponds, with the formation of CdSiO_3 and $\text{CdO} \cdot \text{Al}_2\text{O}_3$, whereas at lower temperatures a partial volatilization takes place; the low enrichment observed below 200°C is related to the formation of CdSO_4 at this temperature, according to the thermodynamic equilibrium calculations.

4 CONCLUSIONS

Heavy metals partitioning between different fractions in FB combustors, using OOW and subbituminous Spanish coal as a fuel at two different scales, has been studied.

Thermodynamic equilibrium calculations were performed to evaluate the influence of different compounds in the distribution and mode of occurrence of heavy metals in co-combustion processes.

Heavy metals were collected and analyzed from three different locations of the facility: bottom ash, before particle retention system (economizer) and the bag filter. The results showed that trace metals volatility was low because samples were mainly collected from the economizer and in the bag filter.

Hg, Cd and As show higher volatilization than the rest of the metals studied. A small enrichment is observed in the ashes from the bag filter and the economizer, between 150-400°C. A partial volatilization is observed for arsenic, presenting a major retention in the ashes than the mercury, with similar RE values for the different ash samples collected (slightly major in the filter), which agrees with thermodynamic equilibrium calculations.

5 REFERENCES

- [1] A. A. Khan, W de Jong, P.J. Jansens, H. Spliethoff. Biomass combustion in fluidized bed boilers: Potential problems and remedies, *Fuel Processing Technology* 90 (2009) 21-50.
- [2] P. García-Ibáñez, A. Cabanillas, J.M. Sánchez, Gasification of leached orujillo (olive oil waste) in a pilot plant circulating fluidized bed reactor: Preliminary results, *Biomass and Bioenergy* 27 (2004) 183-194.
- [3] L.L. Baxter, Influence of ash deposit chemistry and structure on physical and transport properties, *Fuel Processing Technology* 56 (1-2) (1998) 81-88.
- [4] B. Miller, D.R Dugwell, R. Kandiyoti, The influence of injected HCl and SO₂ on the behaviour of trace elements during wood-bark combustion, *Energy Fuels* 2003; 17: 1382-91.
- [5] ML. Contreras, J.M. Arostegui, L. Armesto, Arsenic interactions during the co-combustion processes based on thermodynamic equilibrium calculations, *Fuel* 88 (2009) 539-546.

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