CO-GASIFICATION OF BIOMASS: EFFECT ON THE FATE OF TRACE ELEMENTS

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Abstract

The effect of the co-gasification of biomass with coal and pet-coke on the fate of trace elements was evaluated in the 335 MW Puertollano Integrated Gasification Combined Cycle (IGCC) plant. Sampling of coal, pet-coke, biomass, limestone, slag and fly ash was undertaken from co-gasification tests with 6, 8 and 10% olive pit addition. Samples of effluent from flue gas washing and elemental sulfur from the S recovery unit were also collected from 0 and 6% biomass co-gasification tests to evaluate and compare the abatement capacity of gas cleaning systems. The increase in the proportion of biomass co-gasification (6 to 10%) resulted in: i) the increase of the concentrations of K, P, Mg, Na, and Cl in slag and fly ash (Cl only in fly ash) simultaneously while reducing the FA/slag ratio of K, As, B, Cu, Ge, Mo, Ni, Pb, Sb, Se, Tl and Zn K, iii) the increase of the volatile behavior at fly ash removal temperatures, of B (48-64%), P (0-45%), Cd (0-56%), Cu (0-38%), Pb (11-44%), Se (28-77%) and As (0-42%); iv) High (>80%) and relatively constant volatile proportions of Hg, S, and Cl. The abatement efficiencies for the above elements in the gas cleaning system are not modified in a large extends between 0 and 6% biomass co-gasification, keeping the emission levels below the limit and thresholds of the European regulations.

1. INTRODUCTION

The biomass use in power plants as alternative fuel has been enhanced worldwide in the last years by partial replacement of fossil fuels, since it is assumed that biomass do not contribute to the greenhouse effect since the neutral CO_2 balance. However, this consideration may be not satisfactory for current policies, and the environmental effects from bio-fuel production might be worse than those from fossil fuels[1]. Although extensive research on biomass characteristics and properties for it use as fuel, has been developed the effects on ash behavior and fate of trace elements in biomass combustion/gasification as well as on properties of biomass firing wastes (bottom ash/slag, fly ash) still not fully understood. For instance there are a large number of biomass types (wood, agricultural, herbaceous, aquatic, animal, human or industrial biomass wastes) with different composition depending on source[2]. Generally, biomass may contain relatively high concentrations of Ca, Cl, K, Na, P and/or S, but also in a number of trace elements of environmental concern (Hg, As, Cd and Sb

among others)[3-5]. Recently a review on chemical composition of biomass and derived problems on its use on power generation with has been published[2].

The specific characteristics of each biomass fuel may modify the fate of trace elements in the (co) combustion/gasification with respect to that of coal combustion/gasification. Currently, most of the studies on behavior of inorganic matter in biomass firing are based on thermodynamic equilibrium models. Studies at pilot and industrial scale are then being necessaries to ascertain potential changes on volatile behavior of trace elements and the physical, chemical and leachable properties of combustion/gasification by-products.

The co-gasification of biomass is thought as a promising strategy for reducing CO_2 emissions. Coupled with the aforementioned neutral CO_2 balance, gasification generates pressurized CO_2 flow with low content of impurities, reducing the pretreatment procedures required for geological storage of CO_2 generated in power plants. Studies on the partitioning of trace elements in commercial Integrated gasification Combined Cycle (IGCC) plants still scarce and most of them based on experiments carried out at laboratory and pilot plant scale[6-10], and on modeling of the gas phase[11,12]. Studies on partitioning of elements at the largest worldwide industrial IGCC plant in Puertollano (Spain)[13] fed with coal and petroleum coke, revealed the following partitioning for major and trace elements at fly ash removal temperatures: (a) high volatile elements (>70% in gas phase): Hg, Br, I, Cl and S; (b) moderately volatile elements (up to 40% in gas phase and 60% in fly ash): As, Sb, Se, B, F, Cd, Tl, Zn and Sn; (c) elements with high condensation potential: (>90% in fly ash): Pb, Ge, Ga and Bi; (d) elements enriched similarly in fly ash and slag 30–60% in fly ash: Cu, W, (P), Mo, Ni and Na; and (e) low volatile elements (>70% in slag): Cs, Rb, Co, K, Cr, V, Nb, Be, Hf, Ta, Fe, U, Ti, Al, Si, Y, Sr, Th, Zr, Mg, Ba, Mn, rare earth elements (REEs), Ca and Li. This study pointed out the relevance of organic Cl input on increasing the volatile proportion of a number of trace elements, specially that of As, Sb, and Tl, and of limestone dosages on enhancing slagging of S, B, Cl, Cd and low volatile elements, respectively.

In view of the above findings and the expected high organic Cl content of biomass fuels, co-gasification of biomass may be regarded as potential factor for increasing the volatile fraction of most trace elements in IGCC plants. In this study the effect of the co-gasification of biomass (olive pit) with coal and pet-coke on the fate of trace elements was evaluated in the 335 MW Puertollano IGCC plant. This plant is commonly fed with a mixture of a local high volatile bituminous coal rich in metals and semi-metals[14] and pet-coke, supplied by an oil refinery. Limestone is added (2-4%) to the feed fuel blend as a fluxing agent. Sampling of coal, pet-coke, biomass, limestone, slag and fly ash was undertaken from co-gasification tests with 6, 8 and 10% olive pit addition to the feed fuel blend. Samples of effluent from flue gas washing and elemental sulfur from the S recovery unit were also collected in 0 and 6% biomass co-gasification run tests to evaluate and compare the abatement capacity of gas cleaning systems.

2. EXPERIMENTAL
2.1. Sample collection and operational conditions
Three sets of samples different co-gasification with different olive pit addition (6, 8 and 10%) run tests at the Puertollano IGCC plant were investigated. Each sample set containing simultaneously collected samples of coal, pet-coke, biomass, limestone, feed fuel blend, slag and fly ash. Sample of elemental sulfur and effluent from gas cleaning system were also collected simultaneously to the aforementioned streams in 6% biomass co-gasification run test. In these co-gasification test the IGCC plant was operating (feed fuel mixtures and input and output flows) at the conditions summarized in Table 1. In this power plant, the fuel, following pulverization (down to <100 μm) and drying, is pressurized (to 25 bars) and carried to the gasifier in an inert environment of N_2. The pulverized fuel enters the gasifier through four burners set at 90^oC and is mixed with O_2 (85% purity). The gasification process is carried out at $1200\text{-}1600^oC$ and 25 bars. The slagging properties of the gasifier results in a high production (90%) of molten ash removed from the bottom of the gasifier in liquid form. The slag then enters a water bath, where is cooled and crushed. The remaining 10% of the ash is entrained by the gas. The fuel particles undergo the pyrolysis and gasification processes. The gases produced are first cooled down to 800^oC when leaving the gasifier with a recycled quenched gas flow (235^oC). When leaving the gasifier, the gas is successively cooled down to 400 and 265^oC in high and medium pressure boilers, respectively. In the pressure boilers high and intermediate pressure steam (127 and 35 bars, respectively) is produced, which is sent to the combined cycle heat steam regenerator boiler. After re-heating the steam is expanded into the steam turbine. The ashes are removed from the gas at 265° C by means of ceramic candle filters. By this process the dust content of the gas is reduced to <3 mg/Nm^3. The gas, free of particles, is carried to the gas cleaning and desulphurization unit. Halides and other impurities (HCl, HF, NH_3, HCN and H_2S) are removed from the gas using a venturi scrubber with NaOH as a neutralizer agent. The sulfur is removed by conversion of H_2S to elemental sulfur. Then, the gas is expanded in a 200MW gas turbine. A 135MW steam turbine burns the steam generated in the heat recovery steam generator. The main chemical and mineralogical features of the feed fuel, slag and fly ash were investigated according to the following procedures:

Table 1. Proportions in the feed fuel and inputs and outputs flows of solid and liquid streams in the olive pit co-gasification tests at the Puertollano IGCC power plant.

Input (%)	Test 1	Test 2	Test 3
coal	42.3	40.5	39.6
pet-coke	49.7	49.5	48.4
% olive pit	6.0	8.0	10.0
Limestone	2.0	2.0	2.0
Input & output (tn/h)			
coal	40.0	40.5	38.2
pet-coke	40.0	40.5	38.2
limestone	1.9	1.7	1.9
olive pit	5.7	8.0	9.7
feed fuel	94.5	92.3	51.6
slag	20.1	20.0	9.9
fly ash	3.0	2.5	1.3
elemental S	3.0	2.7	1.7
Effluent gas washing m^3/h	70	72	

2.2. Analysis

The moisture and ash content were determined at 105 and 750 ^{o}C, respectively following the ASTM recommendations. The content of major and trace elements were determined by means of Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). A special two step sample digestion method for the analysis of potentially volatile elements in coals and fly ash devised by Querol et al.[15] was used to dissolve the samples prior to the analysis. The content of Hg was determined by Gold Amalgam Atomic Absorption Spectrometry (GA-AAS, AMMA-LECO) directly on solid and liquid samples. The Cl and F contents were determined by the Eschka[16] method and subsequently measured by selective electrode. The mineralogy of solid samples was determined by X-ray powder diffraction (XRD) with a 218 Bruker D5005 diffractometer with monochromatic Cu Kα1,2 radiation operated at 40KV and 219 40mA., from 4 at 60° of 2theta range, and a step size of 0.05° and 3s/step. The particle size distribution of the fly ash samples was investigated by means of a laser light scattering-based particle size (Mastersizer2000), with a working range from 0.1 to 1000µm. An ethanol media with an ultrasound bath prior to the particle size analysis was used in order to avoid potential dissolution of salts.

3. RESULTS AND DISCUSSION

3.1. Characterization of feed fuel and limestone

The coal, pet-coke and limestone fed in the olive pit co-gasification tests show similar physical, chemical and mineralogical properties than those fed in the standard operational conditions of the Puertollano IGCC power plant. The Puertollano IGCC plant is low moisture (3–7%) and high ash (36–52%), highly volatile bituminous coal, rich in a large lumber of trace elements[13]. It is worth mentioning the common high contents of Cl of the Puertollano, 6 times higher than the coal worldwide values (180 mg/kg) reported by Yudovich and Ketris[17]. The Cl concentrations in the fed coal raged from 653 to 1178 mg/kg in the olive pit co-gasification tests. These high contents of Cl may be due to their accumulation in Puertollano coals in a post-sedimentary digenetic process from leaching of the interlayered volcanic tuffs[18]. The fed pet-coke in the olive pit co-gasification tests is rich in S (around 4%), V (1013-1213 mg/kg), Cl (435-460 mg/kg) and Ni (191-256 mg/kg) while limestone shows also high Cl contents (around 2000 mg/kg).

The olive pits show low moisture (around 7% after air drying), low ash content (around 10%) and low amounts of crystalline phases (mainly fine quartz and Mg silicates particles) with a predominant organic matrix (Figure 1). It is worth mentioning the relatively high concentrations of K (2.1-3.6 %), Cl (0.4-1.0%) and also of Ca, P, Al, Mg, Na, and S and the relatively low content in trace elements (Table 2). Potassium and Cl, together with Ca, occur mainly within the organic matrix of olive pits and in very minor amounts as fine (5-10µm) particles of KCl (Figure 1).
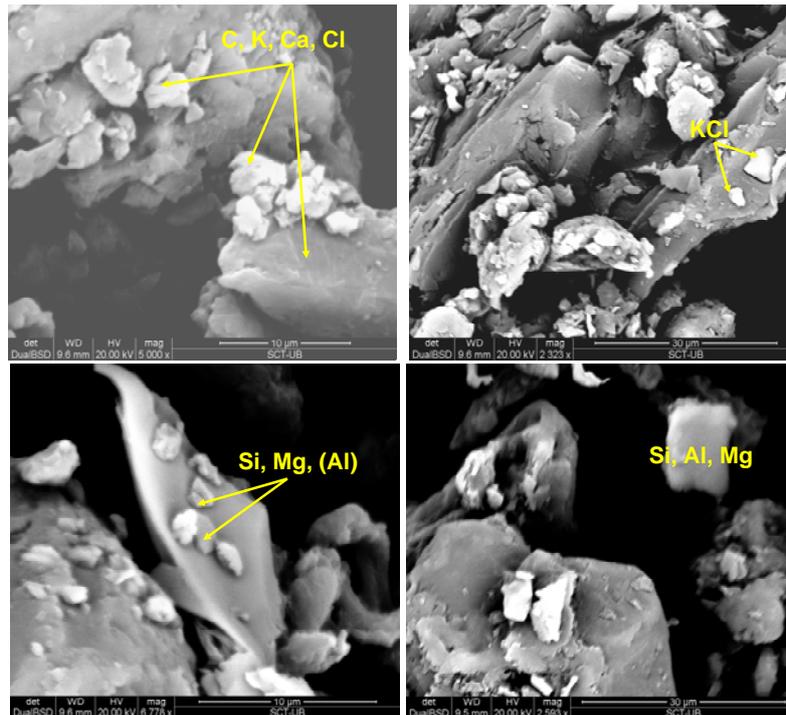
Figure 1. SEM microphotographs of organic K-Ca-Cl (a), KCl (b) and Mg (Al) silicates particles embedded in the predominant organic matrix of olive pits.

3.2. Source of major and trace elements.

According to the characteristics of the coal, pet-coke, olive pit and limestone and their proportions in the feed fuel, coal is the main source (>80%) for most elements (Al, Fe, K, Mg, Na, Si, Ti, As, Ba, Be, Co, Cs, Cu, Cr, Ga, Ge, Hg, Li, Nb, Pb, Rb, Sb, Sc, Sn, Sr, Y, Zn and Zr), pet-coke supplies the highest proportions of S (83-85%), Mo (76-82%), V (85-94%) and Ni (73-88%) and limestone that of Ca (67-92%). The main contribution of olive pits are K (21-38%), P (49-66%), Cl (34-62%) and, Na (8-35%) supplying the highest proportions with the highest biomass dosage. The major organic affinity of most of the elements supplied by pet-coke (Cl, V, Ni) and olive pit (K, P, Cl) may play a significant role on the volatile behaviour of elements in co-gasification.

3.3. Effect of biomass co-gasification on slag and fly ash composition

The mineral composition of IGCC slag and fly ash is not deeply modified by the co-gasification of olive pits with respect to that generated in the co-gasification of coal and pet-coke[18,19]. Slag and fly ash are are mainly made up (>95%) of an amorphous Al-Si glass. Traces of pirrotina/troilite are found in specific slag samples, while galena (PbS), sphalerite and wurtzite (ZnS), phyrrhotite ($Fe_{1-x}S$), and nickeline (NiAs) are the crystalline phases of IGCC fly ash present in XRD detectable levels (>1% wt). Most of these phases are condensed from reducing vapour species in cooling flue gas.

The concentrations of major and trace elements in olive pit co-gasification slag and fly ash samples are in the range of that produced in the co-gasification of coal and pet-coke. According to the proportions of olive pit and coal in the feed fuel blend (Table 1) the concentrations of K, P, Mg, Na, and Cl are slightly higher than mean values of these elements in the Puertollano IGCC slag and fly

ash (Cl only in fly ash) while those of elements supplied by coal (mainly As, Pb, Zn) are slightly lower than the mean values.

Table 2. Concentrations of major and trace elements in the olive pits fed in the biomass co-gasification tests.

%	Test 1	Test 2	Test 3
Al	0.1	0.3	0.6
Ca	0.2	0.7	0.9
Fe	0.1	0.2	0.3
K	2.1	3.6	2.8
Mg	0.1	0.3	0.3
Na	0.6	0.1	0.4
P	0.1	0.2	0.2
S	0.1	0.2	0.2
Ti	0.003	0.01	0.02
Cl	1.0	0.4	0.8
mg/kg			
As	5.3	<0.01	<0.01
B	51.9	43.7	42.0
Ba	8.7	21.6	38.9
Be	<0.01	<0.01	<0.01
Bi	<0.01	<0.01	<0.01
Cd	<0.01	<0.01	<0.01
Ce	2.7	2.9	5.9
Co	<0.01	<0.01	<0.01
Cr	5.4	5.9	6.9
Cs	<0.01	<0.01	<0.01
Cu	13.6	22.7	21.6
Ga	<0.01	<0.01	<0.01
Ge	<0.01	<0.01	<0.01
Hf	<0.01	<0.01	<0.01
La	<0.01	<0.01	2.8
Li	0.0	2.4	3.6
Mn	16.0	39.3	79.5
Mo	1.4	<0.01	<0.01
Nb	1.1	<0.01	<0.01
Ni	4.4	5.5	5.4
Pb	5.7	67.0	104.0
Rb	15.0	16.2	16.3
Sb	<0.01	<0.01	<0.01
Sc	<0.01	<0.01	<0.01
Se	1.1	<0.01	<0.01
Sn	<0.01	<0.01	<0.01
Sr	14.6	20.3	24.3
Th	<0.01	<0.01	<0.01
Tl	<0.01	<0.01	<0.01
U	<0.01	<0.01	<0.01
V	17.1	9.9	9.3
W	6.8	3.5	4.4
Y	<0.01	<0.01	1.7
Zn	31.6	30.9	26.0
Zr	2.9	3.5	5.8

A significant effect of the co-gasification of olive pits is to reduce the fly ash/slag (FA/s) concentration ratio of K, As, B, Cu, Ge, Mo, Ni, Pb, Sb, Se, Tl and Zn with the increase of olive pit dosages in the feed fuel blend. This may indicate a higher volatile fraction of the above elements at fly ash removal temperatures or a higher segregation in slag than in fly ash. In contrast the FA/s ratio of Cl tends to increase with the increase of olive pits dosages, suggesting higher condensation of chloride species in fly ash.

3.4. Effect of biomass co-gasification on volatility of elements.

The volatile fraction of elements was calculated by normalizing their concentrations in the input (feed fuel blend) and output streams (fly ash and slag, and including effluent and gypsum for the global mass balance). Due to the lack of gaseous sampling, out/in ratios<1 indicate the volatile fraction of a given element. An error of 10% was estimated for this procedure. The elements displaying a partial volatile behavior at fly ash removal temperatures in the co-gasification of olive pits are (Table 3): Hg, S, Cl, P, As, B, Cd, Cu, Pb, Sb, Se, Sn, Tl, Zn and K. Mercury (99.7-99.9%), S (90-95%), and Cl (81-96%) are the elements displaying the highest proportions in gas phase, attaining similar values among olive pit dosages. The volatile proportion of the above elements is in the range reported for co-gasification of coal and pet-coke and, according to Font et al[13] may be classified as highly volatile elements (>70% in gas phase). The volatile fraction of the remaining elements is in the 0-76% range, and is markedly increased with the increase of the olive pit dosage for P, As, Cd, Cu, Se and Tl (Table 3). With the exception of Se and in 10% co-gasification test (highly volatile, 76% table 3), and according to the classification of elements in IGCC plants[13] these elements may be classified as moderately volatile elements (around 40 % in gas phase and 60 % in fly ash). The volatile fraction of most of these elements is higher than obtained in the co-gasification of coal and pet-coke (As, B, Pb..) and a number of elements retained exclusively in fly ash and slag (P and Cu) are partially volatile with the co-gasification of olive pit, especially at dosages of 10 %.

The co-gasification of olive pits increase the proportion of organic Cl and that of other elements (S, P, K, etc) in the feed fuel blend with respect to that of co-gasification of coal and pet-coke. As stated in previous studies[13] the organic Cl and the limestone dosages are key factors to modify the volatility of a number of elements (As, Se, Sb, Zn, Pb, among others). To corroborate the influence of these parameters on the volatility of elements in biomass co-gasification, the results obtained in the present study are compared with that obtained in co-gasification of coal and pet-coke. The sum of Cl supplied by olive pits and pet-coke, normalized to the respective input flow, was estimated as the total input of organic Cl in the gasifier in olive pit co-gasification and that of pet-coke in the co-gasification of coal and pet-coke. Due to the major inorganic affinity of Cl in limestone and Puertollano coal (present in refractory phosphate minerals, such as apatite, rather than to organic matter)[13], these inputs are not considered as a source of organic Cl. The volatile fractions of As, Se, Sb, B, Tl, Cd, P, Pb, and Sn at fly ash removal temperatures display a positive trend with the input of organic Cl and negative with the limestone dosages. With the exception of P, Sn, and Sb, the volatile proportions of the aforementioned elements show a negative trend with the increase of the limestone dosages. The volatility of Zn

displays a positive trend with the increase of the limestone dosage and no correlation with the input of organic Cl.

The above issues suggest that the generally higher volatility of the aforementioned elements obtained in olive pits co-gasification than in the co-gasification of coal and pet-coke is due to the simultaneous higher input of organic Cl and low limestone dosage. An increased content of gaseous Cl may favor a high occurrence of high volatile As, Tl, Sb, Se, Cd, and Cu chloride species, such as $AsCl_3$ (boiling point 130 ^oC), $SbCl_3$ (220 ^oC), $SnCl_5$ (140 ^oC), $CuCl_2$ (~300^oC), $TlCl_3$ (155 ^oC), $CdCl_2$ (~300^oC) and Se_2Cl_2 (127 ^oC)[20]. The proportion of As and Sb in gas phase could be also controlled by the levels of Ni in the feed fuel[21], available to form nickeline-brethautite in this IGCC fly ash. Conversely, the volatile proportions of Zn, Sn and Cd are reduced when the limestone content in the feed fuel blend increases. The preferential condensation of Zn, Sn and Cd sulfides over the formation of gaseous chloride species may accounts for this. It is worth mentioning the high volatile fractions attained by P (up to 45 %) in the co-gasification of olive pits. This is most probably related to both, the high input of organic P and Cl by olive pit favoring volatilization of P and subsequent formation of PCl_3 (volatile at 76^oC) and/or PCl_5 (160^oC) and/or P_2Cl_4 (180^oC). The high organic affinity of B (60% of the bulk B) in the feed coal[13] and, in pet-coke (close to 100%) accounts for the high volatility of this element in IGCC. As reported by several authors[15,22] the mode of occurrence of B in coal is controlling its volatile behavior during combustion. The occurrence of B in tourmalines or other silicate minerals reduce the volatility, whereas a mainly organic affinity favors the occurrence of B in the gas phase.

Table 3. Volatile fraction of elements at fly ash removal temperatures in the olive pits co-gasification tests. Nd: not determined

olive pit dosage (%)	4	6	10
Hg	99.7	99.9	99.9
S	90.1	95.2	93.3
Cl	81.0	95.8	88.6
B	54.5	47.9	63.9
As	0	12.9	42.0
Se	28.0	nd	76.9
Zn	12.4	4.5	0
Sb	36.8	nd	24.8
Tl	0	0	13.2
Cd	0	nd	56.2
P	0	17.8	45.4
Cu	0	0	37.7
Pb	11.8	nd	44.2
Sn	30.4	nd	34.4

The abatement efficiencies for the aforementioned volatile elements at fly ash removal temperatures in the gas cleaning system are not modified in a large extends between 0 and 6% biomass co-gasification, attaining >90% retention. Most of Cl, B, Zn, As are retained in the effluent after gas washing, while most of S is retained as S^0. Elemental S may retain low proportions of As, Se, and Hg. The abatement of Hg is generally low but the emission levels of this metal

and those of other elements are below the limits and threshold values established by the EU regulation.

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