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Assess of biomass co-firing under oxy-fuel conditions on Hg speciation and ash deposit formation

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ABSTRACT

In the last years oxy-fuel combustion has been seen as an attractive method for oxygenated fuels, such as biomass, for controlling simultaneously the excess of heat arising from coal combustion and flue gas emissions (CO_2, NO_x, SO_2…). However there is a lack of information with respect to the fate of other toxic pollutants found in trace concentrations, such as mercury, in oxy-fuel processes operating with biomass fuels. In addition, the modified conditions and flue gas composition leads to more corrosive environments which needs of previous evaluation to minimize possibly damaging processes in the boilers, furthermore in case of employing biomass of high alkaline compounds contents.

The present work evaluates the effect of oxy-combustion processes of sub-bituminous coal and coal/ biomass (thistle) blends on mercury partitioning and speciation, under both air and different oxy-fuel combustion atmospheres, by means of a bubbling fluidized bed combustor at laboratory scale. HSC Chemistry 6.1 was supplemented for the interpretation of the experimental results and for the analysis of ash deposits formation.

Hg speciation was seen to be more affected by oxy-fuel combustion during the co-firing tests than in coal combustion, with an increment in Hg oxidation at low temperatures ($T < 350\,^{\circ}C$) and mainly for oxygen concentrations over 30% v/v. This effect is highly related to variations produced in chlorine speciation in the oxy-fuel atmospheres, in which ash deposition and corrosion modifications were seen to be also involved, with a reduction of the chlorinated species against an increased in the sulphated compounds concentration.

1. Introduction

Coal and biomass co-firing is becoming more common in existing coal-fired power plants, to reduce the carbon footprint of electricity generation and achieve minor pollutant emissions, compared to firing neat coal, as it is a near term lower-cost option in comparison to the construction of a new biomass-specific fired power plant [1,2]. Other approaches which are being evaluated and adopted by various countries to minimize CO_2 emissions are based on the implementation of new processes for CO_2 capture and storage (CCS). Among these technologies, oxy-fuel combustion is considered as a promising option to ensure the continued use of coal for electric power production [3,4]. In an oxy-fuel combustion process, the fuel is burnt in a mixture of oxygen (instead of air) and recycled flue gas, obtaining a rich CO_2 (95%) and water vapor stream which, after purification and compression, is ready for sequestration [1,5,6].

In the last years, oxy-fuel combustion has been regarded as a more adequate process for those systems operating with high oxygen content fuels, such as biomass. While co-firing has been widely studied under conventional air conditions, few experiences are available to date for O2/CO2 atmospheres. Recent investigations have shown blending of coal with biomass as a way to control the excess heat generated from oxy-combustion of coal [6,7]. More advantages have been reported for coal-biomass oxy-firing, such as an improvement of coal burnout and ignition properties [8,9]. Diverse studies have also shown a decrease in NO_x y SO_2 emissions through oxy-firing [10,11], which indicates that a simultaneous decrease of CO_2, NO_x and SO_2 could be achieved by means of combining oxy-fuel combustion with coal-biomass cofiring, being proposed as a “clean” coal technology.

However, there are special issues, regarding biomass compared to coal, which could have a significant impact on the combustion process and related phenomena, such as the volatile matter content, the ash composition (Cl and alkali content), and the change in fuel particle size [10]. These aspects are closely linked to different concerning processes such as trace metals emissions (TMs) and ash deposition.

The serious impacts caused by TMs into the environment are widely known, and the importance of being considered in combustion research lies in the fact that fuels containing only several parts per million of

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TMs could result in the release of several tons of pollutants [12]. Currently, there is limited literature available with regards to TMs fate in oxy-fuel combustion processes. Up until now, research has been mainly focused on mercury (Hg) [13–22], as it is considered as one of the most problematic TMs emitted during coal combustion, in terms of harm to human and the environmental impact involved, due to its high volatility, toxicity and persistence in the environment. Moreover, the largest anthropogenic source of Hg emissions to air on a global scale is the combustion of coal and other fossil fuels. In this sense it was the first TMs for which emission limits were regulated.

Different authors [23,24] have summarized the key issues concerning Hg emissions and control in oxy-combustion systems (standard limits, changes in Hg speciation, impact of Cl, NO_x and SO_3 species/concentration variations, effectiveness of Hg removal) concluding that the oxy-fuel combustion flue gas may change Hg partitioning and emission requiring re-evaluation of Hg-sampling protocols and control strategies for oxy-fuel combustion.

With regards to oxy-coal combustion effect on Hg speciation, different authors have encountered significant differences in Hg fate during oxy-firing with respect to air combustion, such as lower Hg emissions during oxy-combustion of bituminous and sub-bituminous coals but little change for lignite [25,26]. However, other studies have shown a significant increase in Hg concentrations in flue gas during oxy-firing [27], but also in the $Hg^{(2+)}/Hg(tot)$ [19–29]. Increasing O_2 during oxy-firing has also been seen to enhance the proportion of oxidized Hg (Hg^{2+}), while increasing sulphur reduced the extent of oxidation [28]. Most authors have explained this impact of oxy-firing on Hg speciation, compared to that under air-firing conditions, as consequence of the CO_2-rich flue gas re-circulation to the boiler [30]. Other researchers [20], have observed SO_2, NO_x, HCl and H_2O vapor, as the main agents involved in Hg°/Hg^{2+} ratio changes, being NO_x the main specie involved in Hg oxidation, thereby, similar Hg°/Hg^{2+} proportions would be obtained for similar concentrations of this compounds in the atmosphere, regardless of the major gas constituent was CO_2 (oxy-firing) or N_2 (air-firing). However, until the moment, most reported studies carried out to evaluate the impact of oxy-coal combustion on TMs fate, are referred to coal combustion, while little research [12,31,32] has been developed with respect to these elements in an oxy-firing process of pure of coal-mixed biomass fuels.

Other relevant aspect, for which further research is necessary with regards to biomass addition in oxy-fuel combustion processes, is the effect on ash quality, fouling and corrosion processes, as these more extreme conditions may imply more exigent performance of materials employed in the power plants. Moreover, the use of recycled flue gas may lead to the accumulation of undesirable corrosive species in the boiler [33,34].

In this regard, reported studies [35–37], have shown increased deposition ratios under oxy-fuel conditions in comparison to standard air combustion conditions, although these studies show temperature dependence and fuels/blends ash composition as the major factors affecting gas and ash compositions rather than the combustion environment. In comparison to oxy-coal combustion, a synergetic effect of cofiring biomass with coal, under oxy-fuel conditions has been detected with respect to mitigating deposition formation, improving the burnout and lowers NOx emissions, as result of the reduced peak temperatures [38]

One of the most important changes encountered in these new conditions are the increase in the SO_2 concentration, when using coal, while increasing the share of biomass produced an increment in the SO_3/SO_2 ratio and in the HCl content in the flue gas. However, with respect to the deposits, similar sulphur levels are found when varying the share of biomass, as a consequence of the reaction of sulphur with the alkalis, especially potassium, originating higher levels of K_2SO_4 in the combustion gas [33–39]. Nevertheless, other authors have detected an increase in potassium alumino-silication in comparison to potassium sulfation under oxy-firing, especially for higher Ca:S mole ratios [40,41], In this sense, sulphur and alkali contents of the parent fuels may induce both advantages and disadvantages, as while higher sulphur concentration in the boiler may convert alkali chlorides released from the biomass to sulphates, thus corrosion could be reduced, the higher alkali content in biomass ashes, will potentially increase the sulphur retention in the fly ash when co-firing with coal [10]. Major iron enrichment in fly ashes has been also reported in comparison to air combustion [40,41].

According to the foregoing, the present study performs an analysis of the influence of different oxy-fuel combustion atmospheres on Hg fate and speciation in coal-biomass co-firing processes in fluidized bed combustion processes, in comparison to a conventional combustion process. The effect of this technology will be also evaluated in regards to ash quality and deposits formation processes. The results obtained through this study intend to comprise a knowledge base for the development of Hg control technologies in oxy-firing processes and, to anticipate the potential corrosion phenomena that these new conditions may cause.

2. Experimental

2.1. Fuels analysis

As a first step for this study, a complete characterization of the fuels selected was carried out. Among the available fuels, a sub-bituminous coal (Puertollano coal) and a biomass (thistle) were chosen, as this coal contains a significant amount of mercury (to enter in the process for Hg evaluation) and also, a high quantity of sulphur (of interest for the corrosion study), while thistle present a high concentration of chlorine and alkaline compounds of interest for both the evaluation of the corrosion process and Hg behavior. Table 1 shows the chemical characterization of the samples employed. The proximate and ultimate analyses of the fuels were conducted by utilizing LECO Truspec equipment. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to quantify the minor elements content in fuels (ash analyses), while Hg content was determined by a direct mercury analyzer from Milestone (DMA-80).

Table 1
Fuels analysis.

Sample	Coal	Thistle
Proximate analysis (% as received basis)		
Moisture	4.0	5.5
Ash	33.5	5
Volatile matter	24.5	74.5
Ultimate analysis (% dry basis)		
C	48.6	44.2
H	3.8	6.2
N	1.0	0.7
S	0.71	0.19
O	12.3	42.5
Cl	0.07	1.26
Calorific value (MJ/kg)		
HHV, w.b.	18.91	16.75
HHV, d.b.	19.70	17.73
LHV, w.b.	17.95	15.28
Ash analysis (g/kg, as received)		
Na	0.7	6.0
K	4.2	8.7
Ca	4.6	9.2
Mg	2.5	2.1
Al	41	0.7
Fe	26	0.60
Si	98	0.030
Trace metals (μg/g)		
Hg	0.27	0.011