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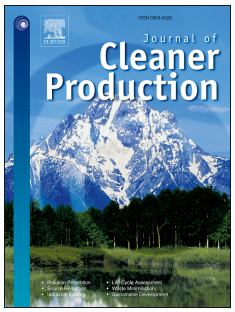

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D.T. Pio, L.A.C. Tarelho, T.F.V. Nunes, M.F. Baptista, M.A.A. Matos

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Daniel Torrão Pio (D.T. Pio): Methodology, Investigation, Formal analysis, Writing – Original Draft, Writing – Review & Editing, Visualization

Luís António da Cruz Tarelho (L.A.C. Tarelho): Conceptualization, Methodology, Investigation, Writing – Review & Editing, Supervision, Project administration

Teresa Filomena Viera Nunes (T.F.V. Nunes): Methodology, Investigation

Miguel Filipe Baptista (M.F. Baptista): Investigation

Manuel Arlindo Amador de Matos (M.A.A. Matos): Methodology, Investigation

Co-combustion of residual forest biomass and sludge in a pilot-scale bubbling fluidized bed

D.T. Pio*, L.A.C. Tarelho, T.F.V. Nunes, M.F. Baptista, M.A.A. Matos

Department of Environment and Planning & Centre for Environmental and Marine Studies (CESAM)

University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

*Corresponding author: danieltp@ua.pt (D.T. Pio)

Abstract

Keywords: biomass, sludge, bubbling fluidized bed, combustion, chlorine

Abstract

In this work, the co-combustion of residual forest biomass from eucalyptus and its blend with different amounts of primary and secondary sludge from the pulp and paper industry was studied in a pilot-scale bubbling fluidized bed reactor. The main objective was the determination of sludge addition influence on the overall process and on the composition of the exhaust gases, with emphasis on chlorine emissions, namely present in the solid phase (fly ashes) and in the gaseous phase (hydrogen chloride), and nitrogen oxides emissions. The co-combustion process of residual forest biomass with primary sludge (up to 5% in mass) and secondary sludge (up to 10% in mass) was successfully demonstrated as a valid energy valorization option. Except specific cases, no significant emissions increase of nitrogen oxides, carbon monoxide or hydrogen chloride were found with the addition of sludge. In fact, hydrogen chloride emissions decreased, potentially due to an increase in the chlorine retention in ashes caused by the high inorganic content present in the sludge. This high inorganic content can also lead to a significant increase in ash production during the combustion process. Thus, consequently, without proper maintenance, significant ash accumulation along the combustion system may occur, which can decrease the process efficiency and cause equipment damage.

Word count: 7511 (excluding references)

Abbreviations

BAT	Best Available Technologies
BFB	Bubbling Fluidized Bed
EL	Experiments with secondary sludge
ELP	Experiments with primary sludge
ELV	Emission Limit Value
FTIR	Fourier Transform Infrared Spectroscopy
HTSU	High Temperature Sampling Unit
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
RFB	Residual Forest Biomass

1. Introduction

Sewage sludge is an unavoidable byproduct of wastewater treatment processes (Hao et al., 2018). This byproduct has been accumulating in the recent years due to lack of proper valorization and disposal methods (Sung et al., 2018). In countries that produce pulp and paper, primary and secondary sludges from the pulp and paper industry may account for more sludge production than municipal wastewater treatment plants (Meyer et al., 2018). Co-combustion of these wastes with other fuels (e.g., residual forest biomass) is recognized as possible, due to the relatively moderate calorific value of sludges (Kijo-Kleczkowska et al., 2016; Zhao et al., 2019). This process is also promising because it allows the reduction of the sludge volume to be disposed, as well as its energetic valorization by production of heat and power (Chen et al., 2019). Furthermore, both waste sludge and residual forest biomass (RFB) from eucalyptus are byproducts from the pulp and paper industry and considered as potential alternative fuels and renewable energy resources (Sung et al., 2018). Regarding solid and exhaust gases emissions, it is commonly suggested that adding sludges to the combustion process of Cl-rich fuels may reduce chlorine (Cl) deposition and bed agglomeration, while increasing NOx emissions, due to the sludges high nitrogen content, and Cl gaseous emissions (HCl) (Aho et al., 2010; Aho and Silvennoinen, 2004; Åmand et al., 2006; Åmand and Leckner, 2004).

Cl emissions are associated with diverse problems of deposition and corrosion in combustion systems. During biomass combustion processes, the Cl present in the fuel is released and can be present in both gas phase and solid phase. Furthermore, Cl can ease the mobilization of diverse inorganic compounds (Strömberg and Björkman, 1997), such as alkali metals present in the burning biomass particles, easing the reaction between these and other substances (Xie and Ma, 2014). Thus, Cl contributes to the increase of problems related to the alkali metals, such as corrosion and agglomeration in the combustion system. Depending on the temperature, it is recognized that a high Cl content in the fuel can cause a significant increase of the

emissions of alkali metals (Olsson et al., 1997). Nonetheless, Cl release from the combustion particles can be controlled to a certain point by limiting the maximum temperature of the process (Jensen et al., 2000). Thus, the higher Cl content present in biomass (in comparison with coal (Lokare S.S., 2008)), limit the steam production process conditions in biomass combustion systems, due to temperature limitations (Hupa, 2012; Nielsen et al., 2000; Viklund, 2013).

Cl release during the devolatilization phase is related to the organic and inorganic fractions of Cl present in the fuel. Cl released at low temperature is associated to organic compounds or HCl and can be recaptured in the chars by secondary reactions with available alkali metals (Johansen et al., 2011). Then, re-release of the captured Cl can occur due to KCl sublimation during pyrolysis and combustion at high temperatures (Johansen et al., 2011). Thus, all relevant Cl species involved in combustion processes are highly volatile, and a high volatilization of Cl is expected (Johansen et al., 2011; Loo and Koppejan, 2008).

Accordingly, Lith et al., (Lith et al., 2004) observed high Cl percentage release, including complete dechlorination, during combustion of spruce and fiberboard with process temperature between 500 and 850ºC. Diaz-Ramírez et al., (Díaz-Ramírez et al., 2014) observed Cl release near 50% at temperatures below 700ºC and complete dechlorination at around 800ºC, during brassica and poplar combustion. Strömberg and Björkman (1997) studied the pyrolysis and gasification of different types of biomass (sugarcane trash, switch grass, lucerne and straw rape) and observed that under biomass pyrolysis and gasification conditions, Cl release under 200ºC is not significant, 20-50% of Cl was released at low temperatures such as 300 to 400ºC, and 30-60% of the total Cl was still left in the chars at 900ºC. Jensen et al., (Jensen et al., 2000) studied the release and transformation of K and Cl as a function of temperature during the pyrolysis of straw in a laboratory batch operated reactor. The authors observed the release of Cl in two main phases: 60% was released when the temperature was raised from 200ºC to 400ºC and the remaining fraction was released

at temperatures between 700 and 900ºC. Knudsen et al. (Knudsen et al., 2004), observed that 25 to 75% of the Cl present in the fuel was released to the gaseous phase at temperatures lower than 500ºC, during combustion experiments with different types of biomass. Afterwards, the Cl was released by volatilization under KCl form, mostly between 700 and 800ºC. For temperatures above 800ºC, the authors observed complete dechlorination for all experiments performed.

During devolatilization (200-400ºC), Cl is released to the gaseous phase mainly under HCl form (van Lith et al., 2006); at these relatively low temperatures, the free Cl ion tends to react with hydrogen ions to form HCl, but not with alkaline metals to form alkali chlorines. With temperature increase, HCl formation tends to decrease (Xie and Ma, 2014). For higher temperatures, a significant part of Cl is released under KCl form and associated to char combustion (Díaz-Ramírez et al., 2014; Jensen et al., 2000; Knudsen et al., 2004; Xie and Ma, 2014). After formation and release to the gaseous phase in the combustion system, the alkali chlorines tend to condensate over fly ash particles or heat exchangers (Loo and Koppejan, 2008). Thus, part of the released Cl during biomass combustion seems to become associated to the solid phase of the exhaust gases, namely fly ashes, or deposited in heat exchangers, while the other part is emitted in the gaseous phase as HCl in the exhaust gas (Loo and Koppejan, 2008).

Due to the close relation between K and Cl, the release behavior and reaction mechanism of these species is dependent on their initial molar ratio present in the biomass (Johansen et al., 2011). The major Cl compound in biomass is KCl, which is stable in solid phase until temperatures of 700ºC to 800ºC are attained (Johansen et al., 2011); for temperatures lower than 700ºC to 800ºC, the vapor pressure of KCl is negligible (Johansen et al., 2011). Nonetheless, the Cl initially present as KCl can react with functional groups present in the organic matrix of the biomass, leading to release of HCl according to equation 1 (van Lith et al., 2006):

$$R - COOH(s) + KCl(s) \rightarrow R - COOK(s) + HCl\,(g) \qquad \text{(Equation 1)}$$

Jensen et al., (Jensen et al., 2000) suggested that at temperatures between 200 and 400ºC, the original organic matrix of the biomass is destroyed, and Cl can be released from the solid phase and transferred to a liquid tar phase. Afterwards, Cl is further released to the gaseous phase in the form of HCl (g) or suffers secondary reactions with K on the char surface. Some further release of Cl under the form of HCl might be due to the reaction of KCl with functional oxygenated groups present in the chars, where HCl is released and K is bound to the char matrix. Jensen et al., (Jensen et al., 2000) concluded that by using adequate operating conditions, for example, low heating rates and large reactors, HCl emissions in gaseous phase can be significantly minimized during biomass pyrolysis.

As previously referred, the biomass type has a considerable influence on the Cl emissions (Díaz-Ramírez et al., 2014; Knudsen et al., 2004). Some studies suggest that the percentages of Cl emitted, in relation to the Cl content present in the fuel, are significantly higher for fuels with less Cl content, due to the fact that Cl emissions are conditioned by the number of proton donors, such as carboxyl and phenolic groups (Díaz-Ramírez et al., 2014; Knudsen et al., 2004). Cl-rich fuels, such as wheat, rice, brassica, etc., present limited interaction between the inorganic Cl and the proton donating sites, thus, leading to lower Cl percentage release (Díaz-Ramírez et al., 2014). The addition of sludges (typically rich in sulfur) modifies the chemistry involved due to the reaction between KCl and sulfur. Thus, a total removal of Cl from the fly ashes is theoretically possible if sulfur exists in sufficient amounts to react with all KCl present (Equation 2, (Vainio et al., 2013)).

$$2\,\mathrm{KCl(g)} + SO_2\mathrm{(g)} + 0.5\,O_2\mathrm{(g)} + H_2\mathrm{O(g)} \rightarrow K_2SO_4\mathrm{(s)} + 2\,\mathrm{HCl(g)} \qquad \text{(Equation 2)}$$

In the literature, it is also suggested that adding sludges may be beneficial for inhibiting Cl deposits formation due to the following mechanisms (Åmand et al., 2006):

- Sulphur in the sludges may react with potassium, producing sulphate and gaseous hydrogen chloride;

- Potassium chloride may be removed by condensation on fly ash particles added with the sludge;
- Potassium in gaseous phase may react with aluminosilicates present in the sludges;
- The deposits may be mechanically removed by the increased ash flows caused by the sludges.

Thus, with sludge addition it can be expected a decrease of Cl emissions in the solid phase and an increase of Cl emissions in the gaseous phase (Åmand and Leckner, 2004) (HCl, e.g. equation 2). Nonetheless, if the sludges are rich in Ca, Cl retention on ashes might increase while HCl concentration in the exhaust gases decreases. These aspects need to be characterized and studied experimentally.

In this work, the co-combustion process of RFB from eucalyptus with primary sludge (up to 5%wt) and secondary sludge (up to 10%wt) from wastewater treatment was characterized. The sludge resulted from the wastewater treatment in the pulp and paper industry. The influence of the addition of sludge on the overall process and on the exhaust gases composition, with emphasis on Cl emissions, namely present in the solid phase (fly ashes) and in the gaseous phase (HCl), and NO_x emissions, was evaluated. The objective was to properly characterize the impact of the integration of this energy valorization solution for the sludges, on the solids and exhaust gases emissions during the co-combustion operation.

2. Experimental work

The experimental infrastructure used in this work includes a pilot-scale bubbling fluidized bed (BFB) reactor with a combustion chamber of 0.25m diameter and 2.3m height made of AISI 310SS. This infrastructure was previously used for gasification works (Pio et al., 2018, 2017) but was properly updated for the co-combustion of RFB and sludges. The general layout of the updated experimental infrastructure is shown in Figure 1. The bottom bed of the reactor consists of 20kg of sand (98.3%wt. SiO_2

content)) with particle size in range 0.250 mm to 1.00 mm; the bottom bed of the reactor has a static height of around 0.24m above the primary air (fluidizing air) injectors. At typical operating conditions, the expanded (fluidized) bed height level is approximately 0.30m above the distributor plate; the fluidizing bed height level can be controlled by the discharge bed level at port C in Figure 1. The fluidized bed was operated at atmospheric pressure and in bubbling regime, with superficial gas velocity of around 0.28 to 0.30 m/s (depending on the operating conditions), and with average bed temperatures in the range of 800 to 850 ºC. The total combustion air was maintained at 250 NL/min, distributed in 80% primary air (fluidization) and 20% secondary air, in order to maintain the bottom bed and freeboard hydrodynamic conditions. The stoichiometry conditions of the combustion process were controlled by continuously monitoring the O_2 concentration in the exhaust gases, and through proper adjustment of the biomass feed, which was maintained between 3 and 4 kg/h.

The biomass fuel used included distinct types of chipped RFB derived from eucalyptus (*eucalyptus globulus*), different types of pellets produced from distinct fractions of RFB from eucalyptus (branches with leaves, bark, etc.), and mixtures of these types of RFB with primary (up to 5% wt.) and secondary (up to 10% wt.) sludges resulting from wastewater treatment processes in the pulp and paper industry. The pelletizing process of the RFB from eucalyptus was performed to increase the uniformity of the physical characteristics of the fuel and improve the fuel feeding regularity. The RFB from eucalyptus resulted from two different operations, namely from forestry operations, as for example trees logging, and was named eucalyptus RFB type A, and from industrial operations in the context of the pulp and paper industry, namely woodchip production from eucalyptus logs, and was named eucalyptus RFB type B. Both types of RFB were chipped, dried at atmospheric conditions and sieved to a particle size below 5 mm. All the types of biomass were characterized in terms of properties with interest for thermochemical conversion of biomass (proximate and

ultimate analysis, and heating value), as shown in Table 1. Some types of biomass were characterized in terms of inorganics composition, as shown in Table 2.

The operating conditions during the combustion in the pilot-scale reactor were characterized, namely the biomass fuel feed rate, air feed rate, temperature and pressure along the reactor and gas composition at the exit. Table 3 shows information regarding the operating conditions and the respective reference of the experiments performed in this work.

The monitoring of the operating conditions was performed according to the following methodologies:

1) Characterization of the exhaust gases:
    a) O_2 concentration determination in a paramagnetic analyzer (ADC-700);
    b) H_2O, O_2, CO, CO_2, CH_4, NO, SO_2 and HCl determination through heated sampling and analysis (180ºC) with measuring principle by FTIR (Gasmet CEM-II);
    c) Total particles concentration determination through isokinetic sampling in quartz filters and their chemical characterization (Cl, Na, K and Ca). The isokinetic sampling for particle concentration determination was performed downstream of a cyclone and, in some cases, downstream of a bag filter located after the cyclone. The content of Cl, K, Na and Ca in the particles present in the exhaust gases (thinner fly ashes) is determined in terms of the content of soluble inorganic ions (Cl^-, K^+, Ca^{2+} and Na^+) by ion chromatography in liquid phase according to the procedure described by Calvo et al., in (Calvo et al., 2013).
2) Characterization of bottom bed ash and fly ash deposited in different locations of the combustion system;
    a) Determination of chemical elements content (Cl, Na, K, Ca, Mg, Al, Mn and P) was performed in an external laboratory (acid digestion followed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis).

3. Results and discussion

This section includes results regarding the combustion experiments performed, namely, reactor temperature profiles (along time and longitudinal), combustion exhaust gas composition profiles along time (CO_2, H_2O, HCl, NO, CO and SO_2), chemical composition (Cl, Na, K and Ca) of fly ash present in the exhaust gases, chemical composition (Cl, Na, K, Ca, Mg, Al, Mn and P) of bottom bed ashes and of fly ashes deposited in surfaces along the combustion system.

3.1. Temperature profiles

The evolution of temperature with time in different locations along the reactor during the combustion of the different mixtures of biomass follows a similar pattern and shows steady-state conditions of operation. These conditions were observed when using only RFB from eucalyptus or mixtures of this biomass with primary (up to 5%wt) and secondary sludge (up to 10%wt) (Figure 2). The temperature stability, despite the fuel mixtures variability and feeding irregularities caused by the heterogeneous physical characteristics of the RFB, is justified based on the recognized suitable mass and energy transfer characteristics provided by the BFB operation regime (Knoef, 2005; Loo and Koppejan, 2008; Tarelho et al., 2011). The bed material allows the absorption, storage and release of thermal energy and its mixing contributes to the existence of uniform temperature in the bottom bed section. Consequently, the biomass is rapidly converted after being fed to the reactor, due to the high heat transfer. In this work, the bed temperature was maintained between 800 and 850ºC.

The longitudinal temperature profile for the different combustion experiments performed is shown in Figure 3. It is observed that the temperature increases from the inside of the bed to the freeboard zone located immediately above the bed, where the biomass is fed. The maximum temperature is observed close to the secondary air injection. Above this region the temperature decreases with height due to heat losses

through the reactor walls, convection with the flue gas and the existence of a heat exchanger (liquid water with a flow rate of 0.6 L/min) located 1 m above the distributor plate (Figure 1). Similar to the observation performed regarding the temperature profiles along time, it was observed that the introduction of sludge mixed with RFB did not cause major changes in the longitudinal temperature profile.

3.2. Gas composition profiles

In this section, it is analyzed the typical concentration profile along time of different gaseous species (CO_2, H_2O, HCl, NO, CO and SO_2) present in the exhaust gases, during the combustion experiments with different biomass mixtures (Table 3).

3.2.1. CO_2 and H_2O

In Figure 4, it can be observed typical CO_2 and H_2O concentration profiles for the exhaust gases. It can be observed that both CO_2 and H_2O show small fluctuations with time which can be justified by irregularities in the biomass feeding rate and the heterogeneous physical and chemical characteristics of the biomass mixtures used. Nonetheless, for long periods of operation, it can be assumed that the system was operating in steady-state conditions in terms of CO_2 and H_2O concentration. CO_2 concentration was typically between 12 and 17%v (dry gas), which are typical values of industrial combustion systems (Loo and Koppejan, 2008). The addition of primary and secondary sludge did not cause any noticeable change in the CO_2 and H_2O concentration profiles.

3.2.2. HCl

The HCl concentration profiles along time (Figures 5 and 6) show a distinct behavior from the other chemical species (e.g., CO_2, H_2O) analyzed. While these species show a concentration that fluctuate around an average value, the HCl concentration increases immediately after the introduction of biomass until attaining a

291 maximum value. Afterwards, HCl concentration decreases with time until reaching a
292 value that changes only in minor amounts with time. This behavior is more evident in
293 experiments with sludge addition. For these experiments, the addition of sludge to the
294 feedstock mixture caused an immediate decrease of HCl concentration in the
295 combustion flue gases (see Figure 5). This can be justified by the sludges high content
296 in ashes rich in CaO (Tables 1 and 2), which acts as adsorbent for acid species such
297 as HCl. In fact, the addition of Ca is recognized as an effective measure for HCl
298 removal in combustion systems (Xie and Ma, 2014). Therefore, sludge addition seems
299 to promote a decrease of the HCl concentration.

300 Despite the analogous conditions of operation obtained for the different combustion
301 experiments performed (e.g. Figures 2,3 and 4), it is observed that the HCl
302 concentration presents significant differences between experiments (Figure 6). On one
303 hand, this can be justified by the distinct Cl content present in each type of biomass
304 used as a feedstock (Table 1). On the other hand, it seems that lower stoichiometric
305 ratios (assumed by lower O_2 concentration in the combustion exhaust gases) tends to
306 contribute to higher HCl concentration in the exhaust gases, being that for the same
307 fuel mixture and bed temperature, lower HCl concentration values were found for lower
308 O_2 concentration in the exhaust gases (e.g. ELP-5 #2 and ELP-5 #4). This needs to be
309 investigated in future works.

310 It was also observed an effect of the operation time on the concentration of HCl in
311 the exhaust gases (Figure 5), i.e., with the increase of operation time, the concentration
312 of HCl in the exhaust gases tended to decrease. This effect might be related to the fact
313 that at the end of each combustion experiment the reactor bed was replaced by a new
314 sand bed. Thus, each experiment started with a clean bed without biomass/sludge
315 ashes. Therefore, it is reasoned that the concentration of HCl might be influenced by
316 the equilibrium between ash accumulation in the bottom bed and their capacity to
317 adsorb HCl. This effect was particularly relevant during combustion experiments where
318 sludge was included in the biomass mixture used as feedstock; the sludge promoted a

higher introduction of Ca compounds in the reactor, and thus increased the capacity of the ashes to adsorb HCl.

3.2.3. NO

In Figures 7 and 8, it can be observed the NO concentration for the different combustion experiments performed and its relation with the primary and secondary sludges addition. The addition of secondary sludge caused a major increase in NO concentration during the combustion of eucalyptus RFB type A (Figure 7 (a)). This can be justified by the difference between the nitrogen content present in the secondary sludges in comparison to the RFB from eucalyptus (Table 1). Analogous results were obtained for eucalyptus RFB type B (EL-5, EL-10 and EL-10#2). The addition of secondary sludge caused only a slight increase in the average NO concentration during the combustion of pellets from eucalyptus bark (Pellets A and A*), however, it led to the increase of the fluctuation of the NO concentration value (Figure 7 (b)). The addition of secondary sludge did not cause noticeable changes in NO concentration during combustion experiments with pellets from eucalyptus branches (Pellets E, Figure 7 (c)). This can be justified by the already relatively high nitrogen content present in this type of biomass (Table 1). The addition of primary sludge (up to 5%wt) does not seem to promote any major change in the concentration of NO for all the experiments performed (Figure 7 (d)).

Thus, in some cases, it was observed that the addition of secondary sludge promoted an increase in NO concentration in the exhaust gases; however, in general, it was not observed a significant difference between the NO concentration values in experiments performed without sludges addition or with sludges addition in the referred mass percentages. Typically, it was observed that the nitrogen content of the biomass has direct influence on the NO concentration in the exhaust gases. NO concentration values expressed as NO_2 (at 6%v O_2, dry gas) were typically between 215 mg/Nm^3 and 433 mg/Nm^3. The highest values were found during combustion experiments with

pellets from eucalyptus branches, which is justified by the higher nitrogen content present in this biomass (Table 1). For comparison, the values obtained for the NO concentration in these experiments were plotted against the ELV referred in the Best Available Technologies (BAT) reference document for Large Combustion Plants (IPPC 2016, 2016) (180 mg/Nm^3, 6% O_2) in Figure 8. It is observed that the experimental values obtained are always above the referred limit.

3.2.4. CO

In general, it is observed that the concentration of CO in the exhaust gases is below the emission limit value (ELV) (500 mg/Nm^3, 11% O_2, Figure 9 (a)) imposed for biomass boilers in the Portuguese legislation (in Portaria n.º 677/2009 (Governo de Portugal, 2009), Portaria n.º 190-B/2018 (Governo de Portugal, 2018) does not include CO ELVs). Nonetheless, during some experiments the CO concentration value exceeded the ELV (e.g., EL-10# 2, Figure 9 (b)). This is related to significant biomass feeding fluctuations caused by the heterogenous physical characteristics of the biomass used as a feedstock in these experiments. Sludge addition did not promote any visible change in CO concentration.

3.2.5. SO_2

It is observed that SO_2 concentration values are relatively low (Figure 10), which results from the relatively low concentration of sulfur present in the biomass used as a feedstock (Table 1). It is also observed that the addition of sludge did not cause any significant change on the SO_2 concentration profiles, even though the secondary sludges have higher sulfur content than all the types of RFB from eucalyptus tested. This behavior may result from the fact that the sludge incorporation (up to 10%wt) is not high enough to influence SO_2 concentration in the exhaust gases. Furthermore, these sludges have a high Ca content, which can cause retention of SO_2 on ashes

(Vainio et al., 2013). The highest concentration value of SO_2 found was 17.2 mg/Nm^3 (dry gas, 11% O_2) during experiment EL-10, which is significantly lower than the ELV (500 mg/Nm^3, 11%O_2, Figure 10) referred for biomass boilers in the Portuguese legislation (in Portaria n.º 677/2009 (Governo de Portugal, 2009), Portaria n.º 190-B/2018 (Governo de Portugal, 2018) does not stipulate O_2 reference value for SO_2 concentration ELV).

3.3. Particulate matter analysis

3.3.1. Fly ashes in the exhaust gases

In this section, the average particle concentration and composition (Cl, K, Ca, and Na) in the exhaust gases during the co-combustion experiments performed is presented and analyzed.

The average particle concentration in the exhaust gases during each combustion experiment performed is shown in Figure 11. It is typically observed lower particle concentration in experiments with chipped RFB from eucalyptus (EL-0, EL-5, EL-10 and EL-10 #2) than in experiments performed with pellets produced from fractions of RFB from eucalyptus (EL-0 #2, EL-10 #3, EL-10 #4, EL-10 #5, EL-10 #6, EL-10 #7, EL-10 #8, ELP-5, ELP-5 #2, ELP-5 #3 and ELP-5 #4). In part, this is justified by the lower ash content of the chipped RFB (Table 1); bark and leaves typically have higher ash content than fractions of wood. In fact, combustion experiments of pellets from eucalyptus bark (EL-10 #6, EL-10 #8 and ELP-5 #3) and pellets from eucalyptus branches (Pellets E, EL-10 #7, ELP-5 #2 and ELP-5 #4) presented particle concentration significantly higher than other combustion experiments with other types of pellets. Nonetheless, the co-combustion experiment performed with the biomass feedstock with highest ash content (Pellets C, EL-10 #5) did not present higher fly ash concentration in the exhaust gases. Thus, other factors apart from the ash content of the biomass may have influenced the formation of fly ash, such as the physical

characteristics of the pellets (e.g., density and hardness) and the chemical composition of the ashes (Sippula, 2010). Future works should address this behavior.

Two main observations can be made regarding the effect of the addition of primary and secondary sludge on the particle concentration in the exhaust gases. In some cases, the sludge addition seems to promote a small increase of the particle concentration (e.g. EL-10 #3 and ELP-5), which is justified by the higher ash content present in the sludge in comparison to the RFB from eucalyptus (Table 1). In other cases, it was observed the opposite, i.e., the decrease of particles concentration after the addition of sludge (e.g. EL-10 #6, EL-10 #7 and ELP-5 #3). Nonetheless, in these experiments, when the sludge feeding ended, the particles concentration continued to decrease. The justification for this phenomenon may be related to the high content of Ca present in the ashes retained in the bed and on the exhaust duct, which may have prevented the formation of thinner fly ashes. In fact, the major components present in the fly ashes from the exhaust gases are Cl and K (Figure 12), whereas Ca was found as the major element in the composition of bottom bed ashes and ashes deposited in inner surfaces of the combustion system (Figure 15). This will be discussed in the following Section 3.3.2.. Similar results were observed in other works regarding co-combustion of RFB with sludge from the pulp and paper industry (Vainio et al., 2013).

K concentration (Figure 12) in the fly ashes was typically higher for experiments with pellets from eucalyptus bark (e.g., Pellets A*, EL-10 #6, EL-10 #8 and ELP-5 #3) and pellets from eucalyptus branches (Pellets E, EL-10 #7, ELP-5 #2 and ELP-5 #4). Furthermore, a linear correlation between K and Cl concentration was found for the particle matter in the exhaust gas (Figure 13 (a)). This relation is close to the mass ratio 1:0.91 for K:Cl in the compound KCl, which indicates that a significant part of Cl in the fly ashes present in the exhaust gases might be in the form of KCl, as suggested by some other works (Loo and Koppejan, 2008).

Ca and Na concentration values in the fly ashes present in the exhaust gases (Figure 12) are significantly lower than the K and Cl concentration values. Furthermore,

even though Ca has the capacity to remove Cl in gaseous effluents (Partanen et al., 2005), only a weak relationship between Ca and Cl in the fly ashes was observed (Figure 13 (b)). The relatively low concentration value found for Ca in the fly ashes is in contrast with that found for the bottom bed ashes and ashes deposited in inner surfaces of the BFB reactor (Figure 15, Section 3.3.2); in fact, Ca is the main alkali element present in the ashes from the RFB and sludges used (Table 2). The Na concentration in the fly ashes present in the exhaust gases is lower than Ca, however, it is observed a stronger linear relation between the mass concentration of Na and Cl (Figure 13 (c)). Nonetheless, this relation is significantly lower than the mass ratio of 1:1.5 for Na:Cl present in the compound NaCl.

In summary, it is observed that the mass concentration of chemical elements in the fly ashes sampled in the exhaust gases during the combustion experiments shows the following decreasing order of abundance: Cl > K > Ca > Na.

In Figure 14, it is shown the contribution from the gaseous phase (measured as HCl) and the particulate phase (fly ashes present in the exhaust gases) to the emission of Cl during the combustion experiments. It is observed that the concentration of Cl (quantified as the chlorine ion Cl^-, by ion chromatography) in the solid phase (associated to fly ashes in the exhaust gases and denoted as Cl-particles in Figure 14) is higher than in the gaseous phase (associated to HCl and denoted as Cl-HCl in Figure 14) for the combustion experiments performed. It is also observed that the Cl emissions for both solid and gas phases are related to the Cl content in the biomass mixture used as feedstock. For example, experiments with pellets from eucalyptus bark (e.g. Pellets A*, EL-10 #6, EL-10 #8 and ELP-5 #3) or eucalyptus branches (Pellets E, EL-10 #7, ELP-5 #2 and ELP-5 #4), which have a high Cl content (Table 1), caused higher average emissions of Cl in both solid and gaseous phase (Figure 14). Similar to the observations made regarding Cl concentration in the gaseous phase (HCl), discussed in the previous Section 3.2.2, the addition of sludge seems to have caused a decrease of Cl concentration in the fly ashes present in the exhaust gases (e.g. EL-10

458 #2, EL-10 #6, EL-10 #7, ELP-5 and ELP-5 #3), which can be related to the Ca present
459 in the sludge ashes and the respective adsorption of Cl by heavier particles retained in
460 the BFB, e.g., in the bottom bed; however, some exceptions were observed that must
461 be accounted (EL-10 #3, EL-10 #4 and EL-10 #5). This phenomenon should be
462 addressed in future works.
463
464 3.3.2. Bottom bed ashes and fly ashes deposited along the combustion system
465 In this section, results regarding the chemical characterization (Ca, K, Mg, P, Na,
466 Al, Mn and Cl) of samples of bottom bed ashes and fly ashes deposited along the
467 combustion system are presented and analyzed. The chosen locations of the
468 combustion system for sampling the ashes were the bottom bed surface layer, the
469 reactor walls above the distributor plate, a cold (liquid water cooling) deposition probe
470 located 2.2 m above the distributor plate, the bottom of the horizontal exhaust duct of
471 the reactor and the ash retained in the cyclone located downstream of the BFB reactor.
472 The ashes were sampled after the experiments with reference EL-10 #4, EL-10 #6, EL-
473 10 #7, ELP-5 #3 and ELP-5 #4 (Table 3); The average concentration values (Ca, K,
474 Mg, P, Na, Al, Mn and Cl) found are shown in Figure 15.
475 It is observed that Ca is present in significantly higher concentration in the different
476 ash samples than the other analyzed elements (Figure 15). This results from Ca being
477 the main chemical element present in the ashes for both RFB from eucalyptus and
478 sludges (Table 2). Regardless of the sampling location, the average concentration of
479 chemical elements on the ashes is by descending order of abundance:
480 Ca>K>Cl>Mg>P>Na>Al>Mn. This composition is distinct from that observed for the fly
481 ashes in the exhaust gases, where K and Cl were the main chemical elements (Figure
482 12). Nevertheless, K and Cl are still present in relatively high concentration in the
483 bottom bed ashes and deposited ashes along the reactor surfaces. These elements
484 are associated with corrosion processes (Davidsson et al., 2007; Hupa, 2012; Loo and
485 Koppejan, 2008; Nielsen et al., 2000; Vainio et al., 2013), thus, their retention in the

bottom bed ashes is desired. In fact, co-combustion of RFB with sludge from the pulp and paper industry has been referred as beneficial to prevent corrosion from compounds derived from Cl and K (Aho et al., 2010; Aho and Silvennoinen, 2004; Åmand et al., 2006; Vainio et al., 2013), which could be related to the high Ca content of the ashes.

The concentration of the analyzed chemical elements in the bottom bed ashes is significantly lower than in the fly ashes deposited in other locations of the combustion system. This is justified by the fact that even after the combustion process, the bottom bed particle samples are composed mainly of the original sand (98.3%wt. SiO_2 content) and silicon was not analyzed. Nonetheless, the sum of the average concentration of the analyzed chemical elements on the particle samples collected at the surface layer of the bottom bed is around 4.4%wt., which means that the sand from the bed is enriched with typical elements from the ashes of the biomass.

Accordingly, it is observed a trend for the increase of the concentration of the analyzed chemical elements with the increase of the distance to the distributor plate. Furthermore, the maximum concentration value for these analyzed chemical elements was typically found in the ashes collected on the exhaust duct or the cyclone. Some exceptions observed are: experiment EL-10 #4 where Cl concentration decreased from the surface of the bed to the exhaust duct and experiment EL-10 #7 where the highest Cl concentration value was found in the ashes collected in the deposition probe located at the top of the combustion chamber. In fact, the maximum average Cl concentration value was found in the ashes collected on the deposition probe. It was also found that the average sum of chemical elements analyzed (Na, K, Mg, Al, Mn, P, Ca and Cl) in the ashes collected in the deposition probe and exhaust duct was 40.2% and 44.6%wt db, respectively. This shows that the fly ashes deposited along the reactor are significantly enriched in typical elements of biomass inorganics, which in industrial scenarios may lead to relevant corrosion issues.

Thus, the excess Ca introduced through the sludge addition seems to have caused a higher retention of Cl in the bottom bed ashes and fly ashes deposited on solid surfaces exposed to the exhaust gases. This might justify the reduction in HCl concentration in the exhaust gases observed with the addition of sludge, which was previously discussed in Section 3.2.2.

4. Conclusions

The objective of this work was the evaluation of the co-combustion process of RFB from eucalyptus with primary (up to 5%wt) and secondary (up to 10%wt) sludge from the pulp and paper industry in a pilot-scale BFB reactor, with emphasis on NO and Cl related emissions.

The continuous monitoring of the operating parameters, such as temperature and exhaust gas composition along time in the BFB, during the co-combustion process of the different mixtures of RFB and sludge, showed that the reactor was operating under steady-state conditions.

Regarding the composition of the exhaust gases, a continuous HCl concentration decrease with time until reaching an almost constant value was observed during the combustion process. This behavior can be related to the Cl retention promoted by the alkaline elements present in the biomass, such as Ca and K. In fact, sludge addition typically caused a decrease in the concentration of HCl in the exhaust gases, which can be related to the high content of alkaline elements present in the sludge (e.g., Ca).

Regarding NO concentration in the exhaust gases, it was observed that it is mainly influenced by the characteristics of the feedstock used. It was also observed that the addition of sludge to RFB with low N content (e.g. eucalyptus wood chips) caused a significant increase in NO concentration during the combustion process. On the other hand, addition of sludge to RFB with high N content (e.g., eucalyptus bark) did not seem to promote any noticeable increase in the NO concentration. For all the combustion experiments performed, the NO concentration (expressed as NO_2) values

found in the exhaust gases met the stipulated ELV for biomass furnaces in the Portuguese legislation (Portaria 677/2009 (Governo de Portugal, 2009)), but are above the ELV indicated in the BAT reference document for Large Combustion Plants (IPPC 2016, 2016).

Regarding CO concentration in the exhaust gases, it was observed that it is immensely influenced by the regularity of the biomass feeding and that sludge introduction in the fuel mixture did not seem to promote any noticeable changes. Furthermore, by using an adequate control of the feeding conditions and an appropriate stoichiometric ratio, it was possible to meet the stipulated ELV for CO concentration in the exhaust gases from biomass furnaces according to the Portuguese legislation (Portaria 677/2009 (Governo de Portugal, 2009)).

Regarding SO_2 concentration in the exhaust gases, it was observed that this value was significantly lower than the ELV stipulated for biomass furnaces in the Portuguese legislation (Portaria 677/2009 (Governo de Portugal, 2009)). Furthermore, sludge addition to the fuel mixture did not cause a noticeable increase in the concentration of SO_2.

Regarding the fly ashes particles emitted with the exhaust gases, it was observed that Cl and K were the major inorganic chemical elements present in the fly ashes. It is reasoned that these two elements might be in the form of KCl, due to the observation of a linear relation between Cl and K with a mass ratio K:Cl close to 1:0.91. It was also observed that the mass of Cl emitted in the particulate phase was significantly higher than that emitted in the gas phase as HCl.

The characterization of the bottom bed ashes and ashes deposited in inner surfaces along the combustion system, considering the chemical elements Ca, K, Mg, P, Na, Al, Mn and Cl, showed that the average concentration of chemical elements in the sampled ashes is (by decreasing order of abundance) Ca>K>Cl>Mg>P>Na>Al>Mn, regardless of the location of the sampling point. This knowledge is relevant to understand the potential negative effects that ashes can

cause on combustion equipment, such as slagging and fouling, and upon the environment after emission to the atmosphere.

Thus, this work demonstrates the potential of the co-combustion of RFB from eucalyptus with primary or secondary sludge in BFB. Except specific cases, it was not found a significant increase of NO, CO or HCl emissions with the addition of sludge to the fuel mixture. In fact, the addition of sludge typically promoted a decrease of HCl concentration in the exhaust gases, which can be related to Cl retention in Ca rich ashes. Nonetheless, for RFB from eucalyptus with low N content, the addition of sludge to the fuel mixture led to higher NO emissions. Furthermore, the high inorganic content present in the sludge can originate a significant increase in the amount of ash production. The accumulation of these ashes along time and along the combustion system (e.g. heat exchangers), can promote operational problems, such as the decrease of the process efficiency, increase of maintenance operation needs and equipment damage. This must be investigated in future works.

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707 Table 1 – Characteristics of the different types of biomass used as feedstock in the
708 combustion experiments in the pilot-scale BFB.

	Eucalyptus RFB		**Pellets**						**Sludge**	
	Type A	Type B	A	A*	B	C	D	E	Primary	Secondary
Proximate analysis (%wt, db)										
Moisture	11.4	11.8	7.7	10.2	8.3	8.9	8.3	7.9	11.3	20.0
Volatile matter	77.3	80.5	78.3	78.1	78.2	77.1	79.0	77.1	na	na
Fixed carbon	21.5	16.6	16.7	17.5	19.0	15.7	17.7	18.4	na	na
Ash	1.2	2.9	5.0	4.5	2.8	7.3	3.3	4.4	61.5	26.5
Ultimate analysis (%wt, db)										
Ash	1.2	2.9	5.0	4.5	2.8	7.3	3.3	4.4	61.5	26.5
C	49.1	48.2	44.4	46.4	50.6	48.2	50.9	51.4	32.4	36.7
H	6.5	6.2	5.4	5.7	6.2	6.2	6.1	6.1	4.2	5.0
N	0.1	<0.2	0.2	0.7	0.8	<0.2	0.9	1.4	0.5	2.2
S	nd	0.03	0.03	nd	nd	0.03	nd	nd	nd	0.4
O (by difference)	43.2	42.7	44.7	42.3	39.5	38.3	38.6	36.3	1.4	29.0
Cl	0.05	0.05	0.20	0.40	0.14	0.05	0.18	0.38	0.02	0.19

709 wb - wet basis; db - dry basis; np – not available; nd – not determined, below the detection limit of the method, 100 ppm wt.

710

711 Table 2 – Concentration of Ca, Na, K, Mg, Al, Mn and P in the ashes from the different
712 types of biomass used as feedstock in the combustion experiments in the pilot-scale
713 BFB

	Pellets				Sludge	
	A*	B	D	E	Primary	Secondary
Ash elemental analysis	**Ppm wt., db**					
Ca	8060	6960	7910	9480	245000	106166
Na	635	3920	396	952	4290	nd
K	3240	2750	2610	6310	291	1134
Mg	1730	668	546	1421	1800	1608
Al	367	41.9	63.3	61.2	313	869
Mn	219	139	157	99	168	nd
P	302	289	263	511	3450	2500

714 db – dry basis; nd – not determined.
715

716 Table 3 – Combustion experiments reference and respective operating parameters.

Experiment reference	Biomass (%wt.)	Type of RFB	Average bed temperature [ºC]	O_2 (%v, dry gas) in the exhaust combustion gases
EL-0	100% eucalyptus	Eucalyptus RFB type A	804	7.0
EL-0 #2	100% eucalyptus	Diverse pellets	821	8.1
EL-5	5% secondary sludge + 95% eucalyptus	Eucalyptus RFB type A	815	7.0
EL-10	10% secondary sludge + 90% eucalyptus	Eucalyptus RFB type A	810	6.2
EL-10 #2	10% secondary sludge + 90% eucalyptus	Eucalyptus RFB type B	825	7.4
EL-10 #3	10% secondary sludge + 90% eucalyptus	Pellets A	837	7.1
EL-10 #4	10% secondary sludge + 90% eucalyptus	Pellets B	848	7.2
EL-10 #5	10% secondary sludge + 90% eucalyptus	Pellets C	839	6.9
EL-10 #6	10% secondary sludge + 90% eucalyptus	Pellets A*	830	5.9
EL-10 #7	10% secondary sludge + 90% eucalyptus	Pellets E	828	6.0
EL-10 #8	10% secondary sludge + 90% eucalyptus	Pellets A*	836	4.5
ELP-5	5% primary sludge + 95% eucalyptus	Pellets D	837	8.0
ELP-5 #2	5% primary sludge + 95% eucalyptus	Pellets E	819	6.0
ELP-5 #3	5% primary sludge + 95% eucalyptus	Pellets A*	838	5.5
ELP-5 #4	5% primary sludge + 95% eucalyptus	Pellets E	820	7.9

717 Legend: Diverse pellets – Different pellets used during the combustion experiment, namely, commercial pine pellets (2h), pellets A (5h)
718 and pellets B (2h); Pellets A – Pellets from eucalyptus bark resulting from operations in the pulp and paper industry (sample 1); Pellets
719 A*- Pellets from eucalyptus bark resulting from operations in the pulp and paper industry (sample 2); Pellets B – Pellets from eucalyptus
720 branches, resulting from forest maintenance operations, with residual amounts of eucalyptus foliage; Pellets C – Pellets from powdered
721 eucalyptus chips (<1mm) Pellets D – Pellets resulting from eucalyptus RFB type A and type B and eucalyptus foliage; Pellets E – Pellets
722 from powdered eucalyptus branches.

723

Figure 1 – Layout of the experimental infrastructure with the pilot-scale BFB reactor. Dashed line — Electric circuit, Solid line — Pneumatic circuit, A - Primary air heating system, B - Sand bed, C - Bed solids level control, D - Bed solids discharge, E - Bed solids discharge silo, F - Propane burner system, G - Port for visualization of bed surface, H - Air flow meter (primary and secondary air), I - Control and command unit (UCC2), J - Biomass feeder, K - Water-cooled gas sampling probe, , N - Gas sampling pump, O - Gas condensation unit for moisture removal, Y – Computer based control and data acquisition system, Z - Exhaust duct; O2 – Online paramagnetic analyzer for the determination of O_2 (ADC-700), FTIR – Online infrared analyzer for determination of H_2O, CO_2, CO, N_2O, NO, NO_2, SO_2, HCl, NH_3, CH_4, etc., HTSU – High Temperature Sampling Unit, UCD0, UCD1, UCD2 - Electro-pneumatic command and gas distribution units, UCE1 - Electronic command unit.

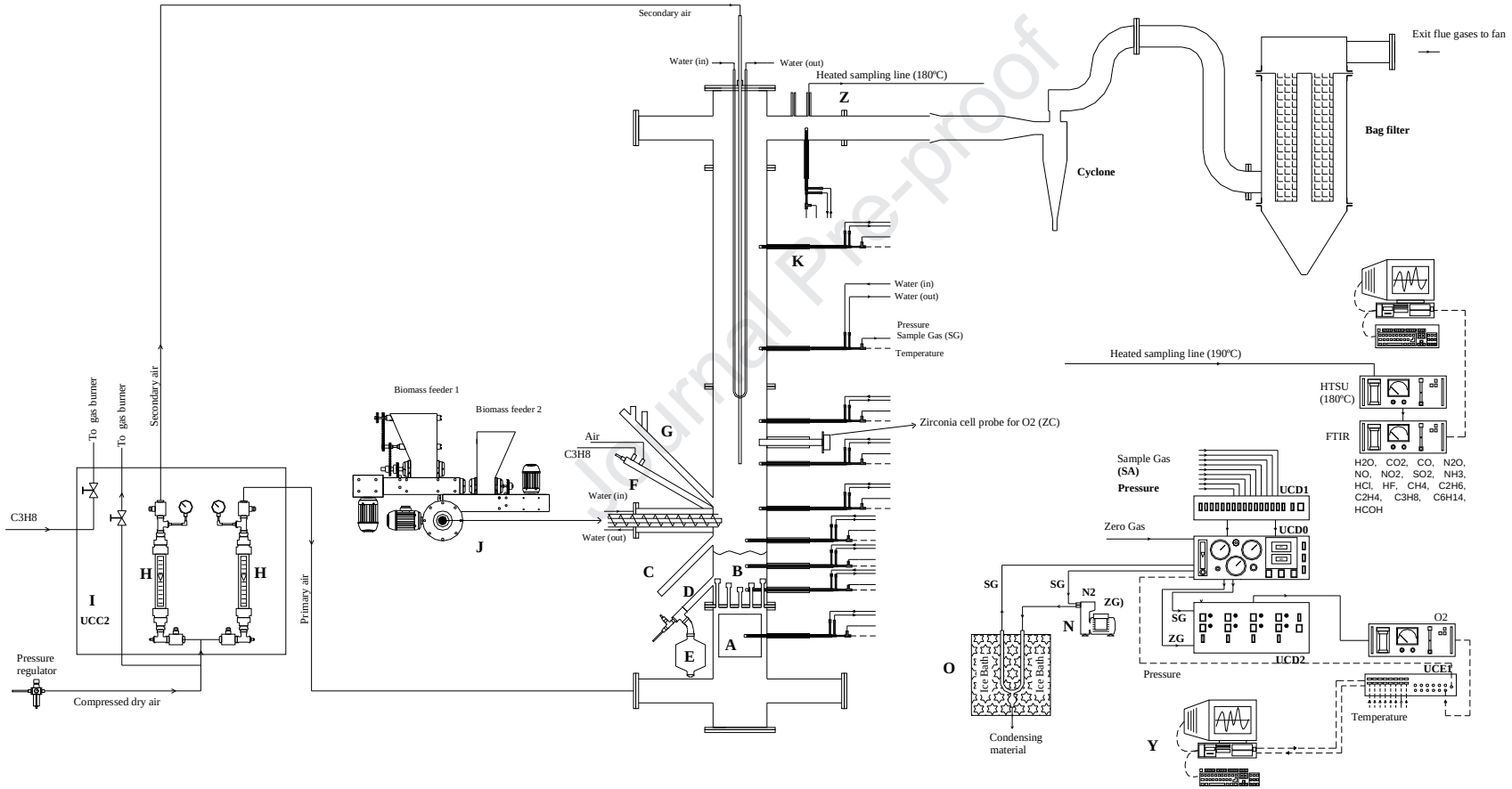
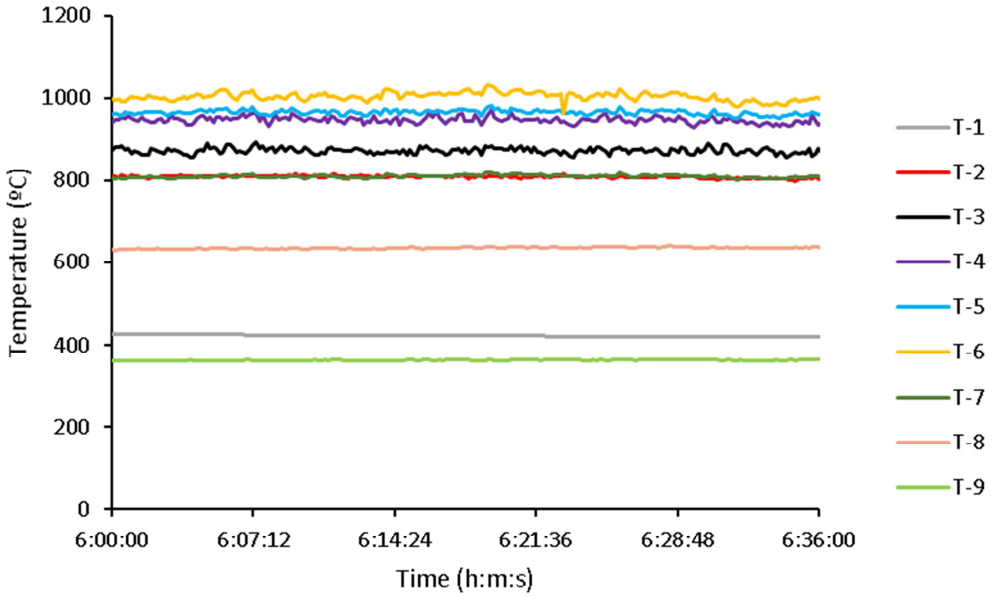
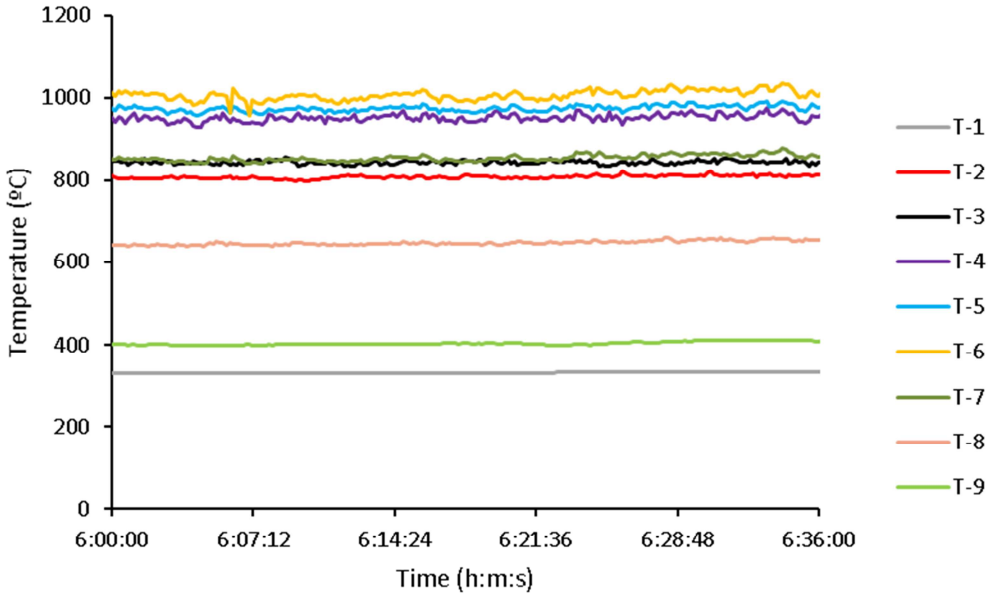


Figure 2 – Typical evolution of the temperature along time at different locations along the reactor height during the combustion experiments: (a) EL-0, (b) EL-10 and (c) ELP-5. Experiments reference according to Table 3. Temperature measurement locations above distributor plate: T1 – 0.05 m, T2 – 0.18 m, T3 – 0.30 m, T4 – 0.45 m, T5 – 0.66m, T6 – 0.86 m, T7 – 1.20 m, T8 – 1.68 m and T9 – 2.90 m.

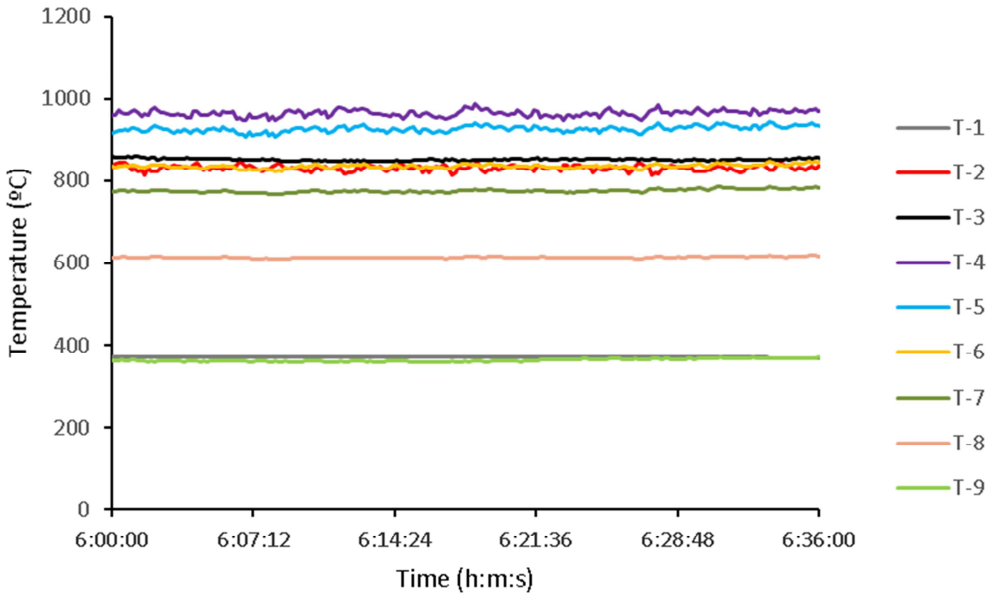


(a)



(b)

Figure 2 (continuation) – Example of the typical evolution of the temperature along time at different locations along the reactor height during the following combustion experiments: (a) EL-0, (b) EL-10 and (c) ELP-5. Experiments reference according to Table 3. Temperature measurement locations above distributor plate: T1 – 0.05 m, T2 – 0.18 m, T3 – 0.30 m, T4 – 0.45 m, T5 – 0.66 m, T6 – 0.86 m, T7 – 1.20 m, T8 – 1.68 m and T9 – 2.90 m.



(c)

Figure 3 – Longitudinal temperature profile in the BFB reactor during the biomass combustion experiments performed. Legend according to experiments references in Table 3.

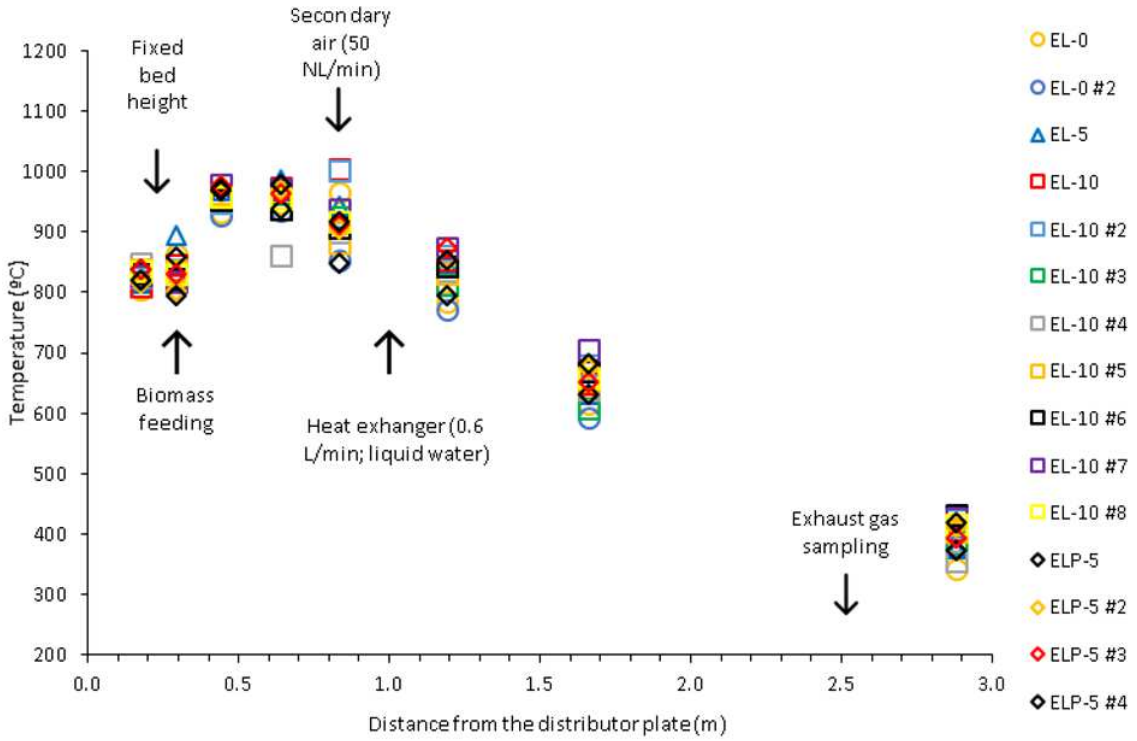
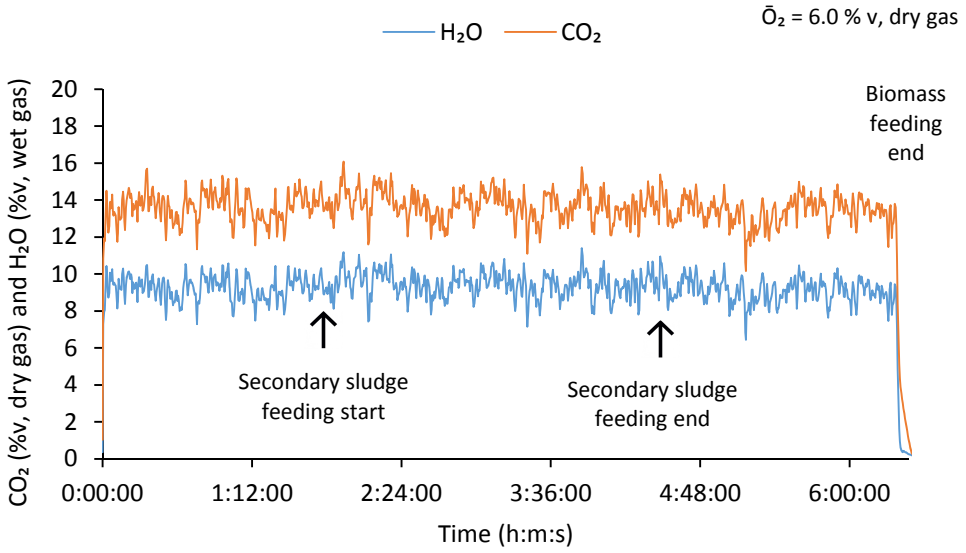
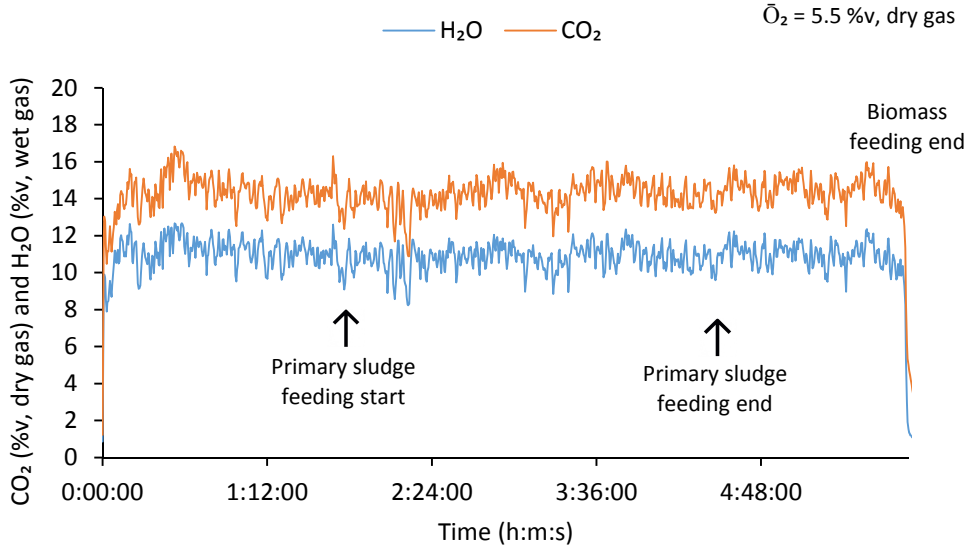


Figure 4 – Typical CO_2 and H_2O concentration along time in the exhaust gases for (a) EL-10 #7 and (b) ELP-5 #3. Experiment reference according to Table 3.

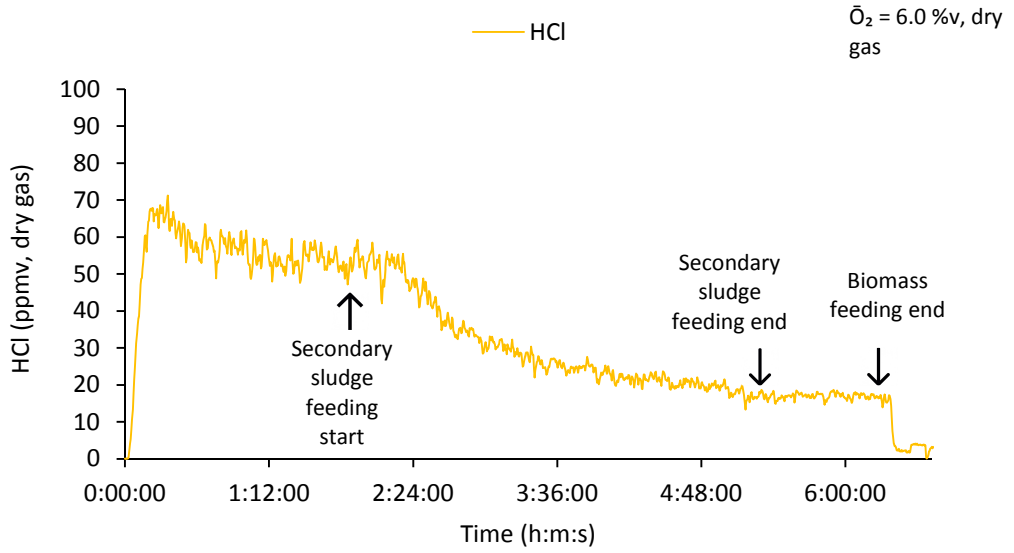


(a)

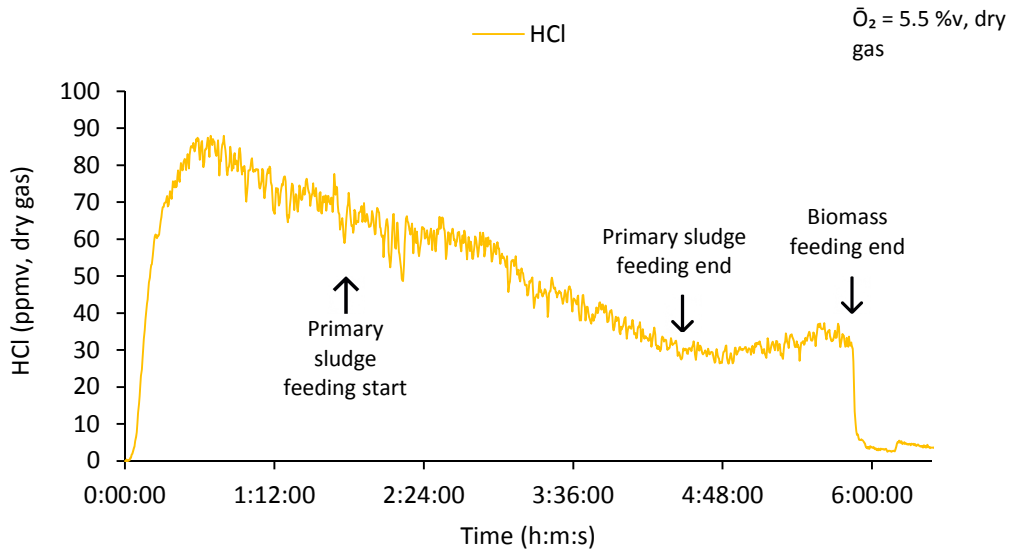


(b)

Figure 5 – Typical HCl concentration along time in the exhaust gases for (a) EL-10 #7 and (b) ELP-5 #3. Experiments reference according to Table 3.

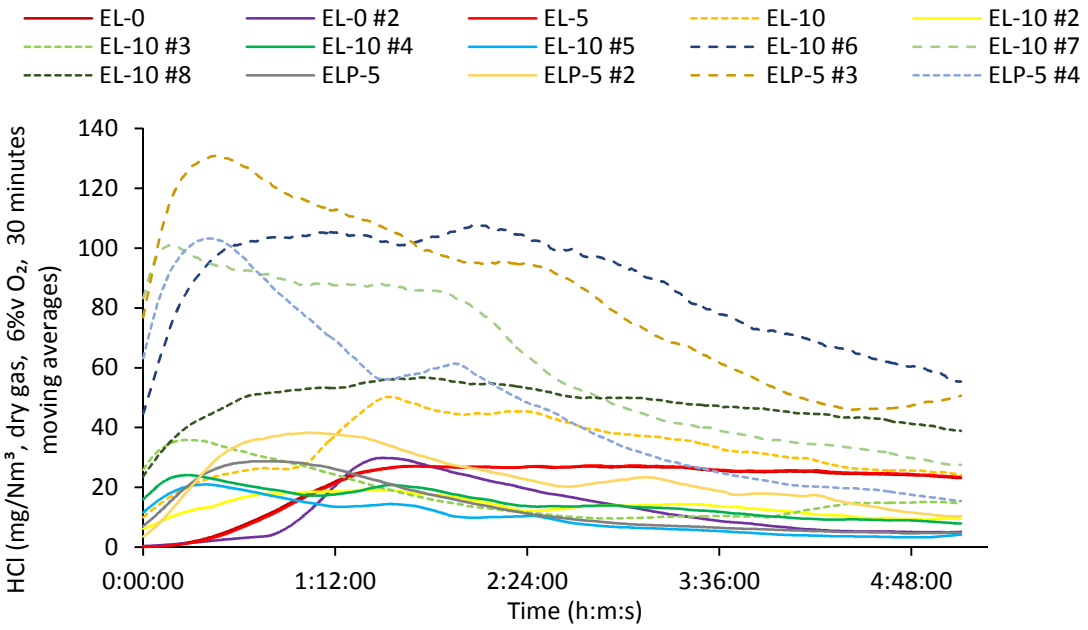


(a)



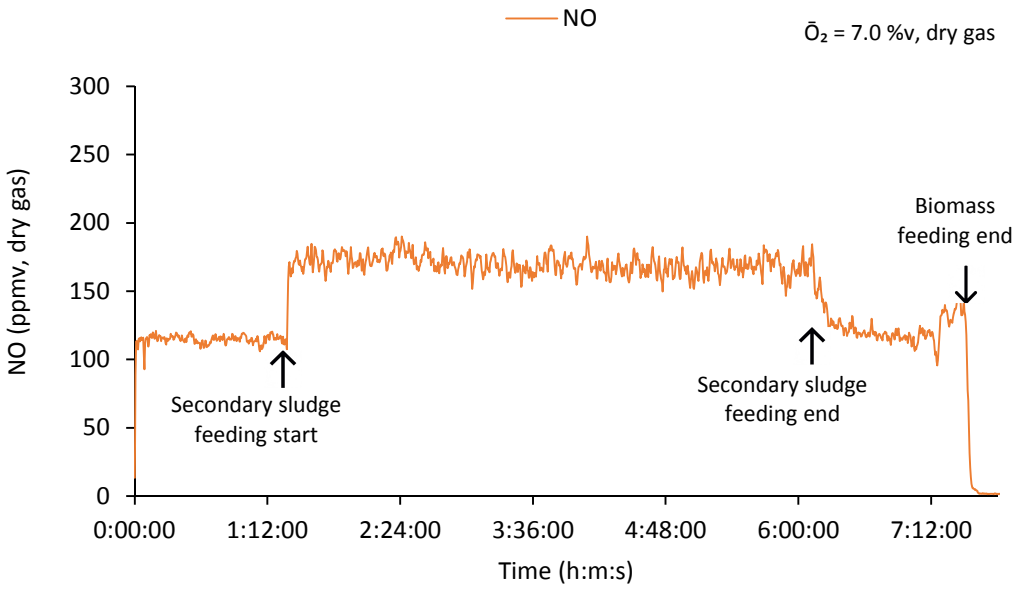
(b)

Figure 6 – HCl concentration along time (30 minutes moving average) for the different combustion experiments performed. Experiments reference according to Table 3.

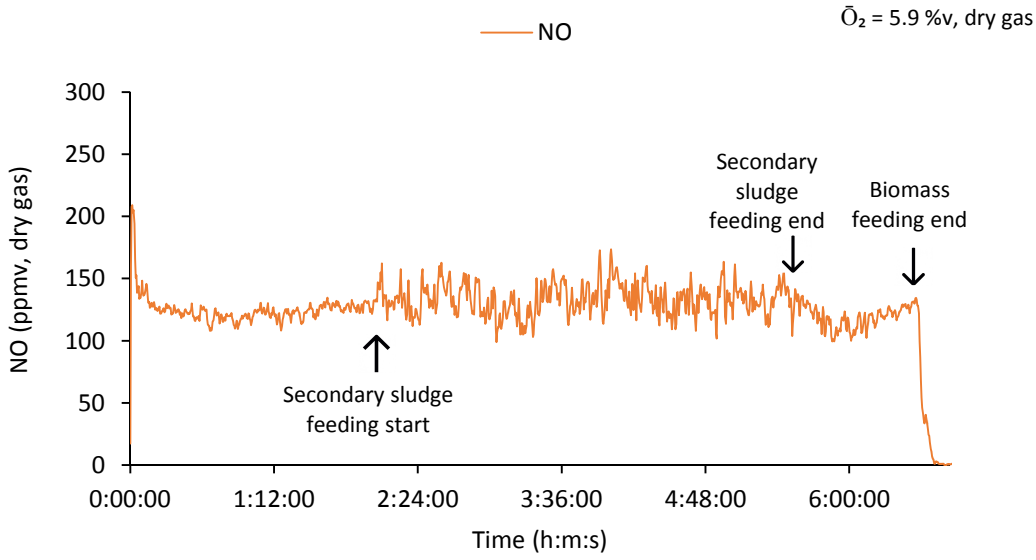


(c)

Figure 7 – Typical NO concentration along time in the exhaust gases for (a) EL-10, (b) EL-10#6, (c) EL-10 #7 and (d) ELP-5 #3. Experiments reference according to Table 3.

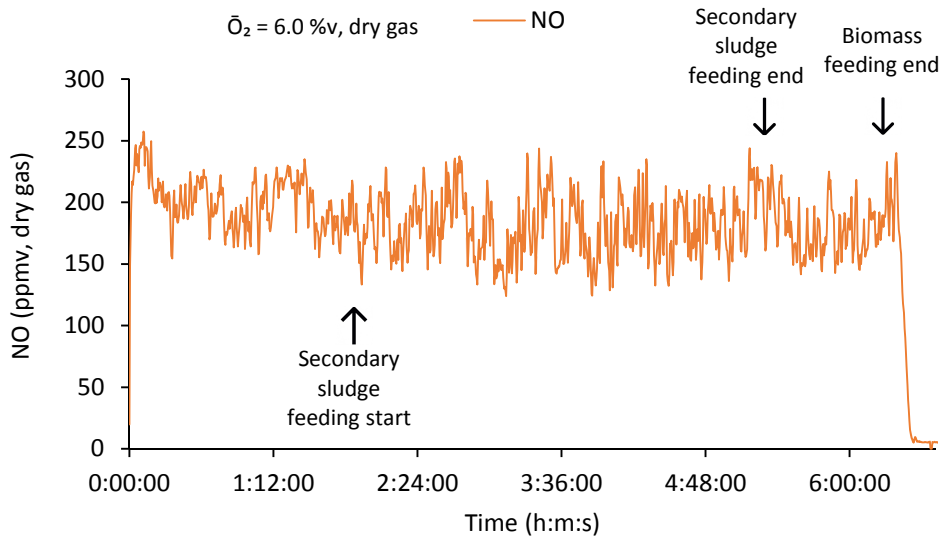


(a)

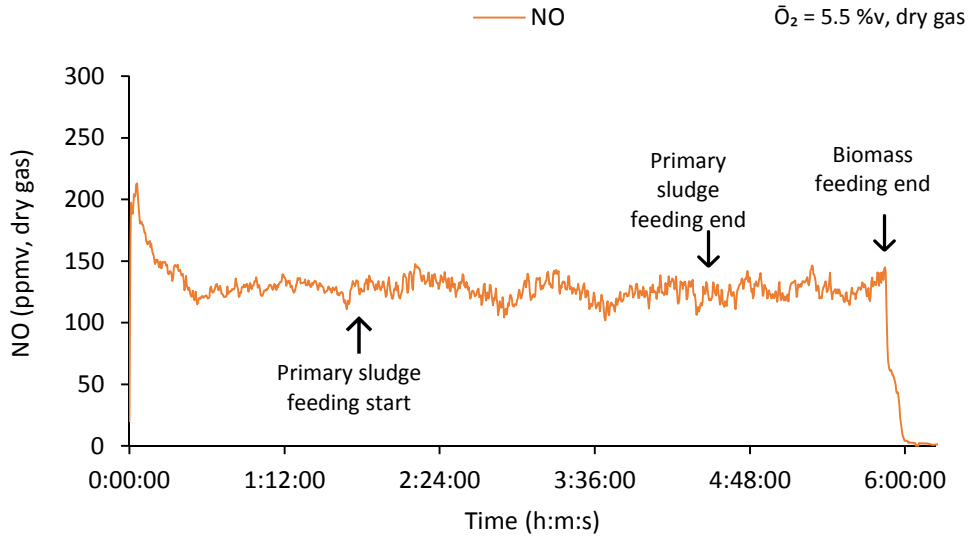


(b)

Figure 7 (continuation) – Typical NO concentration along time in the exhaust gases for (a) EL-10, (b) EL-10#6, (c) EL-10 #7 and (d) ELP-5 #3. Experiments reference according to Table 3.

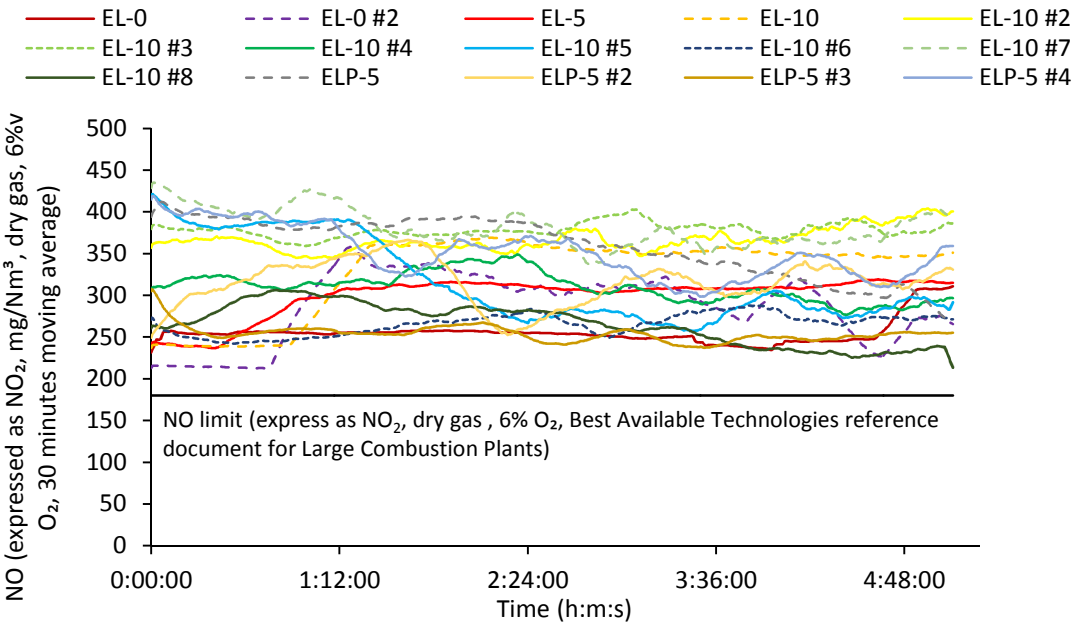


(c)



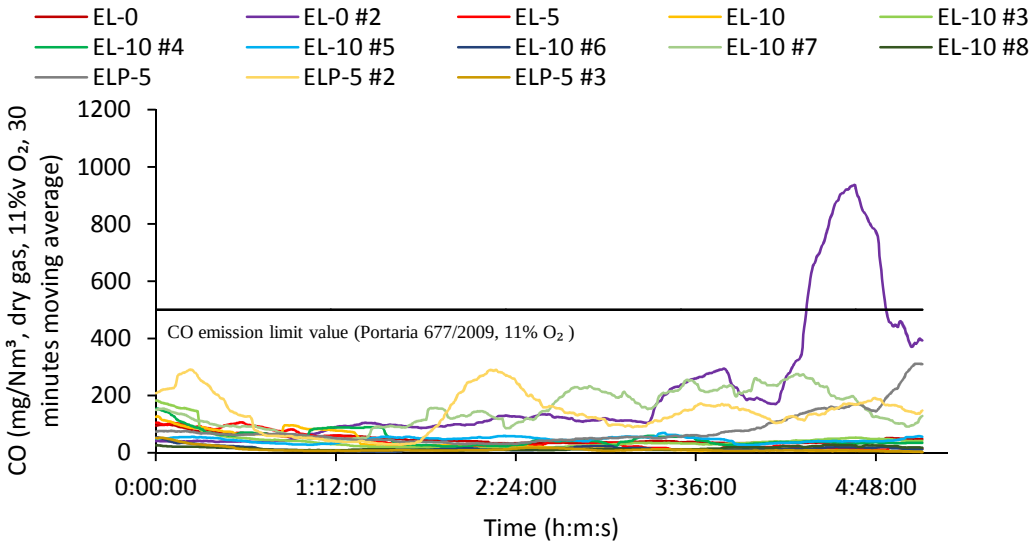
(d)

Figure 8 – NO concentration along time (30 minutes moving average) for the different combustion experiments performed and comparison with the limit value referred on the BAT reference document for Large Combustion Plants (IPPC 2016, 2016). Experiments reference according to Table 3.

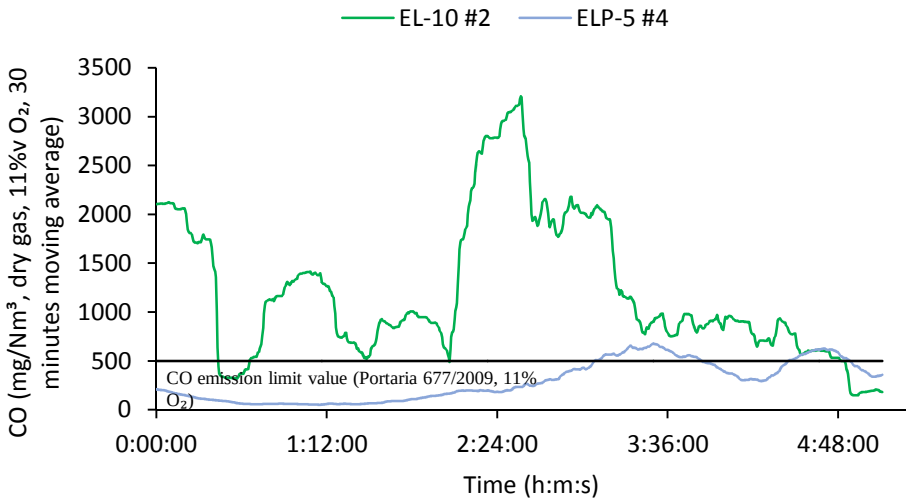


(e)

Figure 9 - CO concentration along time (30 minutes moving average) for the different combustion experiments performed and comparison with the limit value referred to biomass boilers in the Portuguese legislation, in Portaria 677/2009 (Governo de Portugal, 2009): (a) experiments with lower CO concentration values and (b) experiments with higher CO concentration values. Experiments reference according to Table 3.



(a)



(b)

Figure 10 - SO_2 concentration along time (30 minutes moving average) for the different combustion experiments performed and comparison with the limit value referred to biomass boilers in the Portuguese legislation, in Portaria 677/2009 (Governo de Portugal, 2009). Experiments reference according to Table 3.

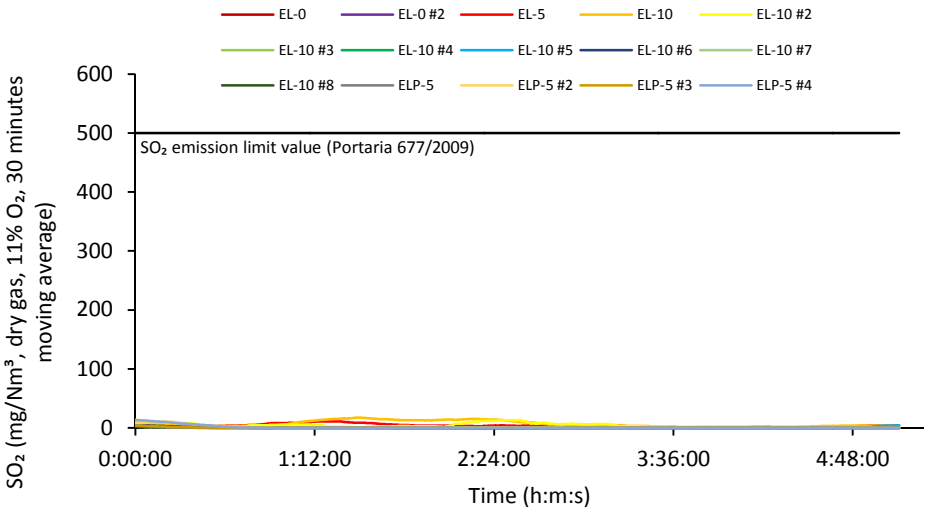
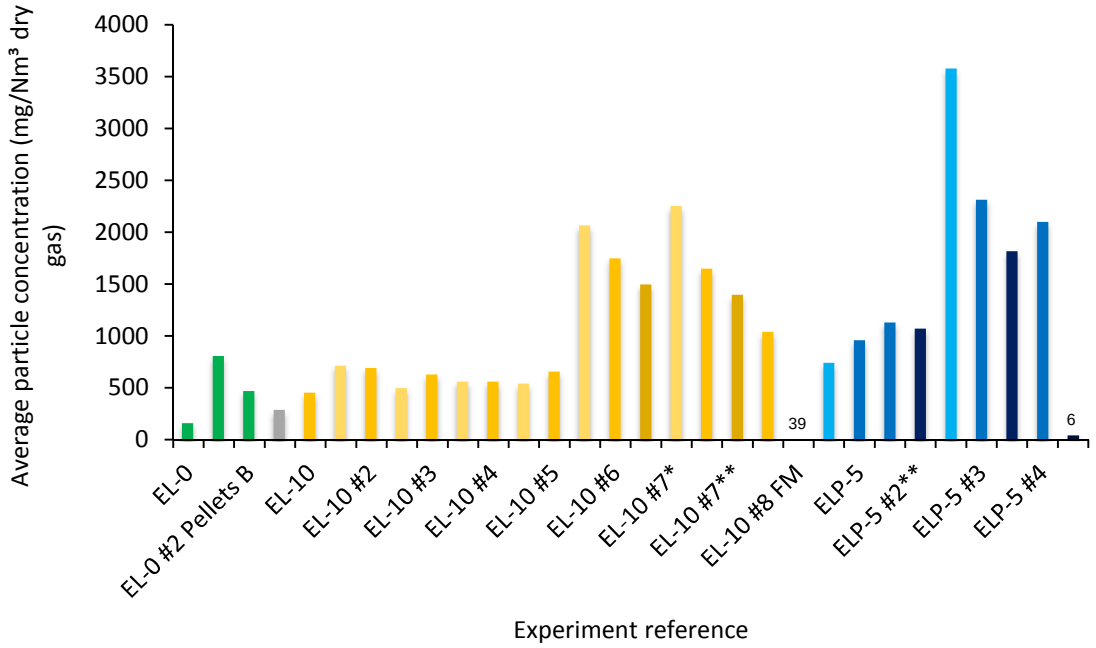


Figure 11 – Average particle (fly ash) concentration in the exhaust gases during the combustion experiments. The gas sampling was performed after the cyclone, except for references with FM, where the gas sampling was downstream of the bag filter. Experiments reference according to Table 3.

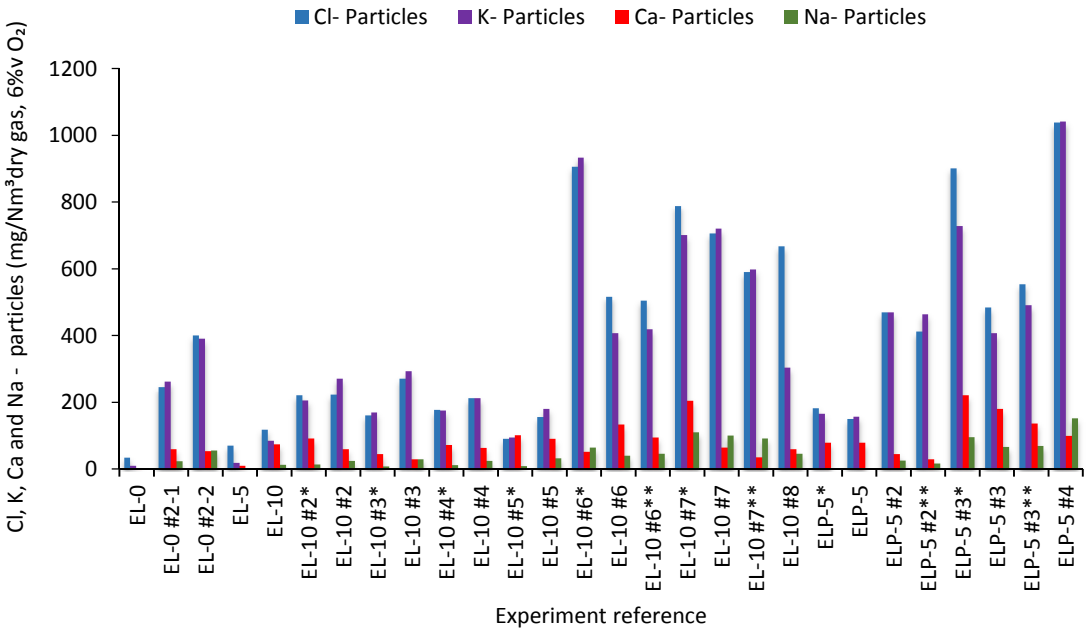


*- Only RFB, before introducing sludge;

**- Only RFB, after the co-combustion process of sludge with RFB;

FM- gas sampling after the bag filter.

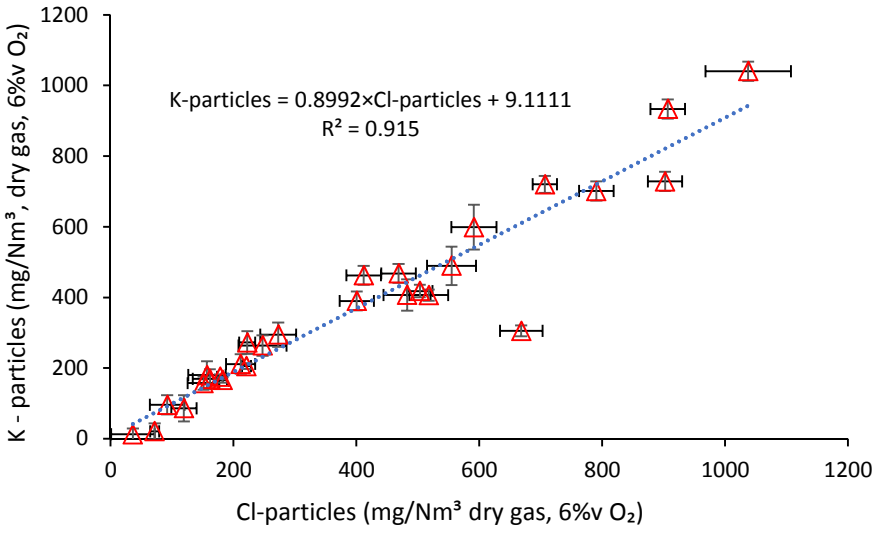
Figure 12 – Average Cl, K, Ca and Na concentration emitted associated with the fly ashes present in the exhaust gases during the combustion experiments. These elements were measured as ion Cl^-, K^+, Ca^{2+} and Na^+, and expressed as mg chemical element/Nm^3 dry gas, corrected to 6%v O_2. Sampling was performed downstream the cyclone (Figure 1). Experiments reference according to Table 3.



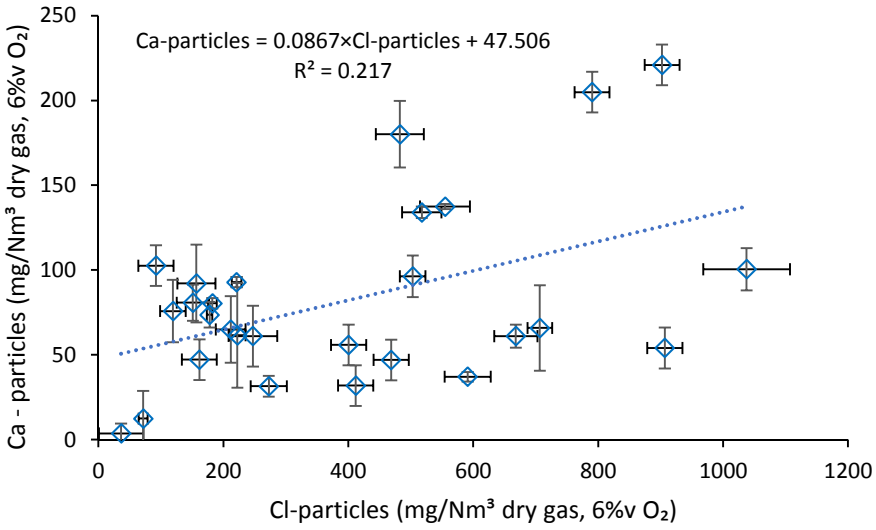
*- Only RFB, before introducing sludges;

**- Only RFB, after the co-combustion process of sludges with RFB.

Figure 13 – Relation between the content of K, Ca and Na with Cl in the fly ashes present in the exhaust gases during the combustion experiments: (a) K and Cl, (b) Ca and Cl and (c) Na and Cl.

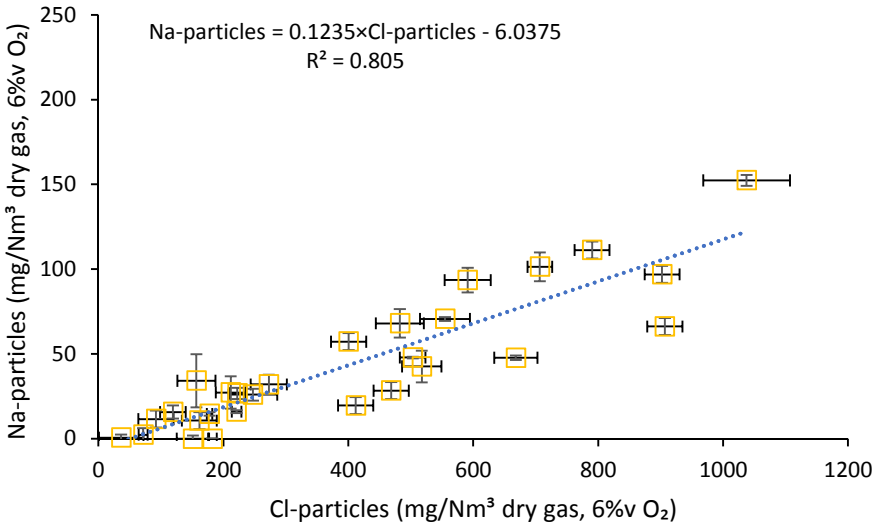


(a)



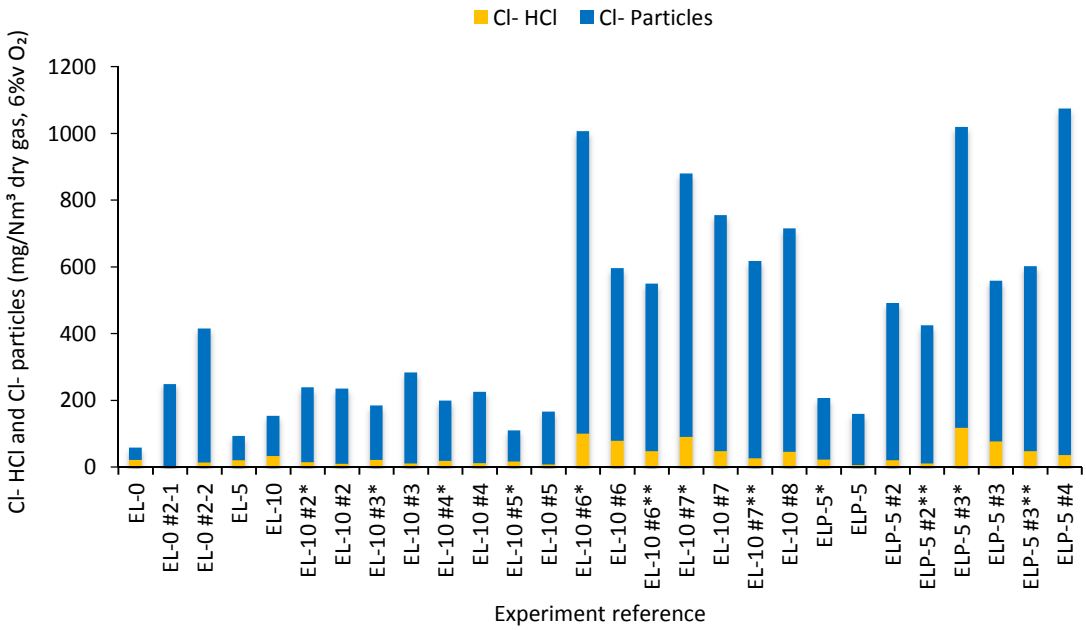
(b)

Figure 13 (continuation) – Relation between the content of K, Ca and Na with Cl in the fly ashes present in the exhaust gas during the combustion experiments: (a) K and Cl, (b) Ca and Cl and (c) Na and Cl.



(c)

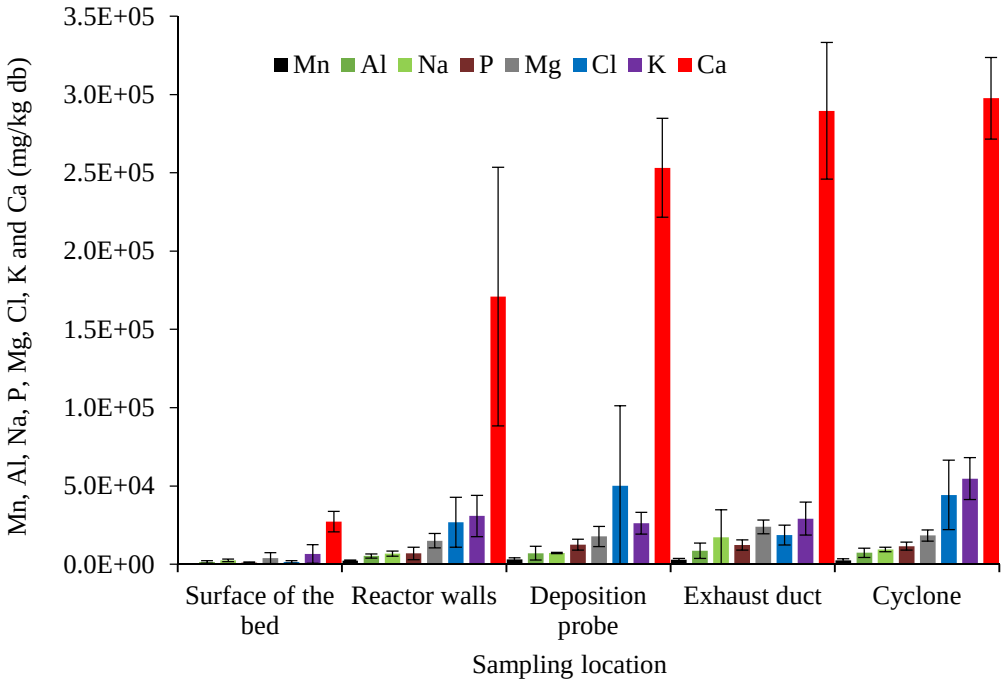
Figure 14 – Average Cl concentration in the solid phase, measured as ion Cl^- in fly ashes (denoted as Cl-particles), and expressed as mg Cl/Nm^3 dry gas corrected to 6%v O_2, and in gaseous phase (denoted as Cl-HCl), measured as HCl in the flue gas and expressed as mg Cl/Nm^3 dry gas corrected to 6%v O_2, in the exhaust gases during the combustion experiments. Sampling was performed downstream of the cyclone (Figure 1). Experiments reference according to Table 3.



*- Only RFB, before introducing sludges;

**- Only RFB, after the co-combustion process of sludges with RFB.

Figure 15 – Average composition (Ca, K, Mg, P, Na, Al, Mn and Cl) (and respective standard deviation) of the ashes deposited or settled in different locations of the combustion system.



Highlights

1. Co-combustion of residual forest biomass and sludge is shown as a valid valorization option;
2. Process stability was attained and demonstrated;
3. NO, CO and HCl emissions did not increase with sludge addition.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: