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Emissions from the combustion of eucalypt and pine chips in a fluidized bed reactor

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ABSTRACT

Interest in renewable energy sources has increased in recent years due to environmental concerns about global warming and air pollution, reduced costs and improved efficiency of technologies. Under the European Union (EU) energy directive, biomass is a suitable renewable source. The aim of this study was to experimentally quantify and characterize the emission of particulate matter (PM_{2.5}) resulting from the combustion of two biomass fuels (chipped residual biomass from pine and eucalypt), in a pilot-scale bubbling fluidized bed (BFB) combustor under distinct operating conditions. The variables evaluated were the stoichiometry and, in the case of eucalypt, the leaching of the fuel. The CO and PM_{2.5} emission factors were lower when the stoichiometry used in the experiments was higher (0.33 ± 0.1 g CO/kg and 16.8 ± 1.0 mg PM_{2.5}/kg, dry gases). The treatment of the fuel by leaching before its combustion has shown to promote higher PM_{2.5} emissions (55.2 ± 2.5 mg/kg, as burned). Organic and elemental carbon represented 3.1 to 30 wt.% of the particle mass, while carbonate (CO₃²⁻) accounted for between 2.3 and 8.5 wt.%. The particulate mass was mainly composed of inorganic matter (71% to 86% of the PM_{2.5} mass). Compared to residential stoves, BFB combustion generated very high mass fractions of inorganic elements. Chloride was the water soluble ion in higher concentration in the PM_{2.5} emitted by the combustion of eucalypt, while calcium was the dominant water soluble ion in the case of pine.

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Introduction

The growing interest in developing alternatives to fossil fuels has led the scientific community and other decision makers to consider other sources of energy (Brunner et al., 2009; Khan et al., 2009; McKendry, 2002; Obaidullah et al., 2012; Vamvuka and Sfakiotakis, 2011). The use of renewable energy sources

will become more important as the reserves of fossil fuels become smaller. The renewable energy sources increase the possibilities for self-sufficiency and can play an important role in reducing the greenhouse gas emissions (Nussbaumer, 2008; Saidur et al., 2011). Under the European Union (EU) energy directive, biomass is an eligible renewable source. The development of competitive biofuel conversion technologies

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with high conversion efficiency, low emissions, and with low operating cost is a challenge (Hustad et al., 1995). Among the technologies available, bubbling fluidized bed combustion (BFBC) is one of the most advantageous. This technology applied to biomass represents an important asset in many industrial processes and is a practical approach for increasing bioenergy use, because it presents several advantages that include high efficiency, fuel flexibility and low environmental impact (Koornneef et al., 2007; Obernberger and Dahl, 1998). Furthermore, this technology also allows a high rate of heat and mass transfer, low pressure drops, and uniform temperature distribution (Anthony, 1995; Werther et al., 2000). BFBC is a technology with high versatility that can be used for burning a very broad range of solid fuels (Anthony, 1995; Calvo et al., 2013; Duan et al., 2013; Kowarska et al., 2013; Leckner et al., 2004; Tarelho et al., 2011; Xie et al., 2007).

Despite the advantages, attention must be paid to operating and environmental problems. There are several factors that can influence operating conditions. The choice of biofuel depends on the option for the conversion process (McKendry, 2002). Plants depend on fundamental processes for growth (Jenkins et al., 1998) that have influence on its chemical characteristics and thus on the emission profiles. Solid biofuels present chemical elements in different concentrations depending on the type and origin of biomass (Obernberger et al., 2006). The chemical composition of biofuels is related to the composition of the soils and with the type of plant species, because different species will take up different compounds from the soil at different extents. The main problems derived from the biofuel chemical composition are related to ash produced during the combustion process. These problems comprise bed agglomeration, slagging, fouling and corrosion (Arvelakis et al., 2001; Hand and Kreidenweis, 2002; Nussbaumer, 2003; Silvennoinen and Hedman, 2013; Spliethoff et al., 2000). Elements like Si, K, Na, S, Cl, P, Ca, Mg, and Fe are involved in reactions leading to ash fouling and slagging. K and Cl are easily volatilized at high temperatures and condense in the convective section, contributing to corrosion, or are emitted as aerosols. Potassium can lead to K silicate formation with low melting points, causing slagging and bed agglomeration (Van Loo and Koppejan, 2008). The characteristics of the ashes may also limit their subsequent use (Hand and Kreidenweis, 2002; Nussbaumer, 2003; Silvennoinen and Hedman, 2013; Spliethoff et al., 2000). BFBC technology helps preventing some ash related problems as a result of the relatively low uniform temperature and good mixing of bed material (Armesto et al., 2002; Vamvuka et al., 2009; Yan et al., 2005). Biomass leaching is an option that can contribute to minimize some operating problems related either to alkali metals (e.g. K and Na), or to other elements, such as chlorine and sulfur. Increasing the ash fusion temperatures allows to reduce the ash related problems like bed agglomeration and deposit formation during combustion (Arvelakis et al., 2001; Bakker et al., 2002; Jenkins et al., 1996; Vamvuka and Zografos, 2004). Particles resulting from biomass combustion are composed of soot, organic and inorganic matter. Operation under stable and efficient conditions generates particulate emissions composed mainly of inorganic compounds. The environmental and health effects of particulate matter are dependent on its physical and chemical properties. Although good combustion conditions lead to lowest particulate emissions, several studies have reported highest oxidative stress, inflammatory, cytotoxic and genotoxic

activities and decreased cellular metabolic activity from particles generated under efficient combustion conditions rather than particles resulting from inefficient combustion (Happo et al., 2013; Uski et al., 2014). The size of the particles generated during combustion is a very important factor. Ultrafine particles (particle diameter < 100 nm) are particularly harmful to human health, because they have a sufficiently small size to penetrate the membranes of the respiratory tract and enter the bloodstream or be transported by the olfactory nerves to the brain (Pöschl, 2005). Hata et al. (2014) found that particles resulting from biomass combustion have a mass that fell within a range of < 100 nm and those particles smaller than 0.43 μm contribute greatly to the total levels of toxic polycyclic aromatic hydrocarbons (PAHs) and water-soluble organic carbon (WSOC).

Studies have shown that BFBC technology has high flexibility to burn a large variety of fuel combinations, while still achieving low levels of pollutant emission (Ghani et al., 2008; Khan et al., 2009). However, gaseous and fine particulate matter emissions have been considered hazardous to human health and control devices are not effective in the elimination of pollutants from the flue gas (Yao et al., 2010; Ye et al., 2012). Taking into account the environmental and human health impact of these emissions and the need to improve operating conditions, a detailed quantification and characterization of emissions is necessary. Although several studies about BFBC of biomass have been developed along the years, the environmental aspects of the technology related to flue gas emissions have been overlooked. As far as we know, only Calvo et al. (2013) have chemically characterized particle emissions from the co-combustion of forest biomass and sewage sludge in a BFBC. In this study, gaseous and particulate emissions from the combustion of pine and eucalypt chips in a pilot-scale BFBC were studied, taking into account operating aspects such as stoichiometry and biomass pre-treatment by leaching. In 2006, the Portuguese government has decided that the production of electricity from combustion plants dedicated to biomass should be 250 MW in 2020 (Teixeira, 2012). The purpose of this research is focused on fulfilling the need of detailed chemical characterization of emission profiles resulting from fluidized bed units, which represent a substantial fraction of the current installed capacity of electricity generation from biomass. In addition to being useful to define the best operating conditions, chemical fingerprints of emissions are needed to: (i) run regional source apportionment models, (ii) improve inventories, (iii) apply air quality models, and (iv) assess potential health effects in the exposed population.

1. Materials and methods

1.1. Fluidized bed combustor

The experimental part of this work was carried out in a pilot-scale combustion installation with a BFBC (Tarelho et al., 2011; Teixeira et al., 2012; Calvo et al., 2013). The infrastructure is constituted by three main components, namely, the reactive system, the sampling and gas analysis system and the control and data acquisition system (Fig. 1). The reactive system is composed of an insulated pilot-scale fluidized bed reactor made in stainless steel (AISI 310 SS). The bottom bed,

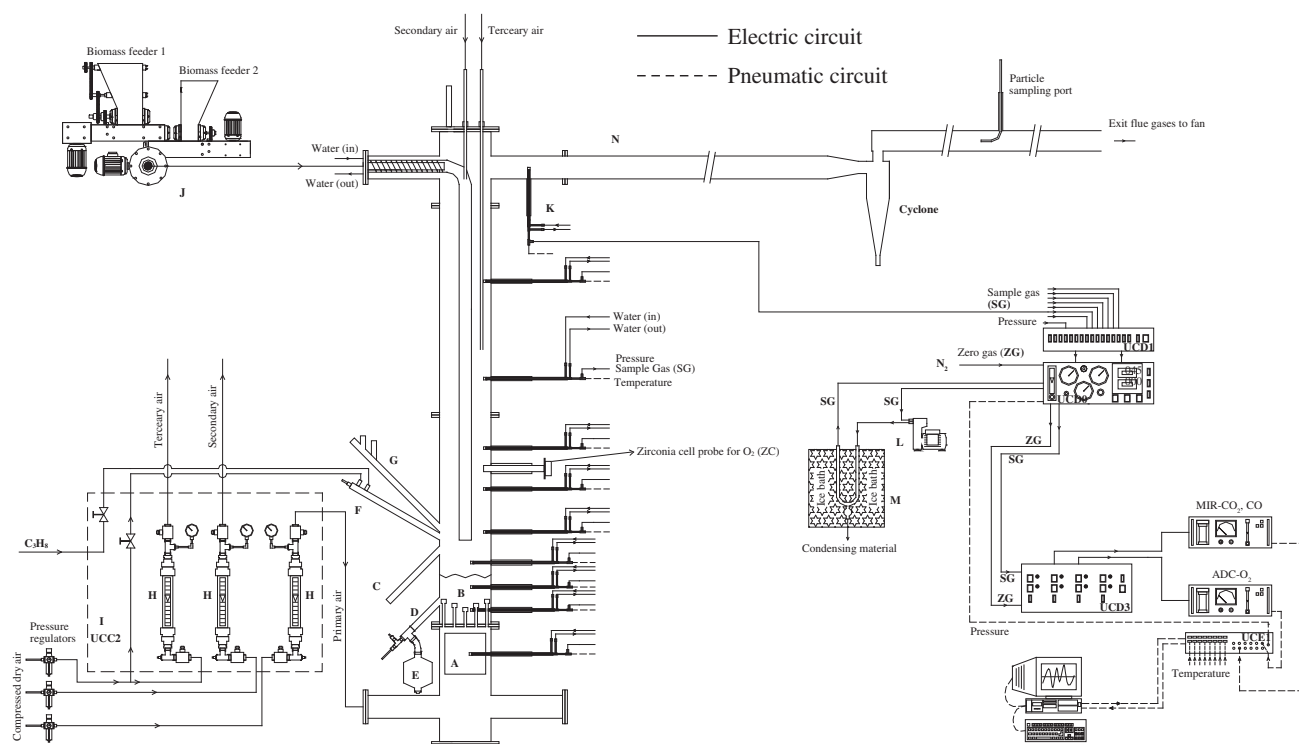


Fig. 1 – Schematic representation of the pilot-scale combustion installation. A: primary air heating system; B: sand bed; C: bed solids level control; D: bed solids discharge; E: bed solids discharge silo; F: propane burner system; G: port for bed surface visualization; H: air flow meter; I: control and command unit; J: biomass feeder; K: water-cooled gas sampling probe; L: gas sampling pump; M: gas condensation unit; N: exhaust duct to cyclone. UCD0, UCD1, and UCD3 refer to command and gas distribution units, UCC2 refers to control and command unit, UCE1 refers to electronic command unit, and ADC and MIR refer to the online analyzers.

with a static height of 0.20 m, consisted of sand particles (mainly composed of quartz) ranging in size between 0.25 and 0.71 mm. The BFBC had an inner diameter of 0.25 m and was 3.0 m in height. It integrated a whole set of accessory elements that allow the operation of the reactor, including a unity responsible for controlling electric and pneumatic circuits. The system also comprised the fuel feed unit and the refrigeration water setup.

The biomass feed system was located on the top of the reactor and allows the independent and simultaneous feeding of two fuels; biomass particles were dropped at the bed surface through a vertical tube located inside the freeboard (Fig. 1). In Portuguese industrial BFB combustors the biomass is typically discharged throughout ports located at the furnace wall and above bed surface. The biomass was injected through rotary valves and air jets in order to spread the fuel at the freeboard region just above the bed, and then the fuel started to dry and devolatilize as it dropped at the bed surface. In the pilot-scale BFB combustor used in the present study, a vertical tube was installed in order to simulate the fuel feeding at bed surface, and to allow the adjustment of the height at which the fuel is dropped-off at bed surface. The configuration used also promoted a pre-drying of the fuel as it fell along the tube in case of using high moisture fuels and the biomass was also fed together with air at bed surface.

The combustion air was distributed in three stages: primary air through the distribution plate, secondary air was added

0.2 m above the bed surface and tertiary air was added at 0.9 m above the bed surface. The supply of tertiary combustion air in the burnout zone allowed to almost completely oxidize the gaseous compounds emerging from the first and second stages of combustion (the lower part of the reactor). The addition of tertiary air to the freeboard region enabled the air to be staged between the bed and the freeboard, for example, for NO_x control (Tarelho et al., 2011), and provided increased gas-phase mixing in order to achieve efficient conversion of the fuel. The injection of combustion air into the BFBC was performed in accordance with the air staged combustion concept.

The pressure and temperature of the combustion flue gases were monitored through nine water-cooled sampling probes located at different heights along the reactor. Two of them were immersed in the bed and the rest of the sampling probes were distributed along the freeboard. Every sampling probe was equipped with an external circulating quenching water sleeve, a cooled particle filter at the rear of the probe, a K-type thermocouple, and a cerablanket plug at the tip, located inside the combustion chamber, in order to filter particles from the flue gas.

The combustion process in a fluidized bed reactor released significant amounts of heat. The refrigeration system of the fluidized bed intended to control the temperature by extracting heat through water cooled probes located inside the reactor. In this system, the working fluid was liquid water and cooling of the fluid was achieved in a refrigeration tower.

1.2. Fuel characteristics

Two types of biomass commonly used in Portugal in industrial combustion facilities for heat and power production were used as fuel in the combustion experiments: residual forest biomass from eucalypt (*Eucalyptus globulus*) and pine (*Pinus pinaster*) felling. The chemical composition of these biofuels is shown in Table 1.

To ensure proper performance of a combustion system, the pre-treatment of biomass is necessary. This pre-treatment can include a refinement of its physical (such as particle size and density) and chemical characteristics. In this work, the particle size of biomass fuels was reduced in order to match the characteristics of the feed system (screw feeder) of the BFBC. Forest biomass residues were chipped, air dried, and sieved to obtain particles with equivalent size below 10 mm. The effect of biomass leaching on the fuel characteristics was also studied. After chipping, a fraction of eucalypt biomass was allowed to leach under atmospheric conditions (leaching by rainwater at atmospheric conditions) over a six-month period. At the end of the leaching period, this biomass was then laid to dry. A more detailed description of the leaching process can be found elsewhere (Teixeira et al., 2012). The goal was to study the effect of leaching on the characteristics of the biomass and on emissions resulting from the combustion process.

1.3. Combustion experiments and operating conditions

During the reactor operation it is possible to distinguish two phases, namely, the pre-heating phase and the biomass combustion phase. The pre-heating phase was conducted with propane combustion in order to raise the temperature of the reactor until the bed reached a value around 500°C; simultaneously, the fluidizing air was heated through an electric oven. After that, the addition of solid fuel was initiated. When the bed temperature reached about 750°C the auxiliary heating systems (gas and electric oven) were switched off and the reactor began to operate only with the addition of solid fuel. The second phase consisted in the operation under stationary conditions at the desired temperature and stoichiometry range.

The experiments were planned to keep similar reactor hydrodynamics. The combustion air was supplied in three stages: primary air (67% of the total combustion air), secondary combustion air (17% of the total combustion air) and tertiary combustion air (16% of the total combustion air). The stoichiometry of the combustion experiments was pre-established and adjusted through the fuel feed rate. A set of eight water cooled probes immersed in the bottom bed allowed the control of the temperature of this zone at the desired value.

The combustion experiments aimed at evaluating the influence of the fuel, stoichiometry and biomass leaching on the flue gas composition and particulate matter characteristics (Table 2). The flue gas sampling (gaseous compounds and particulate matter) was made under steady state operating conditions of the BFBC. The steady state operating conditions were evaluated by continuous monitoring of both temperature and pressure along the reactor height, as well as the exit

flue gas composition; the steady condition was considered as achieved when the bed temperature and the exit flue gas composition were stable along the time.

1.4. Gas sampling and measurement techniques

The gas sampling and analysis system consisted of a set of sampling probes located along the reactor height, a set of electropneumatic control and gas distribution units, a sampling pump, a set of automatic online gas analyzers, a zirconium probe located inside the reactor for *in-situ* monitoring of O₂ concentration, 15 thermocouples and a pressure sensor. Combustion flue gas was sampled through a sampling probe located at 2.2 m height above the distributor plate (Fig. 1). After cooling and drying, the flue gas composition was continuously monitored for O₂ using a paramagnetic online analyzer (model O2-700, ADC, UK) with a Servomex module, and for CO₂ and CO using a non-dispersive infrared analyzer (model MIR 9000, Environnement, France).

1.5. Particle sampling and measurement techniques

Fine particles (PM_{2.5}) were sampled under isokinetic conditions with the reactor operating under steady state conditions. Each filter was sampled over a period that ranged from 5 to 15 min in order to collect sufficient particulate matter for subsequent chemical analysis and, at the same time, preventing clogging of the filters. A low volume sampler (model 2.004.01TCR, Tecora, Italy) was used to collect PM_{2.5} onto quartz filters with 47 mm in diameter. The sampling equipment is constituted by a specific sampling head (PM_{2.5}), a pump operating in a range between 38.0 and 38.5 L/min (at atmospheric pressure and temperature), and a data storage and control unit. PM_{2.5} was collected after a cyclone with approximately 1 m in height and 0.1 mm in diameter (AISI 304 steel plate of 1.5 mm) with tangential inlet. The flue gas temperature in the cyclone was around 135°C, and the pressure drop across it was typically 0.15 m H₂O. In this equipment, the flue gas is submitted to centrifugal and gravitational forces, which promote the removal of some particles (Flagan and Seinfeld, 1998). The collection efficiency of this equipment is high for coarse and heavy particles (>50 µm), but limited for fine particles (Van Loo and Koppejan,

Table 1 – Chemical composition of the solid biomass fuels.

	Eucalypt	Leached eucalypt	Pine
<i>Proximate analysis (wt.%, as received)</i>			
Moisture	11.8	10.4	12.7
Ash	2.53	2.07	1.07
Volatile matter	80.6	81.2	81.6
Fixed carbon	5.12	6.36	4.63
<i>Ultimate analysis (wt.%, dry basis)</i>			
Ash	2.87	2.31	1.23
C	44.58	44.06	48.40
H	5.95	5.73	6.47
N	0.34	0.41	0.17
S	nd	nd	nd
O (by difference)	46.3	47.5	43.74
nd: not determined, below detection limit (100 ppm) of the method.			

2008; Nussbaumer, 2008). For each combustion condition, five replicate filters were sampled.

1.6. Data analysis

The PM_{2.5} and particulate chemical compound emission factors were calculated according to Eq. (1), in which EF_{i,Δt} (mg/kg) is the emission factor of compound i, as burned, in the sampling interval Δt (corresponding to a sampled filter), C_i (mg/Nm³) is the concentration of compound i in the exit flue gas, Q_N (Nm³/sec) is the mean flow rate during the sampling interval, Δt is the sampling interval time (sec) for a filter and Δm (kg) is the mass consumed (dry basis) during the sampling interval.

$$EF_{i,\Delta t} = \frac{C_i \times \Delta t \times Q_N}{\Delta m} \quad (1)$$

The number of PM_{2.5} samples collected in the outlet cyclone duct (0.10 m of internal diameter) during each combustion experiment ranged from 3 to 9. Since the sampling time and thus the mass of fuel consumed during the sampling interval was similar in each experiment, the arithmetic mean of the emission factors was performed in order to estimate global emission factors for each combustion experiment.

For the gaseous components, the emission factors were calculated according to Eq. (2), in which EF_y (g/kg) is the emission factor, dry basis, with y denoted as CO or CO₂, C_i (g/Nm³) is the concentration of compound i in the exit flue gas, dry basis, Q_N (Nm³/sec) is the mean combustion gas flow rate, t (sec) is time, m (kg) is the mass of fuel burned (dry basis) during the sampling interval.

$$EF_y = \frac{C_y \times t \times Q_N}{m} \quad (2)$$

1.7. Analytical methodologies

In order to eliminate organic contaminants, the quartz fiber filters used for particulate matter sampling were baked for 6 hr at 600°C previously to the gravimetric determination with a microbalance (model AG245, Mettler Toledo, Switzerland) (readability—0.1 mg/0.01 mg). For each filter, the weight was obtained from the average of six measurements; the variations were less than 0.02%.

Carbonates in particulate matter samples were determined by acidification with phosphoric acid (H₃PO₄) and determination of the CO₂ evolved. Two punches of 5 mm in diameter were used in each analysis. Blank filters were analyzed for the correction of the obtained values. After flushing out the glass enclosure with nitrogen (N₂), the sample was dipped into the acid solution for about 3 min. After that, the N₂ line was open in order

to carry the CO₂ that evolves to the infrared detector. The quantification of carbonates was carried out by integrating the area under the curve corresponding to the CO₂ concentration read by the analyzer. The N₂ flow rate was about 200 mL/min (at atmospheric pressure and temperature).

The carbonaceous content of PM_{2.5} was analyzed after the removal, by acidification, of carbonates in the samples. To this end, two punches of 9 mm diameter of each sample were exposed to HCl vapors for 5 hr in a desiccator. Subsequently, HCl in excess was removed by keeping the samples in a desiccator over NaOH for 24 hr. The organic carbon (OC) and elemental carbon (EC) of particulate matter were analyzed by a thermo-optical system. Briefly, this method consisted in the volatilization of the particulate carbon and its differentiation into several fractions by means of controlled heating, with subsequent conversion by oxidation to CO₂ for detection. The monitoring of the blackening of the filter using a laser beam and a photodetector measuring the filter light transmittance allowed separating the EC formed by pyrolysis of OC from the one that was originally in the sample (Gonçalves et al., 2014).

To carry out the determination of levoglucosan, elements and water soluble ions, circular filter punches from the various replicate samples were combined and analyzed together in order to obtain mean values for each combustion experiment.

Levoglucosan was determined by high-performance anion-exchange chromatography with pulsed amperometric detection (HPAE-PAD). The chromatograph (model 881, Metrohm, Switzerland) was equipped with an auto sampler Methrom, an amperometric detector for levoglucosan (module 896, PAD mode, Metrohm, Switzerland), and a column Metrosept carb 1 (150 mm × 4 mm id). Particulate matter on each filter punch (1.5 cm²) was extracted with Milli-Q water (10 mL) through ultrasonic agitation. After extraction, the solution was filtrated through a polypropylene puradisc (0.45 μm porosity, 25 mm diameter). The detection limit of the method was 0.075 μg/cm².

Each set of filter punches was subjected to acid digestion (a mixture of 1.25 mL HNO₃, 2.5 mL HF, and 1.25 mL HClO₄) following the method proposed by Querol et al. (2001) for the analysis of major and trace elements by means of inductively coupled plasma atomic emission spectrometry (ICP-AES) (Jarrell Ash IRIS Advantage, Thermo Scientific, USA) and inductively coupled plasma mass spectrometry (ICP-MS) (X Series II, Thermo Scientific, USA), respectively. Three multi-elemental solutions Spec® 1 (rare earth elements, REE), Spec® 2 (alkalis, earth alkalis, and metals) and Spec® 4 (Nb) were used to develop external calibration curves. The mean precision and accuracy fall below typical analytical error and are in the ranges of 3%–5% and <10% for ICP-AES and ICP-MS, respectively, and were controlled by repeated analysis of 0.025 mg of NBS-1633b (fly ash) reference material

Table 2 – Experimental conditions during biomass combustion in the bubbling fluidized bed.

Experiments	Fuel	Particle diameter (mm)	Fuel rate (kg/hr)	Temperature of bed (°C)	O ₂ concentration (vol.%, dry gases)
E	Eucalypt	<10	4.6	808	3.7 ± 0.62
LE	Leached Eucalypt	<10	3.2	807	7.3 ± 0.38
P1	Pine	<10	4.0	804	3.8 ± 0.33
P2		<10	2.4	804	9.6 ± 0.17

(NIST, Gaithersburg, MD, USA). The detection limits were 0.01 ng/m^3 for most of the trace elements analyzed.

The filter punches for cation and anion analysis were placed in a 5 mL screwed cap vial and extracted with 2 mL 2% (V/V) isopropanol (analytical grade, J.T. Baker, USA) and ultrapure water under 10 min mechanical agitation. Extracts were filtered through Millex units and the sample extracts were injected in the ion chromatograph. A dual-system ion chromatograph–conductance detector equipped with a cation isocratic module (model ICS 1100, Dionex, USA), an anion gradient module (model ICS 2100, Dionex, USA), an AS-DV 40 autosampler, and an eluent regenerator system (RFIC-ER, Dionex, USA) was used in this study. This system enables simultaneous injection in both cation and anion modules and determination of cations and anions simultaneously. A detailed description of the method and the system can be found elsewhere (Domingos et al., 2012).

It is not possible to provide particulate mass fractions of elements and water soluble ions in samples from pine combustion under condition P1 (pine, 4.9% O_2) given that, because of the need to repeat the analyses of the carbonaceous fraction (OC, EC and CO_3^{2-}), the leftover filter area was not sufficient to carry out the determination of inorganic constituents.

2. Results and discussion

2.1. Operating conditions

The pressure and temperature profiles along the reactor height during the combustion experiments are shown in Fig. 2. The maximum pressure value was reached at the level of the primary air injectors, on the base of the bubbling fluidized bed. Pressure decreased with bed height and was almost uniform along the freeboard height. The values in the freeboard were close to atmospheric pressure. Differences between absolute pressure values in the BFBC during the combustion experiments are related to differences in the value of atmospheric pressure in the days when the experiments were carried out.

Temperature peaked just above the biomass feeding location and secondary air injection (0.40 m above the distribution plate). The high temperature occurring here is related to the gas phase combustion of volatiles released from

biomass, which mainly occurs in this zone (Calvo et al., 2013; Tarelho et al., 2011). Temperature increased from inside the bed to the freeboard, reached its maximum value above the biomass feeding and secondary air injection points, and decreased in the space above. In general, the temperature in the freeboard was higher than that observed inside the bed. For the experiments E (combustion of eucalypt) and P1 (Table 2), the lowest temperature was observed in the bed. During the combustion of pine under higher stoichiometry (P2) and leached eucalypt (LE), for points located at 1.70 m above the distributor plate, the temperature decreased to values lower than that observed inside the bed. The highest temperatures in the BFBC were observed during combustion of pine chips with lower stoichiometry (P1). The O_2 concentration in the BFBC decreased with the decrease in stoichiometry, i.e., with the increase of the biomass fuel/combustion air ratio. Considering that the combustion air flow rate was maintained constant for the distinct combustion experiments, higher fuel rates originated higher thermal energy output, and thus higher temperatures in the BFBC. The temperature profiles along the reactor height observed in the present work are similar to those observed in other studies (Tarelho et al., 2011).

2.2. Gaseous emissions

The CO_2 , CO and O_2 concentration in the exit flue gas along time during the combustion experiments are shown in Fig. 3. The CO_2 profile over time showed a behavior complementary to that observed for O_2 , i.e., the CO_2 concentration decreased when the O_2 concentration increased, reflecting the relationship between reactant (O_2) and product (CO_2) in a chemical reaction.

The CO_2 concentration in the flue gas from eucalypt combustion was, on average, higher ($17.2 \pm 0.94 \text{ vol.}\%$, dry gases) in the experiment E and lower ($12.9 \pm 0.40 \text{ vol.}\%$, dry gases) in the experiment LE, due to the higher stoichiometry of the latter. For combustion of pine chips, the P2 experiment generated the lowest CO_2 concentration ($10.7 \pm 0.22 \text{ vol.}\%$, dry gases), while the lowest stoichiometry (P1) produced a flue gas with an average CO_2 concentration of $16.6 \pm 0.29 \text{ vol.}\%$ (dry gases).

Due to the lower stoichiometry, the average CO concentration in the exit flue gas from the combustion of eucalypt

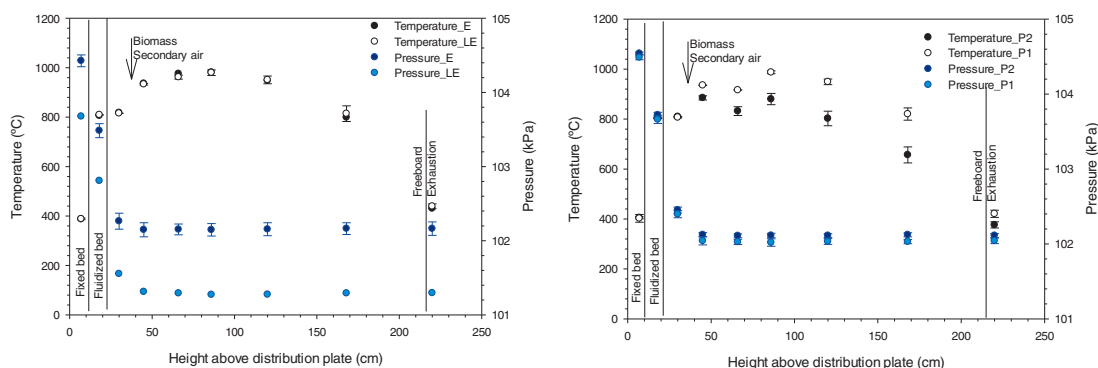


Fig. 2 – Longitudinal temperature and pressure profiles along the pilot-scale bubbling fluidized bed combustion (BFBC) during eucalypt and pine combustion experiments. E, LE, P1, and P2 refer to Table 2.

chips was higher in experiment E (5636 ± 2024 ppmV) (Fig. 3). Although operating under steady state conditions, the CO concentration profiles over time in the experiments with eucalypt showed fluctuations. These fluctuations were related to irregularities in the fuel feeding, and a consequence of the physical characteristics of the chipped eucalypt.

During the experiments with leached eucalypt, the average O_2 and CO_2 concentrations in the exit flue gases were 7.3 vol.% and 525 ± 164 ppmV (dry gases), respectively (Table 2). This lower CO concentration is due to a higher combustion efficiency associated with higher stoichiometry when compared to that observed during experiment E with chipped eucalypt. Nevertheless, it was also observed that the biomass feeding conditions were improved (less fluctuations) during leached eucalypt combustion, because the biomass particles were more breakable and easily transported by the screw feeder.

For a similar O_2 level in the exit flue gases, the CO concentration during pine combustion was lower than that observed during eucalypt combustion (see experiments P1 for pine and E for eucalypt in Table 2 and Fig. 3). A more stable feeding of chipped pine when compared to chipped eucalypt may explain this result. Thus, CO concentrations presented lower fluctuations for pine than for eucalypt.

The CO concentration in the exit flue gas during the combustion of pine with lower stoichiometry (P1) (622 ± 252 ppmV, dry gases) was higher than with higher stoichiometry (P2) (32.2 ± 9.8 ppmV, dry gases). This latter promotes a more efficient oxidation of the fuel (char and volatiles).

The highest CO_2 emission factor was observed for the combustion of pine with higher stoichiometry (P2) (Fig. 4a). Higher carbon content in pine (Table 1) and better combustion efficiency (lower CO concentration, Fig. 2) contribute to a higher CO_2 emission factor. The CO emission factors for eucalypt chips were higher in experiment E when compared

with LE (Fig. 4b) due to a lower combustion efficiency. Leaching the fuel and using a higher stoichiometry seem to be effective ways of reducing emissions of compounds from incomplete combustion (Fig. 4b). The t-test ($\alpha = 0.05$) revealed that the difference between the two conditions was statistically significant ($p = 0.0001$). In a similar way, when the fuel was chipped pine, a higher CO emission factor was observed during the combustion with lower stoichiometry (P1), when compared to the operation with higher O_2 concentration (P2). The difference between the P1 and P2 experiments was found to be statistically significant ($p = 0.0209$). For similar stoichiometry, the CO emission factor was lower for pine than for eucalypt (Fig. 4b). There was a significant difference between CO emission factors from the two fuels ($p = 0.0022$). As stated before, despite differences in reactivity of the two biomass fuels, this can also derive from a more regular feeding of pine.

2.3. Particulate matter emissions

Generally speaking, primary fine particles can be divided into three categories according to their origin and formation mechanisms: ash (inorganic), soot (elemental carbon) and organic material. Ash originates from inorganic non-combustible material introduced into the furnace, while soot and organics are combustible material (Sippula, 2010). The nucleation mode consists of aerosols composed mainly of volatiles that are formed as exhaust gases dilutes and cools. The growth mechanisms of aerosol particles, which are at the origin of the accumulation mode, involve vapor condensation, coagulation, agglomeration, surface reactions and adsorption (Valmari, 2000). A detailed explanation of the particle formation mechanisms can be found elsewhere (e.g. Obaidullah et al., 2012; Biedermann and Obernberger, 2005). Some works refer that fly ashes formed during biomass combustion in

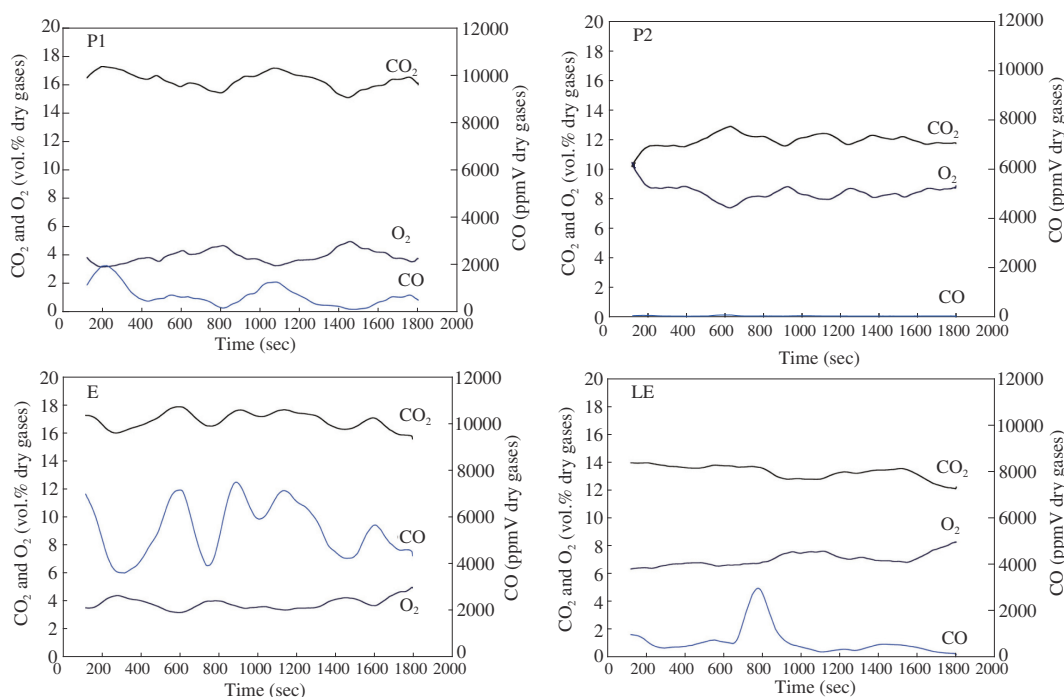


Fig. 3 – CO, CO_2 and O_2 concentrations in the exit flue gases along time, during eucalypt and pine combustion experiments.

fluidized bed are dominated by particles with diameters in the range between 5 and 25 μm (Eldabbagh et al., 2005).

Fine particle ($\text{PM}_{2.5}$) mass emission factors depend on many features, including fuel characteristics and combustion conditions, as shown in Fig. 4c. $\text{PM}_{2.5}$ emission factors for softwood (pine) combustion ranged between 16.8 ± 1.00 and 29.3 ± 3.09 mg/kg of fuel (as burned). The lowest $\text{PM}_{2.5}$ emission factor was observed when operating the reactor with high O_2 percentages (P2), i.e., particulate emissions increased with the decrease in stoichiometry. The difference between the $\text{PM}_{2.5}$ emission factors of the experiments P1 and P2 was statistically significant ($p = 0.0209$). Emission factors for hardwood (eucalypt) combustion ranged from 33.0 ± 10.8 to 55.2 ± 2.55 mg/kg of fuel (as burned). The highest $\text{PM}_{2.5}$ emission was registered when leached eucalypt was burned (LE), although under these conditions a higher O_2 concentration in the flue gases compared to chipped eucalypt (E) was used. The difference between the particle emission factors for these two experiments (LE and E) was statistically significant ($p = 0.0001$). The difference between the $\text{PM}_{2.5}$ emission factors resulting from the combustion of pine and eucalypt, for similar stoichiometry, was not statistically significant ($p = 0.5821$).

Calvo et al. (2013) studied fine particles from co-combustion of forest biomass and sewage sludge from a pulp and paper industry, using the same pilot scale BFBC of the present study, and reported emission factors of $(4.0 \pm 0.2) \times 10^3$ mg $\text{PM}_{2.5}$ /kg of fuel (as burned) and $(3.7 \pm 0.5) \times 10^3$ mg $\text{PM}_{2.5}$ /kg of fuel (as burned) for the flue gas before and after the cyclone. The difference between the much higher emissions factors reported by Calvo et al. (2013) and those observed here are related to the biomass fuel characteristics. The fuel used by Calvo et al. (2013) was composed of 40 wt.% sewage sludge and 60 wt.% of forest biomass residues. A huge difference between fuels regarding the ash content was reported: 1.41 wt.% for forest biomass versus 57.4 wt.% for sewage sludge, thus explaining the high $\text{PM}_{2.5}$ emission. In this context, attention must be paid to the characteristics of the biomass used as fuel, because they can greatly influence the particulate matter emissions.

2.4. Particulate matter composition

The health effects caused by particulate matter are dependent on its physical and chemical properties (Bølling et al., 2009; Lamberg et al., 2011). These properties are a function of biomass fuel and combustion conditions, which may present

high variability (Bølling et al., 2009). Particles produced under conditions of complete combustion are more likely to induce cellular damage than particles generated in poor combustion conditions with higher dosages (Leskinen et al., 2014).

Fig. 5 presents the mass balance obtained by adding up the concentrations of the chemical constituents of $\text{PM}_{2.5}$. OC accounted for around 2 wt.% (LE) to 18 (P1) wt.% of the $\text{PM}_{2.5}$ mass. The difference between the OC mass fraction in $\text{PM}_{2.5}$ produced when burning leached and non-leached eucalypt was not statistically significant ($p = 0.2341$). For pine combustion under distinct operation conditions (P1 and P2), the difference in the OC content in $\text{PM}_{2.5}$ is statistically significant ($p = 0.0348$). Following the procedure of Alves et al. (2011), organic matter (OM) was obtained by multiplying the organic carbon mass by a factor, which generally takes values between 1.2 and 2.2, to account for hydrogen, oxygen, nitrogen and other atoms associated with OC (Chazette and Lioussse, 2001; Hegg et al., 1997; Pöschl, 2005; Turpin and Lim, 2001). The multiplicative factor depends on the aerosol composition, its origin and the degree of aging (Puxbaum and Tenze-Kunit, 2003; Stelson and Seinfeld, 1981). The OM/OC ratio adopted in the present study was 1.9, which can be considered reasonable for biomass burning particles (Alves et al., 2011). Organic matter accounted for about 3 to 6 wt.% of the $\text{PM}_{2.5}$ mass. Contrary to traditional combustion appliances (e.g. fireplace and woodstove), levoglucosan in $\text{PM}_{2.5}$ emitted by the BFBC was always below the detection limit ($0.075 \mu\text{g}/\text{cm}^2$), suggesting that this anhydrosugar, normally pointed out as a good biomass burning tracer, may be highly dependent on combustion parameters. This anhydrosugar is formed during conditions of incomplete combustion resulting from the thermal breakdown of the cellulose, hemicellulose and lignin that are released at low temperatures (300 to 500°C) without being further burned (Bølling et al., 2009; Simoneit et al., 1999). In agreement with the present study, Schmidl et al. (2011) has found that levoglucosan was detected in all samples from manually fired wood combustion systems, but not during conditions of efficient combustion using automatically fired systems. Hedberg et al. (2006) observed that the measurement of levoglucosan emissions show large variations depending on the type of stove, biofuel quality, and operator behavior.

EC accounted for around 2 (P2) to 12 (P1) wt.%, whereas carbonates represented 2 (P1) to 9 (LE) wt.% of the $\text{PM}_{2.5}$ mass (Fig. 5). The differences between either the EC or the carbonate content of $\text{PM}_{2.5}$ from experiments with leached and non-leached fuel (eucalypt) were statistically significant

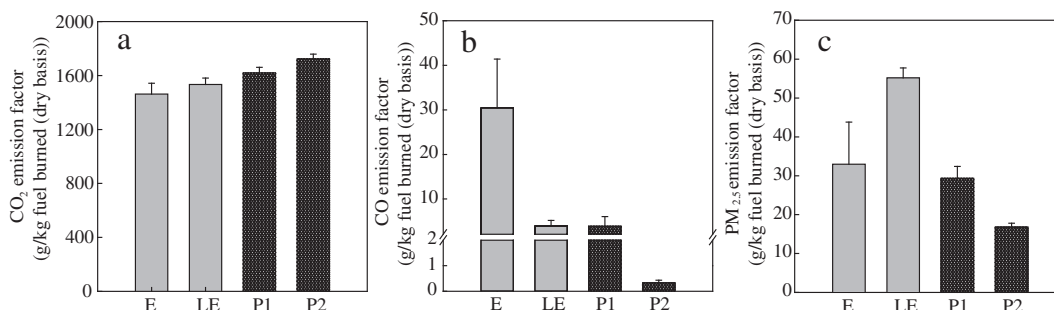


Fig. 4 – (a) CO_2 , (b) CO, and (c) $\text{PM}_{2.5}$ emission factors during eucalypt and pine combustion experiments.

($p < 0.0001$ and $p = 0.0034$ for EC and carbonate, respectively). For pine combustion with different O_2 levels (experiments P1 and P2), a statistically significant difference was observed ($p = 0.0119$ and $p = 0.0197$ for EC and carbonate, respectively). Unlike residential biomass combustion appliances, whose particulate matter emissions present a high carbonaceous content (Alves et al., 2011; Fernandes et al., 2011; Fine et al., 2004; Gonçalves et al., 2010; Schmidl et al., 2011), fluidized bed combustion of biomass seems to generate relative lower amounts of OC and EC in fine particles, as observed in the present study and elsewhere (Calvo et al., 2013). In the present study, the OC/EC ratio ranged from 0.8 to 2.0 for eucalypt and from 1.5 to 1.6 for pine combustion. These values are close to the ratio of 2.2 reported by Calvo et al. (2013). The pre-treatment of the fuel before the combustion process contributed to the increase of EC emissions, thereby lowering the ratio. Fernandes et al. (2011) tested three different types of domestic heating appliances. The lowest OC/EC ratios were obtained for the combustion in the more sophisticated combustion appliance, while the highest were found for the open fireplace. Another observation resulting from their study was the much lower ratio observed for the combustion of softwood (pine) compared to the combustion of hardwood (eucalypt), which is in agreement with the results of the present study. Particles from incomplete combustion, such as soot, condensable organic particles or char, are not expected to be present in significant concentration in flue gases from BFBC, because these equipments operate under more efficient combustion conditions (Khan et al., 2009). Higher OC and EC mass fractions in $PM_{2.5}$ are generally observed when the combustion is more inefficient (Bølling et al., 2009; Fernandes et al., 2011; Obaidullah et al., 2012; Schmidl et al., 2011).

Calvo et al. (2013) found a total carbon (OC + EC) and carbonate (CO_3^{2-}) content in $PM_{2.5}$ of 1.9 and 20 wt.% after the cyclone, respectively. The higher carbonate content in $PM_{2.5}$ in the study of Calvo et al. (2013), compared to the values observed here (2.3–8.5 wt.%), is related to the characteristics of the fuel. Calvo et al. (2013) used a fuel mixture including sewage sludge from the pulp and paper wastewater treatment, with a high percentage of calcium carbonates

(Tchobanoglous et al., 2001). During the combustion process, some carbonate in the sewage sludge is released with fly ashes, thus contributing to the relatively high content in $PM_{2.5}$.

Inorganic elements accounted for about 48% to 55% (wt.%) of the $PM_{2.5}$ mass (Fig. 6). Among them, Ca, Fe, K, Mg, Na, P and S were present in all $PM_{2.5}$ samples. This is in agreement with the findings by Nussbaumer (2003), who reported that submicron and supermicron particles in fluidized bed combustion were composed of K, Cl, S, Na and Ca, while coarse particles were mainly constituted by Ca, Si, K, S, Na, Al, P and Fe. Most of these chemical elements do not exist as single elements in particulate matter, but rather combined in other forms, such as oxides (e.g. CaO, Na₂O, Fe₂O₃, Al₂O₃, MgO, K₂O, P₂O₅, SO₃). For example, potassium, which represents one of the most abundant elements in particulate matter emissions, is generally found as K₂SO₄ in submicron fly ashes (Valmari, 2000). This element can also be found as KCl and K₂CO₃ (Obaidullah et al., 2012). After conversion of major chemical elements to oxides, it was observed that the inorganic fraction accounted for 71 to 86 wt.% of the $PM_{2.5}$ mass (Fig. 5). It should be noted that this mass fraction is slightly underestimated since other elements, such as Si, were not analyzed. The particulate matter emitted from biomass combustion in industrial type combustion systems consists mainly of inorganic compounds (Calvo et al., 2013), whereas, when using manually fired systems (as domestic combustion equipment), high amounts of particulate carbonaceous material are emitted (Schmidl et al., 2011). Soot and organic particles are formed under poor combustion conditions (Bølling et al., 2009; Boman et al., 2004; Obaidullah et al., 2012), whereas inorganic particles are formed under conditions of nearly complete combustion (Nussbaumer, 2008).

The $PM_{2.5}$ samples from combustion experiment P2 presented a high inorganic content. Ca, K, Mg, Na and S contributed to more than 95% of the total mass of inorganic elements. $PM_{2.5}$ from the combustion experiment with leached eucalypt (LE) showed the lowest inorganic content. Leaching of easily soluble forms of some elements (e.g. KCl) during the pre-treatment process of the biomass by rainfall may explain this result (Teixeira et al., 2012). In fact, in the present study, the potassium content in $PM_{2.5}$ decreased from experiment E (non-leached fuel) to experiment LE (leached fuel), as also happened with Na and S. This suggests that a fraction of water soluble constituents, such as K and Na, was removed from the fuel by leaching. On the other hand, the relative amount of other elements like Ca, Fe, Mg and P have increased in $PM_{2.5}$ from the combustion of leached eucalypt, compared to non-leached eucalypt (Fig. 6). The relative enrichment of these elements in fine particles after leaching can be associated with a lower leaching ability.

The composition of fly ashes from the combustion of different biomass fuels show considerable differences between coarse and fine particles that are driven out with the flue gas (Jokiniemi et al., 2001; Teixeira et al., 2014; Obernberger and Supancic, 2009). For example, during wood chip combustion, the Ca content decreases from coarse to fine fly ashes, while the K content increases. Heavy metals like Pb suffer a notable increase in the fine fly ash fraction (Brunner et al., 2001; Obernberger and Supancic, 2009). Thus, it is important to characterize fine particles emitted during biomass combustion in distinct

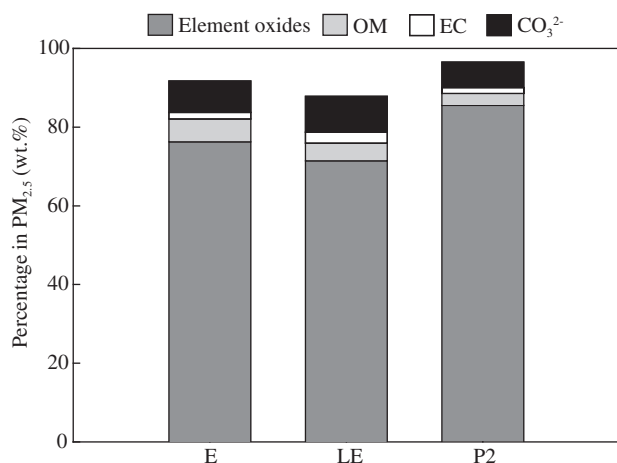


Fig. 5 – Chemical composition of $PM_{2.5}$ from eucalypt and pine combustion. OM: organic matter; EC: elemental carbon.

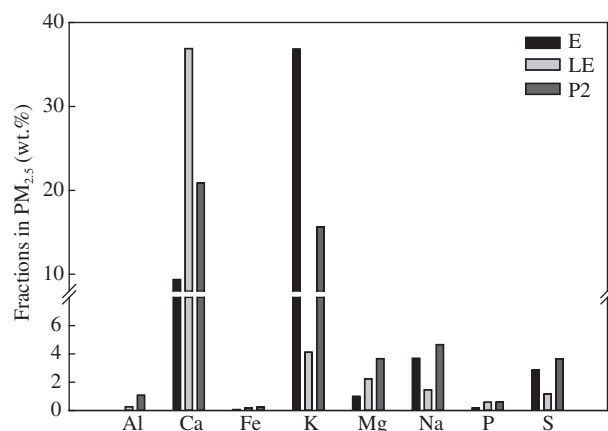


Fig. 6 – Mass fractions of major chemical elements in PM_{2.5} during eucalypt and pine combustion experiments.

systems, because this size fraction is able of penetrating deeper into the human respiratory system.

In the present study, K was the predominant element in PM_{2.5} for experiment E, while in experiments LE and P2 the major element was Ca. Other studies have suggested that pine combustion generate lower amounts of potassium in fine particles (Schauer et al., 2001). The lower potassium mass fraction in PM_{2.5} may be related to the fact that lower K levels are found in pine wood than in eucalypt (Biedermann and Obernberger, 2005). It has been also reported that the Ca content in coniferous wood is lower compared to deciduous wood (Biedermann and Obernberger, 2005; Vassilev et al., 2010). However, in the present study, the lowest mass fraction of Ca was observed in PM_{2.5} from experiment E. Calcium in particulate matter emissions from the combustion of forest residues can also be somehow related to the forest soil and other impurities mixed with the fuel (Valmari, 2000).

The mass fraction of the minor elements in PM_{2.5} samples was very low (Fig. 7). Among those elements, Cr was one of the most abundant (1.6 wt.% of PM_{2.5} mass). This high content of Cr may be mostly associated with abrasive or corrosive wearing of stainless steel from the pilot-scale BFBC walls, as a result of chemical and thermal decomposition of the material in contact with the flue gases. Other elements like Rb, Sr, Mo, and Ba found in the fly ashes account altogether for 0.2 to 0.3 wt.% of the particulate matter mass (Fig. 7).

Some volatile elements (e.g. Cd and Zn) mainly vaporize during combustion and later condense on the surface of the fly ashes or form aerosols (Biedermann and Obernberger, 2005). Among heavy metals, Zn, Sn, Cd, Tl and Cu were present in all samples. The contribution of these elements to the total mass of metals was low, not exceeding 0.3 wt.% (Fig. 7).

The water-soluble ions accounted for about 0.51 to 2.39 wt.% of the PM_{2.5} mass (Table 3). The combustion experiments with leached eucalypt (LE) generated the lowest water soluble ionic content in PM_{2.5}. This can be explained by the fact that during rainfall leaching an important part of elements in water soluble forms could be already been leached out, as already discussed. The water soluble cation with higher contribution to the mass of PM_{2.5} in combustion

experiments of leached eucalyptus (LE) and pine (P2) was Ca²⁺, accounting for 0.23 and 0.65 wt.%, respectively. For combustion experiments with eucalypt (E), Cl⁻ was the soluble anion in higher concentration (1.05 wt.%), while K⁺ was the major soluble cation (0.73 wt.%) in the PM_{2.5} samples. In fact, Cl⁻ and K⁺ are often combined in the biomass and ash components and are highly water soluble. In the present study, the K⁺ content in PM_{2.5} samples from softwood combustion (pine) was much lower than in samples from hardwood (eucalypt) combustion. Some ions like phosphate, lithium, formate and pyruvate were below the detection limit of the method (Table 3). Potassium in fine particles has been used as a tracer of biomass burning emissions. Alves et al. (2011) studied the composition of fine particles resulting from residential wood combustion and observed that Cl⁻ and K⁺ were the major ionic compounds in the combustion flue gas samples. The mass fractions of soluble ions Cl⁻ and K⁺ were higher in particles from the combustion of eucalypt than from pine. Although the type of combustion equipment was very different from the one that was used in the present study, the same trend was observed.

3. Conclusions

This paper constitutes one of the very few attempts so far to comprehensively characterize particle emissions during biomass combustion in a fluidized bed combustor. Despite the limited number of experiments, the results obtained suggest that combustion conditions and type of fuel have a significant impact on the chemical composition of emissions. For the combustion of eucalypt chips, it was observed that pre-processing steps applied to biomass, such as rainfall leaching, could be an effective way to improve the combustion process. For pine chips, the highest CO emission factor was observed during the combustion with lower stoichiometry. The PM_{2.5} emission factors for softwood (pine) combustion ranged between 16.8 ± 1.0 and 29.3 ± 3.1 mg/kg of fuel (dry basis). The lowest PM_{2.5} emission factor was observed when operating the reactor with higher stoichiometry (higher O₂ content in combustion flue gases). For hardwood (eucalypt) combustion, the PM_{2.5} emission factors ranged from 33.0 ± 10.8 to 55.2 ± 2.5 mg/kg of fuel (dry basis). The highest emission was observed for the combustion of leached eucalypt despite the higher stoichiometric conditions. The PM_{2.5} mass was mainly composed of inorganic matter, while organic compounds represented a much smaller fraction. Organic and elemental carbon accounted for 3.1 to 30 wt.%, whereas carbonate represented between 2.3 and 8.5 wt.% of PM_{2.5} mass. The levoglucosan content in the PM_{2.5} mass was always below the detection limit of the method, suggesting that, contrary to what happens with residential combustion equipment (fireplaces and woodstoves), it cannot be used to trace emissions from biomass combustion in fluidized bed reactors. Ca, K, Mg, Na and S were present in all PM_{2.5} samples, representing a significant mass fraction (higher than 48 wt.%) of particulate mass. Water-soluble ions accounted for about 0.51 to 2.39 wt.% of PM_{2.5} mass, with Cl⁻, K⁺ and Ca²⁺ representing the major ionic components in samples from the combustion of eucalypt and pine.

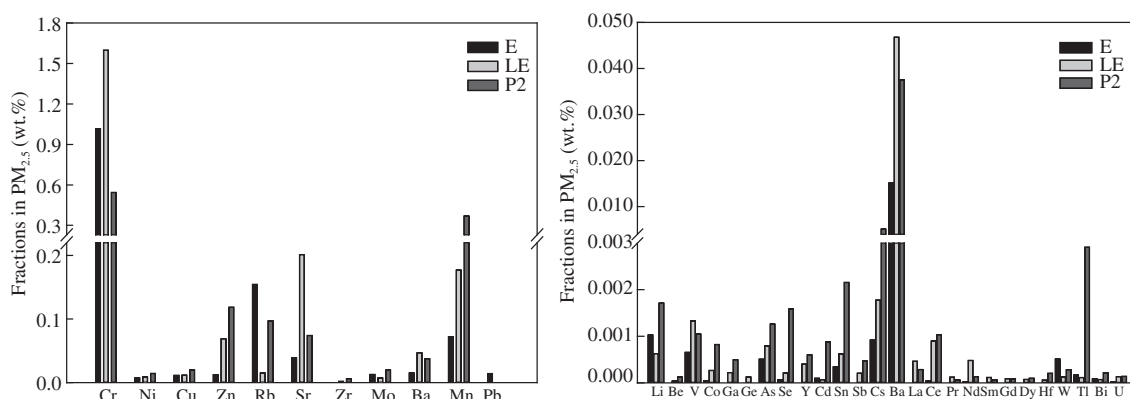


Fig. 7 – Mass fractions of minor elements in $PM_{2.5}$ during eucalypt and pine combustion experiments. Sc, Nb, Eu, Tb, Ho, Er, Tm, Yb, Lu, Ta, and Th were all below the limit of detection.

This work has demonstrated the feasibility of the combustion of residual forest biomass in BFBC. The biomass fuel characteristics and operating conditions influence the performance of the process and respective emissions. A comprehensive chemical composition of fine particulate matter ($PM_{2.5}$) was obtained, constituting an important tool for increasing the knowledge on emissions from BFBC. This information may also be useful for inventorying emissions from related combustion plants, as well for estimating their contribution to the atmospheric pollution levels through receptor modeling. Additional experiments with different feeding rates and stoichiometric conditions should be made to increase the knowledge about the process.

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Table 3 – $PM_{2.5}$ mass fractions of water-soluble ions.

	E (wt.%)	LE (wt.%)	P2 (wt.%)	Detection limit (µg/L)
Fluoride	nd	nd	nd	0.94
Acetate	nd	nd	nd	1.21
Propionate	0.01	0.01	0.01	2.72
Formate	nd	nd	nd	1.77
Butyrate	0.02	nd	0.02	1.72
Pyruvate	nd	nd	nd	0.83
Chloride	1.05	0.04	0.30	1.67
Nitrate	nd	nd	nd	1.23
Succinate	nd	nd	nd	0.98
Sulfate	0.30	0.08	nd	4.84
Oxalate	nd	nd	nd	0.74
Phosphate	nd	nd	nd	2.11
Citrate	0.06	0.02	0.07	1.92
Lithium	nd	nd	nd	0.50
Sodium	0.08	0.01	0.05	0.70
Ammonium	0.00	nd	nd	0.75
Potassium	0.73	0.04	0.08	0.50
Magnesium	0.14	0.08	nd	1.00
Calcium	0.01	0.23	0.65	3.00

nd: not detected, below detection limit of the method.

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