

EMISSIONS FROM THE COMBUSTION OF EUCALYPTUS AND PINE CHIPS IN A FLUIDISED BED REACTOR

C.A. Alves^(a), E. Vicente^(a), M. Duarte^(a), L. Tarelho^(a), E.R. Teixeira^(a), T. Nunes^(a), C. Colombi^(b), V. Gianelle^(b), A. Sanchez de la Campa^(c), J. de la Rosa^(c)

^(a) Centre for Environmental and Marine Studies, Department of Environment, University of Aveiro, 3810-193 Aveiro, Portugal

^(b) Regional Centre for Air Quality Monitoring Air Quality, Environmental Monitoring Sector ARPA Lombardia, 20129 Milan, Italy

^(c) Associate Unit CSIC-University of Huelva “Atmospheric Pollution”, University of Huelva, Campus El Carmen, E21071 Huelva, Spain

ABSTRACT: Interest in renewable energies has increased in recent years due to environmental concerns about global warming and air pollution, reduced costs and improved efficiency of technologies. Under the EU energy directive, biomass is an eligible source of renewable energy. Among others, the technology of fluidized bed combustion represents an important asset in many industrial processes because it presents several advantages. The aim of this study was to experimentally quantify and characterize the emissions of particulate matter (PM_{2.5}) resulting from combustion in a pilot-scale bubbling fluidized bed combustor with variations in fuel (pine and eucalyptus chips), and operational conditions. The variables evaluated were the stoichiometry used and, in the case of the eucalyptus, the leaching of the fuel. The CO and PM_{2.5} emission factors were lower when the stoichiometry used in the experiment was higher. The treatment of the fuel before its combustion has showed to be an effective way to reduce the CO emissions. However, the PM_{2.5} emissions were higher when the leachate eucalyptus was used. The particulate mass was composed mainly of inorganic matter. Organic and elemental carbon represented 3.7 to 29.8% (w/w) and the carbonate (CO₃²⁻) represented between 2.3 and 8.5% (w/w) of the particles mass.

Keywords: biomass, chemical composition, combustion, fluidized bed, particle emission

1 INTRODUCTION

The growing interest in the search for and development of alternatives to fossil fuels, with control of CO₂ emissions has led the scientific community and other decision makers to consider other sources of energy [1-5]. The production of energy using renewable sources will become more important as the reserves of fossil fuels become smaller [6]. The renewable energy sources increase the possibilities for self-sufficiency and can play an important role in reducing the greenhouse gases emissions [6,7]. Under the EU energy directive; biomass is an eligible source of renewable energy. The development of biofuel conversion technologies with high conversion efficiency, low emissions, competitive and with low operating cost is a challenge [8]. Among the technologies available for combustion the bubbling fluidized bed (BFB) 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 production because it presents several advantages that include high efficiency, fuel flexibility and low environmental impact [9,10], furthermore the technology also allows a high rate of heat and mass transfer, low pressure drops, and uniform temperature distribution [11,12]. The bubbling fluidized bed combustion (BFBC) is a technology with high versatility that can be used for burning a very broad range of hydrocarbon based fuels [11,13-16].

Despite the advantages attention must be paid to operating and environmental problems. There several factors that influence operating conditions. The choice of the biofuel depends on the option for the fuel conversion [2]. Plants depend on fundamental processes for growth [17] that have influence on its chemical characteristics and thus on the emission profiles. The solid biofuels present different elements at different concentrations depending on the type and origin of the biomass [18]. The chemical composition of the biofuels are related to

the composition of the soils and with the type of plant species since the different types of species will take up different compounds from the soil to different extents. The main problems derived from the biofuel chemical composition are related to ash, which is produced during biomass combustion. These problems are for instance bed agglomeration, slagging, fouling and corrosion [19-23]. Elements like Si, K, Na, S, Cl, P, Ca, Mg, Fe are involved in reactions leading to ash fouling and slagging. The K and Cl elements play an important role in this aspect since they 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 silicates formation with low melting points causing slagging and bed agglomeration [24]. The characteristics of the ashes besides causing operational problems during the combustion process may also limit its utilization [19-22]. The BFBC technology presents the possibility of preventing some ash-related problems as result of the relatively low uniform temperature and good mixing of bed material [25-27]. The fuel leaching is an option to solve some operational problems related with alkali metals like K and Na, and also chlorine and sulfur. Decreasing the ash fusion temperatures allows to reduce the ash related problems like bed agglomeration and deposit formation [23,28-30].

Studies have showed that BFBC technology has the capacity for the combustion of a large variety of fuel combinations keeping low emissions [1,31]. However, gaseous and fine particulate emissions have been pointed out hazardous effects to human health and control devices are not effective in the elimination of pollutants from the flue gas [32,33]. Taking into account the environmental and human health impact of these emissions and the need for improve the operational conditions, a rigorous quantification and characterization of emissions is necessary. Although several studies have been performed the environmental aspect has been overlooked.

In this study, gaseous and particulate emissions from the combustion of pine and eucalyptus chips were studied. The parameters that had been investigated were the fuel, the stoichiometry and the effect of biomass leaching. The combustion experiments were conducted in a pilot-scale bubbling fluidized bed combustor.

2 MATERIALS AND METHODS

2.1 Fluidized bed combustor

A fluidized bed is a heterogeneous reactor, in which a solid and a gas phase are involved. The fluid (gas phase) is forced to pass through a bed of solid particles. The fluidized bed reactor is constituted by a first zone where the solids concentration is high, so-called bed and a second zone above the bed where the solid concentration is much lower called freeboard. Thus we find in the reactor a volume of particles (bed) of varied nature (biomass ash, sand) supported by a gas distribution plate. The particles are kept in vigorous movement through the air moving upward in the bed.

The experimental part of this work was carried out in a pilot-scale combustion installation with a bubbling fluidized bed combustor (BFBC) [15,16,34]. The infrastructure is constituted by three systems, 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 a pilot-scale fluidized bed reactor made in stainless steel (AISI 310 SS) insulated in height; the bottom bed, 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. It has also an inner diameter of 0.25 m and 3.0 m in height. It also has a whole set of accessory elements that allow the operation of the reactor, including a control unity responsible for controlling the electric circuit of reactor operation and the pneumatic circuit of gases. The system also comprises the fuel feed unit and the water cooling system.

The combustion air is distributed in two stages. The primary air through the distribution plate consisting of 19 injectors, and the secondary air through a standpipe located within the freeboard. The secondary air is added 0.20 m above the bed surface with the biomass fuel. The biomass feed system is located in the top of the reactor and allows the independent and simultaneous addition of two fuels. The biomass particles are dropped at the bed surface through a vertical tube located inside the freeboard.

The pressure, temperature and composition of the combustion flue gases were monitored through nine water-cooled sampling probes located at different heights along the reactor. Two of them are immersed in the bed and the rest of the sampling probes are distributed along the freeboard. Every gas 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 retain the particles present in the flue gas sampled.

The combustion process in a fluidized bed reactor releases significant amounts of heat. The refrigeration system of the fluidized bed intends to control the

temperature in the reactor by extracting heat through cooling probes located inside the reactor. In this system the working fluid is liquid water and cooling of the fluid is achieved in a refrigeration tower.

2.2 Fuel characteristics

In this work it was studied the combustion of two types of biomass used in Portugal in industrial facilities for heat and power production, and includes residues from eucalyptus (*Eucalyptus globulus*) and pine (*Pinus pinaster*) felling. The chemical composition of the solid biomass fuel is shown in Table I.

Table I: Chemical composition of the solid biomass fuels.

Proximate analysis	Eucalyptus	Leached Eucalyptus	Pine
(% wt, as received)			
Moisture	9.03	7.41	9.04
Ash	1.74	1.41	0.60
Volatile Matter	83.12	83.92	85.05
Fixed Carbon	6.11	7.26	5.32
Ultimate analysis			
(% w/w, dry basis)			
Ash	2.91	2.31	1.25
C	45.29	45.08	49.08
H	6.17	5.87	6.38
N	0.03	0.51	0.15
S	nd	nd	nd
O (by difference)	45.59	46.23	43.14

nd – not determined, below detection limit of the method.

In order to have the biomass with a set of adequate characteristics to ensure optimal performance of the combustion system, it is necessary the pre-treatment of biomass. This pre-treatment can include a refinement of its physical characteristics (such as particle size, density) and also chemical characteristics. In this work, the size of the biomass particles was reduced in order to match the characteristics of the biomass feed system of the BFBC. It was also studied the effect of biomass leaching (at atmospheric conditions) on the characteristics of the fuel. Forest biomass residues were chipped, air dried, and sieved in order to obtain particles with equivalent size below 10 mm.

After chipping the eucalyptus biomass, a fraction was allowed to leach under atmospheric conditions (leaching by rainwater) during a six-month period. At the end of the leaching period this biomass was then also placed to dry. A more detailed description of the leaching process can be found elsewhere [34]. The goal was to study the effect of leaching on the characteristics of the biomass and on the emissions resulting from the combustion process.

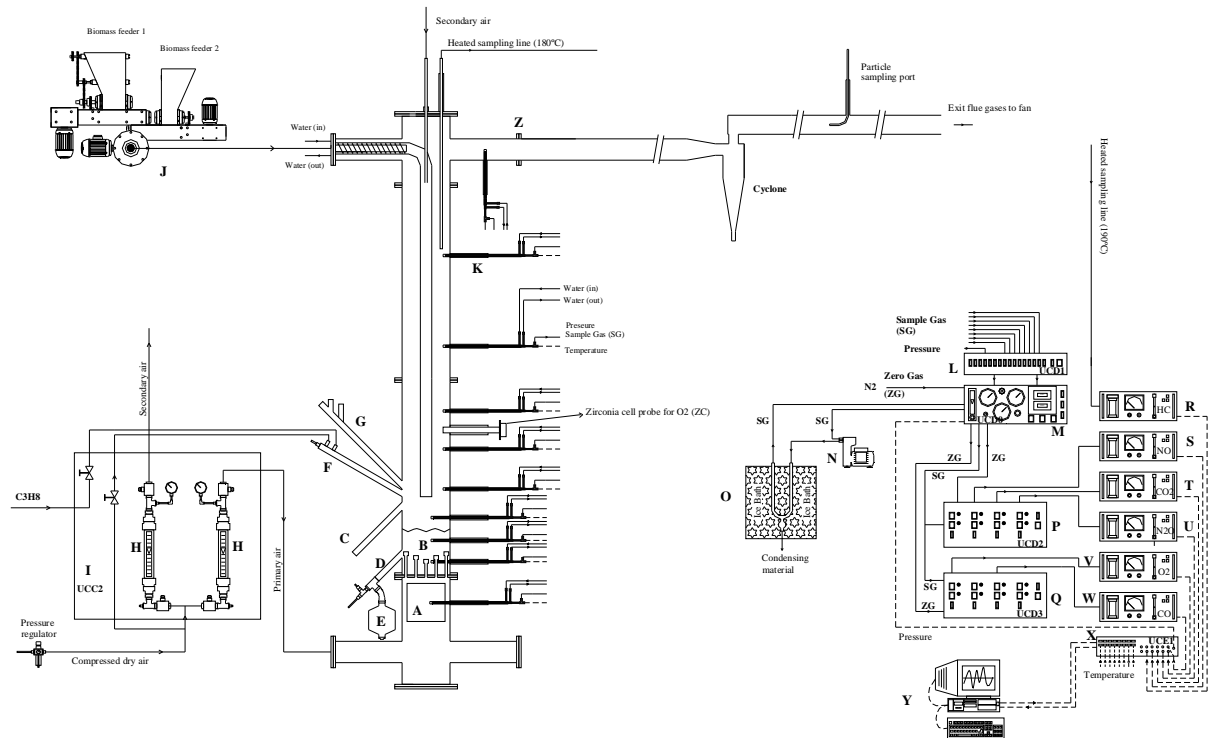


Figure 1: Schematic representation of the pilot-scale installation. Dashed line - Electric circuit, Solid - Pneumatic circuit, A - Primary air heating system, B - Sand bed, C - Bed solids level control, D - Bed solids discharge, E - Bed solids discharge silo, F - Propane burner system, G - Port for bed surface visualization, H - Air flow meter, I - Control and command unit, J - Biomass feeder, K - Water-cooled gas sampling probe, L, M, P, Q - Command and gas distribution units (UCD0- UCD3), N - Gas sampling pump, O - Gas condensation unit, R, S, T, U, V, W - Automatic on-line gas analyzers (CO_2 , O_2 , CO), X - Electronic command unit (UCE1), Y - Computer data acquisition and control system, Z - Exhaust duct to cyclone.

2.2 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 is conducted with propane combustion in order to raise the temperature of the reactor and the fluidizing air heating is performed through an electric oven until the reactor reaches the temperature of 500°C . After that, the addition of the solid fuel is initiated, and when a temperature of about 750°C is reached in the bed, the auxiliary heating systems (gas and electric oven) are switched off and the reactor begins to operate only with the addition of solid fuel. The second phase consists in the operation under stationary conditions in the desired temperature range.

The experiments were planned to keep the reactor hydrodynamics similar during the period of study. The combustion air was supplied in two stages. The primary air (80% of the total combustion air) and the secondary combustion air (20% of the total combustion air). The **Table II:** Experimental conditions.

stoichiometry of the combustion experiments was pre-established and adjusted through the fuel 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 freeboard temperature was controlled by modifying the biomass moisture.

The combustion experiments were performed in order to evaluate the influence of the fuel, stoichiometry and biomass leaching on the flue gas composition and particulate matter characteristics (Table 2). The flue gas sampling for characterization (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 the temperature and pressure along the reactor height and exit flue gas composition; the steady condition was considered as achieved when the bed temperature and the exit flue gas composition did not show significant differences along the time.

Experiments	Fuel	dp (mm)	Moisture content (%)	Fuel Rate (kg/h)	T_{bed} ($^\circ\text{C}$)	O_2 (%)
E1	Eucalyptus	<10	29.2	4.4	806	3.3 ± 0.2
E2		<10	26.3	4.1	810	4.0 ± 0.3
LE	Leaching Eucalyptus	<10	12.6	2.6	807	7.6 ± 0.4
P1	Pine	<10	17.9	2.8	804	8.4 ± 0.1 to 10.3 ± 0.4
P2		<10	20.4	3.2	804	4.9 ± 0.0

2.2 Gas sampling and measurement techniques

The system of gas sampling and analysis consists of a set of sampling probes located along the reactor, 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. The exit flue gas composition was sampled in a probe located at 2.20 m height above the distributor plate.

The continuous motorization of the O₂ concentrations was made by a paramagnetic online analyzer (ADC WA-558G, model 02-700 ADC) with a Servomex module. The CO₂ and CO was monitored by a non-dispersive infrared analyzer from (Environment MIR 9000).

2.2 Particle sampling and measurement techniques

Fine particles (PM_{2.5}) were collected under isokinetic sampling conditions, using a low volume sampler and quartz filters. The particles sampling was carried out after the cyclone. Before entering the cyclone the flue gas was cooled and diluted with atmospheric air to decrease its temperature; the temperature in the cyclone was around 135°C, and the pressure drop across the cyclone was typically 15 mm H₂O. At this equipment the particles in the effluent are submitted to centrifugal and gravitational forces that promote the removal of some particles from the flue gas [35]. The collection efficiency of this equipment is high for coarse and heavy particles (> 10 µm), but limited for fine particles [6,24].

2.2 Analytical methodologies

In order to eliminate organic contaminants the quartz fiber filters used for particulate matter sampling in this work were baked for 6 hours at 600 °C. Previously to the gravimetric analysis with a microbalance Mettler Toledo AG245 (readability- 0.1mg/0.01mg) the filters were placed 48 h in equilibrium in a room with controlled temperature and relative humidity. To avoid contact with contamination sources the exposure of filters to atmospheric air was avoided. The filters were transported and stored in a desiccator and kept in petri dishes. For each filter, the weight was obtained from the average of six measurements; the variations were less than 0.02%.

The carbonates quantification was made by the sample acidification with phosphoric acid (H₃PO₄). Two punches of 5 mm in diameter were used in each analysis. Blank filters were analyzed for the correction of the obtained values. The system includes a reaction cell analyzer, a CO₂ mass flow meter and a data acquisition system. The cell analyzer system is composed of a bubbler containing phosphoric acid (20%) to which two pipes are connected, one that allows the entry of gases into the system and one for the gases outlet. Upstream there is a teflon filter that removes droplets, preventing them from entering the CO₂ analyzer, which can lead to its damage.

The sample is placed in the sample holder inside the bubbler and is performed the system purge with nitrogen (N₂) to be observed that there are no traces of CO₂ closing then the line to N₂ bubbler. Subsequently the sample holder is open to drop the filter into the solution entering this into contact with the acid for about 3 minutes. Finally the N₂ line is open in order to released CO₂ by reaction of carbonates with H₃PO₄. The flow rate of nitrogen was about 200 mL min⁻¹. The carbonates

quantification was carried out by integrating the area under the curve corresponding to the CO₂ concentration read by the analyzer.

The carbonaceous content in the PM_{2.5} was analysed after the removal, by acidification, of the carbonates in the samples. To this end, two punches of 9 mm diameter of each sample were exposed to HCl vapors for 5 hours in a desiccator. Subsequently, the excess HCl was removed by keeping the samples in a desiccator over NaOH for 24 hours. The organic carbon (OC), elemental carbon (EC) and total carbon (TC = OC + EC) of particulate matter deposited on the quartz fiber filters during burning tests were analyzed by a thermo-optical system for transmittance. Briefly, this method consists, in the volatilization of carbon particulate sampled and their differentiation into several fractions by means of a controlled heating, with subsequent conversion by oxidation to carbon dioxide for detection. The analysis is performed in two stages under different atmospheres, the first being an inert atmosphere (absence of O₂) and the second an oxidant atmosphere. In the first phase takes place the controlled heating of the sample in nitrogen atmosphere (100% N₂) along with volatilization of carbonaceous organic compounds (OC) and pyrolysis of some of these compounds (POC). In a second step, after volatilization of the organic carbon, the atmosphere is changed to a mixture of N₂ and air (containing about 4% O₂ in the mixture), and simultaneously with the rise of the temperature occurs the volatilization and oxidation of the remaining carbonaceous material (POC and EC). The phenomenon of organic compounds pyrolysis that occurs in the first stage is inevitable and consists on the process by which the OC, at high temperatures, changes its chemical composition acquiring a structure similar to the EC, being subsequently analyzed as such. The monitoring of the blackening of the filter using a laser beam and a photodetector measuring the filter light transmittance allows separating the elemental carbon formed by pyrolysis of organic carbon and that it was originally in the sample.

The determination of levoglucosan was performed by ion chromatography (IC). The chromatograph Methrom 881 was equipped with an auto sampler Methrom 863 and an amperometric detector for levoglucosan (module 896, PAD mode), column Metrosept carb 1 (150 mm x 4 mm id). Particulate matter on each filter punch (1.5 cm²) was extracted with Milli-Q water (10 ml) through ultrasonic agitation. After the extraction the solution was filtrated through a polypropylene puradisc (0.45 µm porosity, 25 mm diameter).

For the determination of the metals content of the sampled PM_{2.5} a fraction of each filters was subjected to acid digestion (1.25 ml HNO₃; 2.5 ml HF; 1.25 ml HClO₄) following the method proposed by [36] for the analysis of major and trace elements by means of Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Three multi-elemental solutions Spec® 1 (rare earth elements, REE), Spec® 2 (alkalis, earth alkalis, and metals) and Spec® 4 (Nb) were used to construct an external calibration curve. The mean precision and accuracy fall below typical analytical error and are in the range 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 (NIST, Gaithersburg,

MD, USA). The detection limits obtained were 0.01 ng m⁻³ for most trace elements analyzed.

3 RESULTS AND DISCUSSION

3.1 Operating conditions

The longitudinal pressure and temperature profiles along the reactor height are shown in Figure 2. The

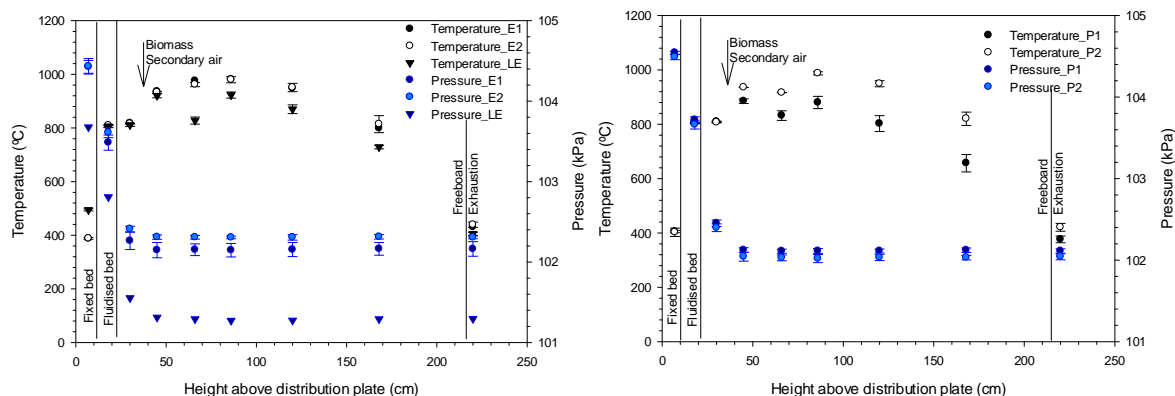


Figure 2: Longitudinal temperature and pressure profiles along the pilot-scale BFBC during the combustion experiments with eucalyptus and pine. Legend according to table II.

The temperature reaches the maximum value just above the biomass feeding location and secondary air injection (0.40 m above the distribution plate). The higher temperature recorded in this location can be related to the volatiles combustion that occurs mainly in this zone [15,16]. For the experiments E1, E2 and P2, the lower temperature was observed in the bed, and increases in the freeboard, reaching the maximum value above the biomass and secondary air injection, and decreases in the space above (Figure 2); nevertheless, the temperature in the freeboard was always higher than that observed in the bed. During pine combustion with 8-10% O₂ in the exit flue gases (P1) and with leached eucalyptus (LE) the temperature at 1.70 m above the distributor plate is lower than that observed inside the bed. The higher temperatures in the BFBC were observed during combustion of pine chips with 4% O₂ in the exit flue gases (P2). The lower concentration of O₂ in the BFBC is associated with the lower stoichiometry experiments (that is, higher ratio biomass fuel/combustion air). Higher fuel rate originates higher thermal energy output during combustion in the BFBC for the same amount of combustion air. The temperature profiles along the reactor height observed in the present work are similar to those observed in other studies [16].

3.2 Gaseous Emissions

The The CO₂, CO and O₂ concentration in the exit flue gas along time during the combustion experiments are shown in Figure 3.

The CO₂ concentration reached its minimum value

maximum pressure value is reached at the level of the primary air injectors, at the base of the bubbling fluidized bed. The pressure decreases with bed height and it is almost uniform along the freeboard height; the pressure along the freeboard is close to the atmospheric pressure. Differences between 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 done.

when the O₂ concentration was maximum. This trend was verified for all the combustion tests performed.

The CO₂ concentration in the flue gas during eucalyptus combustion was in average higher in the E1 (17.5 ± 0.3 %v, dry gases) experiment and lower in the LE experiment (12.8 ± 0.6 %v, dry gases), and its related to the higher stoichiometry of the later. For pine chips combustion, the P1 experiment generated the lowest CO₂ concentration (11.1±1.2 %v, dry gases), and the lower stoichiometry (P2) produced a flue gas with average 15.1%v (dry gases) CO₂ in the flue gas.

The average CO concentration in the exit flue gas during combustion of eucalyptus chips was higher in the experiment E1 (6150.2±1016.3 ppmv) (Fig. 3). Although operating under steady state conditions, the CO concentration profiles along the time in the experiments with eucalyptus (E1 and E2) have showed fluctuations as can be seen in Fig. 3. These fluctuations could be related to the irregularity in the fuel feeding.

The experiments with leached eucalyptus were performed with an average concentration (dry gases) of oxygen in the exit flue gases of 7.6 %. The CO average concentration in the exit flue gas was 598.5±57.5 ppmv (dry gases). The combustion of leached eucalyptus allows a reduction in the CO emissions when compared with the non-treated eucalyptus. This fact can be related with the improvement of the fuel characteristics. However, the higher stoichiometry during combustion of leached eucalyptus also contributes for a higher efficiency on fuel conversion.

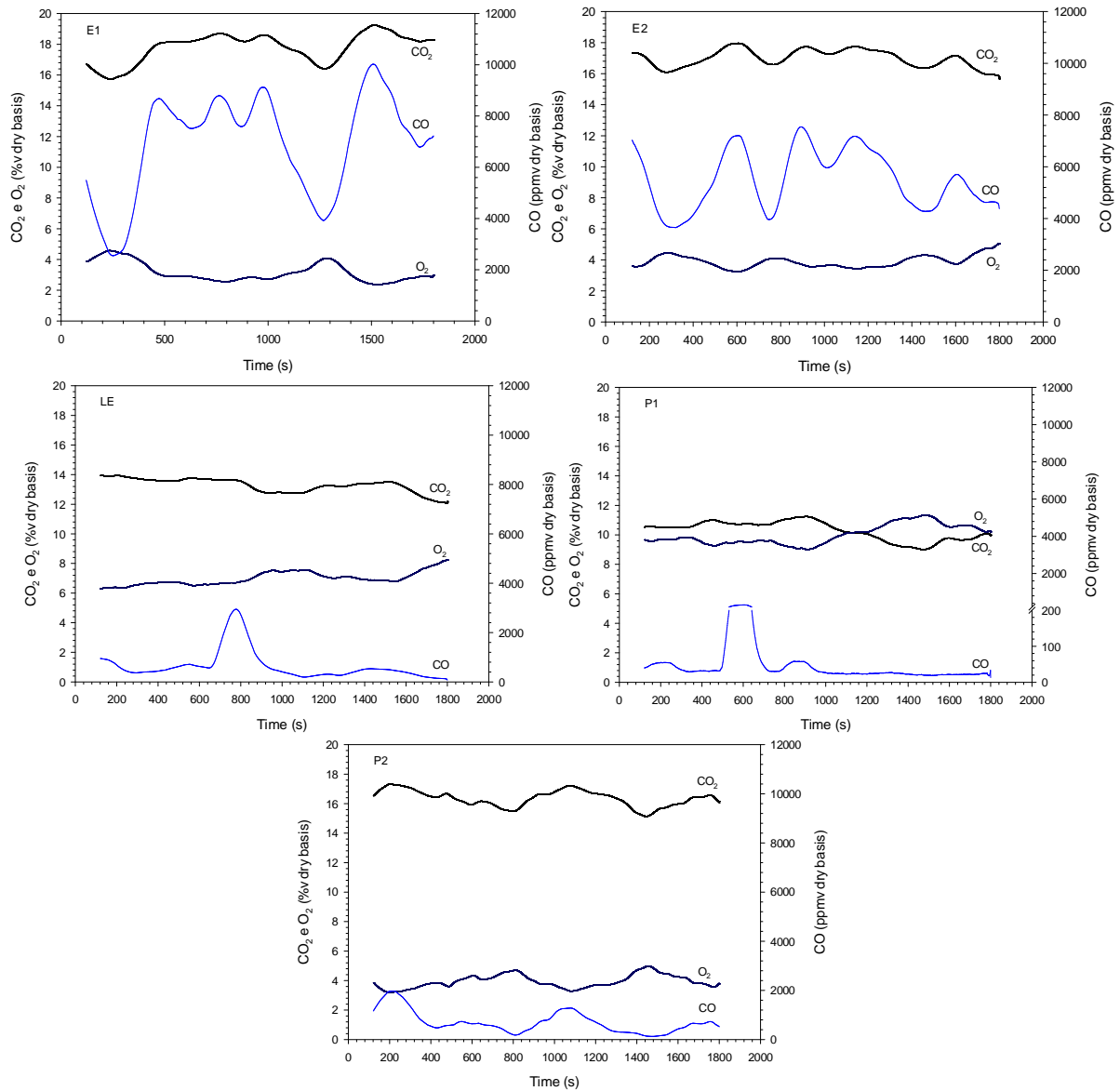


Figure 3: CO, CO₂ and O₂ concentrations in the exit flue gases along time, for each experiment.

When the fuel was pine chips the higher CO average concentration in the exit flue gas was observed during the combustion with lower stoichiometry (P2) (710.0 ppmv, dry gases) and the lower in the experiment with higher stoichiometry (P1) (40.0 ± 16.2 ppmv, dry gases). The higher stoichiometry promotes a more efficient oxidation of the fuel (char and volatiles).

It is observed that the CO concentration in the flue gases during the combustion of eucalyptus (E1 and E2) is much higher than that observed during the combustion of pine (P2); those experiments were performed with a similar stoichiometry. The combustion of pine chips was more stable and generated lower fluctuations in the CO concentration when compared with the eucalyptus experiments; this can be related to a more regular feed of pine, and a consequence of the fuel transport properties.

The CO₂ emission factors are presented in Fig. 4. The higher CO₂ emission factor was observed during pine combustion, and the lower emission factor was observed during eucalyptus combustion. This result is explained by the higher carbon content of the fuel derived from pine

(Table I).

Fig. 5 shows the CO emission factors for the combustion experiments. The CO emission factors during combustion of eucalyptus chips were higher in the experiment E1 when compared with the E2 experiment, and this is related to the lower stoichiometry of the first. Leaching the fuel and using a higher stoichiometry is an effective way for reducing the emissions of unburned compounds (Fig.5). In a similar way, when the fuel was pine chips the higher CO emission factor was observed during the combustion with lower stoichiometry (P2). The fuel characteristics play an important role in the emission factors observed during the pine and eucalyptus combustion. Lower CO emission factors were observed during pine combustion when compared to eucalyptus using similar stoichiometry. This can be a result of a more regular feeding of pine when compared to eucalyptus, thus originating less fluctuation in flue gas composition and a more efficient fuel conversion in the case of pine (Fig. 3).

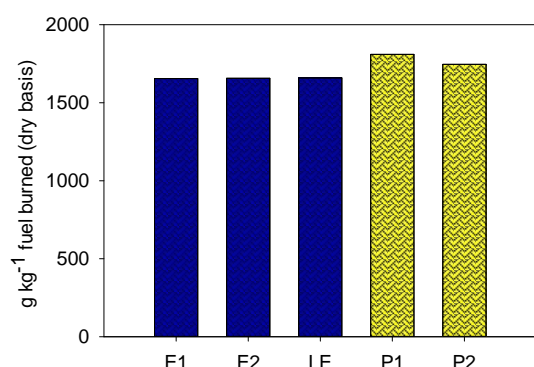


Figure 4: CO₂ emission factors.

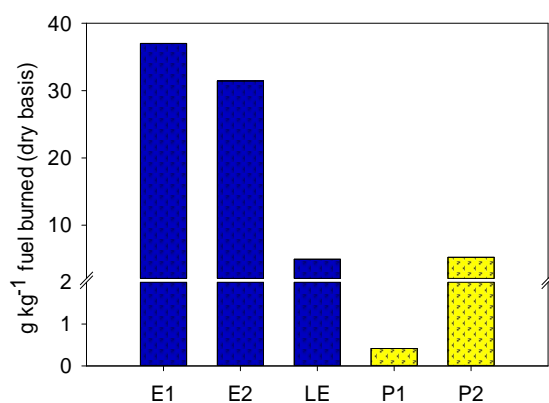


Figure 5: CO emission factors.

When the fuel was pine chips the higher CO emission factor was observed during the combustion with low stoichiometry (P2) and the lowest in the experiment P1. The CO reduction can be result of the volatiles combustion that takes place in the upper part of the reactor leading to a temperature rise and enhancing the burnout. The fuel characteristics can also play an important role in the emission factors that can be observed during the pine and eucalyptus combustion. The pine combustion generated lower emission factors compared with eucalyptus using similar stoichiometry.

3.2 Particulate emissions

Fine particles are formed through pre-existing particles and from species that are volatilized during the combustion process [37]. A detailed explanation of the particles formation mechanism can be found elsewhere (e.g. [3,38]). The fly ashes formed during the combustion in fluidized bed combustors are dominated by particles with diameters in the range between 5 to 25 μm [39].

Fine particle mass emission factors depend on many features including fuel characteristics and combustion conditions as can be seen in Fig. 6.

The PM_{2.5} emission factors for softwood combustion ranged between 15.30 ± 2.91 and 17.50 ± 1.84 (mg kg⁻¹ of fuel, as burned). The lowest PM_{2.5} emission factor was observed when operating the reactor with high O₂ content (P1). Particulate emissions increase with the decrease of the stoichiometry (Fig. 6).

The emission factors for the hardwood combustion ranged from 16.00 ± 3.93 to 45.3 ± 2.08 (mg kg⁻¹ of fuel, as burned) for the different tests performed. The highest PM_{2.5} emission was registered when the leachate eucalyptus was burned (LE).

Calvo et al. [15] studied the aerosols present in the flue gas from co-combustion of forest biomass and sewage sludge from a paper pulp mill industry in the same pilot-scale fluidized bed used in the present study. The authors observed an emission factor of 4.0 ± 0.2 g PM_{2.5}·kg⁻¹ of fuel (as burned) and 3.7 ± 0.5 g PM_{2.5}·kg⁻¹ of fuel (as burned) for the flue gas before and after the cyclone. The high difference observed in the emission factors may be related to the fuel composition and to the fact that a mix of two fuels was burned. The final fuel used by [15] was composed of 40% w/w of secondary sewage sludge and 60% w/w of forest biomass residues. There was a huge difference between the fuels regarding the ash content. Whereas the forest biomass presented 1.41% w/w the sewage sludge presented 57.41% w/w. The nitrogen and the sulphur content in the sewage sludge were also higher than in the forest biomass. Thus, attention must be paid to the fuel used in the combustors since the emissions are highly variable.

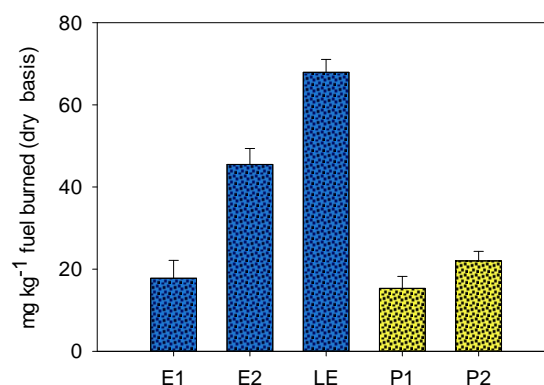


Figure 6: PM_{2.5} emission factors.

3.3 Particulate composition

The health effects caused by particulate matter are dependent on its physical and chemical properties [40,41]. These properties are function of the combustion conditions that may present high variability [40]. The particles produced in conditions of complete combustion are more likely to induce cellular damage than the particles generated in poor combustion conditions with higher dosages [42].

Fig. 7 presents the mass balance performed through the chemical analyses of the particulate matter sampled.

In order to perform a mass balance is necessary to convert the organic carbon in organic mass since the organic matter consists of carbon associated with other elements. The total amount of organic mass is estimated multiplying the OC concentration of by a factor that takes values between 1.3 and 2.2 [43-46] depending on the aerosol composition, its origin and the degree of aging [47,48]. The organic mass/organic carbon ratio adopted in the present study was 1.6. The mass balance was performed using the methodology proposed by [49].

The organic mass in the fine particles samples accounted for about 2 to 7% w/w of the PM_{2.5} mass. Contrarily to traditional combustion appliances (e.g.

fireplace and woodstove), levoglucosan in $PM_{2.5}$ emitted by the BFBC was always below the detection limit, suggesting that this anhydrosugar, normally pointed out as a good biomass burning tracer, may be highly dependent on combustion parameters. The elemental carbon has contributed with around 1 to 2% w/w carbonates 6 to 7% w/w of the total fine particle mass. Unlike residential combustion appliances, that presents high carbonaceous content in the particulate matter sampled [49-53] the fluidized bed combustion generated low amounts of OC and EC in fine particles [15]. Particles from incomplete combustion, such as soot, condensable organic particles or char are not expected to be significant, because these combustors operate under efficient combustion conditions [1].

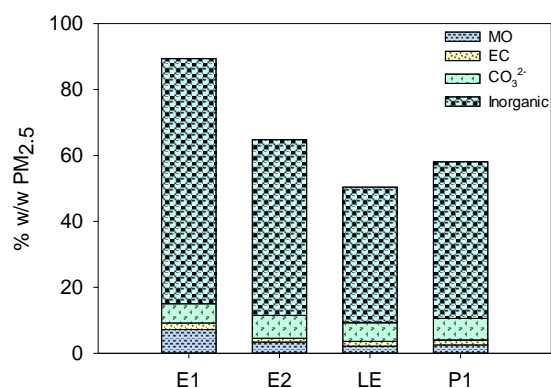


Figure 7: Chemical composition of $PM_{2.5}$.

The inorganic material accounted for about 41 to 74% of the $PM_{2.5}$ mass (Fig. 7). It is necessary to take into account that the chemical elements are not as single elements in the particulate matter. Thus, the inorganic fraction of particulate matter has been underestimated. For example, potassium, which consists in the major emitted element during the experiments, is generally found as K_2SO_4 in the sub-micron fly ashes released [37]. This element can also be found as KCl and K_2CO_3 [3]. The particulate matter emitted from combustion in automatically fired systems consists mainly of inorganic potassium salts, on the other hand, when using manually fired systems high amounts of carbonaceous material is emitted in the particulate matter [50]. Soot and organic particles are formed under poor combustion conditions [3, 40,54] whereas the inorganic particles are formed in conditions of nearly complete combustion [6].

The carbon related mass fraction in the particulate matter is presented in the Fig.8. Organic and elemental carbon represented 3.7 to 29.8% (w/w) of the particulate mass emitted during the combustion process. The organic and elemental carbon present in the particulate matter is related to the combustion conditions presenting higher contribution when the combustion is more incomplete [3,40,50,51,55]. Carbonate (CO_3^{2-}) represented between 2.3 and 8.5% (w/w) of the fine particles. Calvo et al. [15] found a TC/ $PM_{2.5}$ ratio after the cyclone of 1.9% (w/w) and a carbonate content of 20% (w/w) of the total $PM_{2.5}$ mass. The higher carbonate content in particulate matter in the study of [15] is related to the fuel that was used. The sewage sludge presents in its composition a high percentage of calcium that can be related to the wastewater treatment [56]. The calcium present in the sewage sludge during the combustion process can be

transformed into carbonates and others forms like limestone contributing for the high content of calcium based compounds in the particulate matter sampled.

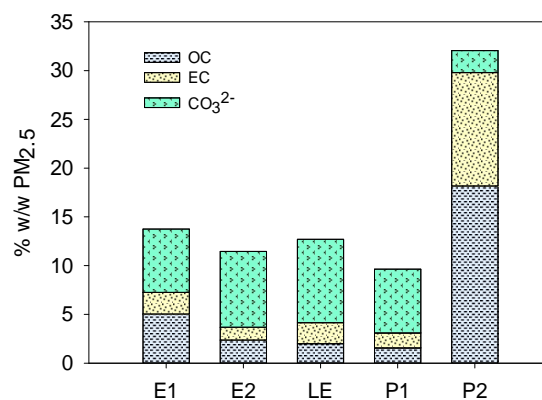


Figure 8: Mass fraction of carbon forms in particulate matter.

Among the trace elements obtained by ICP-MS/AES the Ca, K, Mg, Na and S were present in all the samples. These elements had a great contribution to the total mass of metals (Fig. 9). The fine particles containing sulphate, produced during the combustion process, are an issue of concern due to their detrimental health effects since the exposure to these particles have been found correlate with cancer mortality [57]. The $PM_{2.5}$ samples obtained in the experiment E1 presented higher inorganic content the elements mentioned above have contributed to more than 80% of the total metal mass. The experiment with leachate eucalyptus (LE) presented the lowest metal content as expected. Teixeira et al. [34], in the co-combustion of forest biomass residues with sewage sludge in a pilot-scale BFBC, found that the main chemical elements removed from ashes during leaching with water were sodium, potassium and chlorine. In the study here presented it was verified that the potassium and sodium had suffer a reduction in the particulate matter from the experiments E1 and E2 to the experiment LE. This fact suggests that these compounds are easily removed from the fuel by leaching. Other elements like Ca, Fe, Mg and P have increase in the samples collected from the leachate eucalyptus wood smoke. The relative enrichment in the fine particles after leaching can be related with the lower leachability of these elements.

The typical contents of nutrients and heavy metals presented by [58] in ash resulting from the combustion of different biomass fuels in fixed bed furnaces show that considerable differences between the coarse and the fine fly ashes can be found. The coarse fly ashes accounts for 2 to 20% of the total ash generated and the fine particles 2 to 15%. For wood chips combustion the Ca content decreases from coarse to fine fly ashes and the K content increases. The heavy metals like Pb suffer a notable increase in the fine fly ashes fraction. Thus it is important to characterize the fine particles emitted by the combustion since are the fraction capable of penetrate deeper in the human respiratory system.

The potassium was the predominant element in all the experiments excluding the experiment performed with pine (P1) that presented higher amounts of calcium and much lower potassium when compared with the experiments performed with eucalyptus. Other studies

have suggested that the pine combustion generate lower amounts of potassium in the fine particles [59]. The lower potassium content in the fine particulate matter can be related to the pine chemical composition that presents lower potassium content compared to the eucalyptus [38]. It was been reported that the Ca content in coniferous wood was lower compared to deciduous wood [38]. However, in the present study it was observed higher mass fraction of this element in the experiment P1. Ca element in the combustion of forest residues can be attributed in some extent to the sand and others impurities that the fuel contains [37].

The mass fraction of the minor chemical elements in PM_{2.5} samples was very low (Fig. 10). Among those elements, the Cr was one of the most abundant. Its contribution for the total mass of metals in the fine particles has reached 3.5%. This high content of Cr should be influenced by the destruction of stainless steel from the reactor walls, in result of chemical and thermal decomposition of the material in contact to the flue gases. Other elements like Rb, Sr, Mo, and Ba were found in the fly ashes account altogether with 0.2 to 0.7% of the particulate matter.

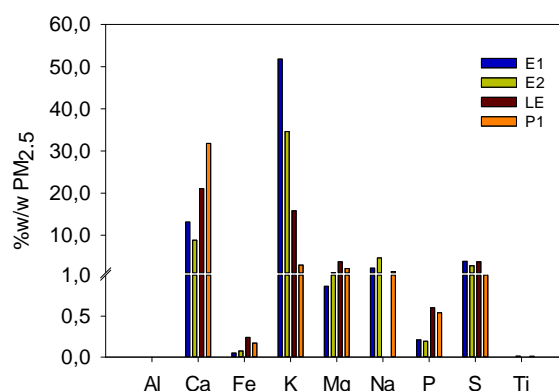


Figure 9: Mass fraction of major chemical elements in PM_{2.5} (% w/w).

Heavy metals can be found in the fly ashes since the volatile heavy metals (Cd and Zn) mainly vaporize during combustion and later condensate on the surface of the fly ashes or form aerosols [38]. Among the heavy metals the Pb, Zn, Sn, Cd, Tl and Cu were present in all of the samples. The contribution of these elements to the total mass of metals in the samples was low, not exceeding 0.3%.

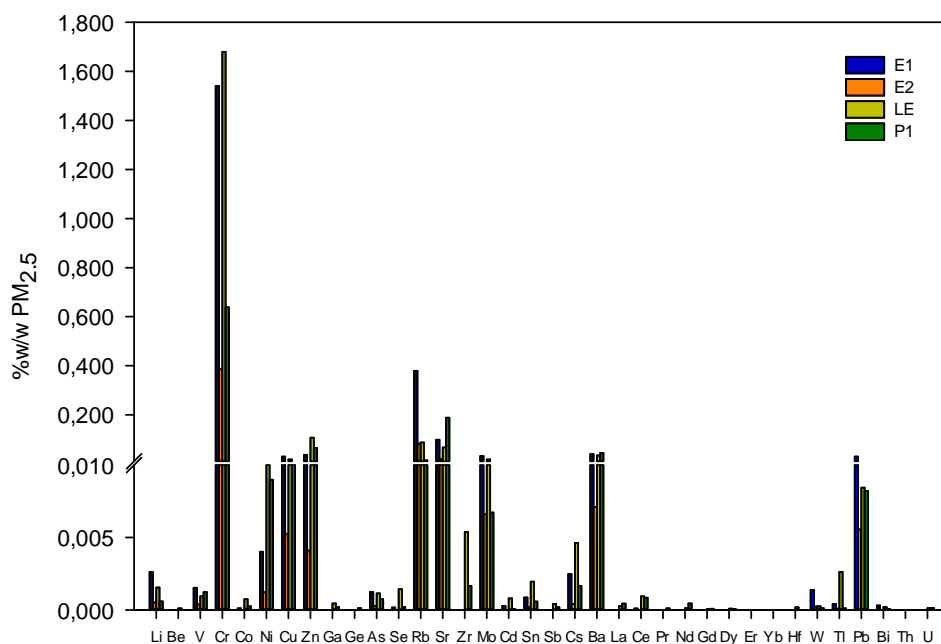


Figure 10: Mass fraction the minor chemical elements in PM_{2.5} (%w/w).

4 CONCLUSIONS

This paper reports a comprehensive effort to characterize particle and gaseous emissions from the combustion in a fluidized bed combustor. The combustion conditions and type of fuel used had showed to have a great contribution on emissions, and on its chemical composition.

For eucalyptus combustion it was observed that a slightly difference in the O₂ content could influence the gaseous emissions. The CO emission factors were lower when the stoichiometry used in the experiment was

higher. The pre-processing steps applied to biomass have showed to be an effective way to reduce the emissions of unburned compounds. For pine chips combustion the higher CO emission factor was recorded during the combustion with low stoichiometry as expected.

The PM_{2.5} emission factors for softwood combustion ranged between 15.30 ± 2.91 and 17.50 ± 1.84 (mg kg⁻¹ of fuel, as burned). The lowest PM_{2.5} emission factor was observed when operating the reactor with high O₂ content. The emission factors for the hardwood combustion ranged from 16.00 ± 3.93 to 45.3 ± 2.08 (mg

kg⁻¹ of fuel, as burned). The highest emission was observed for the experiment performed using the leachate eucalyptus.

The mass of the smoke particles were composed mainly of inorganic matter, while organic compounds represented a small fraction. The Ca, K, Mg, Na and S were present in all the samples and had a great contribution for the particulate mass. The carbon content in the particulate matter was low. Organic and elemental carbon represented 3.7 to 29.8% (w/w) and the carbonate (CO₃²⁻) represented between 2.3 and 8.5% (w/w) of the fine particles mass. Levoglucosan was always below the detection limit.

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