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# Emissions from residential combustion of certified and uncertified pellets

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## Abstract

The aim of the present study was to evaluate the relationship between fuel certification and gaseous and $PM_{10}$ emissions and their composition. Two pellets labelled as ENplus A1 (certified pellets R and P) and a non-certified brand of pellets were tested in a pellet stove. The impact of operating conditions on emissions was also evaluated. The highest carbon monoxide (CO, 2.7-6.1-fold) and total organic carbon (TOC, 1.9-11-fold) emissions were observed for certified pellets R. Nitrogen oxide (NO) emissions were higher for non-certified pellets (2.5-3.2-fold). The compliance of gaseous emissions with the Ecodesign thresholds was not ensured by certification. Certified pellets P generated significantly lower $PM_{10}$ emissions than the other two types of pellets at medium and nominal loads. Water soluble ions represented from 36 to 68 %wt. of the $PM_{10}$ mass. The combustion of certified pellets P and non-certified pellets generated total carbon $PM_{10}$ mass fractions ranging from 23 to 50 %wt., whereas pellets R resulted in lower mass fractions (7-14 %wt. $PM_{10}$). The chromatographically resolved organic compounds were dominated by anhydrosugars and alkanols. Pyrene and retene were the most abundant among polyaromatic hydrocarbons.

**Keywords**: Certified pellets; Chemical composition; Gaseous emissions; Non-certified pellets; Pellet stove; $PM_{10}$ emissions

# 1.Introduction

Increasing environmental concerns associated with fossil fuel consumption and EU bioenergy targets led to an increase in renewable energy production and utilization (European Union, 2019). Woody biomass meets an important share of Europe's renewable-energy demand (AEBIOM, 2017). Among wood-based fuels, pellets offer numerous advantages and are particularly attractive (Obernberger and Thek, 2010), as evidenced by the strong growth of the pellet market over the years. In 2017, EU28 countries consumed around 24.1 million tonnes of wood pellets with nine million tonnes used for residential heating (Bioenergy Europe, 2018).

Key drivers behind the household's heating system choice are the fuel price (Martinopoulos et al., 2018; Sandro et al., 2019; Thomson and Liddell, 2015) and also the environmental benefits (Thomson and Liddell, 2015). Despite the fact that pellet combustion heating devices allow achieving lower emissions compared with traditional firewood combustion in batch mode operated appliances (Vicente and Alves, 2018), this technology is strongly dependent on stove/boiler design (e.g. fuel feeding system: bottom, horizontal or top fed, burner pot configuration) (Polonini et al., 2019; Verma et al., 2013; Win and Persson, 2014) and fuel physical (e.g. pellet length, particle density, durability, bulk density) (Garcia-Maraver et al., 2014; Wöhler et al., 2017) and chemical properties (e.g. fuel ash content, S, Cl and K contents) (Lamberg et al., 2013; Schmidt et al., 2018; Tissari et al., 2008) for optimal performance. Furthermore, the user can still affect the emissions by adjusting the stove or boiler to operate at different heat output levels (nominal load or partial load). Generally, researchers found higher gaseous and particulate emissions when the pellet appliance is operated under partial loads (Schmidl et al., 2011; Venturini et al., 2018, 2015; Verma et al., 2013).

The fuel quality is directly interconnected to consumer's satisfaction with respect to pellet based residential heating (Sandro et al., 2019). In fact, besides its impact on emissions, the use of lower quality raw materials for pellet production, with high content of ash and critical inorganic elements (e.g. alkali metals, Cl, S and Si), can result in ash related problems (e.g. corrosion, slagging and fouling) (Carvalho et al., 2013; Fournel et al., 2015a; Öhman et al., 2004; Rabaçal et al., 2013; Zeng et al., 2016). Taking into account the importance of ensuring the quality of pellet fuels, many European countries, such as Germany, Austria, Sweden and Switzerland, developed their own standards (Verma et al., 2011). In order to harmonise the European pellet market, the EN 14961-2 introduced a common standard for residential pellet fuels, which displaced all other national standards across the EU (e.g. DIN-52731, DIN plus, Ö-Norm M-7135, SS-187120). The European standard for wood pellets was followed a few years later by the international standard (ISO 17225-2). The ENplus certification scheme ensures consumers that the standard requirements are met (EPC,

2013). Worldwide, the number of countries with ENplus certified producers increased from 7 to 44 between 2011 and 2017. The share of ENplus certified pellets on the European market was 70% in 2017 (Bioenergy Europe, 2018). Over the years, several studies focused on assessing how the fuel labelling ensures compliance with the European standard requirements for a specific quality class (Duca et al., 2014; Pollex et al., 2018; Sandro et al., 2019). Duca et al. (2014) analysed chemical and physical parameters of commercial bagged pellets during a three-year period. The research results revealed that certification is useful to guarantee a high pellet quality. More recently, Pollex et al. (2018) evaluated 249 high quality pellet samples to assess the potassium content. The authors reported huge variation in this ash forming element among the tested samples and highlighted that the current limitation of fuel ash content is not enough to ensure low ash forming elements, such as potassium, in the pellets. Several studies have reported linear relationships between PM emissions and fuel K content (Lamberg et al., 2013; Zeng et al., 2016). Fine particles are mainly formed by vaporisation of ash forming elements (e.g. K, Na, S, Cl and easily volatile heavy metals, such as Zn and Pb) and subsequent nucleation and condensation due to flue gas cooling (Obernberger et al., 2006; Obernberger and Thek, 2006; Tissari et al., 2008).

Several studies have focused on emissions from certified pellets. The main goal of most of them was to compare emissions from pellets manufactured from alternative raw materials with those obtained from the combustion of a high quality fuel (Mack et al., 2019; Schmidt et al., 2018; Verma et al., 2012). Other studies reporting the performance of certified pellets aimed to evaluate the effect of combustion appliance operation on emissions (Schmidl et al., 2011; Verma et al., 2013; Win and Persson, 2014). More recently, Venturini et al. (2018) investigated the emissions from the combustion of three wood pellets of distinct quality classes. The combustion of pellets with similar quality in the same combustion appliance and under similar combustion conditions was performed by Arranz et al. (2015) and Fachinger et al. (2017). While the study of Arranz et al. (2015) focused mainly on the gaseous emissions, the latter entails a more detailed characterisation, including PM emissions and chemical speciation. Fachinger et al. (2017) reported slight differences in the gaseous emissions and PM chemical composition from the combustion of two types of pellets both complying with the threshold values defined for class A1 pellets (EN plus A1).

Despite the valuable data provided by the mentioned studies, the emissions from combustion of pellets sold in the Portuguese market are still poorly typified. The aim of this work was to evaluate the emissions (gaseous compounds and particulate matter) and the PM chemical composition from the combustion of two different brands of pellets with certification ENplus A1 and one brand of pellets without certification, all of them manufactured in Portugal. The effect of stove operation on emissions and PM chemical composition from the combustion of each type of pellets was also evaluated.

## 2.Methodology

### 2.1.Combustion experiments

The experimental infrastructure and main features of the combustion appliance used in the present work are described in detail in previous publications (Vicente et al., 2019, 2015). Combustion tests were performed using a commercially available residential stove equipped with top feed burner and with a rated nominal power output of 9.6 kW. Pellets are automatically fed from the stove internal storage tank to the combustion chamber by an auger screw feeding system and ignited by an electrical resistance. The combustion air is driven by an electric fan through an intake at the back of the stove and supplied under the pellet bed through holes in the burner pot. Another internal fan is responsible for circulating air through a heat exchanger and directing it back to the room. The stove power output can be set at five different levels through a control panel on the top of the stove. The combustion air and fuel feed rate are regulated automatically depending upon the chosen load setting. To investigate the influence of biofuel quality on emissions, three types of pellets were tested: two different brands of commercial pellets labelled as ENplus A1 certified pellets (certified pellets R and P) and non-certified pellets. For each pellet, three operation conditions were tested including nominal load and partial load (lowest and medium settings). The fuel feed rate for each fuel was determined by prior calibration of the screw feeding system for the three levels of power output under analysis. The measurements were performed in triplicate by recording the time spent to empty a known amount of pellets from the storage tank as a function of the load setting selected. In addition, the fuel was weighed before pouring it into the storage tank and after the combustion test in order to verify the fuel consumption rate. The fuel properties were determined according to international CEN/TS standards and are listed in Table 1. The threshold for the moisture content (≤10 %wt.) (EPC, 2013) was met for all the pellet brands. As regards ash content, pellets R satisfied the requirements for the A1 class (≤0.7 %wt.), while the other two pellet types had a slightly higher ash content. The carbon, hydrogen, and sulphur contents of the pellets under analysis in the present study are similar to those reported in the literature for wood and woody biomass pellets (Obernberger and Thek, 2004). However, the nitrogen contents of the certified pellets are higher than the maximum values allowed for the highest quality class (≤0.3), whereas the non-certified pellets show a N-content higher than that allowed for the lowest quality class (≤1.0) (EPC, 2013).

133         Table1. Proximate and ultimate analysis of pellet types used in the combustion experiments.

| Proximate analysis | Unit | Certified pellets R | Certified pellets P | Non-certified pellets |
|---|---|---|---|---|
| Moisture[a] | wt.%, as received | 7.2 ± 0.04 | 8.0 ± 0.03 | 7.3 ± 0.03 |
| Ash[b] | wt.%, dry basis | 0.43 ± 0.03 | 0.77 ± 0.01 | 0.84 ± 0.01 |
| Ultimate analysis[c] | | | | |
| C | wt.%, dry basis | 49.7 | 48.7 | 49.4 |
| H | | 6.3 | 6.1 | 6.2 |
| N | | 0.71 | 0.78 | 1.02 |
| S | | < 0.01 (Lq) | < 0.01 (Lq) | < 0.01 (Lq) |
| O (by difference) | | 42.9 | 43.7 | 42.5 |
| Lower heating value[d] | MJ kg$^{-1}$ | 18.47 | 18.50 | 18.53 |

134   Lq – limit of quantification; [a] CEN/TS 14774; [b] CEN/TS 14775; [c] CEN/TS 15104; [d] CEN/TS 14918

135

136       The flue gas temperature was monitored at several points along the combustion and exhaust
137 system (combustion chamber, at the pellet stove exit and at the exit of the chimney) using K-type
138 thermocouples (Table 2). The flue gas composition was monitored continuously using a Fourier
139 transform infrared spectrometer (FTIR, Gasmet, CX4000). The determination of the $O_2$
140 concentrations was made by a paramagnetic analyser (ADC, O2-700 model) after flue gas drying.
141 The operational parameters for each pellet type are presented in Table 2.

142       Particulate matter sampling was carried out in a dilution tunnel, under isokinetic and steady
143 state conditions, through a stainless-steel probe positioned centrally in the dilution tunnel cross
144 section using a low volume sampler.

145

146       Table2. Operating parameters of the stove for the combustion of certified and non-certified pellets.

| Pellet type | Operation mode | Temperature in the combustion chamber (°C) | Temperature at the exit of the chimney (°C) | Fuel mass rate (kg h$^{-1}$) | Power output (kW) | $O_2$ (%) |
|---|---|---|---|---|---|---|
| Certified pellets R | Low power | 548 ± 17.7 | 68.3 ± 0.31 | 0.92 ± 0.12 | 4.7 | 15.3 ± 0.23 |
| | Medium power | 540 ± 15.9 | 70.5 ± 9.3 | 1.05 ± 0.04 | 5.4 | 15.5 ± 0.56 |
| | High power | 617 ± 9.9 | 85.6 ± 0.45 | 1.19 ± 0.10 | 6.1 | 14.3 ± 0.34 |
| Certified pellets P | Low power | 744 ± 5.0 | 94.2 ± 2.43 | 1.26 ± 0.08 | 6.5 | 14.0 ± 0.21 |
| | Medium power | 718 ± 24.2 | 99.6 ± 0.65 | 1.48 ± 0.03 | 7.6 | 14.4 ± 0.28 |
| | High power | 740 ± 21.4 | 112 ± 1.31 | 1.74 ± 0.11 | 8.9 | 13.8 ± 0.31 |
| Non-certified pellets | Low power | 648 ± 61.9 | 67.6 ± 2.00 | 1.32 ± 0.05 | 6.8 | 11.2 ± 0.31 |
| | Medium power | 717 ± 9.6 | 85.0 ± 1.79 | 1.55 ± 0.03 | 8.0 | 11.3 ± 0.32 |
| | High power | 775 ± 4.8 | 89.3 ± 10.2 | 1.84 ± 0.09 | 9.5 | 10.9 ± 0.16 |

147

148    The sampler (TECORA, model 2.004.01) encompasses the $PM_{10}$ sampling head, a pump operating

149    at 2.3 $m^3$ $h^{-1}$, and a control and data storage unit. The mean gas velocity and temperature, in the

150    dilution tunnel and chimney exit, were monitored by a Pitot tube (Testo AG 808) and K-type

151    thermocouple, respectively. $PM_{10}$ samples were collected on pre-baked (6 h, 500 $^\circ$C) quartz fibre

152    filters (Pallflex®) and weighted with a microbalance (RADWAG 5/2Y/F).

153

154    ## 2.2.Analytical techniques

155

156    Organic and elemental carbon: The carbonaceous particulate fractions were quantified by a

157    thermal optical method. Organic carbon (OC) was measured in a nitrogen atmosphere and elemental

158    carbon (EC) in a 4% oxygen 96% nitrogen atmosphere at controlled heating. Correction of pyrolytic

159    conversion of OC to EC was achieved by monitoring the transmission of light through the filter with

160    a laser beam and a photodetector. A non-dispersive infrared (NDIR) $CO_2$ analyser quantifies

161    continuously the $CO_2$ released from the thermal volatilisation and oxidation of different carbon

162    fractions.

163    Water soluble ions: Ion chromatography analysis was performed by means of an ICS-5000

164    instrument (Thermo Scientific) equipped with an auto sampler and ion-exchange columns. For the

165    analysis of anions, the instrument was equipped with Ionpac AS11-HC-4 µm (2 × 250 mm), mobile

166    phase: 30 mM potassium hydroxide. For analysis of cations, the instrument was equipped with a

167    DIONEX Ionpac CS16 analytical (3 × 250 mm), mobile phase: 30 mM methanesulfonic acid. After

168    electrochemical suppression (AERS 500 (4 mm) and CERS 500 (4 mm) suppressors), quantification

169    was performed with a conductivity detector. Calibration was performed using external standards

170    diluted from a stock solution supplied by Thermo Scientific. A portion of each sample (2 punches 9

171    mm) was extracted with Milli-Q water (1.5 ml) under ultrasonic agitation (30 min).

172    Organic compounds: Portions of the filter replicate samples were combined and firstly

173    extracted by refluxing dichloromethane (300 ml) for 24 h. After filtration, the pieces of filter were

174    subsequently extracted by sonication with methanol (75 ml, 30 min). The total organic extract,

175    obtained from the two extraction procedures, was dried and then fractionated by vacuum flash

176    chromatography with silica gel into different classes of organic compounds. The different organic

177    extracts were subsequently dried before the analysis by gas chromatography-mass spectrometry (GC-

178    MS). Before the analysis, fractions that included more polar compounds (alcohols, acids and sugars)

179    were silylated in sealed vials with N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA).

180

## 2.3. Statistical analysis

The significance of differences between emissions under distinct operational loads and types of pellets was evaluated by one-way ANOVA, followed by Bonferroni's post hoc test. Three measurements were performed for each pellet type under each operational condition. In the absence of normality or homogeneity of variances, as assessed with Shapiro-Wilk and Levene's tests, respectively, the transformation of the variable was performed. Pearson correlations were computed and the respective coefficient were presented as r. A value of $p < 0.05$ was considered statistically significant. All the statistical analyses were performed with IBM SPSS Statistics Version 24.

# 3. Results and discussion

## 3.1. Gaseous emission factors

CO emission factors (EFs) varied according to fuel and stove operation mode (Table 3). The highest CO EFs were recorded during the combustion of certified pellets R (2.7-6.1-fold) under the three operational conditions tested ($p < 0.05$) and were inversely correlated with the temperature in the combustion chamber ($r = -0.849$, $p = 0.004$). The temperatures recorded in the combustion chamber were significantly lower during the combustion of this type of pellets in comparison with the temperatures reached during the combustion of pellets P and non-certified pellets ($p < 0.05$). Temperature is an important factor on the fuel reaction rates, hampering an efficient fuel conversion if too low (Brunner et al., 2009). The physical characteristics of pellets (pellet durability, proportion of fines, pellet length and diameter) can affect the combustion performance and consequently the emissions (Garcia-Maraver et al., 2014; Obernberger and Thek, 2004; Wöhler et al., 2017). In fact, Wöhler et al. (2017) burned three softwood pellet samples, differing only in length, and reported a decrease in the fuel mass flow into the combustion chamber for longer pellets. The authors argued that this reduction led to an increase in the level of residual oxygen, which decreased the combustion temperature, resulting in higher CO emissions for the combustion of long pellets compared to short pellets.

The influence of stove operation on CO EFs was only significant for the certified pellets. The trend observed for these two pellet types was distinct. While the combustion of pellets P generated lower CO EFs under minimum load operation in comparison with both medium and nominal load ($p < 0.05$), CO EFs from pellets R were significantly lower at nominal load than under

214 medium power output ($p < 0.05$). Venturini et al. (2015) reported 1.4 times higher CO emissions for
215 the combustion of wood pellets in a stove at partial load than those at nominal load. More recently,
216 a similar trend was observed by the same researchers for three different quality pellets (Venturini et
217 al., 2018). A more accentuated difference in CO emissions under different load operations was
218 reported by Tissari et al. (2008) (10-fold) and by Schmidl et al. (2011) (15-fold) for the combustion
219 of wood pellets. CO emissions can be highly variable, even using automatically fired stoves and high
220 quality pellets (Table 3).

221 　　　　In small scale combustion systems, nitrogen oxides are mainly formed from the fuel nitrogen
222 since the temperatures necessary to activate the other two mechanisms (thermal and prompt $NO_x$
223 formation) are not reached (Brunner et al., 2009; Nussbaumer, 2003). In the present study, NO EFs
224 were similar for both certified pellet brands at all operation modes and similar to the EFs reported by
225 Win and Persson (2014) (Table 3). On the other hand, the combustion of non-certified pellets resulted
226 in NO EFs 2.5-3.2-fold higher ($p < 0.05$) in comparison with certified pellets, which might be related
227 to the fuel N content (Table 1).

228 　　　　The main compounds contributing to the TOC emissions were formaldehyde ($CH_2O$),
229 propane ($C_3H_8$) and ethane ($C_2H_6$) for the combustion of certified pellets R and P, and non-certified
230 pellets, respectively. The TOC and individual hydrocarbon EFs are displayed in Fig. 1. Under the
231 minimum operation mode, certified pellets R generated significantly higher TOC emissions (4.6-6.1-
232 fold) than the other two types of pellets ($p < 0.05$). When operating the stove at medium power
233 output, certified pellets R and P generated the highest and the lowest TOC emissions, respectively ($p
234 < 0.05$). Nominal load operation led to 2.5-4.8-fold significantly lower emissions from pellets P in
235 comparison with the other pellet types ($p < 0.05$).

236 　　　　The release of $SO_2$ varies as a function of the fuel sulphur content (Carvalho et al., 2013),
237 which is generally low in woody biomass fuels (Vassilev et al., 2010). In the present study, the
238 sulphur content of pellet fuels was below the quantification limit. Thus, the $SO_2$ EFs were low,
239 ranging from $0.59 \pm 0.46$ to $6.4 \pm 2.8$ mg $MJ^{-1}$ (Fig. 2). A significant difference between the medium
240 and nominal loads was only registered for certified pellets R. Under nominal loads, no significant
241 differences were observed in the $SO_2$ EFs from the combustion of different pellet types. Partial loads
242 led to significantly lower emissions from the combustion of non-certified compared with the certified
243 pellets P (lower load) and R (medium load). The $SO_2$ EFs obtained in the present study are
244 comparable with those previously obtained for the combustion of wood pellets (Brassard et al., 2014;
245 Fachinger et al., 2017). Higher $SO_2$ emissions were reported by Orasche et al. (2012) for the
246 combustion of certified pellets (20-87 mg $MJ^{-1}$) in a pellet stove under different operation conditions.

9

247            Table 3. CO, NO, $NO_x$ and PM EFs (mg $MJ^{-1}$) found in the present study and comparison with data from the literature.

| Fuel Certification | PM fraction | Operation mode | CO | NO | $NO_X$ | PM | Reference |
|---|---|---|---|---|---|---|---|
| Certified pellets R (ENplus A1) | $PM_{10}$ | Low power | 589 ± 111 | 66.1 ± 1.34 | 105 ± 0.502 [b] | 37.7 ± 1.60 | This study |
| | | Medium power | 710 ± 44.1 | 62.0 ± 2.81 | 101 ± 4.89 [b] | 40.5 ± 1.48 | |
| | | High power | 407 ± 135 | 65.0 ± 2.94 | 101 ± 5.96 [b] | 44.5 ± 1.04 | |
| Certified pellets P (ENplus A1) | | Low power | 122 ± 11.4 | 64.1 ± 0.578 | 98.4 ± 0.887 [b] | 36.2 ± 6.19 | |
| | | Medium power | 149 ± 2.34 | 68.9 ± 3.78 | 106 ± 5.79 [b] | 21.9 ± 1.61 | |
| | | High power | 151 ± 5.30 | 70.1 ± 2.55 | 107 ± 3.91 [b] | 23.2 ± 2.59 | |
| Non-certified pellets | | Low power | 182 ± 56.3 | 179 ± 12.9 | 276 ± 19.0 [b] | 29.8 ± 9.68 | |
| | | Medium power | 117 ± 38.3 | 198 ± 8.64 | 303 ± 13.5 [b] | 43.5 ± 4.83 | |
| | | High power | 108 ± 23.2 | 172 ± 6.19 | 264 ± 9.49 [b] | 46.2 ± 1.01 | |
| DIN+ pellets | TSP | Partial load | 259 ± 7.53 | 79 ± 1.53 | N/A | 78 ± 9.5[c] | Venturini et al. (2018) |
| | | Nominal load | 176 ± 5.13 | 83 ± 1.53 | N/A | 46 ± 9.3[c] | |
| EN 14961-2 | N/A | Cold start | 1390 | N/A | 256 | 110[c] | Orasche et al. (2012) |
| | | Nominal load | 413 | N/A | 165 | 36[c] | |
| ENplus A1 pellets (1) | $PM_1$ | Full cycle[a] | 400 ± 60 | N/A | N/A | 11 ± 3[d] | Fachinger et al. (2017) |
| ENplus A1 pellets (2) | | | 430 ± 60 | N/A | N/A | 17 ± 5[d] | |
| DIN+ pellets | PM | Nominal load | 66 - 78 | N/A | N/A | 56 – 77[c] | Ozgen et al. (2014) |
| DIN+ pellets | TSP | Nominal load | 193 ± 12 | N/A | 80 ± 20 | 23 ± 3[e] | Schmidt et al. (2018) |
| SS 187120 | $PM_{2.5}$ | High power | 16 ± 2 | 63 ± 1 | N/A | 55 ± 3[c] | Win and Persson (2014) |
| | | Medium power | 23 ± 2 | 63 ± 1 | N/A | 43 ± 6[c] | |
| | | Low power | 48 ± 5 | 60 ± 1 | N/A | 55 ± 5[c] | |
| ÖNORM M7135/ DIN+ pellets | $PM_{10}$ | Start-up phase | 116 | N/A | 81.2 | 8.5[c] | Schmidl et al. (2011) |
| | | Full load | 33.2 | N/A | 83.2 | 7.9[c] | |
| | | Partial load | 488 | N/A | 78.6 | 3.0[c] | |

[a]Full and partial load operation, start-up, load change and shut down procedures; [b]$NO_X$ as $NO_2$; N/A - information not available; [c]dilution tunnel; [d]consecutive ejector diluters; [e]chimney

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249       Hydrogen fluoride (HF) EFs were low (Fig. 2) and similar to the EFs reported in the

250    literature for the combustion of wood pellets (Vicente et al., 2019). Although no significant

251    differences among operational loads for each pellet type was recorded ($p < 0.05$), EFs were

252    significantly higher for non-certified pellets in comparison with the certified biofuels ($p < 0.05$)

253    for all operating conditions. Hydrogen chloride (HCl) emissions also showed the influence of the

254    burnt fuel, being higher for certified pellets P than for the other two pellet fuels ($p < 0.05$) for all

255    operating conditions, which might indicate higher Cl content in this type of pellets. The HCl EFs

256    obtained in the present study (Fig. 2) are comparable to those documented in previous studies for

257    the combustion of wood pellets (Brassard et al., 2014; Lamberg et al., 2013; Tissari et al., 2008;

258    Vicente et al., 2019).

259

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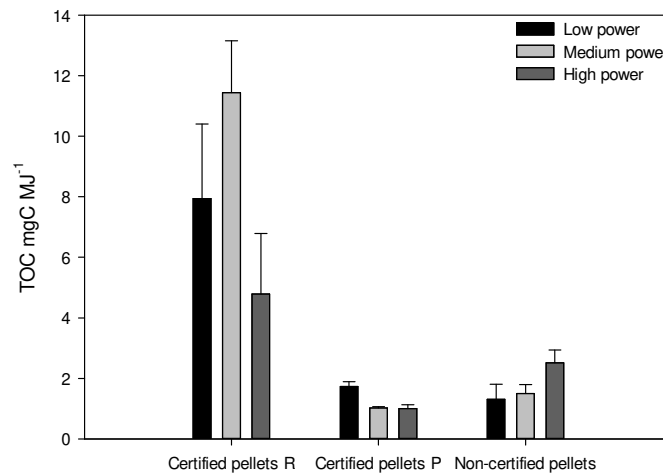


261
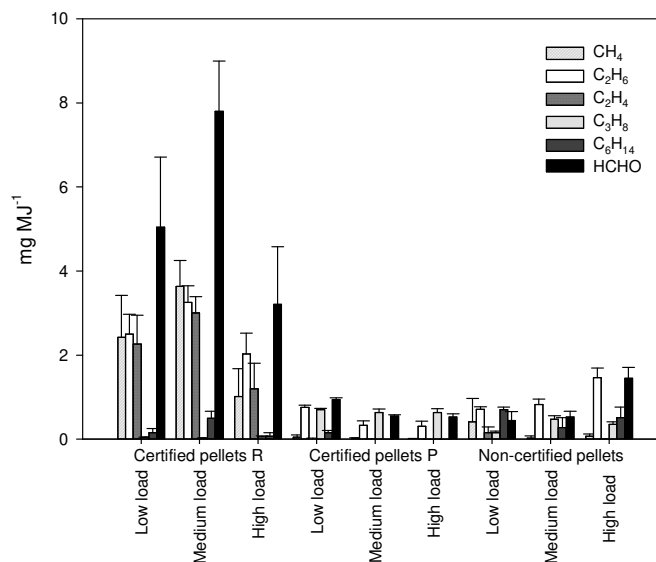
262    Figure 1. Emission factors of TOC and individual hydrocarbons ($CH_4$, $C_2H_6$, $C_2H_4$, $C_3H_8$, $C_6H_{14}$ and

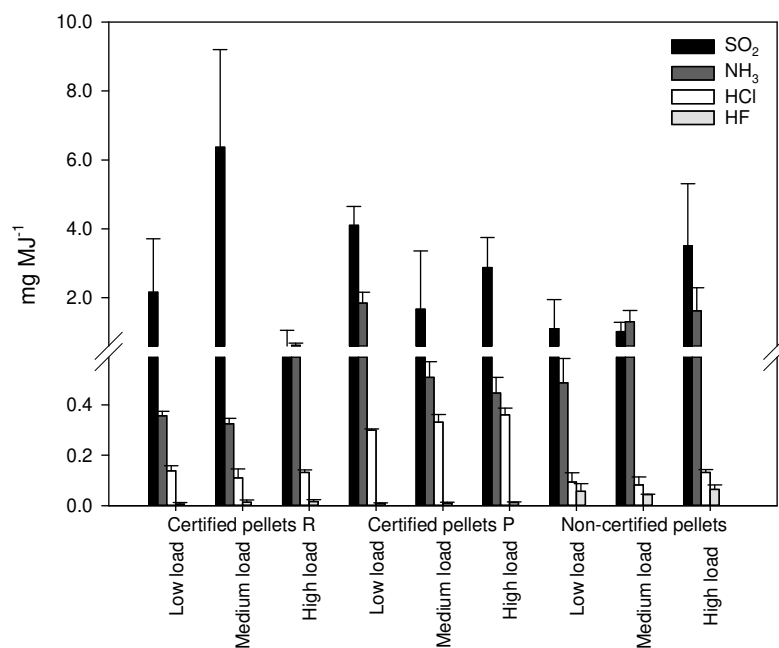263                   HCHO) from pellet combustion.

264

265    In the present work, NH$_3$ was produced in small amounts, which is in agreement with

266    studies reporting emissions from woody pelletised fuels (Brassard et al., 2014; Fournel et al.,

267    2015b; Vicente et al., 2019). The EFs obtained for the combustion of certified pellets were

268    significantly lower than for non-certified pellets at nominal and medium load operation (p < 0.05).

269    However, the lowest level of power output generated significantly higher emissions for certified

270    pellets P in comparison with the other two pellet types (p < 0.05). A positive correlation was

271    found between the power output and NH$_3$ emissions for the combustion of certified pellets R (r =

272    0.797, p = 0.010) and non-certified pellets (r = 0.767, p = 0.016).

273    The Commission Regulation 2015/1185 (European Commission, 2015) (implementing

274    Directive 2009/125/EC - Ecodesign requirements for energy-related products (Directive

275    2009/125/EC, 2009)) establishes the emission requirements for 2022. The CO emissions of the

276    pellet stove were below the regulated limit (300 mg Nm$^{-3}$ at 13% O$_2$, nominal load) for certified

277    pellets P and non-certified pellets. However, during the combustion of pellets R, CO emissions

278    (575 ± 125 mg Nm$^{-3}$ at 13% O$_2$) exceeded that limit. Non-optimal combustion conditions, such

279    as low combustion temperatures, can increase CO emissions, even in automated combustion

280    appliances.

281



283    Figure 2. Emission factors of SO$_2$, NH$_3$, HCl and HF from pellet combustion.

284

285    As discussed above, NO$_X$ emissions from residential combustion are closely related to

286    the fuel N content rather than the combustion technology employed. In the present study, NO$_X$

287    emissions were below the Ecodesign limit (200 mg m$^{-3}$ expressed as NO$_2$ at 13% O$_2$, nominal

288  load) for the combustion of certified pellets but above this value for non-certified pellets (337 ±

289  31.1 mg Nm$^{-3}$ of NO$_X$ expressed as NO$_2$ at 13% O$_2$).

290

291  **3.2. Particulate emission factors**

292

293  Regardless of type of pellet burned, PM$_{10}$ average EFs ranged from 23.2 ± 2.59 to 46.2 ±

294  1.01 mg MJ$^{-1}$ when operating at nominal load. These results are similar to the ones reported in

295  the literature for the combustion of certified pellets under full load operation (Table 3).

296  The PM$_{10}$ emissions from the combustion of the three pellet types under different loads

297  presented substantial variations. Pellets P generated the highest PM$_{10}$ EFs at the lowest power

298  output, which were significantly different from those recorded at the other two operational loads

299  (p < 0.05). No significant differences were found between the EFs for the operation of the pellet

300  stove at medium and nominal loads. Contrasting with that, pellets R generated significantly higher

301  PM$_{10}$ emissions at nominal load than under the minimum and medium level of power output (p <

302  0.05). Similarly, for the combustion of non-certified pellets, significantly higher PM emissions

303  were recorded at nominal load compared with the operation under the lowest level of power output

304  (p < 0.05). Most researchers found a decrease in PM$_{10}$ emissions when operating pellet stoves at

305  nominal loads (Boman et al., 2011; Riva et al., 2011; Venturini et al., 2018, 2015). However, Win

306  and Persson (2014) evaluated different combustion appliances at different loads and reported that

307  for the majority of the units tested, no linear correlation between particle emission and combustion

308  power was observed. The authors pointed out that PM emissions may be influenced by the change

309  in fuel load, due to the fact that the O$_2$ level and combustor temperature may vary with fuel load

310  and excess air.

311  Under the minimum power output, PM$_{10}$ EFs were similar, regardless the type of pellets,

312  while increasing the load led to significant differences, ranging from 1.8 to 2.0-fold, between the

313  EFs of certified pellets P and the other two types (p < 0.05) (Table 3). PM emissions were

314  significantly lower at increased loads for certified pellets P, whereas no significant differences

315  were recorded between certified pellets R and non-certified pellets. The PM$_{10}$ emissions were

316  below the Ecodesign emission limit for all types of pellets. PM$_{10}$ EFs from the combustion of

317  certified pellets R and non-certified pellets were significantly correlated with the temperature in

318  the combustion chamber (r = 0.733, p = 0.025 and r = 0.799, p = 0.010 for pellets R and non-

319  certified pellets, respectively).

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### 3.2.1. Inorganic ions

The dominant water soluble species in particles resulting from combustion of certified pellets were sulphate, potassium, chloride and nitrate, which globally represented from 35 to 66 %wt. of the $PM_{10}$ mass (92-98% of the total ionic content). The major ions in particles generated from non-certified pellets were chloride, potassium, sulphate and sodium. These ionic species accounted for 43 to 49 %wt. of the $PM_{10}$ mass (92-97% of the total ionic content) (Fig. 3). Venturini et al. (2015) reported a contribution of inorganic ions to total PM in the range from 20 %wt. (partial load) to 37.5 %wt. (nominal load) during the combustion of pellets in a top fed stove. In the present study, the contribution of inorganic ions to the $PM_{10}$ mass was higher.

The significant correlation between potassium and sulphate EFs for both certified pellets ($r = 0.791$, $p = 0.011$ and $r = 0.744$, $p = 0.022$ for pellets R and P, respectively) leads to suppose that particles consisted mainly of $K_2SO_4$. These results are in line with those reported by Sippula et al. (2007). The authors tested 11 different pellet fuels in a top-fed pellet stove and reported that for the majority of the fuels, 60-80% of potassium was in the form of $K_2SO_4$. The predominance of potassium, sulphate and chloride for the combustion of woody pellets in automatic appliances has been reported in other previous studies (Boman et al., 2011, 2004; Lamberg et al., 2011; Tissari et al., 2008; Venturini et al., 2018, 2015). Despite the lower contributions to $PM_{10}$ mass, ammonium, lithium, calcium and magnesium were also detected.

The combustion of certified pellets was the only one that made it possible to observe significant differences in the emission of ionic species. The combustion of pellets R under nominal loads generated significantly higher potassium emissions ($p < 0.05$) than the operation at medium and lower loads.

At the lowest level of power output, no significant differences in the EFs of the ionic species was recorded for the combustion of the different pellets. However, for increased operation loads, the ionic composition of particles varied with the type of biofuel, specially the emissions of chloride, which were significantly higher for non-certified pellets ($p < 0.05$). During the operation at nominal load significantly higher emissions of sulphate were recorded for certified pellets R in comparison with pellets P and non-certified pellets ($p < 0.05$), while potassium emissions were significantly different between biofuels ($p < 0.05$). Also, significantly higher nitrate EFs were recorded for pellets R compared with pellets P for both medium and nominal loads ($p < 0.05$).

Several key factors affect the emission of inorganic compounds during biomass combustion, such as the elemental composition of the fuel, the temperature in the combustion chamber, as well as the volatility of the element (Czech et al., 2018; Jeguirim et al., 2017; Knudsen et al., 2004; Van Lith et al., 2006). In the present study, a positive correlation was recorded

between potassium EFs and the combustion chamber temperature for non-certified and certified pellets R (r = 0.841, p = 0.004 and r = 0.701, p = 0.036 for pellets R and non-certified pellets, respectively).

### 3.2.2.Carbonaceous content

The OC and EC emissions, in the range from 0.188 to 3.31 mg MJ$^{-1}$ and from 2.22 to 14.9 mg MJ$^{-1}$, respectively, were affected by both operating conditions of the stove and pellet type burned. The importance of fuel quality on carbonaceous emissions has been also highlighted in previous studies. Vicente et al. (2015) reported OC EFs ranging from 7.40 ± 1.86 (wood pellets) to 48.7 ± 30.9 (agro fuels) mg MJ$^{-1}$, whereas the EC EFs ranged from 1.77 ± 0.44 (wood pellets) to 54.5 ± 23.5 (agro fuels) mg MJ$^{-1}$. More recently, the combustion of laboratory made acacia pellets under partial load conditions generated EFs of 22.9 ± 9.28 mg MJ$^{-1}$ and 6.82 ± 2.47 mg MJ$^{-1}$ for OC and EC, respectively (Vicente et al., 2019). The carbonaceous emissions obtained in the present study for certified pellets are comparable with those reported by Orasche et al. (2012) and Schmidl et al. (2011) for the combustion of certified pellets in small scale stoves.

The OC and EC EFs from certified pellets P were significantly higher (p < 0.05) under the lowest operational setting compared to medium and nominal loads. The differences in the carbonaceous EFs from pellets R combustion were only substantial for OC, which was significantly lower under nominal load operation. No significant differences were recorded between the operational loads tested for the combustion of non-certified pellets. The effect of operating conditions on the PM carbonaceous content was reported in previous studies. Venturini et al. (2015) documented a 2.7-fold decrease in TC EFs from nominal to partial pellet stove operation. Tissari et al. (2008) compared the OC and EC EFs from the combustion of wood pellets under nominal and partial loads, reporting a 90-fold and a 3-fold increase in EC and OC EFs, respectively, under partial load operation.

The combustion of certified pellets P and non-certified pellets generated total carbon (TC) mass fractions in PM$_{10}$ ranging from 23 to 50 %wt., while pellets R resulted in lower TC contributions to the PM$_{10}$ mass (7-14 %wt. PM$_{10}$). For the combustion of wood pellets, Venturi et al. (2015) observed higher TC contributions to PM mass compared to the values of the present study (45-65% nominal and partial load, respectively). Under minimum and medium operational loads, pellets R generated 2 to 6-fold significantly (p < 0.05) lower EC emissions in comparison with the other two pellet types. Under the lowest fuel load operation, no significant differences were recorded for OC EFs, while under medium loads the emissions were significantly (p < 0.05) lower for certified pellets P. Nominal load resulted in significantly higher emissions of both OC and EC for non-certified pellets. OC EFs from the combustion of certified pellets R were found

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to correlate negatively with the potassium EFs (r = - 0.780, p = 0.013), while for certified pellets P potassium EFs correlated with EC instead (r = - 0.760, p = 0.017). OC EFs from both certified pellets correlated with the TOC EFs (r = 0.741, p = 0.022 and r = 0.861, p = 0.003 for pellets R and P, respectively).

The OC to EC ratios have been widely used in atmospheric sciences for the apportionment of emission sources. For wildfires in Southern Europe, OC/EC ratios ranging from 7 to 69 were reported in $PM_{2.5}$ samples (Vicente et al., 2012). In Chinese temples, where incense is burned intensely, OC/EC ratios were in the range from 2.6 to 17 in $PM_{10}$ samples (Wang et al., 2007). OC/EC values in the range 1.1-14.1 have been reported in emissions from residential coal combustion (Chen et al., 2006). OC/EC ratios below 1 have been described in road tunnel studies where fresh vehicle exhaust emissions represented the dominant source of carbonaceous aerosol (Alves et al., 2016; Cheng et al., 2010; Pio et al., 2011). In the present study, the OC/EC ratios varied widely, ranging from 0.04 (certified pellets P, highest power output) to 1.4 (certified pellets R, medium power output). Thus, the characteristic OC/EC ratios for identifying biomass combustion are not valid for certified pellets in advanced combustion technology.

For mass balance calculations (Fig. 3), the analysed OC was converted into organic matter (OM), considering an OM/OC ratio of 1.6. The contribution of OM was low, never exceeding 20 %wt. of the $PM_{10}$ mass (Fig. 3).
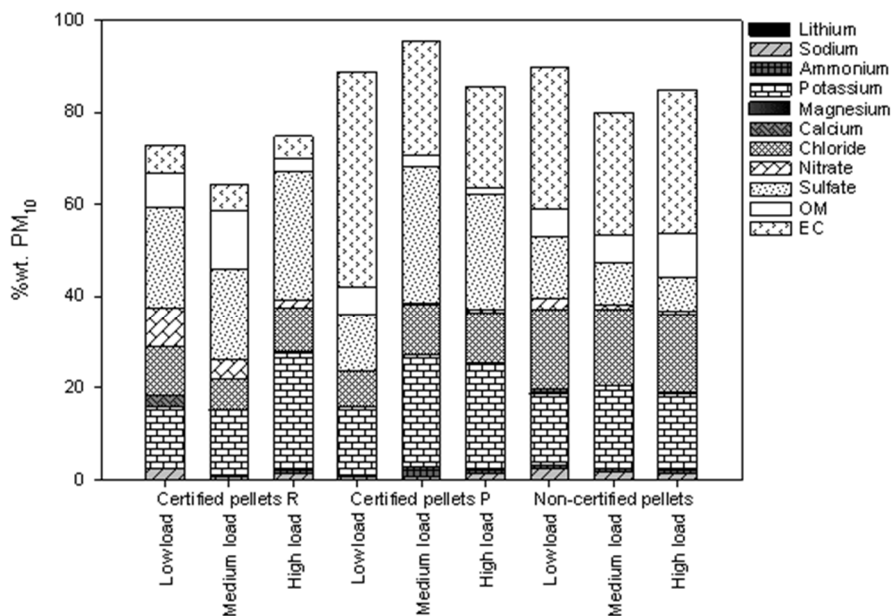


Figure 3. Chemical composition of $PM_{10}$ ($\Sigma$ chemical constituents = OC $\times$ 1.6 + EC + inorganic ions) for the combustion of the distinct pellets under different operating conditions.

### 3.2.3. Organic speciation

A large variety of PM-bound organic species were emitted during the combustion of pellets, namely saccharides, resin acids, polycyclic aromatic hydrocarbons (PAHs), alkanes, sterols, n-alkanols, phenolic compounds, among others (Tables 4 and 5). Organic compounds were dominated by alkanols (non-certified pellets) and saccharides (certified pellets P and R).

Numerous sources contribute to atmospheric n-alkanes, such as higher plant waxes (emitted from leaf abrasion or from biomass combustion), open burning of plastics, fossil fuel combustion and biogenic detritus, including microbial sources (Alves, 2008). The relative source input of PM-bound n-alkanes can be identified by diagnostic parameters, such as the carbon preference index (CPI), defined as the sum of odd-over even-carbon numbered n-alkanes from $C_{11}$ to $C_{35}$, and by the carbon number of the compound with maximum concentration in the homologous series ($C_{max}$). Natural vegetation waxes consist of longer chain (> $C_{20}$) n-alkanes. Oros and Simoneit (2001b) reported an odd to even carbon number predominance (CPI from 0.5 to 3.4) in conifer wood smoke particles and $C_{max}$ highly variable in the range from $C_{20}$ to $C_{33}$. Higher CPIs ranging from 2.1 to 11.8 (Oros et al., 2006) and from 2.6 to 6.8 (Oros and Simoneit, 2001a) were reported for the combustion of grass and deciduous trees, respectively. In the present study, the n-alkane series comprised homologues from $C_{11}$ to $C_{35}$. The $C_{max}$ was observed for $C_{11}$ for non-certified pellets and certified pellets R, while for certified pellets P the maximum was recorded for $C_{25}$. For non-certified pellets and certified pellets R, it was not possible to calculate a CPI value due to the absence of even carbon numbered n-alkanes. For certified pellets P, the CPI was 1.8. Globally, this organic class represented a $PM_{10}$ mass fraction of 1.25, 7.96 and 596 $\mu g\ g^{-1}$ for non-certified pellets and certified pellets R and P, respectively. The dominant alkenes in $PM_{10}$ emitted during the combustion of certified pellets were octadecene (certified pellets P, 103 $\mu g\ g^{-1}$ $PM_{10}$) and tricosene (certified pellets R, 13.5 $\mu g\ g^{-1}$ $PM_{10}$), while non-certified pellets generated a higher PM mass fraction of squalene (12.1 $\mu g\ g^{-1}$ $PM_{10}$).

n-Alkanoic acids were identified as a major compound class in samples from the combustion of deciduous and conifer trees, as well from grasses (Oros et al., 2006; Oros and Simoneit, 2001a, 2001b). These compounds are a major class in conifer smoke samples as they are the units of plant fats, oils and phospholipids (Oros and Simoneit, 2001b). In the present study, n-alkanoic acids showed a strong even to odd C number predominance, with CPI (even-to-odd homologues) of 4.7, 6.0 and 6.3 for PM from non-certified pellets, and certified pellets R and P, respectively. For the combustion of pellets P, $C_{max}$ was observed at $C_{16}$ (palmitic acid), which is in good agreement with literature data on biomass combustion emissions (Oros et al., 2006; Oros and Simoneit, 2001a, 2001b). For pellets R and non-certified pellets, the $C_{max}$ was observed at $C_{18}$ (stearic acid). This organic class represented a $PM_{10}$ mass fraction ranging from 4.31 (certified pellets R) to 1011 $\mu g\ g^{-1}$ (certified pellets P). Unsaturated fatty acids were also detected in $PM_{10}$ from pellet combustion. The highest mass fractions were recorded for 9-octadecenoic acid (oleic acid) for non-certified and certified pellets R and 9-cis-hexadecenoic (linoleic acid) for pellets P.

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456       Numerous sources, such as biomass combustion, vehicular exhausts, cooking and marine

457    bacteria, have been pointed out as contributors to dicarboxylic acids (Kawamura and Bikkina,

458    2016, and references therein). In the present study, the most abundant n-alkanedioic acids in $PM_{10}$

459    samples were malic, adipic and thapsic acids for non-certified and certified pellets P and R,

460    respectively. Dicarboxylic acids accounted for $PM_{10}$ mass fractions ranging from 0.255 (certified

461    pellets R) to 110 $\mu g \ g^{-1}$ (certified pellets P).

462       Alkanols from $C_{10}$ to $C_{30}$, maximising at $C_{15}$ (certified pellets P and non-certified pellets)

463    and $C_{16}$ (certified pellets R), were detected in the organic extracts obtained from pellet

464    combustion. In PM samples from the combustion of deciduous and conifer trees, n-alkanols

465    maximised at $C_{22}$, $C_{24}$, $C_{28}$ and $C_{29}$ (Oros et al., 2006; Oros and Simoneit, 2001a, 2001b). This

466    class of organic compounds was dominant for non-certified pellets (23,847 $\mu g \ g^{-1}$ $PM_{10}$). The

467    contribution of alkanols to the $PM_{10}$ mass emitted during the combustion of certified pellets P was

468    also noticeable (21,040 $\mu g \ g^{-1}$ $PM_{10}$), while certified pellets R generated a lower content of these

469    compounds (2.19 $\mu g \ g^{-1}$ $PM_{10}$).

470       The dominant PAHs in $PM_{10}$ from the combustion of certified pellets P was pyrene, where

471    as higher mass fractions of retene were observed in emissions from non-certified and certified

472    pellets R (Table 5). Pyrene has been identified amongst the three most abundant PAHs from

473    biomass combustion (Nyström et al., 2017; Orasche et al., 2013; Pettersson et al., 2011). Retene

474    has also been found as an abundant polyaromatic hydrocarbon from conifer wood combustion in

475    traditional and improved combustion appliances (Ramdahl, 1983; Shen et al., 2012; Vicente et

476    al., 2016). Globally, 4-ring congeners encompassed from 73.3 (certified pellets R) to 220

477    (certified pellets P) $\mu g \ g^{-1}$ $PM_{10}$, representing more than half of total PAHs from the combustion

478    of certified pellets P and non-certified pellets.

479       Monosaccharide derivatives from the breakdown of cellulose have been described as the

480    major organic components in particles from biomass combustion (Simoneit et al., 1999).

481    However, the temperature range within which these compounds are formed (150-350 °C) (Kuo

482    et al., 2008) is surpassed in automatically controlled combustion appliances, such as pellet stoves.

483    In fact, these combustion appliances emit low or undetectable amounts of anhydrosugars (Alves

484    et al., 2017; Schmidl et al., 2011; Vicente et al., 2015). In the current study, these compounds

485    were present in samples from the three pellet fuels with levoglucosan encompassing 0.01 to 0.02

486    %wt. of the particle mass.

487       The levoglucosan to mannosan (L/M) ratio can be employed to distinguish biomass

488    categories. Lower ratios have been described for softwood (1.3-6.0) and higher ratios (10.9-83.4)

489    for hardwood combustion (Fine et al., 2001; Orasche et al., 2012; Schmidl et al., 2011, 2008),

490    since the latter has larger amounts of cellulose than hemicellulose. In the present study, L/M ratios

491    of 6.8, 7.0 and 8.6 were recorded for non-certified pellets and certified pellets P and R,

492    respectively. These values are higher than the ones (around 2) reported by Alves et al. (2017) for
493    pellet combustion in the same stove, indicating that characteristic ratios usually employed to trace
494    biomass types are not suitable for automatically fired combustion appliances.

495           Other saccharidic constituents have been detected and identified in the smoke plume from
496    a wildfire, comprising monosaccharides (e.g. erythrose, arabinose, ribose, galactose, glucose,
497    mannose, fructose and rhamnose), disaccharides (sucrose and maltose) and polyols (glycerol,
498    erythritol, arabitol, mannitol and inositol) (Vicente et al., 2011). Zhang et al. (2013) reported
499    significant inositol levels in aerosols from broadleaf shrub combustion, suggesting its potential
500    use as tracer for green foliage. In the present study, three polyols were detected (glycerol,
501    erythritol and quebrachitol). Although many other saccharides were present in the samples, its
502    quantification was not possible due to similar fragmentation patterns and isomerism among many
503    compounds.

504

505    Table 4. Oxygenated compounds mass fraction ($\mu g\ g^{-1}\ PM_{10}$) detected in particles emitted in the flue
506    gases during the combustion of the three pellet types in the stove.

| Compounds | Non-certified pellets | Certified pellets P | Certified pellets R |
|---|---|---|---|
| **Saccharides and polyols** | | | |
| Levoglucosan | 90.3 | 68.9 | 153 |
| Mannosan | 13.3 | 9.88 | 17.8 |
| Galactosan | 8.57 | 5.68 | 57.0 |
| Meso-Erythritol | 1.34 | 19.3 | 0.016 |
| Glycerol | 193 | 211 | 1.314 |
| Quebrachitol | 0.218 | nd | 0.001 |
| Other saccharides and polyols | 6.57 | 20947 | 40.6 |
| *Total saccharides and polyols* | 313 | 21262 | 269 |
| **Phenolic compounds** | | | |
| Benzyl alcohol | 37.3 | 305 | 30.9 |
| Coniferyl alcohol | nd | nd | 0.148 |
| Vanillin | 2.75 | 3.20 | 2.54 |
| Vanillic acid | bdl | 0.481 | 2.97 |
| Syringic acid | 0.051 | bdl | 0.204 |
| Sinapyl alcohol | nd | nd | nd |
| Cinnamic acid | 1.503 | 1.16 | 10.4 |
| Hydrocinnamic (coumaric) acid | nd | nd | 8.15 |
| 3-Methoxy-4-hydroxycinnamic (ferulic) acid | nd | nd | 0.155 |
| Benzoic acid | 22.0 | 32.0 | 0.845 |
| 4-Hydroxybenzaldehyde | 26.4 | 23.6 | 3.98 |
| 4-Hydroxybenzoic acid | 1.71 | 2.33 | 0.596 |

| | | | |
|---|---|---|---|
| 4-Phenylphenol | nd | nd | 0.163 |
| 2,4-Di-tert-butylphenol | 104 | 1.64 | 14.7 |
| Resorcinol | 0.141 | 0.343 | 0.729 |
| 4-Hydroxyphenylethanol (tyrosol) | 28.3 | 132 | nd |
| 5-Isopropyl-3-methylphenol | 0.236 | 1.67 | nd |
| 2-Isopropyl-5-methylphenol (thymol) | nd | nd | 1.63 |
| Isoeugenol | 1.06 | 1.19 | nd |
| 2-Methoxy-4-propylphenol | 1.56 | 0.979 | nd |
| 2,6-Di-tert-butyl-1,4-benzoquinone | 32.3 | 38.6 | 0.965 |
| Hydroxyacetophenone | 3.30 | 11.8 | 1.35 |
| *Total phenolic compounds* | 263 | 556 | 80.4 |
| **Resin acids** | | | |
| Abietic acid | 2.84 | nd | bdl |
| Dehydroabietic acid | 7.08 | bdl | 54.1 |
| Isopimaric acid | 1.06 | 0.744 | 1.19 |
| *Total resin acids* | *11.0* | *0.744* | *55.3* |
| **n-Alkenoic acids** | | | |
| 9-Hexadecenoic (palmitoleic) acid | 3.14 | bdl | 0.238 |
| 9-12-Octadecadienoic (linoleic) acid | 2.85 | 0.773 | 0.060 |
| 9-Octadecenoic (oleic) acid | 22.3 | bdl | 3.64 |
| *Total n-alkenoic acids* | 28.3 | 0.773 | 3.94 |
| **n-Alkanoic acids** | | | |
| Octanoic (caprylic) acid | bdl | bdl | 0.765 |
| Nonanoic (pelargonic) acid | 34.5 | 11.2 | 0.619 |
| Decanoic (capric) acid | 12.8 | bdl | 0.774 |
| Undecanoic acid | 2.47 | 1.54 | bdl |
| Dodecanoic (lauric) acid | 12.1 | 10.6 | 0.133 |
| Tridecanoic | 10.1 | 32.1 | nd |
| Tetradecanoic (myristic) acid | 80.6 | 139 | bdl |
| Pentadecanoic acid | 57.5 | 60.4 | bdl |
| Hexadecanoic (palmitic) acid | 129 | 363 | bdl |
| Heptadecanoic acid | 12.0 | 27.1 | bdl |
| Octadecanoic (stearic) acid | 296 | 300 | 1.42 |
| Nonadecanoic acid | 1.81 | 5.91 | bdl |
| Eicosanoic acid | 10.4 | 10.2 | bdl |
| Docosanoic acid | 9.95 | 8.93 | 0.362 |
| Tetracosanoic acid | bdl | 37.3 | bdl |
| Hexacosanoic acid | 3.24 | 3.36 | 0.237 |
| *Total n-alkanoic acids* | *673* | *1011* | *4.31* |
| **n-Alkanedioic acids** | | | |

| | | | |
|---|---|---|---|
| Butanedioic (succinic) acid | 3.972 | 28.8 | bdl |
| Octanedioic (suberic) acid | bdl | 19.0 | bdl |
| 1,5-Pentanedioic (glutaric) acid | 3.876 | 9.16 | bdl |
| Butanedioic (malic) acid | 84.9 | 3.82 | bdl |
| Hexanedioic (adipic) acid | 2.707 | 43.7 | bdl |
| Nonanedioic (azelaic) acid | 0.964 | bdl | bdl |
| Decanedioic (sebacic) acid | 0.866 | 2.43 | bdl |
| Hexadecanedioic (thapsic) acid | 2.34 | 3.57 | 0.255 |
| *Total alkanedioic acids* | *100* | *110* | *0.255* |
| **Other acids** | | | |
| Glycolic acid | 32.6 | bdl | bdl |
| Levulinic acid | 4.70 | 28.9 | bdl |
| 3-Hydroxypropionic (hydracrylic) acid | 27.8 | 31.1 | bdl |
| Glyceric acid | 72.5 | 145 | bdl |
| 3-Hydroxybutanoic acid | 4.44 | 6.83 | bdl |
| 3,4-Dihydroxybutanoic acid | bdl | 15.4 | bdl |
| Pinic acid | bdl | bdl | 10.5 |
| Citric acid | 0.850 | 2.53 | nd |
| Podocarpic acid | 0.014 | nd | bdl |
| Lactic (2-Hydroxypropanoic) acid | nd | nd | 14.5 |
| Pyruvic (2-oxopropenoic) acid | nd | nd | 0.653 |
| 2-Furoic (2-furanocarboxylic) acid | nd | nd | 1.75 |
| *Total other acids* | *143* | *230* | *27.4* |
| **Alkanols** | | | |
| Decanol | nd | 0.910 | 0.026 |
| Dodecanol | 928 | 564 | 0.658 |
| Tridecanol | 564 | 1335 | nd |
| Tetradecanol | 9306 | 7953 | bdl |
| Pentadecanol | 12822 | 10815 | 0.012 |
| Hexadecanol | 129 | 156 | 0.920 |
| Heptadecanol | 24.1 | 40.4 | nd |
| Octadecanol | 20.6 | 108 | bdl |
| Docosanol | 22.4 | 48.1 | bdl |
| Tricosanol | 6.24 | 13.6 | 0.004 |
| Tetracosanol | nd | nd | 0.567 |
| Pentacosanol | 3.74 | 1.01 | 0.005 |
| Heptacosanol | 0.541 | 0.591 | bdl |
| Octacosanol | 20.0 | 3.15 | bdl |
| Tricontanol | 1.22 | 1.97 | bdl |
| *Total alkanols* | *23847* | *21040* | *2.19* |
| **Sterols** | | | |
| Cholesterol | 13.0 | 15.8 | bdl |
| β-Sitosterol | 6.03 | 10.5 | bdl |
| Stigmasterol | nd | nd | bdl |

| | | | |
|---|---|---|---|
| 5-Cholestan-3-ol (dehydrocholesterol) | nd | nd | bdl |
| *Total sterols* | *19.1* | *26.3* | *bdl* |
| **Phthalates** | | | |
| Bis(2-ethylhexyl)phthalate | bdl | bdl | bdl |
| Benzyl butyl phthalate | 2.12 | 1.09 | 1.55 |
| Bis(2-ethylhexyl)adipate | 1.11 | 2.77 | 1.18 |
| Di-n-butyl phthalate | bdl | 5.74 | 85.25 |
| Diethyl phthalate | bdl | bdl | bdl |
| Dimethyl phthalate | nd | nd | 0.01 |
| *Total phthalates* | 3.23 | 9.59 | 88.0 |
| **Other hydroxyl compounds** | | | |
| 2-Methylcyclohexanol | 1.15 | nd | bdl |
| 2,3-Pinanediol | nd | nd | 0.026 |
| 1-Monopalmitin | 149 | 172 | 1.70 |
| 1-Monostearin | 177 | 191 | 13.1 |
| 1-Monolauroyl-rac-glycerol | 0.448 | 0.476 | nd |
| (-)-Isopulegol | nd | nd | 0.016 |
| *Total other hydroxyl compounds* | *328* | *363* | *14.8* |

bdl- below detection limit; nd- not detected

507

508      The alkylphenol 2,4-di-tert-butylphenol was the most abundant (104 µg g$^{-1}$ PM$_{10}$)
509    phenolic compound in PM$_{10}$ from the combustion of non-certified pellets, whereas certified
510    pellets yielded higher particulate mass fractions of benzyl alcohol (305 and 30.9 µg g$^{-1}$ PM$_{10}$ for
511    certified pellets P and R, respectively). These two phenolic compounds have been reported in
512    particles from wildfires (Alves et al., 2011) and combustion of acacia pellets (Vicente et al.,
513    2019). Lignin, a large and complex polymer in wood tissues, is mainly derived from the
514    polymerisation of p-coumaryl, coniferyl and sinapyl alcohols. The relative proportions of
515    biomonomers are specific to the class of plants (Gelencsér, 2004; Simoneit, 2002). In the present
516    study, the methoxyphenols vanillin and vanillic acid, with a guaiacyl structure, were always
517    present in the particulate samples from certified pellets combustion. The presence of products
518    from coniferyl-type lignin pyrolysis and the low mass fractions of syringic acid indicate
519    combustion of softwood pellets (Gelencsér, 2004; Simoneit, 2002). Pflieger and Kroflič (2017)
520    evaluated the toxicity of guaiacol and its nitro derivatives generated during its aging in the
521    tropospheric aqueous phase. The authors used the *Vibrio fischeri* bioluminescence assay to assess
522    the toxicity and concluded that, according to the European legislation, all the studied compounds
523    are harmful.

524      Sterols are constituents of plant lipid membranes and waxes (Oros and Simoneit, 2001a).
525    β-Sitosterol has been described as the most abundant sterol in wood smoke from wildfires
526    (Vicente et al., 2011), charcoal combustion in barbecue grills (Vicente et al., 2018) and Chinese

527     cooking, which is characterised by the high consumption of vegetables (Zhao et al., 2007). In the

528     present study, β-Sitosterol was found at mass concentrations from 6.03 (non-certified pellets) to

529     10.5 (certified pellets P) µg g$^{-1}$ PM$_{10}$, whereas it was below de detection limit for pellets R.

530

531     Table 5. PAH mass fractions (µg g$^{-1}$ PM$_{10}$) in the particulate matter emitted in the flue gases during the

532     combustion of the three pellet types in the stove.

| Compounds | Non-certified pellets | Certified pellets P | Certified pellets R |
|---|---|---|---|
| Acenaphthene | bdl | bdl | bdl |
| Fluorene | 7.22 | bdl | bdl |
| Phenanthrene | bdl | 4.28 | 1.72 |
| Anthracene | 0.067 | 0.790 | 0.120 |
| Acenaphthylene | nd | bdl | bdl |
| Retene | 105 | 88.9 | 177 |
| Fluoranthene | 45.7 | 96.5 | 26.9 |
| Pyrene | 51.1 | 101 | 23.5 |
| Chrysene | 33.1 | 15.7 | 13.9 |
| Benzo[a]anthracene | 12.8 | 6.90 | 9.00 |
| Benzo[b]fluoranthene | 5.50 | bdl | 6.91 |
| Benzo[k]fluoranthene | 6.18 | bdl | 5.55 |
| Benzo[e]pyrene | 6.52 | 0.150 | 5.99 |
| Benzo[a]pyrene | 3.58 | 0.261 | 6.11 |
| Perylene | bdl | 0.906 | 0.157 |
| Dibenzo[a,h]anthracene | bdl | bdl | 0.625 |
| Indeno[1,2,3-cd]pyrene | bdl | bdl | 4.89 |
| Benzo[g,h,i]perylene | 0.369 | bdl | 5.77 |
| *Total PAHs* | 277 | 315 | 288 |

533     bdl- below detection limit; nd- not detected

534

535     Resin acids are biosynthesised mainly by conifers and their major biomarkers are

536     diterpenoids that, upon combustion, are released as natural or thermally altered compounds

537     (Gelencsér, 2004; Oros and Simoneit, 2001b). In the present study, the major natural product in

538     the PM samples was isopimaric acid, with mass fractions ranging from 0.744 to 1.19 µg g$^{-1}$ PM$_{10}$.

539     Dehydroabietic acid has been described as one of the major oxidation products of resin acids

540     (Oros and Simoneit, 2001b). In the present study, this compound has been detected at mass

541     fractions ranging from 7.08 (non-certified pellets) to 54.1 (certified pellets R) µg g$^{-1}$ PM$_{10}$,

542     whereas it was below de detection limit for pellets P. Dehydroabietic acid has been pointed out

543     as suitable biomarker for distinguishing combustion emissions of softwood from hardwood (Fine

544     et al., 2004, 2001; Gelencsér, 2004). However, under atmospheric conditions, this compound may

545     be unstable, suffering degradation by OH radicals (Lai et al., 2015). Thus, its concentrations may

not fully represent the impact from softwood burning when used as a tracer in source apportionment studies.

## 4.Conclusions

The effects of pellet quality, based on certification criteria, on gaseous and PM emissions and chemical composition were studied in a top fed pellet stove. Three pellet brands were used, including two certified pellets (EN plus A1) and one brand without certification. The combustion of these pellets was studied in the stove under three levels of power output (lowest, medium and highest).

The chemical properties of the three pellets were compared with the ENplus certification requirements. Both brands of certified pellets did not fulfil the ENplus A1 standards regarding the nitrogen content, while one of the certified brands revealed a slightly higher ash content than the quality criterion. Although the ENplus certification scheme includes audits of certified companies, it should be mandatory to producers periodically and randomly analyse samples of biofuels since the quality of the raw material may not be reproducible, compromising the quality of the final product.

The main conclusion that can be withdrawn from this study is that fuel certification does not totally ensure high combustion performance and low emissions. The combustion of two brands of ENplus certified pellets, with identical quality class (A1), resulted in distinct emissions and different behaviour under different operating conditions. Generally, certified pellets P performed better than the other two pellet types. While the combustion of certified pellets R generated the highest CO and TOC emissions, noncertified pellets yielded the highest NO emissions and, under nominal load operation, $NH_3$ and carbonaceous compounds bound to PM. In fact, both pellets generated emissions surpassing the thresholds set by the Ecodesign directive. Despite the high emissions, the highest power output and lowest excess of air were observed for the combustion of non-certified pellets. On the other hand, the lowest temperatures in the combustion chamber were recorded for certified pellets R. Considering the distinct behavior recorded for each fuel under different loads, it is not possible to point out the optimal operation condition. The pellet stove employed in this study, like most in-use stoves across Europe, is not equipped with a complete control system to measure the fuel supply into the combustion chamber, temperature or flue gas oxygen. The improvement of small-scale technologies for wood pellet combustion might prevent such high variability in emissions due to fluctuations in fuel quality. Further research work should also focus on the physical characteristics of wood pellets and how these parameters affect the combustion conditions and emissions. This information can be

581 valuable to propose stricter thresholds in European legislation to reduce emissions from
582 residential biomass combustion.

583     Substantial differences were observed in the composition of $PM_{10}$, depending on the
584 biofuel burned and operating conditions. The combustion of certified pellets P and non-certified
585 pellets generated higher carbonaceous mass fractions in $PM_{10}$ than certified pellets R. $PM_{10}$ was
586 mainly composed of inorganic constituents, which differed quantitatively with the type of pellet
587 and stove operating conditions. Potassium, one of the most abundant water soluble ions, was
588 positively correlated with the combustion chamber temperature for two of the tested fuels. Retene
589 and pyrene were the dominant PAHs in $PM_{10}$ from pellet combustion. Levoglucosan was detected
590 in all samples and the highest mass fraction was recorded for certified pellets R (1.7-2.2 times
591 than non-certified pellets and certified pellets P, respectively). Phenolic compounds were
592 dominated by coniferyl-type lignin pyrolysis products, in accordance with the composition of
593 softwood lignin. Several other polar constituents were quantified in $PM_{10}$ samples also including
594 various types of acids, sterols, and polyols. The contribution of these compounds to the $PM_{10}$
595 mass varied with the pellet type used.

596

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