

Article

Influence of Varieties and Organic Fertilizer in the Elaboration of a New Poplar-Straw Pellet and Its Emissions in a Domestic Boiler

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Abstract: Pollutants resulting from domestic combustion would have harmful effects on public health, causing disturbances in the atmosphere chemistry and the climate. In this work, the emissions from the combustion of pellets made of 80% poplar (organically fertilized) and 20% cereal straw (*Triticum aestivum*) have been analysed. Poplar wood from I-214 and AF-8 clones was obtained from fertilized and non-fertilized plots (CONTROL). Dairy wastewater treatment (MUD) and dehydrated sewage sludge (BIOSOLIDS) were the fertilizers employed. BIOSOLIDS-I214 pellets had lower quality standards, so its combustion was omitted. A flue gas sample was sampled together with the particles emitted. The I-214 MUD sample had the highest emitted CO value (1505 mg/MJ). Regarding HCl emission factors, there was a homogeneity in the results linked with the Cl content present in the raw material. A higher particle emission was associated with pellets with higher ash content. Particles were composed mainly for elemental carbon (26–80 mg/MJ), except I-214 MUD. I-214 pellets had the indicators of incomplete combustion and, therefore, major contaminants emission and major environmental impact. Thus, both the poplar clone and the organic fertilizer influenced the parameters and emissions analysed. Therefore, special attention must be paid to both characteristics.

Keywords: biomass; combustion gases; emission factors; organic fertiliser; poplar clone

1. Introduction

The basis of energy production in both developed and developing countries has been fossil fuels. In fact, it is possible to affirm that many European countries still depend heavily on fossil fuels [1]. However, accompanied by a series of encouraging policies [2], the energy landscape is changing in favour of the use of renewable energy and, in particular, of biofuels [3]. The literature is showing that readily available fossil fuels are running out and that, conversely, more productive renewables may be approaching and even surpassing oil and gas in net power generation in many cases [4]. As an important alternative energy source to conventional fossil fuels, biomass is one of the most promising [5,6]. The quality of biomass as a fuel can be estimated from proximate analysis, ultimate analysis, and energy content [7].

Within the different biomass types, biomass of a lignocellulosic nature is considered a guarantee resource as biofuels not only because they are available in a renewable way but also because they do not have a net increase in the release of CO_2 into the atmosphere [8]. It is a heterogeneous



of lignocellulosic biomass options available, such as briquettes or pellets [10]. Although pellets were barely known in most parts of Europe 20 years ago, today, they are an established and valuable renewable energy source [11]. They are formed by densified biomass, and their quality depends on chemical, mechanical, and physical biomass properties [12]. The main advantages linked to them include avoidance of significant levels of emissions compared to fossil fuels [13], a potential reduction in heating costs, an increased comfort [14], and an improvement in calorific value in relation to biomass without densification [15,16]. Besides, pellet quality can be improved using co-pelletization [17–19]. This blending process helps with many of the problems present in different raw materials [20] at the same time that energy use is granted to materials that could be considered wastes.

Among the different options available for obtaining energy using biomass, densified or not, combustion, gasification, and pyrolysis of several sources are emerging technologies with great potential for industrial implementation [21]. This biomass thermal degradation is, however, a complex process mainly because of the large number and the diverse nature of the reactions involved [22].

Direct combustion is possibly one of the most widely used technologies for obtaining energy from fuel. It is known that the process consists of two stages: devolatilization-combustion of the most volatile components and the coal combustion stage. [23]. During combustion, approximately 80% of the initial biofuel is converted into volatile products [24]. Likewise, the use of small-scale stoves has increased as an energy alternative using different types of pellets [25]. However, certain conditions are required for combustion to be completed, such as air supply, high temperatures, prolonged residence time, and a complete mixture of fuel components [26]; sometimes, it is difficult to guarantee with these stoves used. While automated furnaces normally operate under ideal conditions, hand-fed wood stoves have more variable emissions. The result is the additional unwanted product emission partially oxidized and harmful to the environment and human health [27] such as CO, NO_x , SO_2 , and particulate matter (PM). PM is a solid matter mixture with other liquid materials suspended in air [28] linked to air and health pollution problems [29]. PM5 (PM with aerodynamic diameter $\leq 2.5 \,\mu$ m) and PM10 (PM with aerodynamic diameter $\leq 10 \,\mu$ m) are the most usual diameter values to refer to these particles (PM2.5 and PM10, respectively). PM2.5 contains a significant portion of carbonaceous aerosols composed of both organic carbon (OC) and elemental carbon (EC) [30]. Carbonaceous PM, a class of material found in primary and secondary particles, has typically been divided into two classes: BC (Black Carbon) and OC (Organic Carbon). Neither BC nor OC have a defined chemical composition. The term BC is generally associated with solid forms of carbon emitted by incomplete combustion, while OC refers to a complex mixture of different carbon compounds found in primary and secondary particles. Organic particulate matter is a complex mixture of many classes of compounds [31]. While OC contains diverse organic compounds [32] contributing to solar ration dispersion and absorption [33], EC, emitted during incomplete combustion processes, has a similar structure to impure graphite [34] and it is both considered a good indicator of harmful emissions from combustion sources and a useful parameter to evaluate the efficacy of air pollution control strategies [35]. For its part, black carbon is also considered an additional indicator of adverse health and climate effects of airborne particles [36,37].

In this work, the emissions of a new pellet (currently under patent process, P201830823) were studied. This new material consisted of a mixture of poplar wood, organically fertilized and for which energy potential has been previously demonstrated [38,39], and cereal straw (wheat). Hence, with this work, the authors wanted to identify the differences associated with employment of an organic fertilizer in the associated emissions for this new material. In the same way, similar operating conditions to a commercial boiler for domestic heating were done in order to compare the emissions with other fuels.

2. Materials and Methods

2.1. Biomass Samples

The biomass pellets were formed by 80% poplar wood and 20% wheat straw (*Triticum aestivum*). Regarding poplar (*Populus*) trees, two different clones were used: I-214 (*Populus* × *euramericana* I-214) and AF-8 (*Populus* × *euramericana* AF-8). This choice was based on the widespread use of both for biomass purposes in the European continent [40,41]. Poplar wood was obtained from fertilized and non-fertilized plots (CONTROL). In this work, two organic fertilisers were used. They consisted of a dehydrated composted sewage sludge (called BIOSOLIDS) and a sludge from dairy wastewater treatment (named MUD) [38]. This way, both the cereal straw and the sludge, considered on many occasions as waste, were used.

For pellet production, poplar wood was chipped using a Viking [®] GB460 chipper (Waiblingen, Germany). Then, wheat straw and chipped wood were milled employing a Spain yulong-PelletSolucion[®] GXP 65 × 27 hammers mill (Salamanca, Spain). Later, samples were mixed and pelletized in a SKJ120 model flat die pellet mill of the same firm (Salamanca, Spain) than the previous instrument. Finally, pellets were dried using an Econ[®] S+L 360D pellet dryer (Weisskirchen/Traun, Austria).

Pellet elemental and proximate analysis together with the calorific value were estimated following a series of standard methods: moisture (UNE-EN ISO18134-1:2016); volatiles (UNE-EN ISO18123:2016); ash content (UNE-EN ISO 18122:2016); higher heating value (HHV) (UNE-EN ISO 18125:2018); carbon, hydrogen, and nitrogen (UNE-EN ISO16948:2015); as well as sulphur (UNE-EN ISO 16994:2017).

Physical and mechanical pellets properties were also determined. Apart from the diameter and length measure, real and bulk densities were estimated. Bulk density depends on both the pore volume and pellet density. It can be estimated, as stated by the EN ISO 17,828 standard, dividing the mass of the bulk materials by the volume of the container. Simple or real density (pellet mass divided by its volume) was measured according the EN ISO 18,847 standard. Finally, mechanical durability is the ability to remain unaltered during handling. High durability means that pellets have a high quality [42,43], whereas low durability implies a change in the bulk density parameter, increasing the transport and storage losses [44]. This parameter is also linked with certain combustion problems in stoves due to the fact that the distribution of the material, with a durability of less than 95% according to the EN ISO 17225-1 standard, would not be homogeneous throughout the boiler burner. Durability was determined according to the EN ISO 17831-1 standard.

2.2. Combustion Equipement

Combustion experiments were carried out in a domestic boiler (Alpes model), manufactured in Portugal by Solzaima S.A, with a nominal power of 9.5 kW (allowing to heat approximately 95 m² of the surface). The boiler is designed to burn pellets with a diameter of 6 mm and between 10 mm and 30 mm in length. This equipment has an internal tank with 20 kg capacity and a feeder that supplies biomass to the combustion chamber through a feeding port. The same equipment that appears in [45] was employed (Figure 1). This boiler can also operate with automatic and manual modes.

The pellet boiler was placed on weighing scales with a resolution of 20 g, which allowed for control of biofuel consumption throughout the test. The primary air enters through the holes in the lower part of the grill, while the secondary air enters through the holes in the upper part of the combustion chamber. The primary is driven by an electric fan and continuously measured during combustion using a mass flow meter.



Figure 1. Installation scheme: modified from [42]. A—stove; B—combustion chamber; C—grate of the stove; D—air flow meter; E—exhaust duct (chimney); F—gas sampling and analysis system; G—water-cooled gas sampling probe; H—gas sampling pump; I—gas condensation unit; J—pitot tube; K—dilution tunnel; L and M—TECORA PM10 sampling system; and N—fan.

2.3. Combustion Gases Determination

The combustion gas was sampled at the chimney outlet through a sampling line heated to 180 °C and connected to an infrared gas analyser with Fourier transform (FTIR Gasmet, CX4000, Vantaa, Finland). FTIR is a device that has a capacity to measure multiple components, allowing real-time monitoring of carbon monoxide.

2.4. Filter Preparation and Weighing

Quartz fibre filters with 47-mm diameters were used. Before sampling, the filters were burned at 550 °C for 6 h to remove organic contaminants. After that, the filters were closed in properly identified polycarbonate boxes. For 3 days, the boxes were packed in a desiccator to control the moisture. Approximately two hours before weighing, the filters were removed and uncovered to bring them to laboratory conditions (controlled temperature and moisture conditions). The filters were weighed before and after sampling. The filters mass was obtained by averaging five consecutive weighing, without exceeding a difference of more than 10 µg. Weighing was carried out on a Radwag MYA 5/2Y/F electronic scale (Radom, Poland) with a sensitivity of 1 µg.

2.5. Particles Sampling

Isokinetic particle sampling was performed, that is, the sampler input shaft was aligned parallel to the flow stream lines in the same way the gas inlet velocity in the probe was equal to the flow rate in the duct [46]. For particle collection, a low flow sampler connected to the dilution tunnel was used. The sampling point was located in the dilution tunnel final section, where a probe with a 12-mm diameter sampling nozzle was placed to extract the effluent. A low flow particle sampler (TECORA) equipped with a PM10 thermocouple pre-separation head, a pump (operating at a flow rate of approximately 38.33 L/min), as well as a data processing and storage unit was also used.

Because before proceeding with filtration of the sample, the PM_{10} was separated, in the described sampling, the filtration and the inertial impact techniques were used. During each cycle, between 3 and 8 samples of quartz fibre filters were taken. The samples number was conditioned by the following aspects: the pellets types, the filters obstruction, or the irregularities in the boiler operation due to the amount of accumulated ash. In view of these facts, special care was taken such that each burn cycle,

2.6. Organic Carbon, Elemental Carbon, and Total Carbon

characterized by a specific pellet sample, lasted for the same length of time.

Organic and elemental carbon (OC and EC, respectively) determination was done by employing the thermal-optical technique described in Alves et al. [47] and Pio et al. [48], whose work scheme is shown in Figure 2. This allows an optical analysis of the carbon content in a particle filter. It is based on the sampled particulate carbon volatilization and its differentiation into several fractions by controlled heating, with subsequent conversion by oxidation into carbon dioxide for detection. The system consisted of a quartz tube with two heating sections, a laser source, and a nondispersive infrared spectrophotometer for CO_2 analysis. It is based on laser beam transmittance that passes through the sampled filter and the passage of two gas streams: one of nitrogen and another of a mixture of nitrogen and compressed air. The analysis took place in two phases. In the first, the sample was gradually heated under a nitrogen stream with the purpose of volatilizing only the particles related to the organic fraction. Therefore, it is in this phase that the organic carbon fraction pyrolysis takes place, resulting the elemental carbon. This process was controlled by monitoring filter darkening with laser help. In the second phase, air is the gas stream. Employing it, an increase in temperature causes elemental carbon volatilization and oxidation to CO₂. The analysis lasted approximately 24 min, and during this time, all the information was continuously sent to the computer. Temperature, flow, laser signal, and CO₂ concentration data were collected. Finally, by numerical integration, the masses of organic (OC), pyrolytic, elemental (EC), and total carbon (TC) were quantified.



Figure 2. Scheme of the thermo-optical system used: modified from [42]. A—gas bottle; B—quartz oven; B1 and B2—heating zones; C—laser; C1—detector; C2—chopper; C3—amplifier; D—nondispersive infrared spectrophotometer; E—temperature controller; E1 and E2—thermocouplers; F—mass flow meter; G—rotameter; and H—computer.

2.7. Calculation Methods

2.7.1. Biomass Consumption

This parameter is necessary to estimate the emission factors. It was obtained by adjusting the experimental data using a linear equation (Equation (1)) with 0.9966 as the correlation coefficient. This expression was the result of representing the biomass mass over time and, subsequently, applying an adjustment line to a straight line:

$$y = -0.0002x + 122.13 \tag{1}$$

2.7.2. CT, OC, EC, and PM

After collecting the data in the computer, the masses and carbon concentrations were calculated. Initially, the mass values were corrected with the average total carbon value in the white filters using Equation (2):

$$m_i = m_{ia} - m_b \tag{2}$$

where

 m_i —corrected carbon mass of fraction *i* (*i* = TC, OC, and EC) (µg); m_{ia} —carbon mass of fraction *i* analysed (µg); and

 m_b —carbon mass for the same area in the white filter (µg).

The carbon mass linked to the total sampled filter was then determined using Equation (3):

$$m_{iF} = \frac{m_i \times A_F}{N \times A_A} \tag{3}$$

where

 m_{iF} —fraction *i* carbon mass in the analysed filter area (µg);

 A_F —total sampled filter area (m²);

N—analysed circles number by the system (2 for this work); and

 A_A —circle area analysed by the optical term method (m²).

Finally, the concentration of each fraction (*Ci*) was calculated using the sampled volume (*Va*) as well as the mass for each fraction in the total sampled filter (m_{iF}), as shown in Equation (4):

$$Ci\left[\frac{\mu g}{m^3}\right] = \frac{m_{iF}}{Va} \tag{4}$$

The particle concentration (Cp) was obtained by Equation (5):

$$Cp\left[\frac{\mu g}{m^3}\right] = \frac{m_{iF}}{Va} \tag{5}$$

where

ma—difference between the filter mass without sample and the filter mass with sample (μ g) and *Va*—air sampled volume (m³)

2.7.3. Emission Factor (EF)

The particles and carbon fractions emission (OC, EC, and TC) were calculated using Equation (6) as indicated in [49]:

$$EF\left[\frac{g}{kg \ pellets}\right] = \frac{Ci \times 10^{-6} \times V \times A}{CB} \tag{6}$$

where

Ci-concentration obtained in Equation (4);

V—air velocity in the duct (m/s);

A—dilution tunnel area (m^2); and

CB—biomass consumption (kg/s).

Before calculating the emission factors of combustion gases (Equation (8)), the combustion gas concentrations were calculated in Equation (7) (it also needed a unit conversion from ppm to g/Nm³):

$$Cgas\left[\frac{g}{Nm^3}\right] = \frac{Ce \times 10^{-6} \times Mgas}{Va}$$
(7)

where

Ce—gas concentration in ppm; *Mgas*—gas molar mass (g/mol); and

Va—air volume at the chimney temperature and pressure.

As before anticipated, the emission factors (EF) were calculated via Equation (8):

$$EF\left[\frac{g}{kg \text{ pellets}}\right] = \frac{Cgas \ x \ Qar}{CB}$$
(8)

where

Qar—chimney air flow (Nm³/s), estimated by multiplying the chimney area with the velocity measured in the tube.

Finally, to facilitate the value comparison with the literature, EF were converted to (mg/MJ) using the Equation (9):

$$EF\left[\frac{mg}{MJ}\right] = \frac{EF\left[\frac{g}{kg \ pellets}\right]}{CV} \tag{9}$$

where:

CV—biomass calorific value (MJ/kg).

3. Results and Discussion

3.1. Fuel Properties

Pellet properties are shown in Table 2. Despite having 80% straw in its composition, some parameters, namely the carbon, hydrogen, and sulphur content or the HHV, were similar to commercial pellets, manufactured only with forest biomass [50,51]. There was also a clear tendency for elements such as nitrogen, moisture, or ash content to have a concentration more similar to that of agricultural waste pellets than to that of the aforementioned commercial wood pellets [52]. Hence, moisture values (8.3–11.7%) were higher than those typical for lignocellulosic biomass [53], which will have a great influence when assessing emissions during combustion. HHV data were slightly higher than the literature values for the short rotation coppice pellet provided by the ISO 17225-1 standard [54]. Apart from the hydrogen and ash content (which are slightly higher than the results in the literature), the combustible properties of the pellets studied here are similar to those of the commercial ones, even with a higher calorific value and volatile content than those of the wood pellet [55]. To sum up, with a few exceptions, the characterization results (highlighting the carbon content and the calorific values) would allow to think about domestic use of them employing stoves that use radiation and convection systems for heat distribution.

3.2. Pellets Physical and Mechanical Properties

These values can be seen in Table 1. The diameter and length of the pellets produced were standardized. According to EN ISO 17225-2, the length of the pellets produced must not exceed 40 mm. This particularity was fulfilled for all the pellets analysed; 600 kg/m³ is the minimum value established by ISO standards for solid biofuels for the bulk density of the pellets produced; the value, the previous one, was not reached in any case. According to European guidelines, 1000–1400 kg/m³ should be the accepted standard range for a single pellet density [55]. Except the BIOSOLIDS-I-214 combination, the rest of the samples were in this range. This pellet was also the one with a lower value for durability parameter (91.33%). Hence, the overall results linked to the BIOSOLIDS-I-214 pellet were far from the quality standards established for commercial pellets UNE-EN ISO 17225-2:2014 (part 2). For this reason, this pellet was left out of the combustion tests. When compared with the wood pellet, density and durability results were similar [50,56]. With respect to the real density values, the mixtures executed here had higher values than those of the pellets from cereal straw [57].

		Length (cm)	Diameter (cm)	Real Density (kg/m ³)	Bulk Density (kg/m ³)	Durability (%)	Reference
CONTROL	I-214	2.45 ± 0.2	0.66 ± 0.1	1033.84 ± 7.44	540.23 ± 5.50	98.15 ± 0.21	This work
	AF-8	3.68 ± 0.3	0.64 ± 0.0	1146.46 ± 9.37	470.88 ± 3.74	99.27 ± 0.15	This work
MUD	I-214	2.75 ± 0.1	0.67 ± 0.1	1075.29 ± 7.23	466.33 ± 3.22	97.71 ± 0.28	This work
	AF-8	2.10 ± 0.1	0.66 ± 0.0	1040.34 ± 8.89	499.88 ± 4.99	99.14 ± 0.20	This work
BIOSOLIDS	I-214	3.02 ± 0.2	0.67 ± 0.2	926.78 ± 6.60	510.80 ± 5.12	94.42 ± 0.22	This work
	AF-8	2.92 ± 0.2	0.65 ± 0.0	1025.64 ± 9.41	499.43 ± 5.03	98.59 ± 0.23	This work
Wood pellet		1.58	0.65	1150	630	98.3	[50,56]
Wheat straw pellet		1.47	0.42	852	649	98.3	[57]

Table 1. Physical and mechanical properties of pellets.

Table 2. Pellet fuel properties.

		Proximate Analysis (%)							Ultimate Analysis (%)			HHV ^c (MJ/kg)	Reference
		C ^a	H ^a	N ^a	S ^a	Cl ^a	O ^b	Moisture ^a	Ash ^a	Volatiles ^a	FC ^b		
CONTROL _	I-214	48.9 ± 0.3	5.9 ± 0.1	2.1 ± 0.0	0.02 ± 0.00	0.05 ± 0.00	43.0 ± 0.1	8.3 ± 0.1	5.6 ± 0.1	80.3 ± 1.0	5.8 ± 0.1	19.28 ± 0.37	This work
	AF-8	49.1 ± 0.4	5.9 ± 0.1	1.8 ± 0.0	0.02 ± 0.00	0.10 ± 0.01	43.1 ± 0.1	8.5 ± 0.1	5.2 ± 0.1	78.5 ± 0.8	7.8 ± 0.1	19.37 ± 0.36	This work
MUD _	I-214	49.1 ± 0.5	6.1 ± 0.2	1.9 ± 0.0	0.03 ± 0.00	0.06 ± 0.00	42.8 ± 0.3	11.7 ± 0.1	4.5 ± 0.1	80.1 ± 1.2	3.7 ± 0.1	19.33 ± 0.39	This work
	AF-8	49.7 ± 0.6	6.1 ± 0.1	1.9 ± 0.0	0.02 ± 0.00	0.09 ± 0.00	42.2 ± 0.2	9.6 ± 0.1	5.7 ± 0.1	78.3 ± 0.9	6.4 ± 0.1	19.56 ± 0.42	This work
BIOSOLIDS _	I-214	49.0 ± 0.5	5.9 ± 0.1	0.7 ± 0.0	0.02 ± 0.00	0.05 ± 0.00	44.3 ± 0.1	8.7 ± 0.1	5.3 ± 0.2	79.9 ± 1.1	6.1 ± 0.1	19.46 ± 0.38	This work
	AF-8	49.5 ± 0.2	6.1 ± 0.2	1.9 ± 0.1	0.02 ± 0.00	0.05 ± 0.00	42.4 ± 0.2	10.1 ± 0.1	5.4 ± 0.2	79.0 ± 1.1	5.5 ± 0.1	19.51 ± 0.39	This work
Softwood pellets *		50.64	5.98	0.47	0.00	NE	40.14	7.67	2.77	76.44	13.12	18.21	[55]
Hardwood pellets *		50.37	5.75	0.65	0.00	NE	40.98	7.84	2.25	76.34	13.57	18.04	[55]
Wheat straw pellet *		47.42	5.73	0.83	0.12	NE	37.15	7.16	6.16	71.37	15.31	17.34	[55]

^a In percentage. All values are in dry basis except moisture. ^b Estimated by difference. ^c HHV: high heating value. NE: Not estimated. * Values accuracy determined for each particular element in Lisý et al. [58].

3.3. Biomass Consumption and Air Flow

The combustion airflow and the biomass mass evolution in the boiler were carried out under the same loading conditions. Biomass consumption showed some variations between the different pellets used, which may be related to their physical and mechanical properties (Table 1). The average pellet consumption varied from 600 g/h (I-214 CONTROL) to approximately 900 g/h (AF-8-MUD). The trend that consumption was higher for the AF-8 clone was maintained during the treatments.

3.4. Emission Factors

3.4.1. Combustion Gases

All pellets at some time exceeded the CO concentration of 1000 ppm in the flue gas during the test time. Experiments showed that the O₂ concentration decreased with CO₂ increase in the flue gases. The CO₂ concentration in combustion gases is a complete combustion indicator, while the CO presence is an incomplete combustion indicator. There is a relationship between incomplete combustion and very low combustion temperatures. Experimental results also showed that the highest CO concentrations were obtained during I-214 MUD combustion (Figure 3). This can be explained by the fact that I-214 MUD had a high moisture content, which implied lower temperature values and, consequently, high CO concentration.



Figure 3. CO concentration in the emitted gas during combustion.

For its part, the emission factors of exhaust gases from biomass combustion were calculated, shown in Table 3, by multiplying the gas concentration by the air flow rate obtained during the combustion test divided by biomass consumption. CO₂ values were slightly lower than the stoichiometric values of complete pellet combustion. This fact, together with the presence of small amounts of CO, indicated that combustion of the material did not take place completely. This incomplete combustion may be due to (i) a defect in the boiler by causing nonuniform primary and secondary air currents or (ii) a poor pellet distribution in the boiler, which could be associated with its geometric characteristics (Table 1). Since the same boiler was used for all the tests, the results allowed the authors to verify this work objective: to know if there were differences, in terms of variety and fertilizer, between the different pellets tested. During these same experimental conditions, commercial pellets had lower CO emission factors than those analysed in this study [45,59]. I-214 MUD and I-214 CONTROL pellets had higher CO emission factors and, therefore, the lowest average combustion temperatures.

Hydrogen chloride (HCl) presence in the flue gases is related to the biomass chlorine content and is a significant contributor to corrosion in the boiler [60]. The HCl concentration in the emitted gases during wood pellet combustion is expected to be relatively low due to the low typical chlorine content in the wood [61]. As a consequence of the percentage of wheat-straw used in the mixtures being the same in all the samples, there was a homogeneity in the HCl results in line with the Cl data present in the pellets (Table 2).

BIOSOLIDS

AF-8

 164.9 ± 9.8

 0.04 ± 0.00

					Ũ				
		CO ₂ ^b	CO ₂ ^c	CO ^a	NO ^a	NO ₂ ^a	HCl ^a	SO ₂ ^a	TOC ^a
CONTROL	I-214	164.5 ± 10.3	0.04 ± 0.00	1404 ± 50.2	83 ± 9.5	12 ± 3.1	0.4 ± 0.1	59 ± 10.1	37 ± 8.8
	AF-8	166.9 ± 11.6	0.04 ± 0.00	818 ± 22.3	75 ± 11.7	*	0.5 ± 0.2	65 ± 10.8	16 ± 5.4
MUD	I-214	168.8 ± 10.5	0.04 ± 0.00	1505 ± 48.8	95 ± 15.2	6 ± 2.8	0.4 ± 0.1	81 ± 15.4	49 ± 17.1
	AF-8	167.9 ± 10.0	0.04 ± 0.00	878 ± 35.1	59 ± 13.2	13 ± 5.2	0.4 ± 0.1	10 ± 2.8	12 ± 2.9

 69 ± 9.8

 5 ± 1.9

 0.3 ± 0.1

 28 ± 7.2

Table 3. Emission factors from flue gases.

^a mg/MJ. ^b Grams in dry basis per 100 pellets. ^c Nm³/kJ. * Below the quantification limits.

 941 ± 37.6

 16 ± 4.5

Sulphur dioxide (SO₂) is an acidic gas which is considered an air pollutant that causes acid rain which damages building and corrodes metal structures [62,63]. The SO₂ present in the flue gases was related to the sulphur biomass content. In Table 3, the SO₂ emission factors varied from 10 to 81 mg/MJ. These differences may be related to the fact that, for some pellets, SO₂ could be adsorbed and trapped in the ashes. The MUD-I-214 pellet was the one with the most S content (0.03%) and the one that emits the most SO₂ (81 mg/MJ). Similarly, pellets made with the AF-8 poplar clone were the ones with lower SO₂ emissions. This was possibly attributable to the fact that S and SO₂ remained retained in the ashes [64].

3.4.2. Particles

Particulate matter emission factors were calculated from the set of samplings carried out in all combustion cycles for the different types of pellets under the same operating conditions. Table 4 shows the particles emission factors, total carbon, elemental carbon, and organic carbon. The PM10 emission factors for all pellets were quite high compared to studies which work with other biomass sources [65] or commercial pellets [45]. The ash content presented for the pellet sets evaluated in this work is even higher than that allowed by the European standard EN 14961-2 (Solid biofuels—Fuel specifications and classes—Part 2: Wood pellets for non-industrial use), which may explain the high emission factors for the particles. AF-8 MUD and I-214 CONTROL had the highest ash content (5.7 and 5.6% respectively) as well as the highest emission factors (301 and 290 mg/MJ). Figure 4 showed the relationship between the EF obtained for the different pellets and the respective ash content, showing that the ash content is a parameter that clearly influenced the particle emission factors.

Table 4. Particulate matter emission factors (mg/MJ) from flue gases.

	CON	TROL	Μ	BIOSOLIDS	
	I-214	AF-8	I-214	AF-8	AF-8
Filters	7	4	3	7	7
PM ₁₀	290 ± 54.7	171 ± 32.4	211 ± 21.4	273 ± 28.4	301 ± 45.6
TC	92 ± 20.8	48 ± 29.3	65 ± 21.4	97 ± 22.1	104 ± 25.6
EC	44 ± 32.4	30 ± 33.9	26 ± 6.9	80 * ± 20.6	72 ± 16.9
OC	49 ± 16.4	18 ± 6.6	38 ± 6.9	17 * ± 11.3	33 ± 21.2
OC/EC	1.1	0.6	1.5	0.2 *	0.5

* Indicative values due to limitations in the analysis technique, with overestimation of Elemental Carbon (EC).



Figure 4. Relation between the particulate matter emission factor and the pellet ash content.

During combustion, both soot particles (elemental carbon or black carbon), organic particles (organic carbon), and inorganic particles were emitted. The difference between them was made according to their formation mechanism and origin. The soot and organic particles originated from the combustible material and were formed due to incomplete combustion. The inorganic particles were non-combustible material and appeared under almost complete combustion conditions [66]. In combustion equipment operated manually and intermittently, such as fireplaces and stoves, incomplete combustion conditions are dominant [67,68].

In this study, organic particles predominated. On the other hand, in equipment with more modern combustion technologies, the particles consist of inorganic material [69]. The highest OC/EC ratios have been reported for combustion at low temperatures in chimneys, where the particles are dominated by OC. However, the largest EC mass fraction comes from modern, more efficient, and small-scale units, which contributes to the reduction of the OC/EC ratio [70]. In addition, high combustion temperatures and vigorous flame conditions improve soot particle emissions, increase EC emissions, and therefore decrease the OC/EC ratio.

For the pellets of this work, it was observed that, in general, EC constituted the dominant portion of the carbon particles released (Figure 5). However, the data analysis showed that, during I-214 MUD combustion test, the emitted particulate material was dominated by OC. This result can be explained by the low temperatures in the combustion chamber observed for the I-214 MUD pellet test.



Figure 5. Carbon mass fraction in particulate matter.

The EC and OC emission factors for AF-8 BIOSOLIDS were considered indicative values. This was due to the thermo-optical method limitation because it was a too dark sample (with a large amount of carbonaceous material amount). The problem was related to the laser signal responsiveness, since the light beam in the initial analysis phase could not be transmitted through the filter and, therefore, did not reach the detector. This limitation occurred in the elemental carbon separation from the pyrolized organic carbon, which favoured an OC underestimation, without affecting the TC content.

3.5. Varieties and Organic Fertilizer Influence

Once the different characteristics related to the properties and emissions associated with the samples were analysed, we highlight the trends observed by varieties and/or the fertilizers.

Where varieties were concerned, I-214 was related with higher emissions for most of the parameters analysed, namely CO, NO, SO₂, TOC, or OC. Regarding fertilizer influence, it was also relevant. In this way, MUD fertiliser showed higher emissions for these same parameters whenever variety I-214 was used, and this same fertilizer decreased said emissions for AF-8. This fact is an indicator that the use of a certain organic fertilizer has a different influence on the characteristics of the pellets when applied to clones I-214 or AF-8. The influence of the fertilizer also influenced the physical and mechanical

properties of the pellets. The BIOSOLIDS-I-214 pellet was discarded for the combustion tests because it had lower quality standards than the rest of the pellets analysed.

4. Conclusions

The analysis of pellets consisting of a mixture of poplar wood and wheat straw were studied. Results obtained revealed that physical and chemical samples certainly influenced the operating conditions and emissions in a domestic boiler. The airborne particulate emissions were influenced for both the type of organic fertilised and the poplar varieties employed. The different pellet aggregation states and their moisture content clearly influenced the combustion properties and emissions. The BIOSOLIDS-I-214 pellet was discarded for the combustion tests because it had lower quality standards than the rest of the pellets analysed. Considering the AF-8 clone, it showed the best behaviour under MUD organic fertiliser. Mass biofuel consumption generally followed a linear downward trend. Regarding combustion gases, the highest CO emission factors were recorded for I-214 MUD (>1400 mg/MJ) and linked to its high moisture content. The ashes accumulation in the combustion chamber grate may also have influenced the combustion process. Pellets with a high ash content emitted more particles. This requires special care with the design of the elements for separating the particles in the fume cleaning train of the boiler when pellets like these are burned. As for the particle composition, they were dominated by elemental carbon (values ranging between 26 and 80 mg/MJ). Total carbon represented between 24% and 41% of the particle composition.

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