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Thermal Behaviour and Emission Characteristics of *Arundo donax* L. as Potential Biofuel

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Abstract
The study evaluates the potential of *Arundo donax* L., a perennial herbaceous that can grow in wide varieties of soils with minimal water and nutrient requirements, as a solid biofuel for the production of thermal energy. The biomass was characterized in terms of proximal, chemical, and elemental analysis using standard techniques. The combustion behaviour and thermal efficiency were evaluated by using a domestic stove through the Water Boiling Test. The gaseous emissions from the combustion of *Arundo donax* L. were measured with a portable device and compared with those from other conventional biomasses such as pine pellets, corn cobs, and commercial firewood. The results showed a higher heating value of 17.36 ± 0.171 MJ/kg and an elemental composition based on more than 45% carbon. The WBT revealed both, the shortest time (27.8 min) and the specific fuel consumption (1.1 kg/L), and the highest burning rate (88.8 g/min) for *Arundo donax* L. compared to the rest of the biomasses studied. The flue gas profile revealed CO_2 emissions of 2.6%, similar to pellets and commercial firewood (1.3 and 1.9%, respectively), a percentage of CO lower than corn cobs, although somewhat unstable, and NOx emission of around 197 mg/Nm^3 only higher than pine pellets. These results revealed the technical viability of *Arundo donax* L. as a biofuel for thermal energy production, at least at residential level, contributing to the diversification of renewable sources of bioenergy in a sustainability scenario against climate changes effects.

Keywords *Arundo donax L.* · Biofuel · Combustion · Water Boiling Test · Sustainability

Introduction

The growing energy demand has deepened the search for new sources of sustainable resources to mitigate the impact of anthropogenic activities related to the production and use of fossil energy, which is recognized as the leading cause of climate change [1, 2].

In this scenario, which claims an intense and effective search for clean energy, biomasses play an essential role since they are considered the largest potential renewable energy source. Currently it provides about 10% of the world's primary energy supply and it is expected to contribute up to a third to meet the global energy demand in the future [3]. Biomasses also contribute to the climate-neutrality, as they are assumed as carbon neutral [3, 4]. However, the expansion of the use of biofuels may result in direct or indirect impacts on the environment, biodiversity, local air quality, and pollution due to land use change and agriculture intensification [5], issues that have to be appraised.

The biomass search for energy production should focus on high-productivity and low-nutrient requirement crops also with minimal commitment to the use of land for food purposes. For that, cellulosic crops, crop residues, and woody biomass are considered promising and sustainable bioenergy sources. In particular, perennial rhizomatous grasses have received growing interest mainly due to the high yield potential, their low input demand, and the positive environmental impact relative to the CO_2 emissions reduction [6].

Among various perennial grasses, *Arundo donax* L. (AD), commonly known as giant reed, has been recognized as a promising grass as energy crop [3]. According to Dragoni [7], the advantages of using perennial grasses for energy are the high dry matter yields and the ability to use soil nutrients more effectively than annual crops.

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Besides, this biomass can grow in a wide variety of soils, under reduced rainfed conditions, helping to preserve its quality by mitigating soil erosion and providing carbon sequestration services [7]. Fagnano [8] reported that the cultivation of AD in Italy showed favourable effects on environmental quality, thanks to the improvement in soil fertility (soil organic matter and N increase) and climate change mitigation (C stored in the soil). One of the main environmental problems reported by some authors is that AD can generate invasions, as was described in some areas of the USA [9], as giant reed spreads widely by layering when this biomass is found in flood zones. However, under other conditions, its invasiveness potential is low when managed as a field crop since it does not produce viable seeds, and the expansion via rhizomes is slow [7]. One of the main characteristics of this perennial herbaceous for use as an energy crop is that it has a long useful lifecycle, usually longer than 15 years after implantation [10]. Moreover, some researchers have shown recently the availability of current practices in the agricultural sector that can be adapted to the production and management of this lignocellulosic crop [11] besides to identify the conditions that optimize biomass production per hectare [10].

In Argentina, the primary biomasses used for the generation of biofuels are soybean and corn. The cropping systems have changed in the last decades, mainly due to the increased use of fertilizers, new insecticides, and insect-resistant crops to gain yields. Under this scenario, the agricultural frontiers expanded and displaced forest-type areas, causing growing concern about the environmental footprint [5, 12]. Moreover, one out of four Argentinian households are in energy poverty, being rural households affected to a greater extent, mainly because there is a lack of property infrastructure, the absence of a natural gas network, relatively low incomes, and thermally unsuitable housing [13]. This sector usually uses woody biomass for cooking and heating with low thermal efficiency and severe indoor pollution [14]. Falasca [15] highlighted the challenge to develop new agricultural resources that contribute to retrieve abandoned agricultural lands, encourage rural development, and provide bioenergy without competing with agricultural land for food production. The authors recognized AD as a promising perennial herbaceous that could be cultivated with minimal soil and water requirements, giving attractive dry matter yields in several regions of the country [15]. Moreover, Staples [16] indicated that using any biomass for thermal energy should be considered under the assumption of potential economic development of rural areas, household energy security and diversity, and low greenhouse gas (GHG) emissions. The broadest type of biomasses requires specific knowledge to set up its use and the performance of the involved processes. According to Vassilev [4], knowledge of biomass' physical, chemical, and thermal properties is a fundamental step for its sustainable use. These characteristics define properties, quality, and technologies for using biomass as a fuel, but they are also essential to establish biomass conversion products.

No reference was found in the literature about the behaviour of AD as a biofuel under a combustion process. This work aims to determine the physicochemical and thermal characteristics of this energy crop, analyze the efficiency as fuel for direct use, and identify the viability in terms of energy efficiency and air quality in comparison with other biomass of current use, such as pine pellets, corn cobs, and firewood.

Methodology

Biomasses Samples

AD samples were harvested in the 2020 season from a 2-year-old crop (implanted in 2018). Agronomic trials were carried out in Olavarría field (37°02′05.47″ S, 60°19′08.58″ W) located in the central region of the Buenos Aires province (Southern Pampas, Argentina). The soil for cultivation was an illitic, thermic, Petrocalcic Argiudoll. The depth to the petrocalcic horizon was 0.3–0.7 m. Chemical properties in the top 0.20 m soil were 5.0 g organic matter/kg soil, 6.1 mg P/kg available P (Bray I), and 43 kg/ha N-NO_3. The climate of the region is temperate-humid to sub-humid (mean annual temperature is 14.3 °C). Rainfall has a regular pattern with a historical annual mean of 858 mm [17].

The field experiments were carried out on randomized complete blocks without mineral fertilization. Rhizomes, obtained from a reed bed of a naturalized clone, were used as propagules for the plantation and manually placed in furrows 25 cm deep, and then covered using a disc harrow. The planting density was 10,000 pl/ha with a spatial arrangement of 1×1 m. The experiment was carried out without mineral fertilization and conducted in rainfed. Under these conditions, this crop presented a productivity of 9 t/ha. Although these values are low compared to the values reported by some bibliographies [7], productivity showed an increase in the third year of cultivation, reaching values of 12.5 t/ha, and it is expected to increase with the years of cultivation up to the fifth year, where productivity reaches its maximum [18]. Before there used, AD samples were dried under field conditions [11].

Other conventional biomass usually used for residential heating purposes, such as corn cobs (CC), pine pellets (PP) from *Pinus* sp., and a commercial firewood (CF) of *Condalia*

microphylla (piquillín), were studied for comparative purposes. Corn cobs are the remaining part of the corn ear after stripping the corn kernels, accounting for about 75–85% of the weight of the ear of corn [19]. Pine pellets are a densified solid fuel of pine woods and are defined as biomass particles formed into cylindrical pellets [20]. *Condalia microphylla* also known as Piquillín is a native caducifolius species from Argentina, and a xerophytic and thorny shrub of the Rhamnaceae family, which is usually found in the centre and the west of La Pampa Province [21].

Physicochemical Characterization of Biomasses

The polymeric composition of AD was determined in an extractive-free sample following the standard ASTM (1105, 2001) [22], where hexane–ethanol extractives and hot-water extractives were removed before the polymeric determination. The acid chlorination method (ASTM D1104-56) was applied for the holocellulose determination, and the cellulose and hemicellulose content was determinate following the ASTM (1695–77). The lignin content as acid-insoluble and acid-soluble lignin was determined by the ASTM 1106–96 [22]

The elemental composition of AD (%N, %H, %O, %S, %C) was determined in a Leco® CHN628 Series, Sulfur Add-On Module, and TruSpec Micro Oxygen Add-On Module Elemental Determinators. All determinations were performed in duplicate.

The physical and thermal characteristics and the elemental composition of CC, PP, and CF were found from the literature.

The proximate analysis of the biomasses, in terms of moisture content (ASTM D-4442), ash (ASTM 1102–84), and volatile matter (by differences), was performed according to ASTM standards [22].

Thermal Properties of Biomasses

The heating value is an important property that defines the energy content of any biomass. Several equations were reported in the literature to estimate this property, based on the ultimate analysis (or elemental composition), the proximate analysis, and the chemical composition [23]. In this work, the high heating value (HHV) was calculated according to the modified Dulong's formula (Eq. 1) using the elemental composition of the samples, as follows:

$$HHV\left(\frac{kJ}{kg}\right) = \left[0.3383 * \%C + 1.443 * \left(\%H_2 - \frac{\%O_2}{8}\right) + 0.094 * \%S\right] * 1000 \quad (1)$$

where $\%C$, $\%H_2$,$\%O_2$, and $\%S$ corresponded to the percentage of carbon, hydrogen, oxygen, and sulphur in the biomass, respectively.

The LHV was determinate considering the biomass moisture and the hydrogen content, according to the following equation [24]:

$$LHV\left(\frac{KJ}{Kg}\right) = HHV\left(\frac{KJ}{Kg}\right) - \frac{2499 * (9 * \%H_2 + \%W_b)}{1000} \quad (2)$$

where 2499 kJ/kg is the water vaporization enthalpy at 273 °K, and $\%W_b$ represents the moisture content of the biomass in dry basis.

The Water Boiling Test (WBT)

Water Boiling Test (WBT) version 4.2.3 [25] was applied to evaluate the combustion efficiency of AD. This procedure is an international test protocol developed in 1982 to provide guidelines to test cookstoves' performance with a standardized methodology. The protocol was updated several times, and the last version includes emission guidelines and thermal parameters testing (WBT, Version 4.2.3).

This protocol simulates the cooking process to help understanding the energy transfer from the fuel to the pot and consists of three phases: the cold start (high power phase) in which a pre-weighed bundle of biomass and a cold stove are used; a hot start (high power phase), where a pre-weighed bundle of biomass and a hot stove are used; and simmering (low power phase), where the boiled water from the second phase was simmered for 45 min. In this work, the WBT was carried out in the first phase (cold start), using a domestic stove equipment typical for use in homes in Argentina. In each run, the initial temperature of the stove was 13 ± 2 °C. Over it, 2.5L of water in a 5-L pot without a lid was left to reach the local boiling point of 98.4 °C at 100.83 kPa, corresponding to the local site testing (Olavarría city, 36°54′00″S 60°20′00″W, 196 masl) and measured according to III.D Section (Water Boiling Test, version 4.2.3).

Biomass Used in the WBT

For the WBT, dried AD pieces were put together in ad hoc bundles of 20 cm in diameter and 45.3 ± 4.8 kg/m^3 density, where PP presented the higher density (621 kg/m^3) similar to CF (490–650 kg/m^3), while for CC a cobs density of 147 kg/m3 were found.

Technical Calculations from the WBT

The WBT suggests the use of kindling material to start the fire, according to local practices. In all the tests, five sheets of newsprint were used. Equal amounts of each biomass (500 g) were gradually loaded according to their consumption rate, following the Arora et al. [26] methodology, which did not set a feeding interval, but it was based on visual observation, adding fuel as soon as the flames began to

decrease. Tests were carried out in duplicate. During the cold start phases, the final volume of water (W_{cr}) and the dry biomass consumption (f_{cd}) were measured at the end of each test, along with the time (Δt_c) required to reach the water boiling temperature. Water temperature (T) and elapsed time (t) were recorded every 5 min. From the above measurements, the thermal efficiency, the burning rate, the firepower, and the specific fuel consumption were the parameters calculated for each biomass to evaluate the stove efficiency and to comparatively analyze the performance of each biomass. Following is detailed the calculation of each one.

- The *Thermal Efficiency* (h_c, %) indicates how well the stove can transfer the energy of the biofuel to the cooking pot, considering that the remaining energy is lost to the environment.

$$h_c(\%) = \frac{\Delta E_{H_2O,heat} + \Delta E_{H_2O,evap}}{E_{release,c}} * 100 \quad (3)$$

  where $\Delta E_{H_2O,heat}$ corresponds to the required energy to heat the water, $\Delta E_{H_2O,evap}$ is the energy to evaporate the water, and $E_{release,c}$ represents the energy consumed in the test and calculated as the product between f_{cd} and LHV.
- The *Burning Rate* $\left(r_{cb}, \frac{g}{min}\right)$ indicates how quickly the stove consumes fuel and is a measure of the average grams of biomass burned per minute during the test, calculated as:

$$r_{cb} = \frac{f_{cd}}{\Delta t_c} \quad (4)$$

  where Δt_c corresponds to the total time of the combustion test or the boiling time.
- The *Firepower* (FP_c, W) measures how quickly fuel is burning. It is affected by the stove (size of fuel entrance/combustion chamber) and user operation (fuel feeding rate), and is calculated as:

$$FP_c = \frac{f_{cd} * LHV}{\Delta t_c * 60} \quad (5)$$

- The *Specific Fuel Consumption* ($SC_c, kg/L$) measures the required fuel to boil one litre of water. It is calculated by the equivalent dry fuel used, divided by the litre of water remaining at the end of the test as:

$$SC_c = \frac{f_{cd}}{w_{cr}} \quad (6)$$

Combustion Emissions Measurement

The flue gas was sampled using a hood of 360 mm above the cooking surface (stoves) connected to a flue pipe of 100 mm diameter. The sampling port was located 600 mm after the hood (Fig. 1). A pitot tube connected to a probe was used for differential pressure measurement, gas composition, and temperature.

The flue gas composition was monitored by using a multi-gas analyzer (Testo® 350 XL) every 30 s. The portable device has an electrochemical sensor to measure concentrations of O_2 (%), CO (ppm), NO, and NO_2, and calculated CO_2 (%) and NOx (ppm) as NO plus NO_2 gases. The equipment was calibrated at factory (Calibration Certificate No. 52447–07 06 2021), according to IRAM 35,050 Standard, 1 month before use.

The concentrations of CO and NOx were converted into units according to Eqs. 7 and 8. Factors 1.25 and 2.05 represent the density of CO and NOx in kg/Nm^3, respectively, at normal conditions. The O_2 reference concentration (13%) and the O_2 measured each time allow considering the dilution of the gas due to excess air in combustion.

$$CO\left(mg/Nm^3\right) = \left[\frac{21 - O_{2reference}}{21 - O_{2measure}}\right] * CO(ppm) \times 1.25 \quad (7)$$

$$NOx\left(mg/Nm^3\right) = \left[\frac{21 - O_{2reference}}{21 - O_{2measure}}\right] * NOx(ppm) \times 2.05 \quad (8)$$

The WBT method suggests carrying out a carbon balance to estimate the individual carbon species in the emission (CO, CO_2, and PM) to determine the combustion efficiency. However, as Akagi [27] indicated, it is often difficult to measure all the species; therefore, the modified combustion efficiency (MCE) is usually reported instead and calculated as shown in Eq. 9 [27–29].

$$MCE = \frac{[C]_{CO_2}}{[C]_{CO_2} + [C]_{CO}} \quad (9)$$

where $[C]_{CO_2}$ and $[C]_{CO}$ correspond to the carbon emitted as CO_2 and CO, respectively.

Statistical Analysis

The significance of the differences between the measured parameters was determined by using *F*-test (ANOVA) and Student's *t*-test (mean analysis) at 95% of confidence ($\alpha = 0.05$). All statistical analyses were performed using Statgraphics Centurion XVI (v.16.2.04).

Results

Physicochemical and Thermal Characterization of the Biomass

The physicochemical characterization in terms of moisture, ash, elemental (C, N, H, S, O), and polymeric (lignin,

cellulose, and hemicellulose) composition of all biomasses is shown in Table 1, together with the thermal characteristics in terms of HHV and LHV.

The dry matter of the biomasses resulted high, ranging between 86.68 and 90.01% (values not displayed), with moisture contents lower than 13.3% being CC the biomass with the broadest reported range of moisture (4.6% and 13.26%). According to Zhao [30], the moisture content is a biomass property of significant interest as it impacts combustion temperature, burning rate, and combustible gas production. Also, water evaporation during the initial combustion stage can lead to energy loss, delaying the start of volatile combustion.

Ash content is one of the main factors to consider any biomass as a fuel since the higher the ash content, the lower its quality as fuel [31]. According to Vassilev [4], biomass containing low ash is more desirable as fuel because ash could cause an inappropriate combustion process and it will influence its thermal use [32]; nevertheless, this parameter is mainly species-dependent. In particular, the ash content will define the transport and storage of the ashes and the emissions of particulate matter besides the heater device design and its cleaner process. The ash content in AD was $3.86 \pm 0.00\%$, similar to the value reported by Krička [31] of 3.56% for the same biomass, a value 57.3% lower than CF ($9.03 \pm 0.00\%$) but significantly higher than PP (84.5%).

In addition to the ash content, lignin is another parameter that influences the selection of biomass for energy purposes, mainly because it affects the heating value of the materials [31]. CC revealed the lowest lignin content (11 and 16% db, Table 1), 26 to 49% lower than the values reported for AD of $21.8 \pm 2.5\%$ in this study or the values reported by Shatalov [33] of 20.33%. AD showed higher cellulose and lignin and low hemicellulose content than reed canary grass (42.6% cellulose, 29.3% hemicellulose, 7.6% lignin) and wheat straw (41.3% cellulose, 30.8% hemicellulose, 7.7% lignin) [34]. The results found here do not agree with those reported by Shatalov and Pereira [33], which indicated that AD composition presents lower concentrations of lignin and cellulose than wood but is comparable in hemicellulose. No references were found in the literature regarding CF related to its polymeric and elemental composition.

Table 1 shows the HHV and LHV obtained from Eqs. 1 and 2 for AD of 17.36 ± 0.17 MJ/kg and 15.78 ± 0.17 MJ/kg, respectively; these values resulted similar to those reported by Krička et al. [31] and Faix et al. [35] for the same biomass. The average HHV for CC (18.51 ± 0.5 MJ/kg), PP (19.35 ± 0.2 MJ/kg), and CF (18.40 ± 0.84 MJ/kg) resulted higher than AD; nevertheless, the difference did not result statistically significant (p-value = 0.1686). Other biomasses usually used for thermal energy (HHV) such as pellets from pine forest residues (20.97 MJ/kg) [36], wood sawdust (18.55 MJ/kg), or sugar cane bagasse (17.88 MJ/kg) [37] show similar HHV values to AD, revealing the potential of this perennial herbaceous as a renewable biofuel.

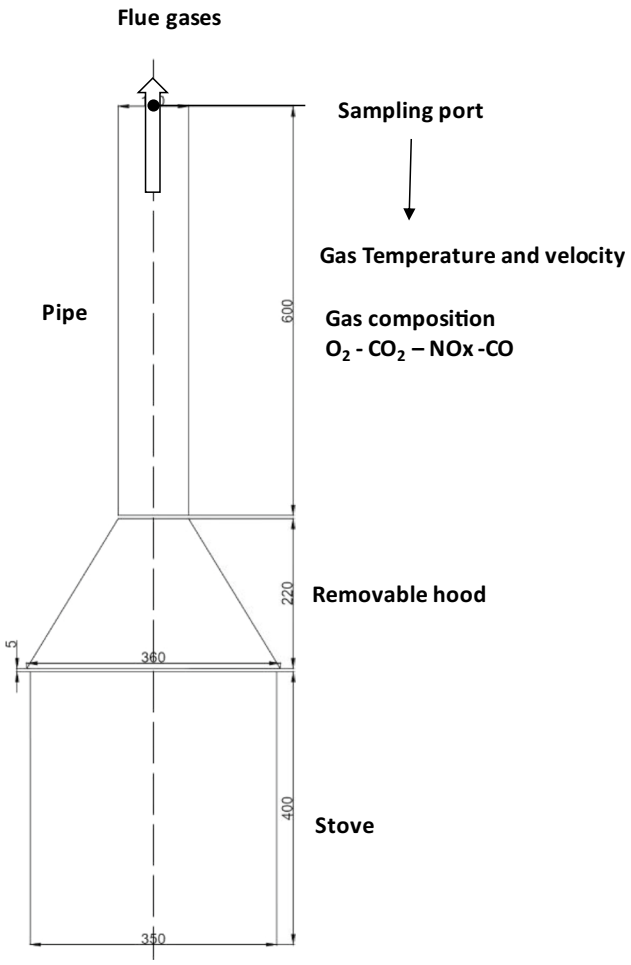

Fig. 1 System used for the flue gas emissions measurement

WBT Test Performance

During the combustion tests, the water temperature (T) at regular time intervals was recorded, together with the total mass used and the time needed to reach the local boiling point. These variables were used to calculate the parameters of Eqs. 3, 4, 5, and 6 during each combustion test. The time required to reach the water boiling point was 27.8 ± 1.4 min for AD, resulting a significantly faster process than with PP, CF, and CC as shown in Table 2. Differences of up 58% indicate a rapid chemical reaction that the structural components of AD exert in contact with the oxygen of the air to produce heat. No significant differences between biomasses were observed in the amount of final water evaporated. However, the dry biomass used to carry out each combustion process was significantly different ($p < 0.05$) since AD required 22% and 48% less amount than CF and CC, respectively.

The water temperature profile (as the average of repetitions) is shown in Fig. 2. AD displayed a constant warming slope of 3.3 °C/min, significantly higher than the rest

of the biomass, which exhibits an average gradient of 1.340 ± 0.099 °C/min.

Although thermal efficiency is a parameter usually used to know the performance of a particular stove to transfer the energy of the biofuel to the cooking pot, in this work, this parameter will be analyzed to compare the behaviour of AD against conventional biomasses used for thermal energy production. As can be observed from Fig. 3, AD showed a higher thermal efficiency (h_c=3.76 ± 0.18%), being 67%, 29%, and 22% upper than CC, CF, and PP, respectively. Lower h_c in CC and CF could result from a higher moisture content, as Vassilev [46] indicated. The analysis of this parameter revealed that CC and PP burned more slowly and with the lower firepower than AD, presenting poor flame, requiring more biomass, and taking longer to boil the water. These results agree with the report by Zhao [30], who indicated that biomasses that burn with flame present greater firepower with significant increases in the heat released. When stoves are used to heat environments, efficiencies lower than 5% correspond to low-efficiency stoves [28]. This study used a conventional stove that is usually used to warm the surrounding environment and to cook, mainly in rural areas or in households that are not connected to the public grid of natural gas or electricity. Therefore, there is a loss of energy through the walls of conductive materials that cause the inefficient heat transfer to the pot, giving low thermal efficiencies. Anyway, these preliminary results revealed that AD behaviour could be considered adequate as a renewable biofuel.

Some low-efficiency stoves have been analyzed in the literature, with similar findings to those obtained in this work. Jetter [47], for an eco-stove feed with oak, informed efficiencies lower than 10%. About the specific fuel consumption (SC_c,) required to reach the boiling of water, AD showed favourable behaviour and exhibited an average consumption of 1.10 ± 0.7 kg/L, significantly lower (p-value 0.0042) than the rest of the biomass studied, mainly CC, that required 110% more amount of biomass (2.32 ± 0.04 kg/L). The combustion burning rate (r_{cb}) is a parameter that helps to determine the thermal quality of fuels, since it represents the maximum fuel burning rate achievable in any device (stoves, boilers, kilns). AD revealed the highest value (88.8 ± 3.7 g/min), resulting in 50, 67, and 90% faster energy release per unit of time compared to CC, PP, and CF, respectively. This behaviour is consistent with the temperature profiles observed in Fig. 2.

According to Onuegbu et al. [48], the burning rate and the heating value of biomass are two factors that, when combined, manage the water boiling time. In this sense, from Fig. 3, it could be observed that there is no direct relationship between the LHV and the amount of fuel consumed. Therefore, the heating value is not the only factor affecting the WBT.

Flue Gas Emission Profiles

Although carbon dioxide is the main product of biomass combustion, these emissions are considered CO_2 neutral, which represent the main environmental benefit of using biomass as an energy source [32, 46]. However, incomplete combustion of biomass can also lead to emissions of unburned C-based pollutants, such as CO, NOx, methane, polycyclic aromatic hydrocarbons, dioxins, furans, tar, soot, and other hydrocarbons [46]. Therefore, the combustion of the biomasses considered in this work was analyzed concerning how they would affect air quality in terms of CO, NOx, O_2, and CO_2 emissions. Data regarding the analysis of the combustion process (average values from data gathered for 10-min intervals) are shown in Table 3. Data acquisition started once the combustion process had reached the steady regime following the methodology suggested by Arranz [36].

MCE is a reasonable proxy for combustion efficiency and represents the percentage of the released chemical energy in the fuel. It also indicates how well the fuel is burned, as an MCE near 0.99 represent biomass that flame and an MCE near 0.8 represent smouldering biomass. At the same time, MCE values between 0.8 and 0.9 suggested roughly equal amounts of biomass consumption by flaming and smouldering [27]. In this sense, as could be observed from Table 3, MCE of AD, CC, and PP resulted higher than 95%, suggesting flaming biomasses. These results agree with those previously observed, where biomass with flaming combustion, as AD, presents higher firepower ($FP_c = 23.3 \pm 1.0$ kW) than those that burns by flaming and smouldering as CF ($FP_c = 13.1 \pm 1.4$ kW).

Chen [29] reported MCE for pellet stove higher than 95%, similar to the result obtained here; the same authors indicate that the MCE for pellet burning is generally higher than that of uncompressed straw burning. These results are in accordance with the one observed in this work, where AD and CC showed lower MCE than PP.

The flue gas temperature and velocity are shown in Table 3. The combustion temperature is a parameter that can influence the emissions of pollutants. As Chen [29] indicated, combustion temperature can be affected by the stove design and protocols used, resulting in different amounts and types of pollutants emitted. Although the combustion temperature was not measured in this work, flue gas temperature (T_{fg}) was used as an indirect indicator, which allows the establishment of relative differences between the burning temperatures of the biomass. Statistically lower ($p\text{-}value < 0.0000$) flue gas temperatures were observed for PP, in agreement with those reported by Koppejan [32], which informed flue gas temperature for pellet stoves of 132 °C and emissions of 104 and 313 mg/Nm^3 of NOx and CO, respectively, similar to those here obtained

Table 1 Physicochemical and thermal characterization of *Arundo donax* L., Pinus pellets, corn cobs, and piquillín

Biomass	α-cellulose (% db)	Hemicellulose (% db)	Lignin (% db)	%N	%C	%H	%S	%O	Moisture (% db)	Ash (% db)	HHV (MJ/kg)	LHV (MJ/kg)	Reference
Arundo donax L.	**58.7 ± 2.9**	**22.6 ± 0.4**	**21.8 ± 2.5**	**0.49 ± 0.00**	**45.54 ± 0.43**	**6.02 ± 0.01**	**0.14 ± 0.01**	**41.52 ± 0.30**	**9.99 ± 0.12[b]**	**3.86 ± 0.00[c]**	**17.36 ± 0.17[1]**	**15.78 ± 0.17[2]**	**This study**
					45.67 ± 0.045	6.17 ± 0.030	0.29 ± 0.001	47.13 ± 0.004	9.01 ± 0.571	3.56 ± 0.216	17.48	16.14	[31]
				0.2	49.4	6.0		44.4			17.4		[35]
	29.18–32.93	32.03–28.48	20.92–21.31							4.77–6.14			[33]
Pinus Pellets	ND	ND	ND	ND	ND	ND	ND	ND	**7.44 ± 0.05[a]**	**0.60 ± 0.00[a]**			**This study**
				0.17	46.7	5.8	0	47.1	10	0.13			[38]
	46.7	24.48	29.4										[39]
	73.99		26.01						9.94	0.87	19.681	18.13[3]	[40]
				1.43	49.40	4.6	0.02	45.82	8.86	0.78	18.29	17.04[3]	[20]
Corn cobs	ND	ND	ND	ND	ND	ND	ND	ND	**13.26 ± 0.27[c]**	**2.79 ± 0.00[b]**			**This study**
	47.27	52.72	16.03										[41]
	48 ± 2	33 ± 2	15 ± 1	0.42	50.2	5.9	0.03	43.5	4.6	1.8	19,14	17.88	[42]
				0.92	46.2	5.42	0.24	47.22	11.74		18,36		[43]
	50.5	31	15	1.3	45.5	6.2		47					[44]
				0.43	44.4	5.6	1.3	48.27	5.1		18,02		[45]
	77.24		15.75							1.16	19.29	17.56	[37]
Condalia microphylla (piquillín)	Piquillín density 490–650 kg/m^3								**13.3 ± 0.18[c]**	**9.03 ± 0.00[d]**			**This study**
											17.5–19.2	16.74[3]	[21]

Bold values were experimentally determined

ND, not determined; *% db*, percentage in dry basis; different letters within a column (moisture and ash) indicate significant differences (p-value > 0.05); moisture (p-value: 0.000); ash (p-value = 0.000)

[1]HHV determined by Eq. 1

[2]LHV determined by Eq. 2

[3]Values calculated from Eq. 2, considering the moisture and H content reported

Average HHV values obtained from the reported values: CC (18.51 ± 0.5 MJ/kg), PP (19.35 ± 0.2 MJ/kg), and CF (18.40 ± 0.84 MJ/kg)

Average LHV values obtained from the reported values: CC (17.34 ± 0.51 MJ/kg), PP (17.59 ± 0.54 MJ/kg), and CF (16.74 ± 0.84 MJ/kg)

Table 2 Parameters recorded during the WBT

Biomass	W_{cr}(L)	f_{cd}(kg)	Δt_c(min)
AD	2.24 ± 0.05^{a}	2.50 ± 0.05^{a}	27.8 ± 1.4^{a}
PP	2.14 ± 0.01^{a}	3.21 ± 0.21^{a}	60.1 ± 1.4^{b}
CC	2.06 ± 0.11^{a}	4.86 ± 0.33^{b}	$80.7 \pm 3{,}3^{c}$
CF	2.19 ± 0.10^{a}	3.21 ± 0.32^{a}	67.3 ± 3.2^{b}
p-value	*0.4748*	*0.0183*	*0.017*

Different letters within a column indicate significant differences (p-value > 0.05)

W_{cr}, final volume of water; f_{cd}, dry biomass used; Δt_c, time to reach the boiling temperature

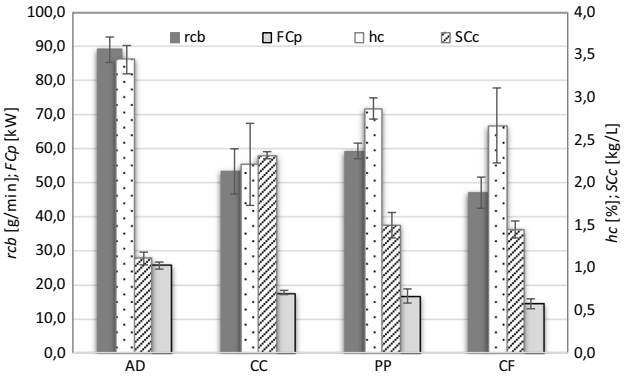

Fig. 3 Measured parameters of the WBT for the studied biomasses. The error bars represent the standard deviation of two replications

for NOx (103.8 ± 11.7 mg/Nm^3), but higher than for CO (46.7 ± 27.7 mg/Nm^3).

The concentration of O_2 and CO_2 and emission rate of CO and NOx from the flue gases of the studied biomasses are shown in Fig. 4. The temporal evolution of the emissions along approximately 400 s was recorded, and through the box plots, the concentration of each gas in a long lapse of approximately 600 s was analyzed. The box plots showed the median, arithmetic mean, and quartiles of each gas concentration and also the maximum, minimum, and outlier values if any.

As can be observed from Fig. 4A, immediately after the starting the combustion, O_2 concentration shows a reduction, reaching a minimum value. The low O_2 concentration may result from the way the biomass is loaded in the stove and the ignited process, behaviour similar to that observed by Arranz [36]. After this stage, the O_2 concentration increases to a stable average value of around 18–19% for all the biomass, except for CC, whose value resulted slightly lower, approximately 17%. Figure 4B shows the evolution of CO_2 concentrations, evidencing a maximum at around 60 s, which correlates with the initial decreasing trend of O_2. AD and CC were the biomasses with the highest maximum CO_2 concentration of 4.3% and 3%, respectively. After achieving the maximum, the CO_2 concentration fluctuated around average values of 2.6%, 3.8%, 1.3%, and 1.9% for AD, CC, PP, and CF, respectively. The values measured in this work for PP were slightly lower than those reported by Arranz et al. [36] for wood pellets, who observed CO_2 emissions in a range between 2.3 and 3.9%, although the variation depends on the material of the pellet.

The CO emissions are mainly influenced by the combustion technology and the process conditions. Low combustion temperature, insufficient oxygen, poor mixing of the fuel with the combustion air, and short residence time contribute to higher CO emissions. PP showed the lower CO emissions (0.54 ± 0.33 mg/s; 47 mg/Nm^3) which could be explained in a higher oxygen content in the fireplace which favours oxidation from CO to CO_2 as Roy [49] indicated, and in a lower moisture content in PP as Mekonnen [28] indicated. Arranz [36] reports CO emissions for pellets between 225 and 2000 ppm depending on the origin of the analyzed pellet, values that are in the range of values for PP. On the other hand, CF generated the highest average volume of emissions (628.2 ± 121.5 mg/Nm^3), followed by CC (552.8 ± 109.6) and AD (388.8 ± 315.9). With the exception of AD, whose CO emissions ranged between 70 and 1000 ppm, the rest of the biomasses showed fairly stable CO concentration over time. The heterogeneity of the biomass, since the entire plant that included cane and leaves was burned, could explain this behaviour.

Results observed of low MCE and higher emissions in CF could be explained by the higher moisture content, which could make the ignition more complex [28], and increases

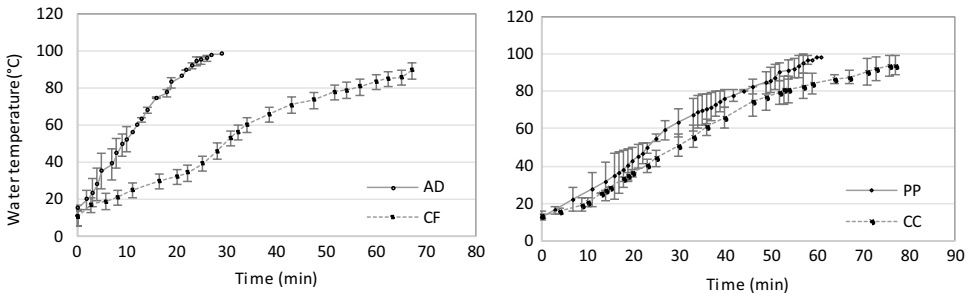

Fig. 2 Water temperature profile during the WBT of each biomass

Table 3 Flue gas velocity (v_{fg}) and temperature (T_{fg}), and emission taxes of CO, NOx, CO_2, O_2, and MCE

	v_{fg}(m/s)	T_{fg}(°C)	O_2 (%)	CO_2 (%)	CO (mg/Nm^3)	NOx (mg/Nm^3)	MCE
AD	2.49 ± 0.46^{b}	264.9 ± 48.2^{c}	18.81 ± 1.10^{b}	2.56 ± 0.70^{a}	388.8 ± 315.9^{b}	197.8 ± 43.1^{b}	95.4 ± 3.4^{b}
CC	2.81 ± 0.37^{c}	348.5 ± 32.3^{d}	17.06 ± 1.41^{a}	3.75 ± 0.40^{d}	552.8 ± 109.6^{c}	248.5 ± 27.0^{c}	97.7 ± 0.9^{c}
PP	2.29 ± 0.91^{a}	150.1 ± 13.1^{a}	19.62 ± 1.11^{c}	1.31 ± 0.10^{a}	46.7 ± 28.1^{a}	103.8 ± 11.8^{a}	98.3 ± 1.1^{c}
CF	2.45 ± 0.54^{b}	203.8 ± 44.2^{b}	18.92 ± 1.34^{b}	1.99 ± 0.33^{b}	628.2 ± 121.5^{c}	241.0 ± 73.2^{c}	90.4 ± 3.6^{a}
p-value	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Different letters within a column indicate significant differences (*p-value* > 0.05)

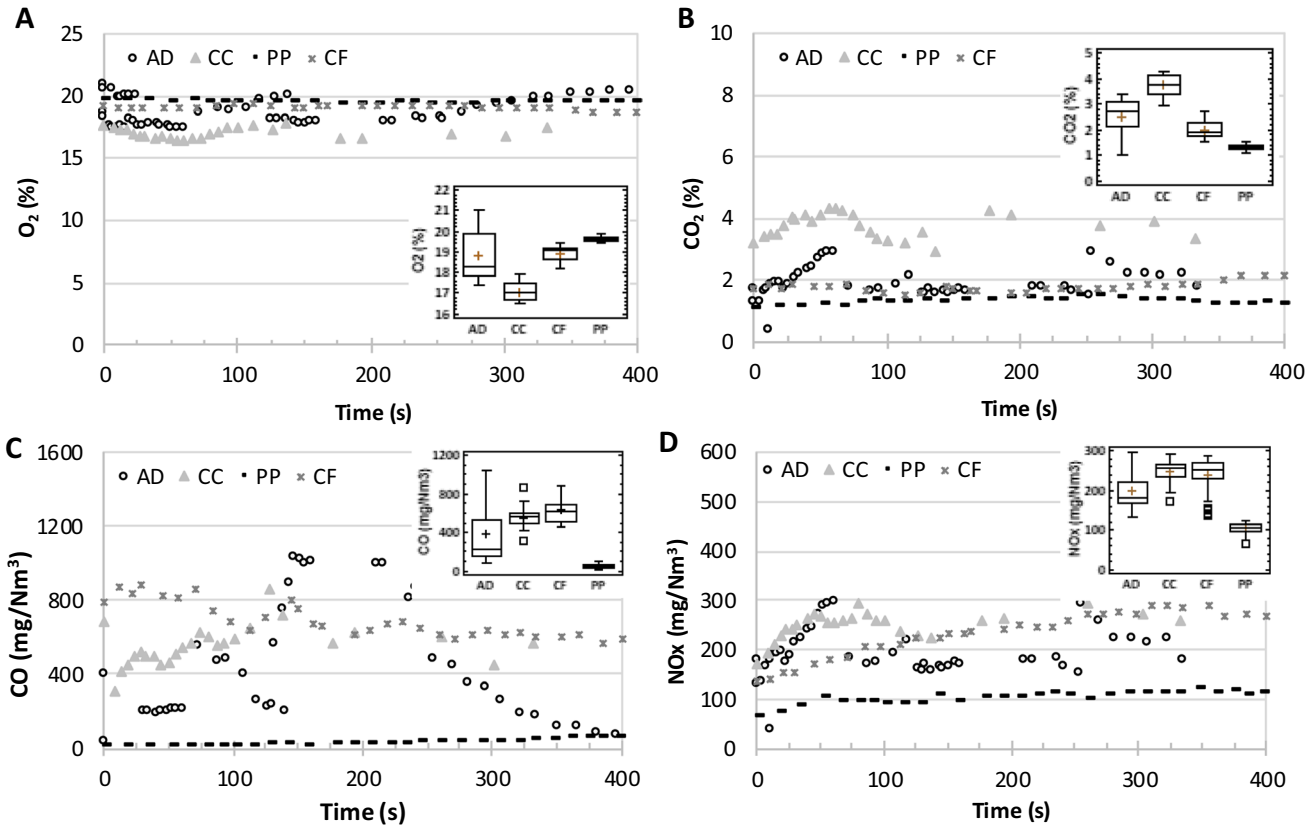

Fig. 4 Emissions of flue gas (**A:** O_2, **B:** CO_2, **C:** CO, and **D:** NOx) from combustion of AD (*Arundo donax* L.); CC (corn cobs); PP (pine pellets); CF (commercial firewood)

the combustion products, such as carbon monoxide (CO) and nitric oxide (NO) as Zhao [30] indicated.

Regarding NOx emissions, each biomass showed a different behaviour; CC revealed an increase over time to reach a maximum of approximately 300 mg/Nm^3, to then decreased up to an average value of 248.5 ± 27.0 mg/Nm^3, value significantly higher than those observed in AD (197.8 ± 43.1 mg/Nm^3) and PP (103.8 ± 11.8 mg/Nm^3). NOx emissions increased when biomass has a higher nitrogen content, with an excess air ratio, and also with the combustion temperature, although at low combustion temperature, the temperature influence became more important than the excess air ratio [32]. Therefore, for the same combustion air conditions as was the case of these tests, NOx emissions are related to the nitrogen content of the biomass and the combustion temperature. The observed low value of NOx emissions in PP could be explained through the lower nitrogen percentage in the biomass (approximately one order of magnitude lower than CC and AD) and the lower flue gas temperature.

In general, PP showed lower CO and NOx emissions, resulting from the densification process, as it was recognized

it could reduce emission pollutants [50]. In comparison, AD showed lower CO and NOx emissions between the non-densified biomasses, evidencing the potential viability as a sustainable biofuel. The advance to the pelletization of AD canes could be the next step in the development of a value chain AD based.

Conclusions

These preliminary results demonstrated the technical viability of AD as an alternative replacement for fossil fuels or woody biomasses. AD presented a low ash content and an LHV in the range of other conventional biomasses. From the WBT analysis, AD showed higher thermal efficiency, which entails a shorter process time to reach the boiling temperature and lower fuel consumption. The flue gas profile of AD exhibited lower CO and NOx emissions than corn cobs and CF but higher than PP, demonstrating the advantage of pelletizing. The densification process could be the next step to value AD on a market scale.

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Author Contribution Verónica Córdoba: conceptualization, methodology, formal analysis, investigation, writing—reviewing and editing. Alejandra Manzur: conceptualization, methodology, writing—reviewing and editing. Estela Santalla: conceptualization, writing—reviewing and editing.

Data Availability "The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request."

Declarations

Conflict of Interests The authors declare no competing interests.

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