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Assessment of wood chip combustion and emission behavior of different agricultural biomasses

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Abstract

The increased interest in using farm-grown biomass for energy production makes it necessary to expand and deepen knowledge on combustion of agricultural residues. The lack of data and studies on solid fuel quality, and combustion related emissions, represents an obstacle to the sustainable development of agricultural biomass industry. In the Mediterranean basin, large quantities of lignocellulosic biomass are obtained yearly from pruning operations carried out largely widespread in fruit plantations such as citrus, grapevine and olive orchards. The most common practice to eliminate this type of residue is the open burning, carried out directly on the field by farmers, without any emissions control or energy recovery. The aim of this study was to obtain a clear description of three different wood biomasses and their behavior during combustion. The physicochemical properties were studied to determine their influence on combustion emissions. Measurements were conducted in laboratory and subsequently carbon monoxide (CO), carbon dioxide (CO_2), oxygen (O_2), nitrogen oxides (NO_x), sulfur dioxide (SO_2), Total Organic Compounds (TOC), and particulate matter (PM) emissions were evaluated during combustion in a 30 kW boiler equipped with a multicyclone filter bags for emission abatement. Principal Component Analysis (PCA) was applied to the data of biomass properties and emissions parameters in order to elucidate which feedstock features had a more determinant influence on the combustion process. Grapevine and citrus showed high N content and consequent high NO_x production. Olive highlighted the best characteristics, high energetic potential and low emissions under regulation limits; in addition, olive pruning residues is the most available woodfuel in the Mediterranean area of Europe, confirming its great potential on agricultural biomass industry sustainable development.

Keyword: Wood Residues Combustion, Emissions, Atmosphere, Pollutants, biofuel

1. Introduction

Wood represents one of the oldest biofuels used for heat and energy generation via direct or indirect burning [1]. The woodfuel conversion technologies are divided into three categories i.e., biochemical, chemical and thermochemical pathways. Respect to first two methods, thermochemical technology is gaining much interest among researchers due to the versatility of the feedstock application [2-4]. The thermochemical processes convert chemical energy in thermal and vice versa because they are made up of endothermic and exothermic reactions at high temperature [5]. In Europe and America, the technology is at the leading level, and its standard system is relatively complete, concluding the entire chain from raw material collection, storage, distribution and application [6]. Since the major fossil fuel resources such as coal, petroleum and natural gas are being rapidly depleted, wood biomass resources are emerging as a promising renewable and sustainable solution. In fact, woodfuel is considered a carbon neutral and renewable source of energy production [7]. The carbon dioxide released during combustion is comparable to that which is absorbed from atmosphere during biomass growth. Consequently, the CO_2 net cycle is in balance and biomass combustion doesn't contribute to the greenhouse effect [8-12]. This importance has resulted in ambitious targets that were further promoted and sustained by EU Directives [13-14] to reduce net carbon dioxide emissions to the atmosphere by increasing the proportion of electricity generated from renewable resources [15,16]. In fact, for over a decade, the European Union has financed an economic contribution to promote the achievement of the new targets for climate and energy policies. Increasing the share of renewable energy to at least 20% of consumption represents one of the objective that the EU energy strategy planned to reach by 2020 and this percentage should increase up to 32% by 2030. For this important objective, the Italian government launched several programs (National Operational Programme - PON; Rural Development Program – PSR; Italian Energetic Program – PEI; Regional Operational Programs - POR) to increase the installed capacity for electricity and thermal production encouraging agriculture and industrial enterprise to use crop residues (pruning residues, waste, etc.) to favor a correct disposal of this waste by using it as fuel [11,12]. These incentives have also favored the installation of small plants and that do not have any particulate control system, given their small size. For this reason, there is a lack of knowledge about the impacts of the biomass energy supply chain on air quality and of the related changes in land. In fact, combustion of biomass causes emissions of gas and particulate matter (PM) which can seriously affect atmospheric processes and human health [17,18]. Several studies showed that agricultural residues burning calls for close attention as it emits significant amounts of greenhouse gases such as CO_2, CO and hydrocarbons, other gaseous pollutants such as SO_2 and NO_x, and smoke particles carrying carcinogenic substances with a wide size distribution [19-21]. In particular, agricultural residues contain less carbon (C) and hydrogen (H) and have higher contents in ash and inorganic elements such as nitrogen (N), sulfur (S), chlorine (Cl), potassium (K) and silicon (Si) respect forest residues. In the Mediterranean area, several tree crops provide large pruning amounts. Especially in Italy, olives, citrus and grapevines guarantee together more than $4x10^6$ tons/year of residual biomass [22]. These crops are widely spread all over the Italian territory; in 2019, olive cultivars had an extension of 1,163,370 ha, while grapevine and citrus 715,599 and 142,654 respectively [23]. The most usual practice for the disposal of these pruning residues is the open burning, with a consequent loss of a resource and uncontrolled pollutants input in atmosphere. While forestry biomass availability for energy in Italy has been widely studied and quantified [11, 24-26], with the development of consolidated management models, residual biomass from agricultural crops, despite its widespread availability, is not enough considered in energy models and economic development. Combustion is the most important process used in this field and the chemical and physical characteristics in the combustion chamber can strictly determinate its quality and the subsequent emission [27,28]. Although residual biomass utilization is considered as a sustainable solution, its uncontrolled burning, injects many different pollutants into the atmosphere that could have a harmful effect on air quality, climate, and human health, especially in winter and in the Mediterranean area where long dry periods can occur. Both open burning of pruning residues and the large use of domestic fireplaces, are atmospheric pollution contributory causes [29]. Emissions from biomass burning are the major source of primary carbonaceous aerosols [30], contributing up to 75% of the global combustion primary organic particulate matter [31]. The macro-pollutants, or traditional pollutants, are those chemical species that are more easily measurable with automatic instruments, more widespread and present in higher concentrations. The concentrations monitoring of these pollutants allows the characterization of the general state of air quality and, as regards the activity carried out in this study, the atmospheric impact of the combustion processes. Particulate matter (PM) emissions from biomass combustion have always been in the focus of air pollution control in many environments [32,33], and attention is still rising while regional or international emission limits tighten and requirements defined in international product standards become stricter. In addition, emission of nitrogen oxides from combustion represents an environmental concern [34]. In fact, nitrogen oxides, collectively referred as to NO_x, are formed in essentially all combustion processes, mostly as nitric oxide (NO) with smaller amounts of nitrogen dioxide (NO_2) and nitrous oxide (N_2O). Nitric oxide is subsequently oxidized to NO_2 in the atmosphere. For fuels with low nitrogen content such as woody biomass, formation of NO arises from fixation of N_2 in the combustion air with elevate temperatures. Nitrogen compounds are acid rain precursors and participate in the generation of photochemical smog. Sulfur dioxide (SO_2) is the most important primary pollutant and arises mainly from the oxidation of sulfur in the combustion processes of coal, oil and diesel. The oxidation of sulfur dioxide produces SO_3 which, reacting with water, generates sulfuric acid, the main responsible for acid rain [35]. Carbon monoxide (CO) is a colorless and odorless gas that is formed by the incomplete combustion of hydrocarbons present in fuels. It has harmful effects mainly on humans and on the environment. The presence of CO in atmosphere at high concentration, more than 100 ppm for several month, leads to a decrease in the ability of bacteria to fix nitrogen in the plants roots. In emissions, CO is monitored mainly because it represents a relevant combustion quality indicator [28]. These gases can cause respiratory problems, acid rain, deposits and corrosion [36-38]. In small-scale appliances, they may disturb the combustion process, reduce efficiency and lead to unwanted shutdowns and higher levels of compounds from an incomplete combustion including carbon monoxide (CO) and PM [39-41]. Therefore, combustion of agricultural residues is considered the most significant sources of fine aerosol in many regions of Europe [42-43]. Hence, a detailed characterization of the sources that deteriorate air quality is required in order to, establish polices for the reduction of the emissions. This paper evaluated three different types of pruned residues highly available in the Mediterranean area, and their emission during combustion are characterized, with the aim to qualify the woodfuel parameters useful to sustainable practices, highest energetic yields and lowest environmental impacts. The aim of this work is to assess the impacts on the air quality during the combustion process of wood residues in small size plants. Therefore, the results of this study are relevant to Italy and other countries with olive, citrus and grapevine groves around the Mediterranean basin, due to the limited number of previous studies on this issue.

2. Materials and Methods

2.1. Biomass composition

Biomass pruning woodchips both comprising heartwood and bark, from different species of the genus *Citrus*, *Vitis* and *Olea*, were collected in November 2019 from different experimental farms of the ARSAC (Regional Company for the Development of Calabrian Agriculture) situated throughout the Calabrian territory (Southern Italy). The experimental nature of these fields permitted to provide not treated biomass in order to understand the real energetic behaviors of pruning. The pruning residues were collected mounting a Peruzzo® shredder machine (Model Cobra Collina 1600) on a Landini tractor (Model 13000 MKII, 95 kW) [44] and successively a Green Technik chipper (Model CIP 1500 PTO) reduced the woodchips of a size smaller than 60 mm to guarantee the correct automatic feeding of the power station. For combustion trials, approximately 100 kg of biomass was available for each species. The moisture content was measured by the Memmert UFP800 drying oven, at 105 ± 2°C, according to the ISO 18134-2 (2017) [45]. For characterization, the dried sample was grinded with the Retsch SM 100 cutting mill for a preliminary size reduction and thereafter through the Retsch ZM 200 rotor mill. Ash content was measured by a Lenton EF11/8B muffle furnace, according to the ISO 18122 [46]. The higher heating value (HHV) was determined by means of an Anton Paar 6400 isoperibol calorimeter and according to the ISO 18125 [47]. The lower heating value (LHV) was calculated from the higher heating value, depending on the hydrogen content. The elemental composition, carbon content (C), hydrogen content (H), nitrogen content (N) was measured with a Costech ECS 4010 CHNS-O elemental analyzer, according to the ISO 16948 [48].

2.2. Emission measurement

The experimental tests on combustion were carried out in November 2019 and conducted on a commercial 30-kW boiler (CSA 30-100 GM, D’Alessandro Termomeccanica, Miglianico, CH, Italy). The boiler is hydronic (use of water as the heat-transfer medium), single fuel, able to consume 7.1 kg h^{-1} of combustible at max work. The mobile grate feeding system allows the use of solid combustible materials such as woodchip and crushed wood waste. Biomasses were burnt in three different days, permitting to cold and clean the boiler after every trial and sampling the overfed material which dropped into combustion chamber (bottom ash). For each experiment, the mass flow of fuel was calculated by dividing the amount of burned fuel by the time of the combustion test. Exhaust gases were directed to an exhaust duct via a flying-ash collection multicyclone. Macro-pollutants measurements were conducted according to EN 14791, 14792 and 15058 [49-51]. The boiler's stack was provided with a port to accommodate the probe (HP1 Dadolab, Cinisello B., MI, Italy) for flue gas sampling; two 180°C lines heaters were used, one for the Total Organic Carbon (TOC) online gas analyzer and another for a multiparametric online gas analyzer, able to detect NO_x, SO_x, CO, CO_2 and O_2. Total gaseous hydrocarbons concentration (TOC) was determined using a Ratfisch RS 53-T heated flame ionization detector (FID) calibrated against propane in air standards, while the multi-gas portable analyzer used was Horiba Model PG-250. The HP5 Dadolab probe and the ST5 Dadolab isokinetic sampler were used to sample PM and metals, respecting European method [52]. PM was sampled by glass microfiber filters and quantified with gravimetric analysis using a Mettler Toledo AL104 Analytical Balance placed in a conditioned room at 20°C and 50% humidity, while quartz filters were used for metals sampling (MK-360 Munktell). Metals in emission were captured by isokinetic sampling probe equipped by a quartz filter (for flying fraction) and a bubbler system containing HNO_3 /H_2O_2, as absorbing solution (for fugitive fraction). The metals content in filters and solutions was determinate with the ICP-MS 7700 Agilent, after samples mineralization with a microwave Milestone START D.

2.3. Statistical Analysis

A multivariate approach has been used to understand better the dynamics involved in biomass combustion, able to take into account many variables analyzed simultaneously [53]. The statistical analysis was entirely conducted in R ver. 3.6.1. Since different data nature and structure were obtained from the experimental design, many statistical tests and analysis turned out to be useful for their comprehension. All characterization analysis was conducted in triplicate. Since the three biomasses description was one of the goals of this study, differences between biomasses were tested through a One Way ANOVA, allowing to evaluate the importance of the biomass qualitative factor on compositional and emission parameters. Thus, the study evaluated if all the compositional and energetic parameters (C, H, N, Ash, Humidity, LHV) are significantly different between the three species. The individuation and of such differences is subsequently obtained with the post-hoc Tukey-HSD test, able to compare groups means and with which was possible to observe weather the variable assumed significant differences according to the plant species. Shapiro-Wilk and F tests were performed to evaluate both normality and homoscedasticity of biomass characterization variables. For emissions variables (CO, NO_x, SO_2, O_2, CO_2 TOC, PM and metals), which weren't normal distributed and homoscedastic, the Friedman test and the Conover test were performed to understand difference between biomasses. Relationships between all variables were studied through simple and multiple linear regression models. The multivariate data analysis was conducted by Principal Component Analysis (PCA) to evaluate the relationships between biomass properties and the combustion emission parameters. PCA is used as an exploratory data analysis for the dimensionality reduction by projecting each data point onto only the first two principal components to obtain lower-dimensional data while preserving data's variation. The parameters shown in Table 1 were used for the only characterization comprehension, allowing the biomass grouping and combustion performances prediction. PCA was conducted on elemental analysis and LHV, on all the characterization parameters and finally on both emissions and characterization data. PCA allows the whole data set to be represented in a way easy to visualize and interpret.

3. Results and Discussion

3.1. Biomass characterization

The use of multivariate statistical methods permitted to draw valuable considerations about correlations between biomass characteristic upon combustion process and emissions. Despite quite similar biomasses were treated (woody tree cultivars) a good classification came out. N content and combustion efficiency certainly influence NO_x production. Elemental analysis reveals differences between biomasses for the nitrogen content. Through a One Way ANOVA is shown how nitrogen percentage changes between samples; a significant *P*-value is observed only for N, while no significant differences were found in C and H between the three species (Table 1). When a Tukey-HSD test is performed, grapevine results the specie with a significantly higher N percentage respect olive and citrus (Figure 1). In literature, it is frequently observed that grapevine and its products are richer in N than other cultivar biomasses [54-56]; and it is assessed the positive effect of vine pruning dispersion as fertilizer, with the possibility to reduce chemical inputs, and increase the sustainability of agroecosystems [57]. Elemental composition does not seem to influence the Heating Values. Despite many models on HHV prediction from elemental composition are described in literature [58] and since only three biomasses are assessed in this study, it wasn't possible to find or apply a regression model able to predict HHV. In fact the multiple regression analysis carried out, brings to a linear model with a very low Multiple R-squared of 0.2. However through analysis of variance (Table 1) is pointed out how LHV changes significantly between the three species, but this trend is not justified by elemental composition; olive shows higher LHV, considerably different from the citrus one, while the high grapevine variability in LHV makes it energetically similar to both citrus and olive (Figure 1f). To verify the three biomasses separation due to elemental composition and LHV, a PCA analysis was performed with only these variables (Figure 2a). The first principal component (PC1) is defined as the direction that maximizes the projected data variance, while the second (PC2) is taken as the orthogonal direction to the first component that maximizes the variance of projected data. PC2, which explains the 34.6% of the data variance, is positively correlated with C and N content, while PC1 (41.4% variance explanation) is mainly positively associated with H, but negatively with LHV, which seems to be less significant for the discrimination of groups since it shows a shorter loading. If the samples distribution is analyzed in Figure 2a, a grouping driven by nitrogen is confirmed; the three biomasses are arranged from left to right in ascending order of nitrogen content, with grapevine showing highest values. In parallel, the variability in the amount of carbon, within olive and citrus, is very clear, in fact they are lengthened on a line parallel to the direction of the carbon loading, confirming a strong carbon content variability within these two biomasses. Such analysis gives a clear result on different groups formation when many compositional data are considered, despite the biomass used are similar and coming all from tree fruit cultivars. Reducing dataset dimension in two components that maintain the data variability of all variables makes it noticeable an overall view of the relationships established between the different parameters in the three biomasses considered. Ashes are significantly determined by the sample kind too (Table 1) and their behavior strictly remark the nitrogen one (Figure 1c-d), showing a significant positive correlation (**P <0.01). The linear regression model applied on these two variables gives a Multiple R-squared of 0.79 and the function obtained was:

$$Ash = 0.29 + 4.03[N].$$

This correlation could be explained by the fact that nitrogen-rich biomasses, in their structure, contain nitrates with elements typically present in ashes such as Si, Ca, K, Mn and others. During combustion, nitrogen is emitted and all the elements connected to it are found in ashes, increasing the percentage of the latter. In literature are also found many biomasses with both high nitrogen content and ash percentage [59,60]. The lack of statistical significance between ash, humidity and LHV trends doesn’t prevent to appreciate what is confirmed in literature, that is ashes and humidity are negatively correlated to LHV. In Figure 3, the energetic behavior of the three species is better explained; factors able to well modeling LHV remain humidity and ashes [61] which result lower for olive, confirming its higher energetic potential. All biomasses arrange themselves on the fitted plane depending on humidity and ash content, providing a quick view on their conduct during combustion. After olive, grapevine shows a higher LHV, despite its higher content of ash, respect citrus. Finally, the citrus biomass seems to be the worst in the combustion processes compared to olive especially. Biomass whole characterization brought to the definition of three distinct groups with different energetic behavior. Through the PCA analysis (Figure 2b) including all variables, it is evident that the two eigenvector PC1 and PC2 explain the 72.6 % of the total variability. It is appreciable how N, Ash and H influence the PC1 and make grapevine so different from olive and citrus, which show lower values of these three variables. Citrus shows the largest variability for PC2 mostly driven by carbon and humidity content. It's also noticeable that parameters like LHV, C and Humidity, mostly explained with the PC2, strongly influence the variability within biomasses groups, while N, H and Ash, explained by PC1, mainly affect the variability between groups. Olive represents the best biomass from an energetic point of view, with highest LHV values, and lowest ash and humidity content. Such a preliminary classification helps to easily group different biomass intended to be burned and give a first important screening on potentialities from both economic and energetic point of view. Such kinds of studies can help researches and policy makers to easily detect during preliminary phases the most potential resources and opportunities in the agricultural biomasses industry field, directing the activities towards the most promising models, saving time and resources.

Table 1 Biomasses characterization results (means ± st. dev.) and P-values of one way ANOVA. Asterix indicates significant differences between groups.

Figure 1 Boxplots of Characterization Analysis: Elemental composition, Ash, Humidity and LHV. Boxes not accompanied by the same letter are significantly different at $p < 0.05$.

Figure 2 Principal Component Analysis biplots, obtained with Elemental Analysis and LHV.

Figure 3 Biomass distribution depending on Ash, Humidity and LHV.

3.2. Macro-pollutants emissions

When emissions are considered is glaring that during combustion grapevine gave the worst results. Despite the same process was performed for any specie to obtain wood chips, the grapevine one had more uneven and filamentous particles, maybe due to the wood and bark nature. Furthermore a piece of woodchip was found in the probe nozzle at the end of grapevine emissions sampling. These events probably could have affected combustion conditions and data acquisition. In grapevine higher values and variability unite carbon oxide and sulfur dioxide emissions (Table 2), suggesting bad combustion conditions, with low temperatures and a CO_2/CO balance shifted towards CO. Such a result follows what other researchers found compering combustion emissions of vineyards pellet with other commercial wood-based pellets [62,63]. As observed in biomass characterization, more NO_x production from grapevine was expected, due to its higher nitrogen content, but when we consider emissions as such, citrus shows considerebly higher values (Figure 4a).If emissions are normalized to an oxygen content of 6%, (Figure 4b) vine NO_x production reaches levels comparable to the citrus ones. This could be explained by the fact that during grapevine combustion unfavorable conditions occurred: low temperatures, high oxigen production (Figure 4d) and consequently diluted emissions. Thus, for grapevine the high NO_x production (Figure 4b), is mostly explained by the higher biomass nitrogen content (Fuel-NO_x mechanism), while for citrus, that shows better combustion conditions and presumebly higher temperature in combustion chamber, a thermal mechanism for the high NO_x emission can be assuemed [64,65]. The weak correlation between NO_x emissions and N fuel content can have several explanations related to combustion efficiency. On the one hand, high concentration of CO or other carbon compounds may inhibit NO_x formation. Carbon monoxide has been shown to enhance the rate of NO reduction over different carbonaceous materials [66]. On the other hand, the catalytic effect of char and ash may also influence NO_x emissions [67]; the NO formed by the char may be re-adsorbed on the char surface and form N_2 by a following reaction with NO or can be reduced by CO catalysed by char [68]. Both when values are normalised or not the low olive nitrogen content causes generally low CO and NO_x emissions (Figure 4a-b), in congruence with what has been seen in literature when olive is compared with other species like almond [69]. Despite its large presence, especially in south Europe, studies on citrus thermal valorization and relative emission monitornig are completely lacking. Also when SO_2 is considered (Table 2), olive gave better results in therm of emissions with lower values than grapevie and citrus, confirming its high energetic and suistainable potential. Data revealed that the problem occurred on the probe nozzle during samplings influenced considerably the PM analysis. In fact for grapevine an improbable value of 1.0 mg/Nm^3 is detected. While citrus and olive show normal PM emission values of 103.05 mg/Nm^3 and 71.28 mg/Nm^3 respectively. Once again olive shows more comforting results from a sustainable point of view. From PCA analysis on emissions parameters, resulted that TOC content didn't affected the biomasses grouping for emissions criteria, probably due to its extremely high variability. The principal components 1 and 2 explain the 86.1% of variability; the component 1 depends mostly from oxygen and carbon dioxide percentage, together with CO content. SO_2 reveals an ambiguous behavior, influencing both PC1 and PC2, while NO_x positively affects PC2 (Figure 5). Can be observed that variables associated to PC1 comprise parameters related to combustion efficiency like CO and O_2; grapevine (in green) is the biomass where these parameters are higher and more influent for the emissions description. Citrus (in orange) shows less variability and the best combustion characteristic with high CO_2 production in emission.The high variability of CO and O_2 in olive and grapevine emissions measurements is appreciable by the spreaded points cloud of these two species in Figure 5. Such differences in emissions variability can be due to different boiler operation during combustion and to different wood chip textures, especially for grapevine. PC2 strongly divided the samples on the base of NO_x and SO_2 indicating emission patterns depending on biomass composition; olive (in blue) is confirmed as a low emitter of nitrogen compounds, while grapevine and citrus emit more NO_x due to compositional and thermal reasons respectively. In Figure 6, both characterization and emission parameter are plotted with a PCA analysis, factors not significant for the discrimination of groups weren't considered. The variables more strongly associated to PC2 are NO_x and LHV, such variables differentiate olive from the other two biomasses. Citrus and grapevine completely differ for PC1 values, in fact they are poles apart, with citrus showing higher CO_2 emission and humidity content, while grapevine differ for the relevant N content and high CO and SO_2 emissions. As can be observed, from emission turns out that citrus has the better combustion parameters, while in laboratory tests citrus showed lowest LHV, suggesting a lower energetic yield too. This contrast could be explained by the significance that wood chips physical properties and storage system can have during combustion [62,63]. As far as macro-pollutants are concerned, the main issue in biomass combustion is nitrogen oxides formation. This study pointed out how NO_x during combustion are very variable and relatable to many factors like boiler setting and biomass composition. Systems able to reduce their formation vary in function of the plant size and consider both management and technical solutions. The first are mostly represented by the biomass choice. Since we saw that composition strongly influences emissions, is recommended to direct the biomass selection through N-poor materials. Obtain a god quality of wood chip is essential too and a better combustion environment can be reached. Thus, small size and low humidity content should be achieved during biomass pretreatment. Otherwise when bigger plants are considered technical solution can be the Selective Non-Catalytic Reduction (SNCR) [70-72] and reburning [73,74] which have been studied extensively. They are available as commercial technologies, typically offering NO_x reductions of the order of 50% [75].

If PM is considered, when small plants are used, isn’t always suitable to install abatement devices that can be usually more expensive than the whole boiler. In these cases small devices like the multicyclone centrifugal filter used in this study, can already give an essential contribution in the abatement of the bigger solid particles produced. When bigger plants are taken into account, many solutions can bring to strong reductions of PM. Experimental campaigns have been already devoted to investigate the operation of a biomass moving grate furnace (350kW) [76]. The research has been set up in order to perform experimental activities in a wide range of test configurations, including baghouse filter evaluation. Definitely technical solutions that could reduce emissions should be carefully planned taking into account the plants kind, the biomass available in the territory and the user necessities.

Table 2 Emissions of CO, SO_2 and TOC (means ± st. dev.). Letters show Conover test results and groups not accompanied by the same letter are significantly different at $p < 0.05$.

Figure 4 Boxplots of NO_x emissions such as (a), normalized to a 6%oxigen tenor (b), CO_2 and O_2. Boxes not accompanied by the same letter are significantly different at $p < 0.05$, by using Conover test.

Figure 5 Biplot obtained by Principal Component Analysis applied to the emission data.

Figure 6 Biplot obtained by Principal Component Analysis applied to emission data together with biomass properties.

3.3. Metals emissions

The regulation in force for plants emissions was considered as a reference: the European Directive (UE) 2015/2193 identifies limits for total heavy metals content in flue gases and only the following elements detected by ICP-MS are included: Cr, Mn, Ni, Cu, Tl, Pb. Emissions from all tested fuels maintained well below this threshold (Table 3), and no significant difference could be detected when comparing different fuels in terms of total heavy metal emissions. In order to understand the relationships between the concentrations of various elements in the flue gas, a PCA was performed from the chemical composition of trace elements in PM10 (Figure 7). In fact, emissions reveal higher content of elements typical of biomass burning such as Ca, K, Al and Na [59] and lower concentration of other trace elements. While the concentrations of Pb, Cd, Cu, Mn, were very low for every biomass considered, olive presents slightly higher values of Ni and Cr, always under regulation threshold. Ni showed concentrations unexpectedly high especially in olive, if we consider that it is a low volatile metal. Also, other studies concerning biomass flue gas analysis detected higher Ni concentration than expected, without a clear explanation [69], such a result should be addressed with further analysis in order to understand its possible causes.

Table 3 Metals concentration in flue gas emissions.

Figure 7 Loading plot of the PCA (PC1/PC3) performed on the metals concentration.

4. Conclusions

The results reported in this study confirmed the idea that agricultural residues would be a potential raw material for energy scope because their availability in comparison with dedicated bio-energy crops support their interest through better recycling and re-using thanks to numerous technological developments. When small and commercial boilers are considered, it is rarely possible to manage precisely the combustion process by regulating oxidizing and fuel loading. In these cases, fuel selection and pretreatment result fundamental to minimize pollution and maximize energetic yields [77,78]. In particular, farmers should firstly choose biomasses with low N content, using woodchip with a low humidity content and regular size. Furthermore, before turn the boiler on the first time is advisable to make fireplace measurements campaign to understand clearly the pollutants amount emitted. In fact, when bigger plants are installed other common practices include the installation of devices capable to monitor the combustion condition and to strongly reduce emission, especially NO_x and PM. The first category includes oxygen sensors for the oxidizing monitoring connected to the fuel charger, in order to obtain better combustion conditions, while the second type includes devices able to decrease the PM production like multicyclone centrifugal or baghouse filters. Such practices can surely help small and medium agricultural enterprises to get more efficient energetically and more sustainable. In this study, a clear distinction between the three biomasses is pointed out with olive residues considered the most advantageous biomass from every point of view, both in terms of emissions and energy yield. Another advantage is the great diffusion of olive pruning and its high availability that could bring to a real sustainable production chain respecting current regulation emission limits. In fact, the bigger pruning availability and the good energetic behavior make olive the best solution in terms of fuel utilization in biomass plants, together with devices able to control and breakdown pollutants emission. Grapevine resulted less indicated for heat generation because of high NO_x and CO emissions. Such a different behavior can be traced back to higher N content inside its structure but maybe also for the heterogeneous matrix particle size which brought to the finding of woodchip in the probe. Anyway, the grapevine physical texture prevented to obtain regular and small chips like olive and citrus. For grapevine therefore is suggested, like observed in literature, a fertilization utilization instead of combustion for heat production. Citrus shows the best combustion conditions, but its N content, together with high temperature, favor both thermal and fuel NO_x generation. Another important issue is PM emissions, efficiently regulated by the multicyclone filter installed after the combustion chamber, except for grapevine that presented the already discussed problem. Results unavoidably underline the necessity to manage pruning burning for heat production purposes, using the best biomasses available, under controlled combustion and with emissions abatement device able to limit pollutants release into the atmosphere. However, further studies are needed to encourage the creation of a biomass supply chain network [79] incoming from agricultural residues. In addition, the quality of wood chips represents an important parameter to apply this biofuel in different type and size of energy plant. Considering a greater diffusion of small farms, the presence of small-medium energy plants will be very likely and consequently the quality of the wood chips will have to assume a great importance to guarantee a correct and efficiency combustion.

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Declaration of competing interest

There is no conflict of interest.

Author contributions

Andrea R. Proto: Conceptualization, Funding acquisition; Investigation. Writing - original draft & editing. Adriano Palma: Investigation, Formal analysis, Data Curation, Writing - original draft & editing. Enrico Paris: Conceptualization, Investigation, Methodology. Salvatore F. Papandrea: Investigation, Methodology. Beatrice Vincenti: Investigation, Validation. Monica Carnevale: Investigation. Ettore Guerriero: Methodology, Investigation. Roberto Bonofiglio: Project administration. Francesco Gallucci: Funding acquisition, Conceptualization, Supervision, Project administration.

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Table 1

Table 1 Biomasses characterization results, expressed by means ± standard deviation, and P-values of one way ANOVA. Stars indicate significant differences between groups.

Compound	Citrus	Grapevine	Olive	P-value
C (%)	48.86 ± 4.42	50.34 ± 0.73	49.58 ± 2.69	0.838
H (%)	5.75 ± 0.62	6.36 ± 0.52	5.00 ± 0.60	0.073
N (%)	0.35 ± 0.06	0.57 ±0.12	0.21 ± 0.06	0.005**
Ash (%)	1.80 ± 0.18	2.71 ± 0.14	0.90 ± 0.03	0.000***
Humidity (%)	12.31 ± 0.06	12.08 ± 0.15	12.15 ± 0.07	0.089
LHV (MJ/kg)	17.95 ± 0.20	18.39 ± 0.37	18.68 ± 0.03	0.033*

Table 3 Metals concentration in flue gas emissions.

mg Nm^{-3}	Citrus	Grapevine	Olive
Na	1.10	0.78	1.19
Mg	0.44	0.31	0.43
Al	1.11	1.02	1.49
K	1.11	1.37	1.74
Ca	1.10	0.73	0.99
Cr	0.02	0.02	0.24
Mn	0.24	0.01	0.01
Fe	0.33	0.23	0.34
Ni	0.03	0.02	0.32
Cu	0.02	0.03	0.06
Zn	0.15	0.10	0.14
Ga	<LOQ	<LOQ	<LOQ

Sr	<LOQ	<LOQ	<LOQ
Cd	<LOQ	<LOQ	<LOQ
Tl	<LOQ	<LOQ	<LOQ
Pb	<LOQ	<LOQ	<LOQ

Table 2

Table 2 Emissions of CO, SO2 and TOC. Data are means ± standard deviations, and letters show Conover test results. Groups not accompanied by the same letter are significantly different at $p < 0.05$.

Emission	Citrus	Grapevine	Olive
Such as	627.76 ± 324.00 c	1852.13 ± 398.30 a	
CO (mg/m^3)			733.03 ± 422.54 b
SO_2 (mg/m^3)	13.30 ± 4.16 c	31.91 ± 7.35 a	1.08 ± 3.26 b
TOC (mg/m^3)	1.25 ± 0.52 a	1.21 ± 0.44 a	1.77 ± 1.18 b
CO (mg/m^3)	1351.16 ± 744.78 c	10402.84 ± 3517.97 a	2396.22 ± 1183.67 b
SO_2 (mg/m^3)	28.15 ± 7.67 c	188.36 ± 107.75 a	2.75 ± 11.11 b
TOC (mg/m^3)	2.72 ± 1.22 c	7.09 ± 4.51 a	6.50 ± 5.67 b

Figure 1 Boxplots of Characterization Analysis: Elemental composition, Ash, Humidity and LHV. Data are means ± standard deviation (n = 3), and boxes not accompanied by the same letter are significantly different at $p < 0.05$, by using Tukey-HSD test.

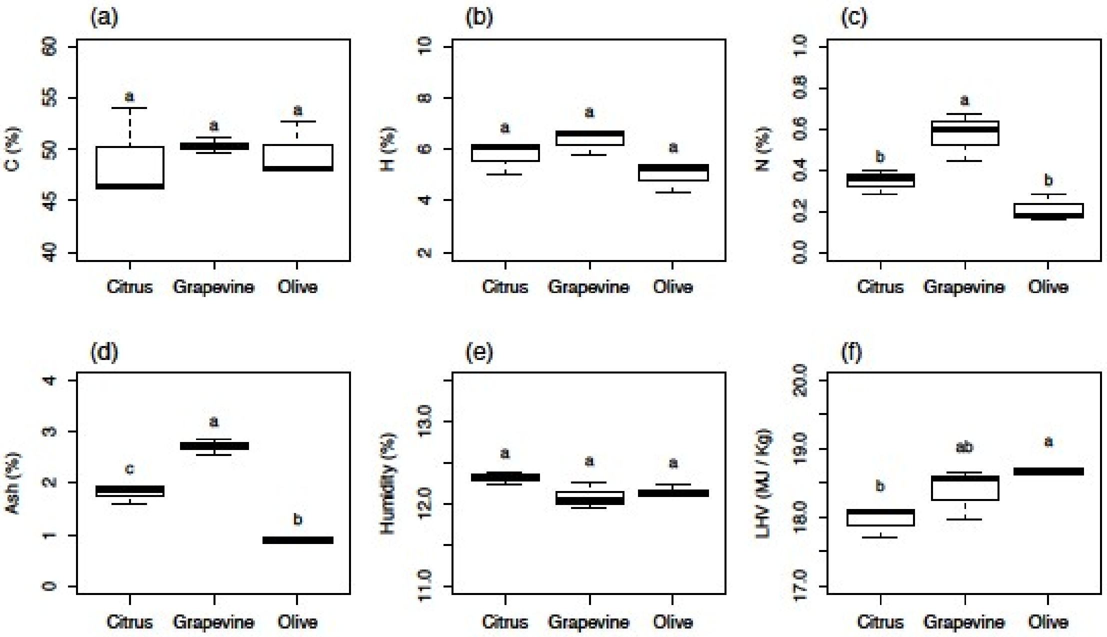

Figure 2 Principal Component Analysis biplots, obtained with Elemental Analysis and LHV.

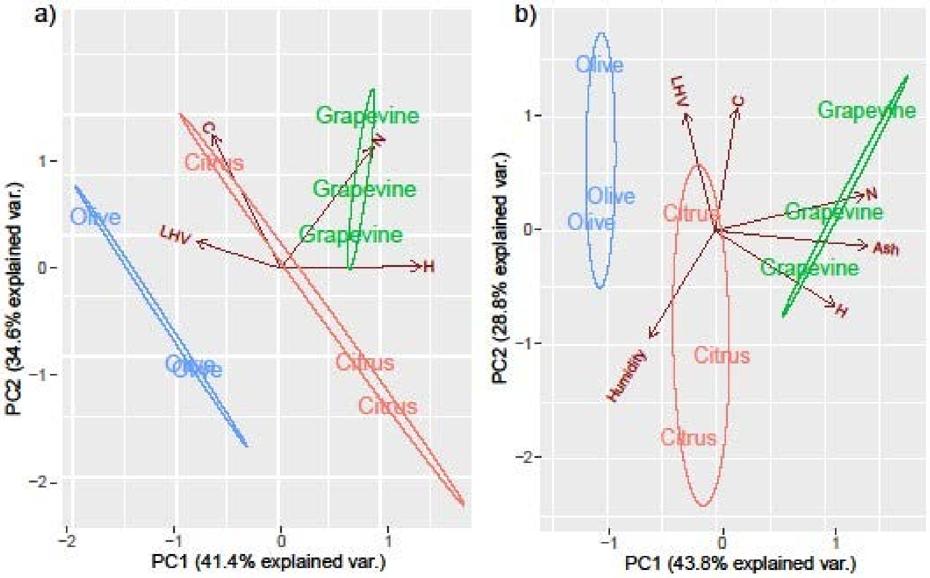

Figure 3 Biomass distribution depending on Ash, Humidity and LHV

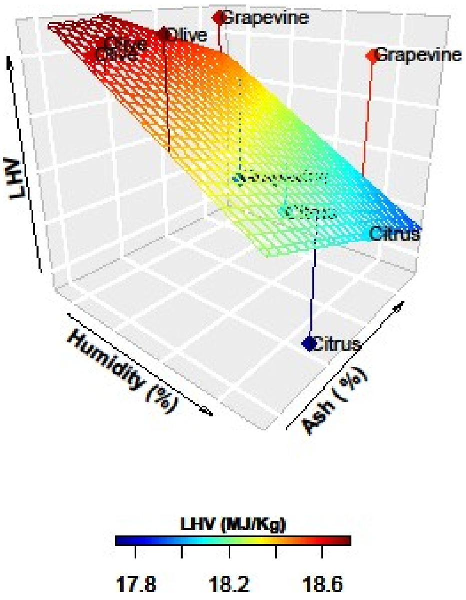

Figure 4 Boxplots of NOx emissions such as (a), normalized to a 6%oxigen tenor (b), CO2 and O2. Data are means ± standard deviation (n = 3), and boxes not accompanied by the same letter are significantly different at p < 0.05, by using Conover test.

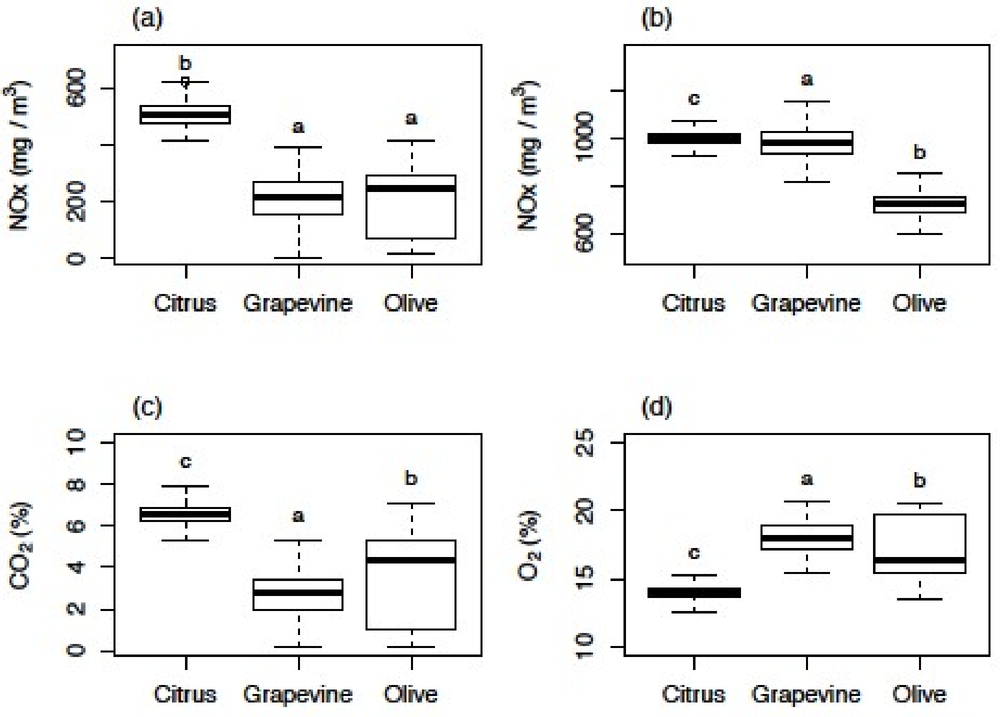

Figure 5 Biplot obtained by Principal Component Analysis applied to the emission data.

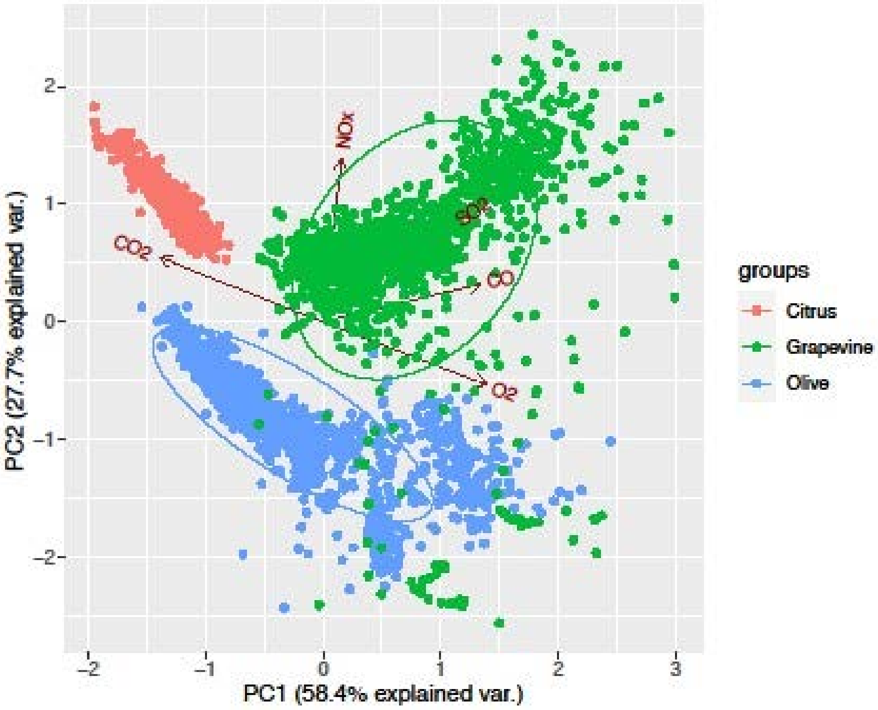

Figure 6 Biplot obtained by Principal Component Analysis applied to emission data together with biomass properties.

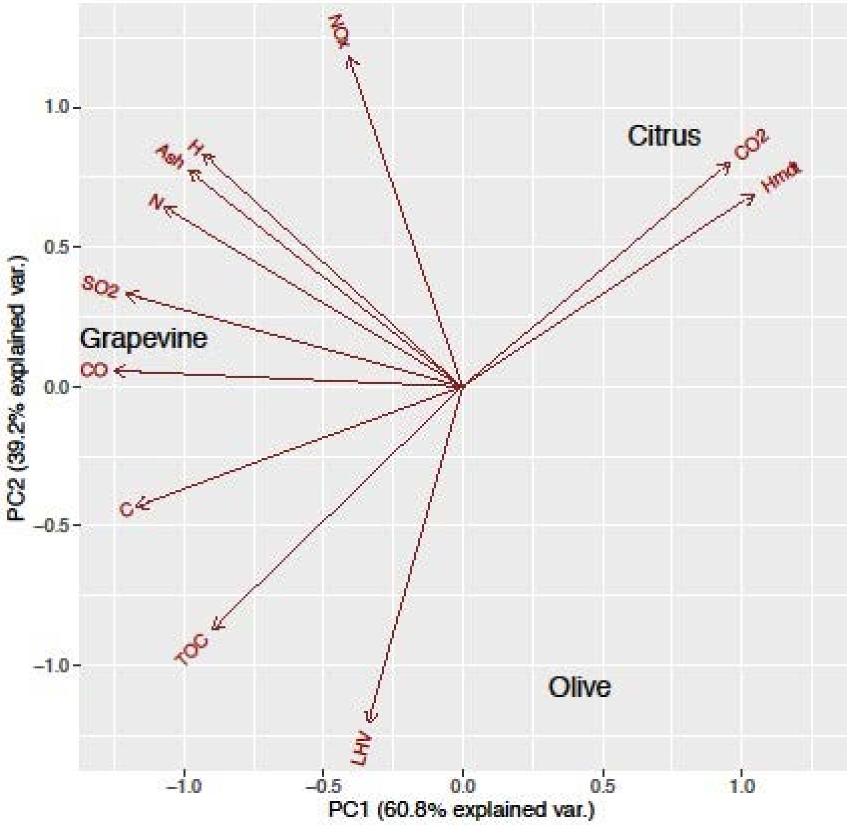

Figure 1 Loading plot of the PCA (PC1/PC3) performed on the metals concentration.