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Study of the Thermochemical Properties of Lignocellulosic Biomass from Energy Crops

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Abstract: The cultivation of short rotation coppice (SRC) is a sustainable and ecological alternative for the production of energy vectors today. For its use, it is necessary to know the thermochemical properties of the biomass produced, as well as the differences between genotypes and varieties. In this work, the thermochemical properties of five different *Populus* clones grow up in Mediterranean basin, with two different age categories, are analyzed. The moisture content, wood density, heating value, ash content, energy density, composition and the volatile matter were measured, separating wood and crust fractions. The mean crust content for all clones was near to 10% but it is observed that the youngest clones have higher content of crust and humidity. The 3 year-old clones generally show lower humidity and ash content and higher density of wood and fixed carbon, consequently showing a higher heating value. In addition, 3 year-old clones are encouraged since they have a lower content of majority and minority elements in proportion that can generate less operating and environmental problems.

Keywords: energy crops; biomass; *Populus*; short rotation crops

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1. Introduction

1.1. Context of Biomass Energy

The continuous increase in the anthropogenic demand for energy implies the progressive depletion of fossil fuels and the increase of pollutant emissions, facts that have forced different governments to stimulate the use and search for alternative sources of energy. Currently, the European Union and other developed countries are promoting a strategy to reduce the emissions responsible for climate change and for the air pollution. In this sense, the objective is to create a sustainable production model considering a triple effect social, economic and environmental. The initiative, initially proposed in Kyoto Protocol, led to the drafting of the White Paper on Renewable Energies of the European Union (EU) [1]. In this regard, later the directive 2009/28/ EC was created which indicates that, in 2020, three objectives should be reached: (i) 20% of the primary energy produced in the Union countries must come from renewable origin, (ii) greenhouse gas emissions must be reduced by 20% and (iii) energy efficiency must be increased up to 20%. Additionally, 10% of fuels used in transport sector must be produced from renewable raw materials [2].

The European technical specification CEN/TS 14588 defines biomass as "all material of biological origin, excluding those that have been included in geological formations undergoing a mineralization process" [3]. This definition, therefore, excludes fossil fuels such as coal, oil or natural gas. Biomass includes residues of agricultural, livestock, forestry and urban origin, as well as energy crops, herbaceous or woody. According to this, biomass covers great heterogeneity in resources and applications associated with this energy source. Additionally, biomass is an abundant resource (the fourth primary energy source after coal, oil and natural gas) and geographically dispersed.

1.2. Wood Fuels and Forest Crops

Wood energy represents, in the developing countries, approximately 15 percent of total primary energy consumption although this value conceals differences at the subregional and national levels. In fact, in 13 countries woodfuels provide up to 90% of energy [4]. On the contrary, in industrialized countries, the total contribution of biomass to total primary energy is reduced to 3%, being used to produce heat and electricity, as well as in domestic applications [3]. Combustion is widely considered as one of the most simple, cost-effective, and environmentally benign thermal-chemical processes to date. Although the direct combustion process is considered as one of the most simple, cost-effective, and environmentally benign thermal-chemical processes to date [5].

Depending on the feeding material and the characteristics of the biomass the uses may be different. The residual biomass can be used directly in methane generation [6], heat cogeneration [7], biogas production [7] and hot water [8]. Biogas resources come from wastewater, empty industrial fruit bunches and live animal manure, pressed fiber and grain husk with a very high potential [7]. Likewise, poultry litter and natural gas co-combustion in a rotating fluidized bed combustion chamber have been proposed as one of the alternative solutions for the use of biomass [8].

However, despite the progress made in the use of biomass at the European level in last decades, biomass continues to be the pending subject of renewable energies in Spain, since it is the only source that has not met the objectives established in the Renewable Energy Plan 2005–2010 in Spain [9] and in the subsequent Renewable Energy Plan 2011–2020 [10,11] despite its high potential.

Biomass is usually classified into two large groups: primary and residual. Primary biomass, usually called energy crops, includes the production and management of different plant types. The residual or processed biomass is that which is extracted from the waste material of different productive activities (agricultural, forestry or industrial). Usually, residual biomass raw materials present more heterogeneity in its composition with implies higher ash content, lower C and H concentration and higher Nitrogen content (lower heating value) [12]. Other classification distinguishes between Short Rotation Forestry (SRF) that focuses mainly on forest species and Short Rotation Coppice (SRC), which normally does not distinguish between woody and herbaceous crops, being this last denomination broader.

Forest crops exploit certain species that are considered as energy efficient, economically profitable and are postulated as alternative for obtaining energy due to their rapid growth rate, greater regrowth capacity, high-energy accumulation per unit of weight and great adaptability to different soil conditions. In this sense, biomass in general and energy crops (in particular) were destined to play a fundamental role in energy plans, both at the European level and at the national level (Spain, PER 2011–2020 [11]).

1.3. Advantages and Drawback of Energy Crops

Several economic, environmental and social advantages are associated to the cultivation and use of energy crops [3,13,14]:

- Around 90% reduction of CO_2 emissions [15]. Part of the CO_2 emissions generated in the combustion process is previously immobilized in the biomass structure during its growth associated with photosynthesis. This balance is known as Life Cycle Analysis, being a disagreement in bibliography related to the CO_2 percentage "captured" by the plants.
- The use of biomass is not dependent on intermittent weather, such as solar or wind energy.
- Contribution to forest maintenance (reduction of the risk of forest fires and pests) and agriculture (use of set-aside land, reduction of erosion).
- Reduction in SO_2 and NO_x emissions due to the low content of sulfur and nitrogen in the elemental composition of the biomass.

- Socio-economic development of rural areas: job creation, development of processing and distribution industries, strengthening of agricultural markets, fixing of rural population.

Although the numerous advantages commented, the cultivation of energy crops presents some drawbacks [16]:

- The handling and management (collection, transport, planting, phytosanitary treatments etc.) implies in turn a significant consumption of energy from fossil sources and high production costs.
- The reduction in CO_2 emissions is lower than expected (up to 90% with respect to the emissions generated in the combustion of fossil fuels [16]).
- Impossibility of total replacement of fossil fuels with fuel produced from biomass due to limited availability of farmland.
- Possible alteration of biodiversity because of the introduction of alien species and large areas of monoculture.

Sweden was the first country which opted for energetic forest species in the 80s, starting with willow plantations for energy production. The good results obtained favored the creation of new plantations in Denmark, Finland and the United Kingdom. However, the edaphological and climatic conditions of Spain mean that the species suitable for energy production must have different characteristics from the species used in northern Europe. For this reason, the first crop cultivated in Spain on a large scale was *Populus* (commonly called poplars), selected by the possibility of diversifying its exploitation in the paper industry in the case of not being profitable as energy crop. This variety has been little studied in the Mediterranean climate but is generating great expectations as an energy crop.

To cultivate profitable energy crops, it is necessary to scientifically determine which are those species whose performance is optimal under certain bioclimatic conditions. Apart from *Populus*, other crops stand such as: eucaenas, willows, paulownias and *Eucalyptus*, which are cultivated in a nursery until they are installed in the field and during the whole process they behave as CO2 sinks. All of them have a high planting density and their felling shifts are short (2, 3, 4 or 5 years) until the tree canopy closes.

Short rotation forest species are selected as energy crops because they meet the following requirements to a greater or lesser extent [17–19]:

- High heating value and quality of the fuel.
- High biomass production in dry basis.
- High youth growth.
- Narrow cups and/or large size of leaves at the top.
- Very fast-growing species.
- Very broad genetic base.
- Brief improvement cycles.
- Ease of vegetative multiplication.
- Regrowth after cutting.
- Adaptability to different soils and climates.
- Resistance to biotic and abiotic stress.
- Low ash content.
- Tolerance to high densities.

Considering all the commented aspects, the characterization of the biomass is a necessary step to evaluate its potential for energy application. Parameters such as the proportion of crust, the moisture content, the density or specific weight, the heating value, the ash and volatile content, the concentration of inorganic elements (including alkali metals) and the relationship between cellulose and lignin are properties must be evaluated to get a complete characterization of the biomass [17].

Short-shift, fast-growing species plantations are currently a promising way to produce electricity and heat either in industrial plants or in homes. The thermochemical and physical properties of the different crops, among them *Populus* gender, are of great interest since they allow to determine the energy potential of this type of biomass and the possible problems derived from the ashes produced in the combustion process. For this reason, a study of thermochemical and physical characterization of the biomass of different genotypes in the climatic conditions of the Mediterranean basin is carried out in this work. From this information, it is possible to evaluate which of the commercial genotypes usually considered as energy crops is the most appropriate for using in the climatic conditions selected (higher energy densities) and which period of cultivate time (2 or 3 years) is more suitable. Additionally, the biomass characterization was carried out for wood and crust, separately, in order to know the influence of both fractions on the properties evaluated and, consequently, to estimate the behavior that these genotypes would have in the combustion process of a power generation central.

2. Materials and Methods

2.1. Plant Material and Location

Five different genotypes, typically used as energy crops belonging to different species or hybrids, were used in this study:

- Clone I-214 belongs to the species *Populus deltoides x Populus nigra*, called *Populus x Euroamericana* (Dode) Clone Guinier I-214 [20].
- Clone AF2 belongs to the species *Populus deltoides 145-86 x Populus nigra* 40 called *Populus x canadensis* Mönch [21],
- Ballotino clone belongs to the species *Populus x canadensis* Mönch, and according to some authors it is called Ballottino [22],
- Clone Monviso belongs to the species *Populus x generosa* 103-86 (*Populus deltoides 583 x Populus trichocarpa* 196) x *Populus nigra* 715-86 (*Populus nigra 12 x Populus nigra* 7), briefly indicated as *Populus x generosa x Populus nigra* clone Monviso [21], finally,
- The clone Viriato, which is the least known, belongs to the species *Populus deltoides* Marsh 20.

The commercial plantations are located in Spain, in the city of Granada, in the area called Vega de Granada. The plots have a slope that ranges from 3.7% to 4.4% and they are considered as irrigated land. The localization and edaphic, physiographic and climatic characteristics of zone are shown in Tables 1 and 2. No fertilization was performed in any of the location studied and irrigation was applied according to the requirements.

Table 1. Location and meteorological factors.

Latitude (°)	37° 10′4.61″ N
Longitude (°)	3° 38′21.76″ W
Altitude (m, asl)	590
Annual mean temperature (°C)	15.9
Mean Maximum/minimum temperature (°C)	29.3/3.7
Absolute maximum/minimum temperature (°C)	40.3/−5.8
Annual precipitation (mm)	368

Table 2. Biophysical factors and measurement methods.

K (pmm–peat mineral soil mix- or mg/kg ms) by atomic emission	76
Mg (meq/100 g) by atomic absorption	2.13
Organic Matter (%) by Walkey-Black	0.9
Electric conductivity (mS/cm) by 1:2.5	0.2
P (pmm or mg/kg ms) by Olsen	4.1
pH by 1:2.5	8.5
Active lime (%)	4.3
Clay/Lime/Sand (%) by ISSS	26.7/46.3/27.7

From the information showed of Table 2 is possible to confirm that the selected soils have a typical sandy texture which matches the cation exchange capacity. These are considered as impoverished soils due to their low concentration in P and K, slightly basic pH and low-medium organic matter, which makes them susceptible to an alternative use for agricultural.

2.2. Design and Management of Plantation

The preparation of the land and the plantation was carried out mechanically, in spring, to allow the stumps to regrowth. The density was 13,200 trees per hectare for AF2, I-214, Ballotino and Monviso, and 15,000 tress per hectare in the case of Viriato. Sampling in the plantations was carried out to the samples collected were representative of the plants, being the population density comparable. Trees were harvested and the fresh weight of aerial biomass (stem and branches) per plant was determined. The characteristics of the plantation are showed in the Table 3, where is observed that four clones of 3 year-old were selected and only one younger (2 year-old). The use of the land by local farmers, as well as commercial limitations and interests limited the possibility of planting other 2 year-old varieties.

Table 3. Biomass name, age and density of plantation.

Species	Clone	Trees per Hectare	Plants Age (Years)
Populus x Euroamericana (Dode) Guinier	I-214	13,200	3
Populus deltoides 145-86 x Populus nigra 40	AF2	13,200	3
Populus x canadensis Mönch	Ballottino	13,200	3
Populus x generosa x Populus nigra	Monviso	13,200	3
Populus deltoides Marsh	Viriato	15,000	2

The sampling should be carried out inside the plantation to avoid the edge effect, i.e., the different growth of the plants in the limit the plot due to changing conditions such as light, irrigation, protection, etc. A representative sample is taken randomly, considering this sample as sufficiently repeatable and reliable of the total plantation. The cut is made at ground level, up to a height about 10–20 cm.

3. Results and Discussion

3.1. Natural Air-Drying

Immediately after cutting, the samples are debarked upon receipt in the laboratory and measurements of diameter, weight and length of the samples are taken which allow to estimate the density of the wood once the dry weight has been calculated. The samples were dried naturally, this process consisting on spreading the sample in an airy place, free of contaminants, avoiding direct exposure to the sun and in as far as possible little traveled. To evaluate the natural air drying for each genotype, the difference between the moisture content before and after natural air drying was calculated. The sample preparation methods were developed according to the methodologies proposed in the technical specification CEN/TS 14780 [23]. The samples were then weighted, cut into chips and dried in an oven to determine the moisture content of according to EN 14774 [24].

3.2. Samples Crust Content

As it was commented previously, the biomass characterization was carried out separating wood and crust fraction. In this sense, the first step necessary in this study is the evaluation of crust content in the samples. Results of this analysis are shown in Figure 1 the error detection associate to the device lower than 0.5%.

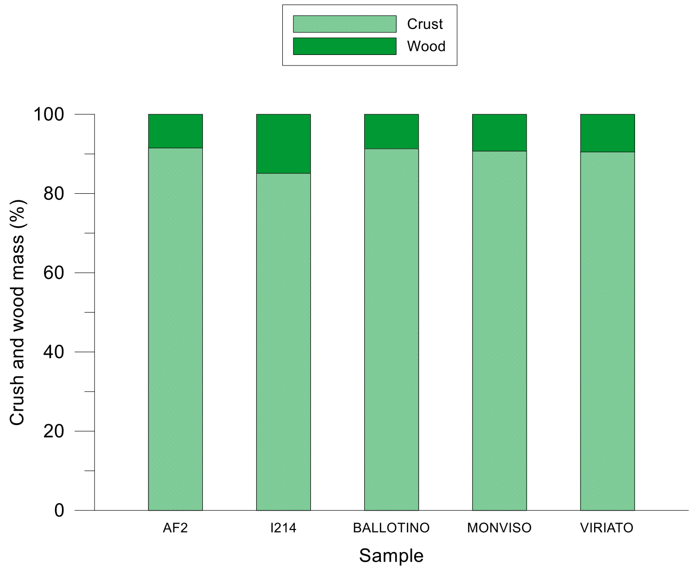

Figure 1. Crust and wood content in mass percent dry basis of the different clones.

The crust content varies from 9.3% to 14.9% in dry basis. Senelwa et al. [25] comment that the crust/wood ratio is lower as the age of the stump increases, although results from clone I-214 are not consistent with this trend because this sample is 3 year-old and it presents a higher crust content than Viriato one. Generally, the mean crust content in the Mediterranean ambient is lower than that reported by Senelwa et al. [25] y Mészáros [26] (11.5–22%).

3.3. Methodology and Standards of the Composition and Properties Measured

The thermochemical properties of lignocellulosic biomass were analyzed in the laboratory. Three repetitions were made for each analysis. Different physical-chemical properties and composition measured in this study are moisture content, particle size distribution, apparent density, lower and higher heating value (LHV and HHV, respectively), elemental analysis (carbon (C), hydrogen (H), nitrogen (N), sulfur (S)), ash content and volatile matter. Additionally, the majority and minority inorganic elements (Al, Ca, Fe, Mg, K, Si, Na, Ti, Mn, As, Cd, Cr, Cu, Ni, Pb, Sb, Mo, V, Co, Zn) present in the lignocellulosic biomass were also determined. In the Table 4, all the properties measured in this work and its the standard associated are detailed.

Table 4. Standards of the composition and properties measured.

Property	Standard
Sample preparation	EN 14780
Moisture content (M_c)	EN 14774-3/EN 14774-2
Wood density	UNE 15150
Heating value (LHV, HHV)	UNE 164001
Ash content (A)	EN 14775
Volatile matter (V)	EN 15148
Carbon (C)	EN 15104
Hydrogen (H)	EN 15104
Nitrogen (N)	EN 15104
Sulfur (S)	EN 15289
Chlorine (Cl)	EN 15289
Oxygen (O)	By difference between C, H, N and S
Mayor elements	EN 15290
Minor elements	EN 15297

The crushing of the wood and the crust, separately, was carried out with a cutting mill (Retsch model SM100) according to EN 14780. Once the samples are prepared (crushed to 0.25 mm and pre-dried) they are dried in an atmosphere of air (or N_2 if the sample is susceptible to oxidation) at 105 ± 2 °C until a constant mass is reached. The humidity data are expressed in units of percentage by mass and are carried out independently (wood and crust). This parameter is evaluated before carrying out the tests for determining the rest of properties (wood density, heating value, ash content, volatile matter, C, H, O, N, S, and Cl content, major and minor inorganic elements) in order to show the results of the properties evaluated on dry or wet basis.

The biomass (wood and crust) used for the rest of the properties analyzed (Table 4) was crushed with an ultra-centrifugal mill (Retsch model ZM 200) in order to reduce the particle size up to 0.5 mm or less (size required by the different analysis equipment) and a weight of approximately 50 g to allow to carry out all the tests.

The higher heating value (HHV) was measured using the calorimeter 6100 PARR, with removable oxygen bomb and bucket. The combustion is carried out at constant volume, so the internal energy change due to combustion with water in the condensed state is the higher heating value at constant volume [26]. From this value, the lower heating value (LHV) is calculated using the Equation (1):

$$LHV_v = HHV_v - 9 \cdot \Delta h^0_{vap,w} \cdot Y_H \quad (1)$$

where LHV_v and HHV_v are the lower and higher heating value measured at volume constant, respectively. $\Delta h^0_{vap,w}$ is the standard enthalpy of vaporization of water and Y_H is the mass fraction of hydrogen in the fuel.

The combustion process in a boiler occurs at constant pressure. For this reason, in order to calculate different parameters related to the efficiency of the power cycle using biomass as fuel, the lower heating value is calculated at these conditions (LHV_p) using the Equation (2), where Y_O is the mass fraction of oxygen in the fuel composition:

$$LHV_p = LHV_v - 619.12 \cdot Y_H - 77.43 \cdot Y_O \quad (2)$$

The elemental analysis, i.e., carbon, hydrogen, nitrogen, and sulfur content, was measured with a CHNS analyzer (LECO model TruSpec) [27,28]. An ion chromatography was used for the chlorine determination [28] and the ash content was analyzed in a furnace following the specifications of EN 14775 [29]. The volatile matter was determined using a furnace according to EN 15148 [30] while the concentration of major and minor inorganic elements in the biomass samples composition were determined specified in the EN 15290 and EN 15297 standards [31,32].

3.4. Moisture Content

Moisture content depends, largely, on the proportion of sheets, fine and coarse material, the time of year, the time elapsed since felling, precipitation and environmental humidity. The importance of this property lies in different aspects: (i) the price of transport (the weight of wet biomass is higher than dry biomass), (ii) the storage because the moisture affects drying time, favors the putrefaction and the possible autoignition during the storage. However, the most important disadvantage associated to the moisture in biomass is the decrease of the heating value, with the consequent price penalty.

Moisture was removed in the samples to avoid uncertainty. For this reason, in this study the content of volatile matter, fixed carbon and ash are normalized on a dry basis (without moisture) because the characteristics of the sample become more significant and comparable with other studies [33].

Figure 2 shows the moisture of the five "clones" selected for this work, separating the fractions of wood and crust. The values of moisture (in percentage) are high which is justified because they are "green samples" (wood+crust). These percentages (between 48–57%) compromise the thermal use of biomass, since the fuel humidity would be not higher than 20% in small-scale installations and in big installations this value would be lower than 40%. It is remarkable the reduction of humidity when the sample is pre-dried, decreasing up to 6% or 8.5% in only one month. From all the samples tested, the clone with the lowest humidity content is Monviso (wood+crust) and the highest value is associated to AF2. Viriato sample (the youngest one) shows the highest value of moisture in the crust, which is justified by the lower lignification of the stem and the higher biological activity of the phloem because of the lower surface/volume ratio.

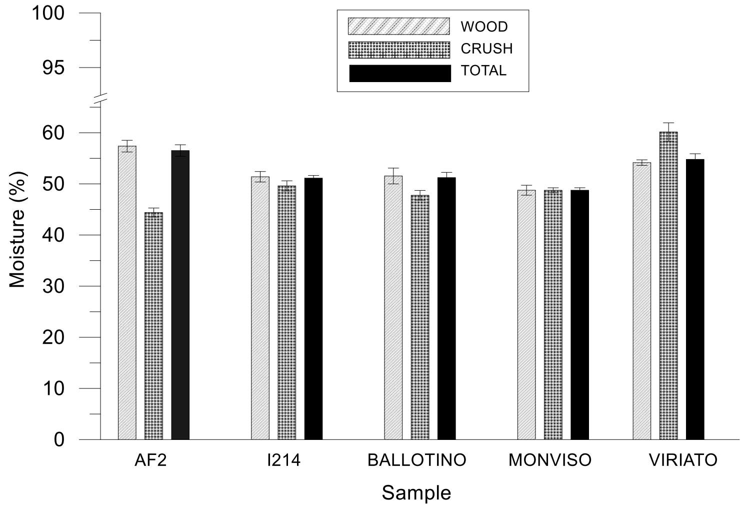

Figure 2. Moisture content (in percentage) of the different clones and fractions.

3.5. Density of Wood Samples

The density of biomass (wood fraction in this case) has influence on the physical-chemical properties and on the fibrosity of solid wood products [34]. This parameter is necessary to estimate the transport and storage costs and the feedstock characteristic of the thermo-chemistry equipment (hoppers, augers, conveyors, etc.). The production of dry wood is directly related to the density of the samples [35].

Results of wood density at the time of cutting, and after the wood drying, are shown in Figure 3. The highest values of wood density were obtained with Ballotino samples in both, wet and dry basis (785 y 381 kg/m^3, respectively), being the results quite different depending on the clon [34]. Viriato samples (the only younger clone, 2 years) show the lowest density because the wood is less lignified. The higher density at the time of cutting do not imply a higher density when the biomass is dry, as is checked for the samples of AF2 y Monviso. Around the 50% of the weight correspond to water, so it would be interesting to study the viability of the dry process in field.

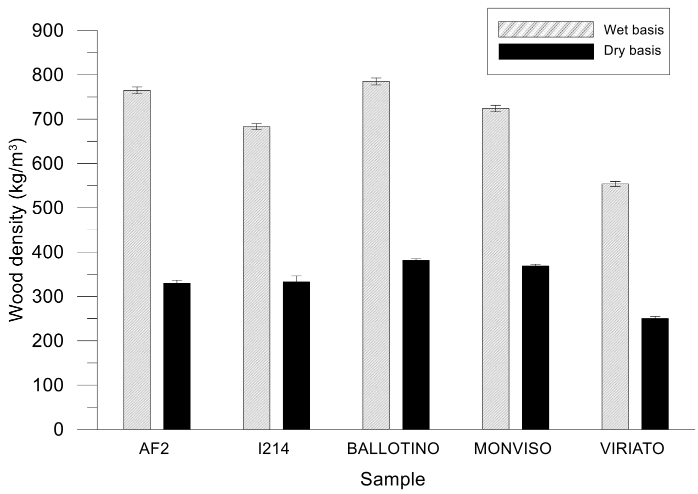

Figure 3. Wood density (kg/m^3) for the different clones in wet and dry basis.

Among 2 year-old clones, that of Viriato is the sample with the lowest density which is due to it is not lignified while for the 3 year-old clones it is Ballotino, in both wet and dry conditions (785 y 381 kg/m^3, respectively). The higher density at the moment of felling does not imply a higher density when the biomass is dry, as it may be checked for the samples of AF2 y Monviso. Around the 50% of the weight correspond to water, so it would be interesting to study the viability of the dry process in field in order to minimize the transport costs.

3.6. Proximate Analysis

Proximate analysis includes the volatile content, ash content and fixed carbon of the fuel, in this case biomass. Regarding volatile content, it has influence in in the reaction velocity whatever was the process: pyrolysis, combustion and/or gasification. In this sense, the design of the biomass processing facilities, i.e., reactors or boilers depends on this parameter.

The results of volatile fraction (%) for all the samples tested are shown in Figure 4. Results obtained for the clones selected in this work are quite high (84.5–87%) compared to those commented in literature, which usually vary from 78.4% to 84.8% [35–37]. No great differences are observed between varieties or age clones, although is considered that the short rotation coppice (SRC) usually shows high volatile content [38,39]. Volatile fraction of crust samples is lower than that wood samples, which is in concordance with its lower heating values (see Section 3.9). Most of the heating value of biomass can be contained in its volatile fraction [40], this fraction could reach up to 80% of the total of the sample. The volatile fraction of biomass used to be higher than in other fuels, e.g., coal (30–50%).

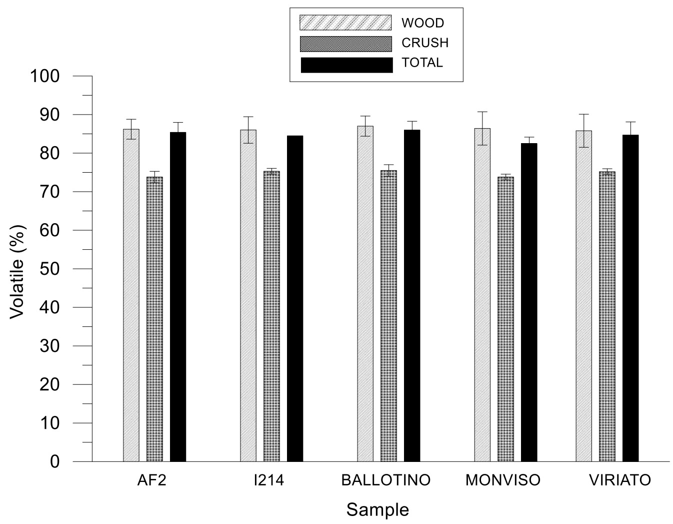

Figure 4. Volatile content (%) in dry basis for the different clones and fractions.

The higher ash content, the lower heating value. Apart from this effect, ash presence favors the deposit formation and heat transfer zones, being all these aspects notable disadvantages and affecting to the plant costs (thermal plant shutdowns for maintenance or periodic cleaning).

Ash content for the wood samples (Figure 5) varies from 0.83% for AF2 to 1.22% for Viriato clone while this content for the crust fractions is quite higher (7.88% for Viriato clone). The biomass ash content commented in bibliography varies from 1.4% and 4.5% [29,40–43] which indicated that the samples selected for this work correspond to high quality biomass which may be penalized by the presence of crust. The higher presence of ashes in crust fractions, and for the young samples, is justified by the lower ratio area/volume and, consequently, its lower biological activity. It is remarkable that the maximum value of this parameter for biomass samples is quite lower than that associated to other fuels such as the coal (5–30%), becoming an advantage for the use of biomass in power generation plants.

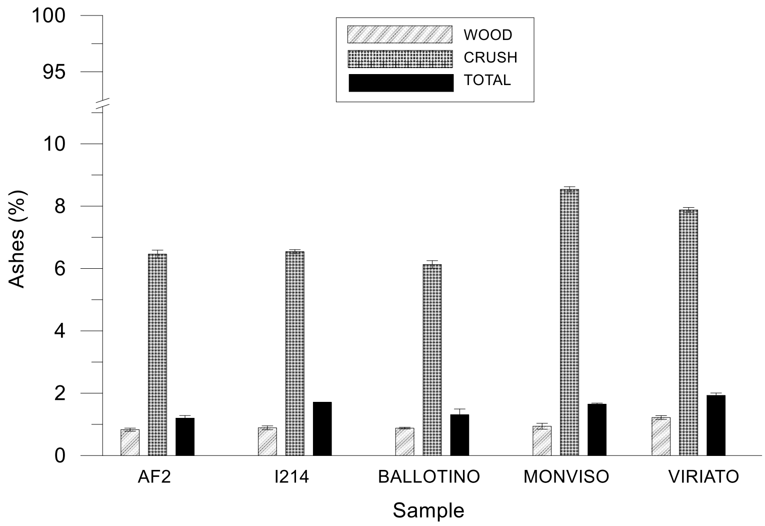

Figure 5. Ash content (%) in dry basis for the different clones and fractions.

The ashes from biomass have two compounds: one intrinsic from composition and other derived from the external contamination (presence of waste material in the feedstock of power plant). Moreover, the ashes analyzed in this work are those generated in the laboratory at 550 °C while the solid waste generated in a thermal plant (ashes and slags) are produced at higher temperatures and, consequently, the composition is not the same than that showed in this work. In this sense, to evaluate its viability of use and economic recovery in depth, the study should be carried out with the solid waste generated in the plant itself.

Volatile matter on convection heating surfaces creates scaling. These compounds are usually alkali metal oxides (K_2O and Na_2O) [44]. Deposition of ashes (e.g., Na_2SO_4, K_2SO_4) via flue gas on the outer tube wall and calcium-based deposit on the inner tube wall by hard water could cause a fouling effect to increase thermal resistance, decreasing the heat transfer rate [45].

The values of fixed carbon content of the different samples analyzed are shown in Figure 6, observing that the values of this parameter of crust fractions are always higher than those of wood. The carbon content has a direct relationship to the heating value (see Section 3.9). Similar values were obtained with the different genotypes selected for this study which indicates the no influence of the age or another sample characteristic.

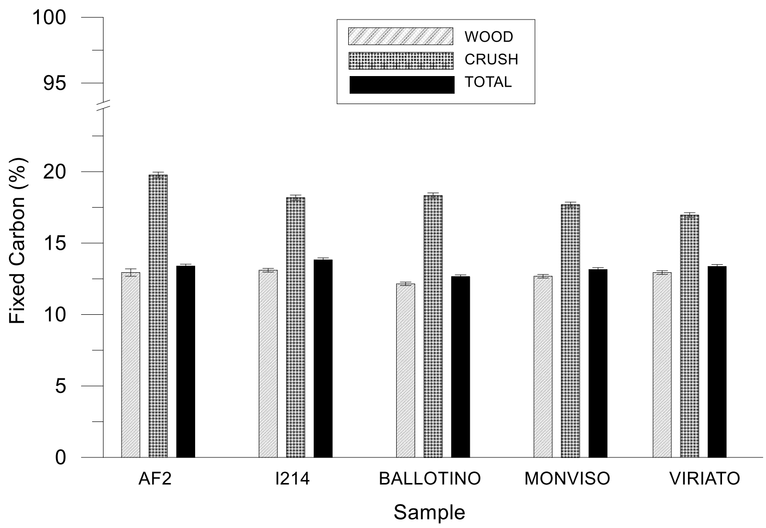

Figure 6. Fixed carbon in dry basis for the different clones and fractions.

3.7. Elemental Analysis

Elemental analysis provides the carbon, hydrogen, nitrogen, sulfur and oxygen content in the fuel. Chlorine, fluorine and bromine can also be included in this analysis. The nitrogen, sulfur and chlorine content of forest biomass is low, a positive factor due to environmental issues (emissions and formation of dioxins) and the implications of the sulfur and chlorine content in the formation of deposits and corrosion in boilers [46]. All results shown are presented on a dry basis in Table 5. In addition, when elemental analysis data on a dry basis is shown, the ash content is included since the oxygen content is calculated by difference to 100 with the rest of the elements (C, H, N, S, Cl) and the content in ashes. In general, and unless otherwise specified, the material studied does not include leaves, since the felling of deciduous species cultivated in short shifts for them to re-grow must be carried out during the vegetative stoppage period.

Table 5. Elemental analysis (ash, C, O, H, N, Cl and S) in percent in dry basis of the different fractions of the clones and weighted total. (-) below detection limit.

	Element	AF2	I-214	BALLOTINO	MONVISO	VIRIATO
		Mean/SD	Mean/SD	Mean/SD	Mean/SD	Mean/SD
Wood	C	49.49/1.20	49.11/1.01	48.93/1.16	49.1/0.97	49.09/0.88
	H	6.36/0.12	6.19/0.10	6.31/0.05	6.05/0.13	6.29/0.12
	O	43.15/1.1	43.63/1.05	43.69/0.99	43.65/0.96	43.16/0.79
	Others (Cl, S, N)	0.16/0.00	0.17/0.06	0.19/0.03	0.27/0.06	0.24/0.03
	Ashes	0.83/0.1	0.89/0.05	0.88/0.07	0.94/0.03	1.22/0.12
	N	0.14/0.02	0.15/0.05	0.16/0.01	0.24/0.03	0.21/0.03
	S	0.02/0.00	0.02/0.00	0.03/0.01	0.03/0.01	0.02/0.00
	Cl	-/-	0/0.00	-/-	-/-	0.01/0.00
Crust	C	48.44/1.25	48.57/0.90	49.33/1.12	46.46/0.97	46.84/1.01
	H	5.77/0.15	5.87/0.09	5.65/0.06	5.41/0.10	5.74/0.15
	O	38.82/1.1	38.59/0.95	38.34/1.12	38.8/0.96	38.77/0.75
	Others (Cl, S, N)	0.5/0.04	0.45/0.11	0.55/0.10	0.78/0.09	0.78/0.10
	Ashes	6.46/0.11	6.54/0.05	6.13/0.09	8.54/0.05	7.88/0.06
	N	0.45/0.03	0.39/0.04	0.5/0.01	0.7/0.03	0.68/0.03
	S	0.05/0.00	0.05/0.00	0.05/0.00	0.08/0.01	0.08/0.00
	Cl	-/-	0.01/0.00	-/-	-/-	0.02/0.00
Biomass sample (wood and crust)	C	49.42/1.20	49.03/0.99	48.96/1.16	48.85/0.97	48.85/0.89
	H	6.32/0.12	6.14/0.10	6.26/0.05	5.99/0.13	6.23/0.12
	O	42.86/1.1	42.90/1.04	43.25/1.00	43.20/0.96	42.69/0.79
	Others (Cl, S, N)	0.18/0.00	0.21/0.07	0.22/0.04	0.32/0.06	0.30/0.04
	Ashes	1.20/0.1	1.71/0.05	1.31/0.07	1.65/0.03	1.93/0.11
	N	0.16/0.01	0.18/0.05	0.19/0.01	0.28/0.03	0.26/0.03
	S	0.02/0.00	0.02/0.00	0.03/0.01	0.03/0.01	0.03/0.00
	Cl	-/-	0.00/0.00	-/-	-/-	0.01/0.00

Elemental analysis of the samples studied is also shown in the Table 5, including mean values and standard deviation of the repetitions made for each sample. Firstly, the nitrogen content varies from 0.1% to 0.7%, values within the typical range of biomass samples. The low content of nitrogen of these samples, compared to other fuels (for example coal), is an advantage for biomass since nitrogen favors the NO_x formation during a combustion process.

The formation of NO_x in the combustion process of whatever fuel, in this case biomass, is mainly due to a thermal mechanism where the high temperature and the presence of nitrogen in the fuel composition are the factors with the highest influence. However, the composition of the fuel in terms of ash, volatile matter and fixed carbon content will also affect the transformation of the released N species. Most solid biofuels obtained from agricultural residual biomass has a high content of volatile matter and a low content of fixed carbon which would reduce the NO_x formation. However, the catalytic effect of ash could be important for some residual biomass that has a high calcium oxide (CaO) content that can give rise to active surfaces capable of catalyzing the reduction of NO and N_2O [47]. The char/ash effect on NO_x destruction was observed during tests in a multi-fuel domestic boiler (40 kW) with poplar pellets, generating very low NO_x production values 47.

The most important information related to the elemental analysis lies in the carbon and hydrogen content because the higher values of these compounds, the higher heating value. The carbon content of the samples varies from 46% to 50% while the range of hydrogen is 5–7%, typical values for biomass. Sulfur content favors corrosion, deposit formation and the production of SO_x. The normal range of sulfur content for coal is 0.5–7.5% and, for this study, the highest value is 0.5% which facilitates its use for energy production. The sample from 2 year-old clone of Viriato showed the highest Cl content, being the values of all samples the typical of biomass. Regarding oxygen content, on one hand decreases the heating value of fuels and in the other hand favors the combustion process because its presence reduces the air necessary in this process. The oxygen percentages of samples studies move between 35–45%.

The most important variations are observed in the nitrogen, sulfur and chlorine contents are summarized in Table 5. Nitrogen varies between 0.35% and 0.95%, sulfur between less than 0.02% and 0.07% and chlorine between 0.004% and 0.01%, generally very low values. On the other hand, the variations of C and H are less significant. Carbon varies between 47.9% and 50.2% and hydrogen between 5.7% and 6.4% [17,43].

3.8. Analysis of Majority and Minority Elements

In this section, the presence of majority and minority elements (different of those corresponding to elemental analysis, C, H and O) is evaluated. From the results showed in Figures 7 and 8 (less than 0.1% the error in the measurements) the following conclusions can be commented:

- Firstly, the majority compounds present in the samples analyzed are: Ca, followed by K, Mg, Si, P and Al (Figure 7a,b). Regarding the crust, Al acquires a relevant importance (Figure 7c,d) which may be due to the fact Al is toxic to plants, being eliminated and becoming part of the crust. Additionally, since Al is part of the clays (land where the plantation is located) it may be deposited in the crust.

Among the minorities' elements (Figure 8a for wood and Figure 8b for crust), the metabolism of plants may be the cause of the high values for Zn because it is a promoter of certain metabolic reactions and serves to activate the enzymatic system.

Therefore, young individuals (for example 2 year-old plants) with higher metabolic activity have a higher content of minority elements, mainly in the fraction of wood. The implications of the composition lie in the hypothetical use of these. Several are suggested:

- Flux material in ceramics, being applied as a flux due to its potassium content.
- The amount of potassium, magnesium and phosphorus present in the ash makes it interesting to use it as a soil nutrient for agricultural use.
- This possible application in agriculture is possible thanks to Ca content of the ashes for correction of acidic soils.
- The low content of heavy metals must be evaluated according to the destination of the ashes (dumping or different uses), taking into account the limits allowed for said destination.
- Na and K, which in combination with S and Cl cause ash deposition and fusion problems and increase corrosion.
- K reduces the melting point of the ashes and can cause jams. It's the high content of this element may be of interest in applications as a flux in ceramic or its use as fertilizers.
- Content of majority and minority elements affects the operation of reactors and boilers (such as in controlling the temperatures of the superheaters) and the maintenance of the plant (periodic cleaning). Other elements such as Mg, Ca, and P increase the melting point of the ash and facilitate the retention of contaminants in them.

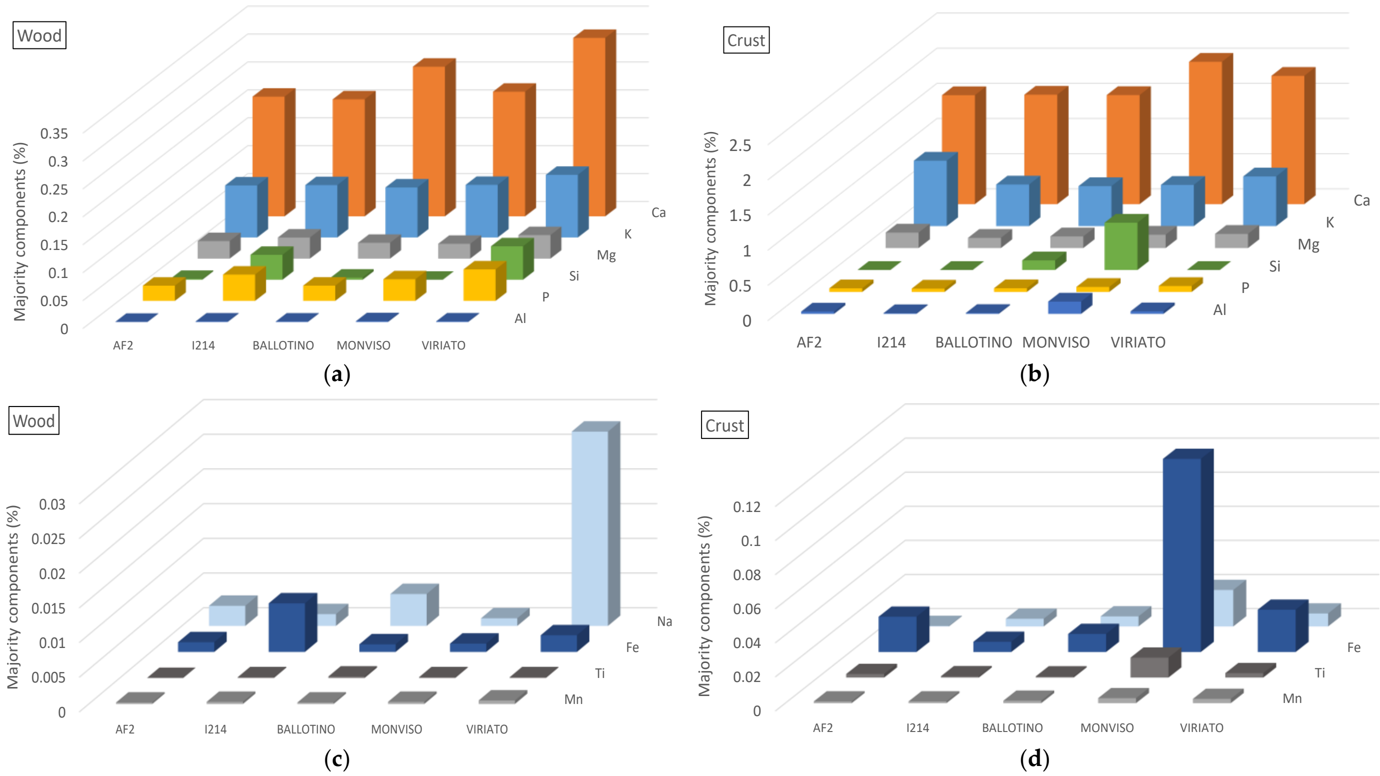

Figure 7. Analysis of majority elements in dry basis for wood (**a**,**c**) and for crust (**b**,**d**).

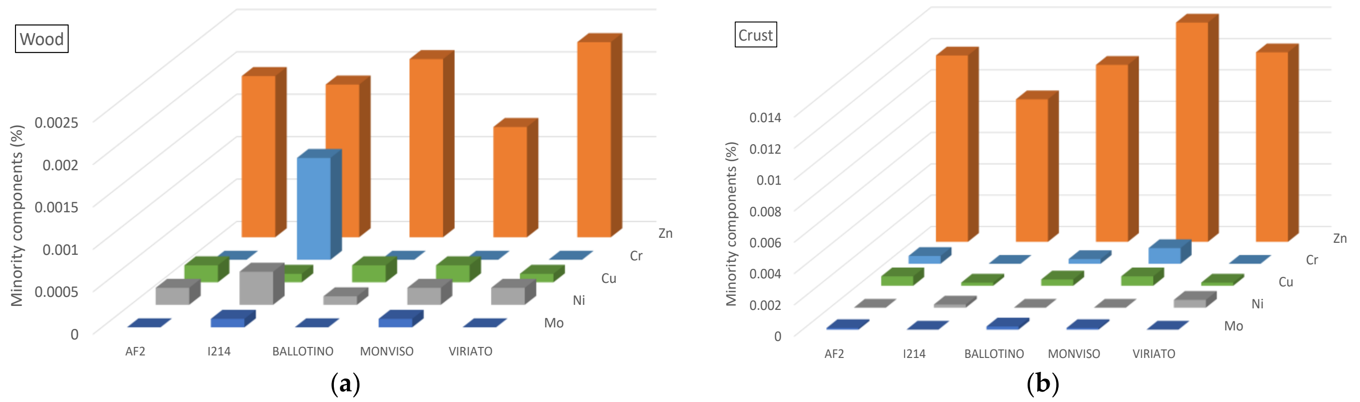

Figure 8. Analysis of minority elements in dry basis for (**a**) wood and (**b**) crust.

3.9. Heating Value

The influence of crust in this parameter is low and, for this reason, values of the total sample are shown in Figure 9. The importance of this parameter mainly lies in the price of biomass. One of the main disadvantages of the biomass is that the values of heating are in the range of 14.5–21.5 MJ/kg while other fuels, i.e., coal, this range is 23–28 MJ/kg.

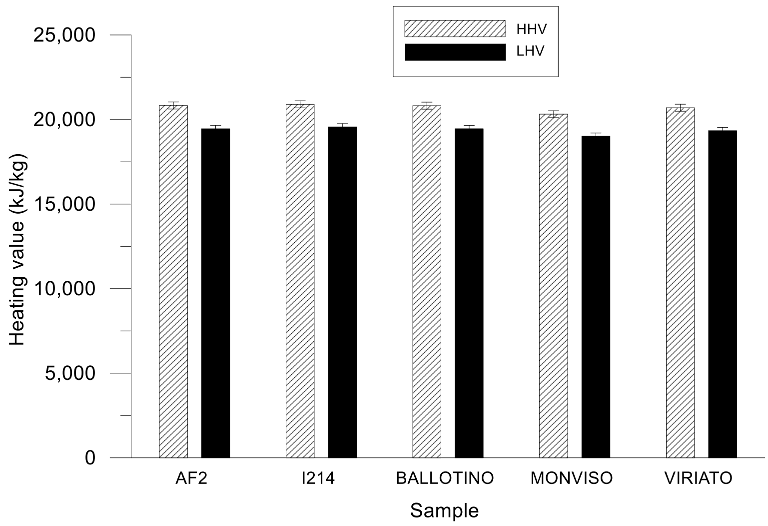

Figure 9. Higher heating value (HHV_v) balanced (crust + wood) and lower heating values (LHVp) for the different clones at dry basis.

All harvested genotypes presented HHV_v and LHV_v which varied between 20.3–20.9 (MJ/kg) and 19.0–19.6 (MJ/kg), both on a dry basis, respectively. Heating values are similar in both age classes (3 years and 2 years), varying its mean value by less than 150 kJ/kg (less than 1% of the value). On the other hand, and within the oldest samples, it is observed that there is a significant decrease in calorific power in the Monviso clone around 600 kJ/kg (≈3%). The comparison of results is facilitated by calculating the calorific value on a dry basis.

Considering the practical use of biomass in a boiler, the lower heating value is more representative because it denotes the energy content available for combustion. The lower values determined for 2 year-old clones would suggest that these genotypes are less suitable. In addition, according to the results of the ash content (Table 5), there are slight differences between the different genotypes. The higher ash and the higher moisture content penalize the heating value of 2 year-old clones (because it has greater biological activity and has not lignified as in the case of 3 year-old). This may be possible due to ash having an inert effect on the heating value [33].

As can be seen in Table 5 and Figures 7 and 8, the values and type of ash for this poplar biomass are very low compared to other types of biomass [48], so this component has lower influence. In the study of Jenkins et al. [49] similar values for volatile fixed carbon and slightly higher values for ash content were obtained with poplar samples. This high ash content would justify the lower HHVv obtained for poplar samples in this work [49]. Other parameter that has influence on the heating value is the moisture in the fuel, which reduces the value of this parameter value compared to that measured at dry basis. The heating values can also be correlated with the carbon concentration among other compounds. According to the bibliography, an increment of 1% in carbon content implies an increase of the heating value by approximately 0.39 MJ/kg [50], which is in the orders of magnitude of the data obtained. As shown in Table 5, the maximum variation of the C content is 0.57% (without considering the deviation of the data), so the carbon content will have an influence lower than 220 kJ/kg between the samples.

3.10. Wood Energy Density (MJ/m^3)

This parameter is calculated from the heating value and the density of the sample. Two types of representations are presented in the Figure 10: one considering the dry wood (0% of humidity) and the other using the humidity at the moment of collection.

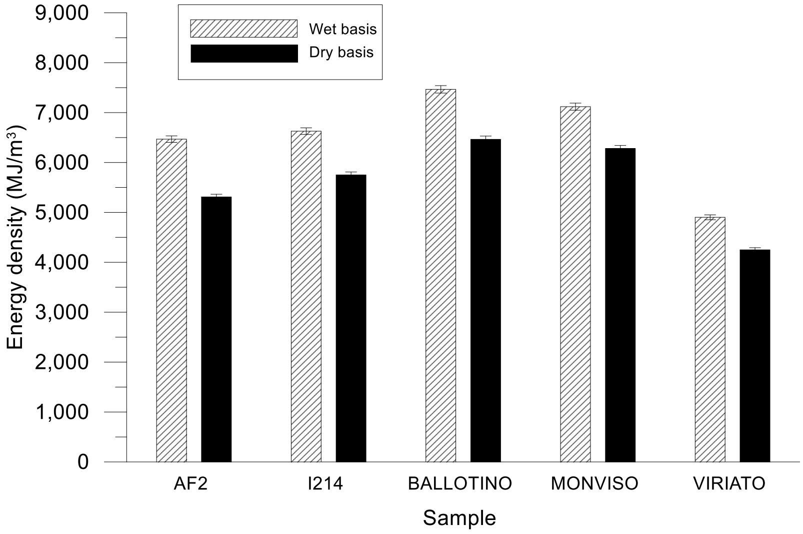

Figure 10. Energy density for the different clones at dry and wet basis.

Regarding to energy density, moisture content can be a limiting factor in biomass transport. The sample of 2 year-old Viriato shows the lowest energy density. In the case of Ballotino and Monviso, although the transport of wet biomass involves a large amount of water in the sample, the energy contained is up to 6465 MJ/m^3 (high value compared to other clones). The transport of this wet biomass may be profitable depending on the costs and benefits, the use to which it will be destined, as well as the benefits and drawbacks that may be generated from the composition of its ashes.

In general, as previously mentioned, 2 year-old clones have a lower energy density and a higher concentration of ashes, so their use should be limited to less demanding applications.

4. Conclusions

In this work, the thermochemical characterization of several *Populus* clones (a species of great interest for its implantation as an energy culture) has been carried out in order to determine which of the clones shows the best properties for its use for energy production. Poplars are well adapted to the Spanish (Mediterranean) climate, and they respond well to local temperatures and light exposure in the growing period. This work provides a wide knowledge of the possible uses of this biomass as fuel in different process of energetic productions.

Crust content in the samples is 10.35% and 9.50%, in dry basis, for 3 year-old samples and 2 year-old samples, respectively. These values are quite low compared to the values reported in literature in other environments, which is an advantage since the possible operation problems associated to this sample fraction is reduced. The youngest clones have higher content of humidity and crust, possibly due to higher biological activity and higher phloem-to-volume ratio.

From the results obtained this study is concluded that the clones grow up in a Mediterranean environment for 3 year-old have a higher heating value, fixed carbon and lower humidity and a greater potential to reduce the problems related to ash. The use of 2 year-old clones is not advisable since the energy density of the wood is very low (although its calorific value per kg is similar) and the moisture content is higher (increasing mass transported without improvement of the total energy content). In this sense, the Viriato clone (2 years) presents higher humidity, high ash content, low density in dry wood and a higher content of minor and major elements, which can cause problems operating and environmental problems. Additionally, 3 year-old samples show higher density values than the Viriatio one, which is justified by their higher lignification of the stem. Heating values are similar in both age classes and are the located in the higher limit of the biomass range.

Notwithstanding the above (advantages of using SRC cultures), it should be taken into account that the clones studied come from crosses of exotic species, which could imply long-term problems, such as alterations in biodiversity (loss of genetic diversity or hybridizations with native species), creation of monocultures, etc. Therefore, it would be advisable to cultivate native species. In addition, it is recommended to use mixtures (multispecific crops) to minimize the impact of diseases and pests.

This knowledge opens paths for the realization of different technical and economic feasibility studies in the future. Additionally, the separately study of wood and crust fractions (usually the total biomass sample is evaluated) provides and added value to this work and it will allow to allocate this biomass, according to its composition, to the most appropriate use in different energy production processes (combustion, gasification, pyrolysis, etc.). Wider research would allow to make production and market simulations of this type of biomass and to evaluate the quality of different biomass raw material for the conversion into electricity and heat.

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