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Characterization of residual biomasses from the coffee production chain and assessment the potential for energy purposes

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10 chain and assessment the potential for energy purposes
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34 ABSTRACT – Chemical quantitative characterization of biomass is relevant for waste to
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36 energy recovery technologies. In the present work, selected agroindustry solid residues
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38 from coffee crops – parchment and coffee shrub, i.e., stem, branches and leaves – were
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40 characterized. Properties such proximate, ultimate and biochemical composition, energy
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42 content, and thermogravimetric analysis, were evaluated. Results showed high values of
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44 higher heating value and volatile matter content. The silica contents are small for all
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46 samples. Additionally, the high content of extractives and lignin, reveal that these residual
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48 biomasses are more suitable for charcoal than cellulose pulp production. The extensive
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50 residue characterization provided valuable data that helped in outcome of the evaluation of
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52 different conversion technologies as being an environmentally friendly alternative,
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54 contributing to sustainable, reliable, carbon-neutral form of modern energy and upgrade the
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5 large quantity of waste generated by the coffee industry into energetically valued residues,
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8 by improving their management.
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11 **KEYWORDS:** Chemical characterization; coffee shrub; waste quantification; waste to
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13 energy
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19 1. INTRODUCTION

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22 Brazil, Vietnam, Colombia and Indonesia are the largest bulk coffee beans
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24 producers in the world, responsible for more than 50 % of world production. The coffee
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26 production chain generates a large quantity of residues from the cherries and shrub. Large
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28 scale around the world. It is estimated that the annual world production of coffee generates
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30 over ten million tons of residues yearly (solid and liquid). This amount excludes the
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32 residues of cultivation (pruning leaves) which are difficult to estimate due to the differences
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34 in agronomic management practices [1]. Organic residues from coffee production represent
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36 a serious source of environmental concern, if discarded inadequately and with poor
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38 management.
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45 With exports amounting to 30.2 million bags of 60 kg in 2017, Brazil is the largest
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47 producer and exporter of bulk coffee beans in the world [2, 3]. The gross amount of bulk
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49 coffee beans (*Coffea arabica* and *Coffea robusta*) produced in Brazil (2017) was 2.78
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51 million tons according to [4], and the total area planted in the country with coffee shrubs
52
53 (*Coffea arabica* and *Coffea robusta*) in 2017 was 2.21 million hectares, where 1.86 million
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55 hectares (84.16 %) were in production [5]. As can be seen in Table 1, Southeastern Brazil,
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5 is the main region of bulk coffee beans production (84.44 % of total bulk coffee beans
6 produced). The environment and climate provide there ideal growing conditions for coffee
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8 shrub.
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13 **Table 1.** Data of estimated amount of planted area, harvested area, total coffee beans
14 produced and residues generated in coffee plantation in Brazil (2016/2017) [4]
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19 Coffee shrub should be periodically pruned and stumped. According to [6], a full-
20 grown coffee shrub weighs on average 15 kg (dry wood). Approximately 25 % of the shrub
21 becomes solid waste in the pruning, which occurs approximately every five years. The
22 pruning frequency depends on the agronomic management practices, production and shrub
23 growing stage. To prune, the secondary and tertiary branches should be cut from the shrub,
24 leaving more space for the primary ones to grow. This rejuvenation should occur after four
25 to five harvests, which means that an average of 32 million tons of residual wood is
26 generated in the from coffee plantations of Brazil annually. To stump, the shrub should be
27 cut down 30 cm in height. The frequency of stumping is linked to the number of shrubs
28 within a given unit of area (planting density): at a sowing density of 2,500 to 3,000
29 shrub·ha⁻¹, the production level will start to decrease after 10 years, at 5,000 shrub·ha⁻¹ after
30 7 years and at 10,000 shrub·ha⁻¹ after 4 to 5 years after planting.
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50 The coffee plantations in Brazil are mostly high-density (5000 shrub·ha⁻¹). Several
51 reports have indicated that coffee beans production may be more suited for high-density
52 plantings; indeed the high productivity, less erosion due to complete land cover, low cost of
53 weeding, better use of the resources, greater efficiency in the workforce, recycling of the
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5 organic material when coffee shrub is harvested [7]. Some evidences suggest that optimal
6 plant density is of about 5,000 shrubs ha⁻¹ for *Coffea arabica*, and no more than 4,000
7 shrubs ha⁻¹ for *Coffea robusta* [7-10].
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14 Furthermore, in bulk coffee beans production, approximately 55 % of the coffee
15 cherry are converted into grain, and the parchment represents 12 % of the fruit on a dry
16 basis [11]. Consequently the estimated production of parchment was 605.81 thousand tons
17 in 2017 in Brazil (December 2016/2017). Therefore, the bulk coffee beans production
18 represents over 2.3 million tons of solid residues being generated per year. As a result of
19 having the greatest bulk coffee beans production, southeastern Brazil is the region with the
20 highest waste generation from coffee plantations, producing more the 80 % of the total
21 amount of waste produced in the country. This amount excludes the leaves (fallen and
22 pruning). However, under normal cultivation conditions, coffee leaves have an average
23 duration of 1.5 years, with defoliation caused by different factors such as inadequate
24 nutrition, water deficiency in the soil, excessive plant burden, disease and crop. When bulk
25 coffee beans are cultivated in full sun, as in Brazil, in the post-harvest period, the leaf
26 defoliation occurs in plants with a normal 30–70 % drop in leaves. Thus, the *Procafe*
27 foundation, in a survey in the state of Minas Gerais (Brazil), estimated that on average
28 5,500 kg (dry basis) per hectare of leaves fall annually in different conditions of *Coffea*
29 *arabica* coffee plantations.
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54 The large amount of waste generated by the agricultural industries is a problem that
55 exists in almost all regions of Brazil. Thus, the waste management is often considered
56 potentially problematic, because its disposal or proper use usually generates high costs that
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5 producers often want to avoid. The thermochemical conversion technologies for recovery
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7 of energy from wastes can play a vital role in mitigating the problems caused by the large
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9 amount of residual waste. In this sense, the residues from bulk coffee beans production can
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11 be used to generate thermal energy to dry agricultural products or to heat animal facilities,
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13 or as fuel to generate mechanical or electrical energy. However, knowledge of the quantity,
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15 physical and chemical characteristics and technologies available for use of residues has
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17 been an hindrance to find an alternative that conserves energy and contributes to
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19 sustainable development.
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26 The concern with the increase of coffee bean productivity has ignored the changes
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28 to the characteristics to the residues provided by the coffee production chain, additionally,
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30 little or partial information exist about its use in the generation of value-added products. In
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32 order to solve some limitations in relation to the use of bulk residual coffee biomass, such
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34 as low energetic density, high content of moisture, high heterogeneity that leads to
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36 difficulties in handling, transport and storage, agricultural / forestry companies and research
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38 centers, suggests solutions for reducing these problems, trough treatments that produce
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40 homogeneous, high yielding, high quality and low cost products, such as biodiesel, biogas,
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42 source of sugars [12], and precursor for production of activated carbon [13, 14].
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49 The aim of this study was to present an extensive characterization of residual
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51 biomasses from the coffee production chain for energy purposes, increasing knowledge
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53 about the alternatives applicable to the energy matrix of countries where the coffee industry
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55 is one of the major agricultural activity, through physical and chemical analyzes that
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57 identify the most important quality indices, the interactions between them, as well as the
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5 quantification of its importance. An extensive characterization of the residues presented in
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7 this work is not readily available in the literature and these results are fundamental tools for
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9 the qualification and quantification of the effects of their properties on conversion
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11 technologies that include thermochemical processes such as pyrolysis, gasification, and
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13 combustion, and physical processes such as briquetting and pelletizing.
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18 2. MATERIALS AND METHODS

19 2.1. *Sampling and preparation for characterization process*

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24 Residues from coffee shrub (*Coffea arabica* L.) cultivation: parchment, leaves and
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26 wood, provided by a rural farm in the municipality of Paula Cândido, MG, Brazil
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28 (20°49'50.0" S 42°55'03.3" W) were used. The plantation was established in 1986, and due
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30 to low productivity, stumping of new plant formation was required. The wood collected
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32 was 11 years old (from after the last stumping period), from a 30-years-old plantation.
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38 The biomasses were ground in an industrial mincing Lippel® brand, and posteriorly
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40 in an electric hammer mill, motor Weg® mark of 10 CV and 3520 rpm, which was coupled
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42 with a screen opening of 2 mm. For samples intended for chemical analysis it was
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44 necessary to further reduce the particle size, using a knife mill type Wiley® Mill Model 4.
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46 The biomasses were finally classified into superposed screen with openings of 40 mesh and
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48 60 mesh according to the American Society for Testing and Materials (ASTM), 1982.
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53 The experiment was conducted according to a randomized design with six
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55 biomasses and two replicates for each characterization. Data were subjected to analysis of
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57 variance (ANOVA). For the large number of tests and variables involved, Bonferroni-
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5 corrected alpha value ($\rho = 0.001$) was employed to reduce the likelihood of spurious
6 correlations. Statistical analyzes were performed on the IBM SPSS® software platform,
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10 2015.

11 12 13 *2.2. Stock estimation of the coffee shrub wood parts.*

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16 The wood samples were previously separated into (I) stem, (II) primary branch and
17 (III) secondary branch according to their diameter, 10 ± 2 cm, 2 ± 1 cm and 1 ± 0.5 cm,
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19 respectively, for individual properties analysis and stock estimation.
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23 24 *2.3. Laboratory procedures for biomass characterization*

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27 An extensive characterization of the solid fuel was performed, evaluating their
28 properties, including proximate and ultimate composition, energy content, several
29 biochemical composition (polysaccharides, lignin, extractives, uronic acids and acetyl
30 group) and thermogravimetric analysis of each residue group.
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38 *2.3.1. Basic density.* The measurement for basic density of wood sample (stem) was
39 determined according to the Scandinavian Pulp, Paper and Board (SCAN-CM) 43:95
40 (1995) standard procedures of 25 disks obtained from different cut sections on the main
41 axis of the shrub. The drying analysis of wood parts of the coffee shrub, (stem, primary
42 branch and secondary branch) with dimensions of 30 cm length and variation of the
43 diameter for each wood part, was conduct in a climate-controlled room with temperature
44 (23 °C–24 °C) and relative humidity (60 %–70 % RH) control. The mass loss of the
45 samples was monitored by periodic weightings until reaching anhydrous mass.
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2.3.2. *Ultimate analysis.* The ultimate analysis shows the content of five major elements: carbon (C), oxygen (O), hydrogen (H), nitrogen (N) and sulphur (S) in the organic phase. The content of these elements was measurement using a Vario Micro Cube CHNS-O equipment with helium as a carrier gas and oxygen as an ignition gas according to the German Institute for Standardization (DIN EN) 15104:2011-04 (2011) standard procedure. The molar ratios of oxygen and hydrogen to carbon were also determined.

2.3.3. *Proximate analysis.* The equilibrium moisture content (EMC) was determined by mass difference. It was considered that equilibrium was reached when the sample weight difference between two successive days was less than the balance accuracy. The volatile matter (VM) analysis was performed according to DIN EN 15148:2010-03 (2010). Ash content (AC) was determined according to DIN EN 14775:2010-04 (2010). Fixed carbon (FC) was calculated as the difference between 100 and the sum of VM and biomass AC. The silica content of the biomasses was measured according to the Technical Association of the Pulp and Paper Industry (TAPPI) T245 cm-98 (1998) and the contents of sodium (Na), iron (Fe), copper (Cu), manganese (Mn), potassium (K), calcium (Ca) and magnesium (Mg) were determined by atomic absorption spectroscopy, according to the SCAN CM 38:96 (1996) procedures. The chloride content was determined by potentiometry using automatic titrator equipped with HI 4107 combination chloride electrode.

2.3.4. *Heating value.* The high heating value (HHV) has determined according to DIN EN 14918:2014-08 (2014) standard procedure, in duplicate, using a bomb calorimeter

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adiabatic IKA300. The net heating value (NHV) of dry matter was determined according to equation (1) of the annex E of the DIN EN 14918:2014-08 (2014).

$$\text{NHV (J}\cdot\text{g}^{-1}) = (\text{HHV (J}\cdot\text{g}^{-1}) - 212.2 * \text{Hydrogen content (\%)} - 0.8 * (\text{Oxygen content (\%)} + \text{Nitrogen content (\%))} * (1 - 0.01 * \text{EMC (\%))} - (24.43 * \text{EMC (\%))} \quad (1)$$

2.3.5. *Chemical composition.* The chemical composition of studied biomass samples was evaluated within the following procedure. The milled samples were extracted successively with ethanol/toluene (1:2 v/v), ethanol and finally water following the TAPPI method T264 cm-97 (1997). This extracted sample (extractive free sawdust) was conditioned in a temperature and relative humidity-controlled room (23±1 °C, 50±2 % RH) until an equilibrium moisture was achieved. The extractions were carried out in duplicate, and the extraction yields were expressed in percentage in relation to the biomasses dry weight. The contents of uronic acids and acetyl groups and anhydrosugars (anhydroglucose, anhydromannose, anhydrogalactose, anhydroxylose and anhydroarabinose) in the extractive-free biomass were determined according to [15],[16] and SCAN-CM 71:09 (2009) standard procedure, respectively. Sugars were measured by a Shimadzu HPLC, coupled to a refractive index detector (RID-10 A), equipped with a Bio-Rad Aminex HPX-87H column (300 x 7.8 mm), and operated at 60 °C with a mobile phase of sulfuric acid 5mM at rate of 0.6 mL min⁻¹. On the extractives-free biomass, the acid insoluble lignin and acid soluble lignin were determined according to TAPPI T 222 om-11 (2011) standard procedure and [17], respectively.

Thermogravimetric analysis was applied to evaluate the gradual rate of mass loss of the biomass as a function of the constant temperature increase. Tests were performed using

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5 a TGA analyzer (SHIMADZU DTG60 Series), by heating a typical sample mass of 4 mg in
6 a purge of nitrogen ($30 \text{ ml}\cdot\text{min}^{-1}$), at heating rates of $10 \text{ }^\circ\text{C min}^{-1}$ with final temperature at
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8 1000 $^\circ\text{C}$.
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10 11 12 13 3. RESULTS AND DISCUSSION 14

15 16 *3.1 Stock estimation of the coffee shrub woods parts* 17

18
19 Table 2 shows stock estimation of the biomass (stem, primary branch and secondary
20 branch) in the coffee shrub.
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25 **Table 2.** Stock estimation of the woods parts (stem, primary branch and secondary branch)
26 in the coffee shrub.
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31 The analysis of Bonferroni presented significant difference between the stem and
32 the branches for diameter and proportion. The stem has greater diameter as it is responsible
33 for sustaining the plant and supporting the weight of the branches with its foliage and fruit.
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35 The coffee shrub represents on average $8.88 \text{ kg wood}\cdot\text{coffee shrub}^{-1}$, the greater
36 contribution is from the stem, followed by secondary branches and primary branches,
37 respectively. The branches represent more than 50 % of the total weight of the shrub, a fact
38 that explains the great importance of the branches in the structure of the system, as it is on
39 which the fruits grow. The growth of the shrub is influenced by age, planting density,
40 cultural practices and weed competitions [7]. The pruning of the shrub occurs
41 approximately every five years to increase the shrub productivity [6]. For energy, the
42 transport of the raw material is a fundamental stage in the chain of energy production. In
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5 this way, the stem provides more amount of stacked biomass than the branches, as a result
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7 of the significant difference between the densities.
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10 3.2 Characterization of residual biomasses from the coffee production chain 11 12 13

14 Table 3 shows a chemical analysis of the residual biomasses from the coffee
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16 production chain.
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19 **Table 3.** Properties of residual biomasses from the coffee production chain.
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23 3.2.1 Basic density of coffee wood. In the average value of basic density of coffee
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25 wood (598.7 kg m^{-3}), negligible variations between the base and the top of the stem were
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27 observed. For energy, high wood density is preferred, resulting in higher mass production
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29 for a given volume of wood [18]. Operational advantages, such as gains in harvesting and
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31 forest transport processes can be achieve, due to the fact that larger volumes of harvested
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33 wood will generate greater specify mass values [19]. According to the measures suggested
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35 by [20], wood basic density for charcoal production should exceed $500 \text{ kg}\cdot\text{m}^{-3}$. The value
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37 found for coffee wood is similar to values reported in the literature for Eucalyptus wood,
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39 that presents basic density between 436 and $668 \text{ kg}\cdot\text{m}^{-3}$ for the species *Eucalyptus pellita*,
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41 *Eucalyptus urophylla* and *Eucalyptus grandis*, traditionally used for energy conversion,
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43 including firewood and charcoal [21].
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50 3.2.2. Ultimate analysis. The biomasses collected are basically composed of carbon
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52 (50.26 \% – 54.41 \% , dry basis), hydrogen (6.13 \% – 6.59 \% , dry basis) and oxygen (35.52
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54 \% – 42.29 \% , dry basis). Small amounts of nitrogen and sulfur were also observed. Biomass
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56 with high values of carbon and hydrogen, contributes the most to the calorific value of the
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5 fuel [22]. The energy generated by thermal reactions is associated with the enthalpy of
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7 carbon, hydrogen and sulfur [23]. The presence of nitrogen and sulfur in the biomass have a
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9 direct impact on the environmental pollution, due to the formation of harmful oxides (NO_x ,
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11 SO_x) from volatile compounds [24]. The content of sulfur observed in the elemental
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13 composition was low (0.20 %–0.43 %). Generally, the S content in biomass varies in the
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15 interval of 0.01 %–2.3 % [25].
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21 The coffee shrub is highly N-demanding, the nitrogen requirements increases with
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23 shrub age especially at the beginning of grain production. If there are not limiting factor,
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25 the nitrogen will promote rapid plant development specifically through the increase in
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27 number of plagiotropic branches per shrub, number of nodes per branch, and number of
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29 fruiting nodes, flowers and leaves per node, which, taken together, are associated with
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31 higher yields in coffee beans [26, 27]. Hence the coffee shrub presents high potential for
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33 nitrate assimilation in leaves as well as in roots. That is the reason of the highest levels of
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35 nitrogen in leaves with significant difference between the other biomasses. The supporting,
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37 slowly growing parts have the lowest nitrogen content. The nitrogen content in biomasses
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39 varies in the interval of 0.10 %–12 % [25, 28]. The values of nitrogen and sulfur found in
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41 this study are similar to other biomasses used for energy, which are environmentally more
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43 advantageous than other sources of thermal energy such as mineral coal.
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50 The molar ratios of oxygen and hydrogen to carbon for the residues studied are
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52 shown in Figure 1. Oxygen is generally present in plant-based fuels, and its presence
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54 decreases the calorific value [29]. Therefore, low H/C and O/C ratios are desirable for the
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56 use of biomass for energy. The samples with low O/C ratio, also have more energetic
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5 content because C-C bonds have higher chemical energy than C-O bonds [30]. In the
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7 biomasses collected, higher O/C ratio can be observed in the primary branch (O/C = 0.63)
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9 with no significant difference among biomasses. In H/C ratio, secondary branch and stem
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11 have the highest value (H/C = 1.48), no significant difference between the biomasses were
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13 found for this property. Parchment appears to have a low value for the heating value
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15 considering the relatively high O/C ratio. This fact may be also associated with high AC.
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17 According to [22], higher proportion of oxygen, hydrogen and inorganic elements,
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19 compared with carbon, tend to decrease the HHV of the fuel.
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26 *3.2.3. Heating value.* [31], reported that heating value is one of the most important
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28 parameters for energy modeling and simulation in thermochemical conversion processes.
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30 For the HHV, Table 3 shows mean values between 18.30–19.45 MJ·kg⁻¹ (dry basis) similar
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32 values are found in literature (18.60–21 MJ·kg⁻¹, dry basis) for residues from coffee
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34 production chain and are analogous to biomasses commonly used in energy generation [6,
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36 32, 33]. NHV shows mean values between 14.11–16.10 MJ kg dry⁻¹. Primary branch has
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38 the higher value of NHV with no significant difference with the other biomasses, mainly
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40 due to its low moisture content and its high HHV, influenced by low AC and mineral
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42 composition. (Table 3).
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48 **Figure 1.** Molar ratios of hydrogen and oxygen to carbon and high heating value for
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50 studied residual biomasses from the coffee production chain
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53 *3.2.4. Proximate analysis.* The proximate analysis aims to quantify the moisture,
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55 volatiles (condensable and non-condensable), fixed carbon and ash biomass content. The
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57 FC content is of special interest since this indicates the potential for charcoal generation
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5 from devolatilized biomass. The FC content in the samples varies in the interval of 14.62
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8 %–21.23 %; secondary branch presents the highest values of FC content with no significant
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10 difference among the biomasses. The biomasses studied presents high values of FC, similar
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12 to FC content mentioned in the literature for biomasses more commonly used in energy
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14 generation, such eucalyptus wood [34, 35]. For VM, the range of values was 74.07 %–
15
16 83.70 %. The primary branch presents the highest volatile matter content (83.7 %),
17
18 significance difference between the other biomasses, and similar to solid fuels as
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20 eucalyptus (82.62 %) and bamboo (84.65 %) [36, 37]. Solid fuels with high VM and low
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22 FC content are more susceptible to thermal degradation [38], requiring less length of time
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24 on a thermochemical process, making the biomass degradation faster compared to fuels
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26 with high FC and low VM content.
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33 Ash is the inorganic solid residue left after the fuel is completely burned [39]. In the
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35 data obtained for ash content, it was observed that the residual biomasses from the coffee
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37 production chain had low ash contents in the range of 1.67 %–4.33 %, except for the
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39 parchment and leaves, which had higher values of 5.84 % and 7.17 %, respectively.
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41 According to [40], [41], in the coffee production chain, the residues from the coffee cherry
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43 typically generate significantly more AC than the coffee woody biomasses, supporting the
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45 data obtained. Few results of coffee shrub leaves have been reported; however, studies from
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47 leaves of different species show that ash content is significantly high compared to the tree
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49 and shrub wood from which it comes: for example [42] reported $16.8 \text{ g}\cdot\text{kg}^{-1}$ - $67.8 \text{ g}\cdot\text{kg}^{-1}$
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51 AC of leaves in different trees and shrub species.
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5 The mineral composition of ash (Table 3) shows that potassium (K), calcium (Ca),
6 chlorine (Cl) and magnesium (Mg) present dominants levels in the ashes, and manganese
7 (Mn), iron (Fe), copper (Cu) and sodium (Na) appeared in small quantities. The values of
8 the minerals showed significant difference in the analysis of Bonferroni between the
9 biomasses for some of the samples. Stem bark, parchment and leaves were the biomasses
10 with more significant difference in the minerals content analysis, this is because the
11 mineral concentration in crop-related biomass is strongly influenced by the type of biomass
12 (herbaceous biomass, wood, fruit and crop residues), and also the harvest time and
13 fertilization practices [43]. The parchment shows the highest content of K (12.09 g kg⁻¹)
14 followed by the leaves. However, these residues and the stem present the lowest values of
15 Cl, 3.16, 4.36 and 3.08, g kg⁻¹ respectively. The stem also evinces low content of K (4.06 g
16 kg⁻¹) as the stem bark (2.94 g kg⁻¹) does.

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35 These minerals indicate potential ash-related problems at high or moderate thermal
36 conversion temperatures [39, 44-48]. The release of Cl and K is a main concern due to their
37 effect on corrosion when biomass is combusted or gasified [49, 50]. They also affect the
38 deposit formation or fouling of heat transfer surfaces [51, 52] and deactivation of Selective
39 Catalytic Reduction (SCR) [53]. Emissions of hydrogen chloride (HCl), methyl chloride
40 (CH₃Cl), Cl₂, or alkali chlorides, mainly potassium chloride (KCl), sodium chloride (NaCl),
41 and calcium chloride (CaCl₂) are not desirable [54-56]. It is preferable to have a chloride
42 content at or below 0.2 % to prevent ash fouling in the thermochemical processes [57].
43 Furthermore, the literature report that in the biomass thermochemical conversion processes,
44 Cl is primarily released during the devolatilization [58]. [59] found that 60 – 80 % of Cl
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5 contained in woody biomass are released during the devolatilization phase in a fixed bed
6 reactor at low temperature. [32], [60] and [61] also observed the reduction of Cl during low
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8 temperatures pyrolysis by 20 %–50 % or more.
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13 The silica contents are quite small for all biomass samples (0 %–0.4 %). The
14 influence of the silica on combustion and gasification processes has been reported at
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16 temperatures higher than 873°C because of the ash deposition propensity in thermal fuel
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18 conversion systems. The presence of minerals increase both, the tendency for ash particles
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20 to stick to heat transfer surfaces and the subsequent rate of strength build-up in ash
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22 deposits. These operational problems are closely related to the chemical composition of the
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24 AC. The gasification process requires a feedstock with less than 5 % ash content, preferably
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26 less the 2 %, in order to prevent the formation of clinkers [62]. To mitigate the negative
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28 effects of minerals in thermochemical conversion processes, [63] suggested a pre-treatment
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30 to reduce their concentration in the fuel, e.g. fuel leaching.
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39 *3.2.5. Chemical composition.* Another important characteristic of biomass is the
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41 composition in terms of the main structural chemical compounds. Data of chemical
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43 composition is presented in Table 3. The dried biomass is composed mainly of about 40 %
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45 to 60 % of cellulose (composed of units of Anhydroglucose linked by glycosidic bonds β 1-
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47 4), 15 % to 30 % of hemicelluloses (matrix polysaccharides) and 4 %–35 % of lignin
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49 (cross-linked phenolic polymers) [39, 64]. However, residues from coffee production chain
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51 contain several other components, including lipids, tannin, polyphenols and nitrogenous
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53 compounds [65-67]. These minor components were not evaluated in this study, but were
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55 considered in the mass balance presented in the Table 3.
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5 The carbohydrate fraction range for the studied samples were 17.90 %–33.25 %;
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7 5.30 %–14.55 %; 0.90 %–2.50 %; 0.90 %–3.30 %; 1.35 %–4.50 % for anhydroglucose,
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9 anhydroxylose, anhydrogalactose, anhydromannose and anhydroarabinose, respectively.
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11 These values are within in the ranges found in studies carried out for biomasses used in
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13 energy production, where the anhydroglucose represent, on average, 46.6 % of the chemical
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15 composition of biomass, varying from 44.5 % to 50 %, the anhydroxylose are the dominant
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17 fraction of the hemicelluloses and represent 10.8 % to 13.2 %, on average of 12.2 % of the
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19 biomass. The other carbohydrates (anhydrogalactose, anhydromannose and
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21 anhydroarabinose) contributed with approximately 0.7 %, 0.6 % and 0.2 %, respectively
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23 [68].
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30 The chemical composition of the biomass exerts a great influence on the results of
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32 energy conversion, affecting the thermogravimetric performance of the process. The
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34 hemicelluloses are more susceptible to the reactions of thermal degradation because of the
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36 presence of hydroxyls connected to its main chain and the absence of crystalline
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38 agglomerates [69]. The branched chains of the hemicelluloses and cellulose are easily
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40 degraded at low temperatures, having maximum peaks loss at approximately 275°C for
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42 hemicelluloses and 350°C for cellulose [70].
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48 For lignin, higher content in biomass leads to more sustainable biofuel production,
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50 because lignin is the chemical component that has a greater thermal stability due to the C-C
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52 bonds between monomeric units of phenyl-propane, and consequently has more stability in
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54 its aromatic matrix contributing for charcoal and products like methanol and bio-oil
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56 formation [71]. The acid insoluble lignin content of the samples evaluated in this study
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5 varied from 24.52 % to 40.98 % and soluble solids from 2.07 % to 3.59 %, similar to the
6 reported values for soluble and insoluble lignin from biomasses used in energy production
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8 such *Eucalyptus grandis*, *Eucalyptus globulus*, *Eucalyptus dunnii* and *Eucalyptus urophylla*
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10 [72], and higher values than those reported in the literature for *Coffea arábica* residues
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12 [40].
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18 The total extractive content ranged from 10.57 % to 24.72 %. Leaves of the shrub of
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20 *Coffea arábica* present a total extractive significantly higher than the other lignocellulosic
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22 materials (Table 3). The high extractive content of the leaves (24.72 %) is mainly due to the
23
24 residual fraction of amino acids, sugars and mucilage of low molar mass not removed
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26 during the milling of the biomass, because the extraction with ethanol / toluene only
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28 extracts substances such as waxes, fats, resins, phytosterols and non-volatile hydrocarbons
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30 [73]. The lowest levels of total extractives were found in the samples of the coffee shrub
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32 wood, corresponding to approximately 50 % of the total extractives verified for the leaves.
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34 Because of high extractive content its use in processes such as the production of cellulose
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36 pulp is not attractive due to the increase in the expense of reagents.
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43 The extractives play an important role in the use of biomass, because they influence
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45 the physical and energetic properties. Depending on their thermal stability, these substances
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47 can contribute to the increase in the yield of charcoal. Some of the extractives are volatile
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49 and therefore they are important in the direct burning of the biomass, because they react
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51 faster and help to maintain the combustion flame. For the production of charcoal, the high
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53 volatile extractive content in the biomass is detrimental because it provides lower
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5 gravimetric yield in charcoal due to the degradation of these substances at low temperatures
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8 [74].
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11 *3.2.6. Thermogravimetric analysis.* Figure 2 shows the thermal behavior of the
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13 residual biomasses of the coffee production chain by Thermogravimetric analysis (TG) and
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15 Differential thermogravimetric analysis (DTG).
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19 **Figure 2.** TG (a) and DTG (b) of the residual biomasses of the coffee production chain.
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22 It is observed that the thermal degradation profiles of the biomasses were similar,
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24 with small differences in the temperatures corresponding to the maximum peaks of the
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26 curve, mainly related to the degradation of the hemicelluloses and cellulose. The
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28 thermogravimetric data (TG) curves and the first derivate data (DTG) curves, usually show
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30 three bands of thermal degradation, which the first one is attributed to the drying of the
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32 biomasses and the other two to the degradation of its main components; it should be
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34 emphasized that each biomass components degrades in different temperature ranges. The
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36 second temperature range corresponds mainly to the thermal degradation of the
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38 hemicelluloses and of cellulose and lignin in smaller proportions. The third thermal
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40 degradation range was then initiated, this temperature range corresponded mainly to the
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42 degradation of the cellulose. The loss of mass for the cellulose needs a greater amount of
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44 energy than the hemicelluloses, due to the depolymerization of the cellulose chain and the
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46 breakdown of its monomer [75], that is the reason the degradation of the cellulose occurs
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48 after the degradation of the hemicelluloses. The degradation peak of lignin is absent, due to
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50 the fact that its thermal decomposition occurs in a wide temperature range [69, 76]. The
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52 table 4 shows the measurements of the mass losses (%) obtained for each biomass,
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5 according to the temperature ranges from T_i (initial temperature) to 600°C, with intervals of
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8 100°C.
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10 **Table 4.** Values of mass loss of biomasses in function of the temperature ranges, in
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12 percentage.
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16 As presented in Figure 2, the combustion process of the samples could be divided
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18 into two stages. The first stage extended from 33°C–127°C; 23°C–105°C; 32°C–107°C;
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20 31°C–101°C; 27°C–121°C; 25°C–102°C for leaves, primary branch, secondary branch,
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22 stem, stem bark and parchment, respectively, which represented the dehydration by
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24 evaporation. The second stage was from 233°C–424°C; 243°C–380°C; 237°C–422°C;
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26 242°C–384°C; 233°C–464°C; 280°C–364°C for leaves, primary branch, secondary branch,
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28 stem, stem bark and parchment, respectively, which represent the liberation of the volatile
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30 compounds. A similar phenomenon was shown in the combustion characteristics of oil
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32 palm fiber and eucalyptus in torrefaction [77]. From Table 4, the mass loss percentage of
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34 the first and second stage in the total mass loss was approximately 8.04 % and 45.02 %;
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36 13.76 % and 58.00 %; 7.63 % and 55.99 %; 9.73 % and 46.00 %; 7.04 % and 64.01 %; 8.00
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38 % and 50.57 % for leaves, primary branch, secondary branch, stem, stem bark and
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40 parchment, in the first and second stage, respectively. As coffee shrub residues are
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42 biomasses, the main composition of the biomasses are cellulose, hemicelluloses and lignin.
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44 Therefore, the combustion of coffee shrub residues corresponds to the combustion of other
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46 biomasses. Cellulose rapidly decomposes between 300°C and 350°C; lignin decomposes
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48 between 410°C and 540°C and hemicelluloses decompose between 198°C and 398°C [76-
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50 78]. Therefore, the mass loss in the second stage of the thermal degradation samples was
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5 because of the decomposition of cellulose and hemicelluloses. The stem and primary
6 branch of the coffee shrub present higher mass losses in the second stage. Probably these
7 biomasses have higher rates of cellulose crystallite. The opposite is observed for leaves,
8 which have the lowest degradation rate and are responsible for the greatest residual mass.
9

10 11 12 13 14 15 16 3.3 Biomass potential for energy purposes 17

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19 Alternative routes for the waste use have been continuously studied and proposed to
20 generate attractive and competitive products, such as solid. Liquid and gaseous fuels
21 (briquettes, pellets, charcoal, bio-oil, biogas), as well as several chemical products, such as
22 natural antioxidants, enzymes, vitamins, cellulose, lipids, proteins, and pigments. Knowing
23 the characteristics of the biomass is a very important factor to understand its influence on
24 the appropriate process of energy conversion. According to the data obtained, the following
25 section describes the effects of the properties of biomasses evaluated in thermochemical
26 and physical processes, as well as their impact on operational and economic parameters:
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- 39 • For direct combustion, wood with high basic density ($>500 \text{ kg}\cdot\text{m}^{-3}$) results in more
40 concentrated fuel energy, due to the greater mass of fuel contained in the same unit
41 volume [79]. In this sense, coffee wood is a desirable material for charcoal production.
42 In addition, the charcoal density will also be higher, resulting in greater strength and
43 higher energy per volume.
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- 45 • High volatile content shows high potential for bioenergy production through the direct
46 conversion of raw material [80]. Charcoal and ash are the main residues obtained from
47 the thermochemical conversion processes. The high volatile content of the stem and
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5 primary branch of the coffee shrub, as well as its low percentage of ash compared to the
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7 other evaluated biomasses make them desirable as feedstock for combustion.
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- 10 • Woody parts of the coffee shrub have high economic potential for energy applications.
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12 The low moisture content reduces transport and storage costs [81]. Additionally, the
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14 energy consumption in the drying stage when subjected to processes such as
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16 gasification, combustion and pyrolysis, decrease.
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- 19 • For the production of bio-oil by fast pyrolysis process, the biomass is subjected to high
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21 temperatures and short vapor residence time. High ash content generates secondary
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23 vapor cracking, reducing the bio-oil quality and liquid yield. However, the presence of
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25 inorganic components such as potassium favors the formation of charcoal [62]. As a
26
27 result, leaves and parchment are desirable biomasses for fast pyrolysis process.
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- 30 • During the processes of combustion, the sulfur is converted into H₂S and SO₂, which
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32 are strong sources of contamination. In this sense, leaves of the coffee shrub are the
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34 least qualified because of the higher content of sulfur. In addition, the sample has the
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36 highest nitrogen content, resulting in the formation of nitrous oxides.
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- 39 • For the charcoal production, biomass with lower fractions of cellulose and
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41 hemicelluloses should be preferred. The parchment of coffee cherry, stem, primary and
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43 secondary branch of coffee shrub experienced a greater thermal degradation than the
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45 other biomasses at low temperatures, probably, due to the high anhydrosugars content
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47 in its chemical composition
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- 50 • The high content of cellulose and high calorific value of the parchment of the coffee
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52 cherry makes it an attractive biomass for use as a direct combustion material.
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- Waste of the coffee production chain are desirable materials for the densification processes, due to their lignin content and humidity, conditions that favoring agglomeration [82]. Briquettes increase energy density of waste materials and reduce storage and transportation, desirable factors for the energy industry.

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The literature does not provide enough information of the evaluated biomasses due to the complexity relation of the sample properties and the conversion processes. However, now it is possible to create a database that allows to classify the energetic potential of the waste from coffee production chain based on its physico-chemical characterization.

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4. CONCLUSIONS

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Residual biomasses from the coffee production chain could be classified as suitable feedstock for thermochemical conversion processes with low moisture content, carrying an average higher heating value, and volatile matter content. Additionally, it was also found, that ash composition is not detrimental to use and low sulfur content corresponding to good environmental performance. The composition of residual coffee shrub biomasses will lead to good product quality for charcoal. Therefore, the characterization of the samples shows that the thermochemical conversion and densification technology is an environmentally friendly alternative. It can be used to upgrading the large quantity of waste generated by the coffee industry into energetic valued residues thus improving their management.

51 52 53

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Table 1. . Data of estimated amount of planted area, harvested area, total coffee beans produced and residues generated in coffee plantation in Brazil (2016/2017) [4]

Region	Planted area (ha·10 ³)*	Harvested area (ha·10 ³)*	Total coffee produced (t·10 ³)*	Residues generated (t·10 ³)	
				Wood	Parchment
Brazil	2270	1914	2777	31654	607
North	90	78	154	1286	34
Northeast	165	148	184	2449	40
Southeast	1942	1621	2345	26795	512
South	46	46	72	762	16
Central-west	27	22	23	362	5

Table 2. Stock estimation of the woods parts (stem, primary branch and secondary branch) of the coffee shrub.

Estimation	Wood Parts of coffee shrub			Total
	Stem	Primary Branch	Secondary Branch	
Diameter (cm)	9.8*	2.3	1.8	
Biomass (kg·coffee shrub ⁻¹)	4.10*	2.24	2.54	8.88
Biomass (%)	46.17*	25.22	28.61	100

*significant difference, using a Bonferroni-corrected alpha value (p=0.001)

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Table 3. Properties of residual biomasses from the coffee production chain

Components	Biomasses						SD ^c
	Leaves	Primary branch	Secondary branch	Stem bark	Stem	Parchment	
<i>Basic density (kg m⁻³)</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	598.7	<i>nd</i>	-
<i>Ultimate elemental^b (wt % dry)</i>							
C	53.97	50.31	51.82	54.41	50.64	50.69	1.80
H	6.55	6.13	6.40	6.59	6.12	6.23	0.21
O	35.50*	42.28	40.06	36.66*	41.16	42.05	2.87
N	3.54*	0.92	1.51	2.13*	1.86	0.82	1.00
S	0.43*	0.36*	0.21	0.21	0.21	0.20	0.10
H/C	1.46	1.46	1.48	1.45	1.48	1.45	0.01
O/C	0.49*	0.63	0.58	0.50*	0.62	0.61	0.06
<i>Proximate composition(wt %)</i>							

5	EHM	16.35	8.70*	9.28*	18.11	10.96	11.09	3.88	
6	VM ^a	74.71	80.62*	75.31	75.63	83.70*	74.07	3.90	
7	FC ^a	18.12	16.95*	21.23	20.03	14.62*	20.09	2.45	
8	AC ^a	7.17*	2.42*	3.45*	4.33*	1.67*	5.84*	2.08	
9	Silica (% of ash)	0.10	0.10	0.10	0.40*	0.15	0.35*	0.14	
10	<i>Minerals (g kg dry⁻¹)</i>								
11	Ca	4.65	4.49	6.41	20.96*	6.29	3.73	6.55	
12	Fe	0.18	0.05	0.11	0.57*	0.07	0.24*	0.19	
13	Mn	0.03	0.04	0.02	0.01	0.01	0.03	0.01	
14	Mg	2.05*	1.17	1.68	2.23*	1.07	1.77	0.46	
15	Cu	0.05	0.02	0.04	0.06	0.02	0.04	0.02	
16	K	10.86*	6.74*	7.96*	2.94*	4.06*	12.20*	3.65	
17	Na	1.19*	0.36*	0.69	0.95	0.68	0.73	0.28	
18	Cl	4.36	7.26	6.80	5.98	3.08*	3.16*	1.83	
19	<i>Heating value (MJ kg dry⁻¹)</i>								
20	HHV	19.45	19.20	19.20	19.20	19.00	18.30*	0.40	
21	NHV	14.68	16.10	15.92	14.11*	15.44	14.81	0.77	
22	<i>Chemical composition (%)</i>								
23	Extractive	24.72*	13.09	13.95	12.19	10.58	21.95*	5.80	
24	Insoluble Lignin ^b	35.52	26.73	29.32	40.98	27.33	24.52*	6.26	
25	Soluble Lignin ^b	3.59*	3.12*	2.93	2.19	2.24	2.07	0.61	
26	Total Lignin ^b	39.11	29.85*	32.25	43.17	29.57*	26.59*	6.37	
27	AnhydroGlucose ^b	19.65*	33.25	29.05	17.90*	31.65	29.60	6.46	
28	AnhydroXylose ^b	5.30*	11.85	10.30	6.25*	12.20	14.55	3.61	
29	AnhydroGalactose ^b	2.50*	1.15	1.45	1.20	0.90*	1.65	0.56	
30	AnhydroMannose ^b	1.10	2.55*	1.70	0.90	3.30*	1.00	0.97	
31	AnhydroArabinose ^b	4.50	1.55	2.90	4.25	1.35	3.45	1.33	
32	Uronic acids ^b	4.80	3.80	4.70	5.20	3.30	5.50	0.84	
33	Total sugars ^b	37.85*	54.15	50.10	35.70*	52.70	55.75	8.70	
34	Acetyl group ^b	1.00	1.8	1.8	1.00	2.80*	2.85*	0.82	
35	<i>Others^b</i>	14.87	11.78	12.40	15.80	13.26	8.97*	2.42	

^adry basis. ^bdry ash free basis. ^cStandard deviation. *nd*-not determined. EHM-Equilibrium Hygroscopic Moisture. VM-Volatile matter. FC-Fixed Carbon. AC-Ash content. HHV-Higher Heating Value. NHV-Net Heating Value.

*significant difference, using a Bonferroni-corrected alpha value (p=0.001)

Table 4. Values of mass loss of biomasses in function of the temperature ranges, in percentage

Biomasses	Temperature rates (°C)						Residual mass (%)
	T _i - 100	100- 200	200- 300	300- 400	400- 500	500- 600	
Mass lost (%)							
Leaves	8.04	1.85	16.94	28.08	9.47	3.16	32.46
Primary branch	13.76	0.92	18.68	39.32	6.34	4.90	16.08
Secondary branch	7.63	1.08	19.45	36.54	6.02	3.00	26.26
Stem Bark	9.73	1.49	14.22	31.78	10.17	3.13	29.47

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Stem	7.04	0.82	17.66	46.35	6.86	4.99	16.00
Parchment	8.00	4.31	24.80	25.77	7.61	4.44	25.07
SD ^a	2.48	1.31	3.52	7.65	1.71	0.94	6.84

^aStandard deviation

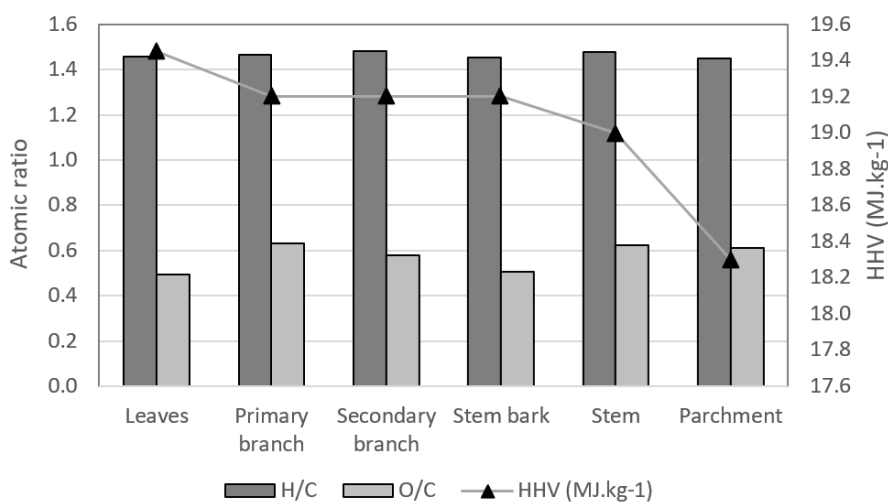


Figure 1. Molar ratios of hydrogen and oxygen to carbon and high heating value for studied residual biomasses from the coffee production chain.

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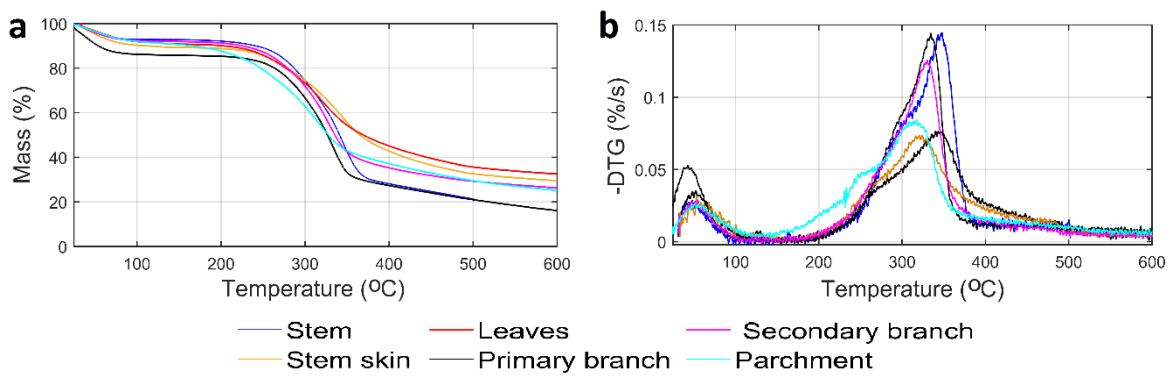


Figure 2. TG (a) and DTG (b) of the residual biomasses of the coffee production chain.

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Table 1. . Data of estimated amount of planted area, harvested area, total coffee beans produced and residues generated in coffee plantation in Brazil (2016/2017) [4]

Region	Planted area (ha·10 ³)*	Harvested area (ha·10 ³)*	Total coffee produced (t·10 ³)*	Residues generated (t·10 ³)	
				Wood	Parchment
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North	90	78	154	1286	34
Northeast	165	148	184	2449	40
Southeast	1942	1621	2345	26795	512
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Central-west	27	22	23	362	5

*Systematic Survey of Agricultural Production - December 2017

Table 2. Stock estimation of the woods parts (stem, primary branch and secondary branch) of the coffee shrub.

Estimation	Wood Parts of coffee shrub			Total
	Stem	Primary Branch	Secondary Branch	
Diameter (cm)	9.8*	2.3	1.8	
Biomass (kg·coffee shrub ⁻¹)	4.10*	2.24	2.54	8.88
Biomass (%)	46.17*	25.22	28.61	100

*significant difference, using a Bonferroni-corrected alpha value ($p=0.001$)

Table 3. Properties of residual biomasses from the coffee production chain

Components	Biomasses						
	Leaves	Primary branch	Secondary branch	Stem bark	Stem	Parchment	SD ^c
<i>Basic density (kg m⁻³)</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	<i>nd</i>	598.7	<i>nd</i>	-
<i>Ultimate elemental^b (wt % dry)</i>							
C	53.97	50.31	51.82	54.41	50.64	50.69	1.80
H	6.55	6.13	6.40	6.59	6.12	6.23	0.21
O	35.50*	42.28	40.06	36.66*	41.16	42.05	2.87
N	3.54*	0.92	1.51	2.13*	1.86	0.82	1.00
S	0.43*	0.36*	0.21	0.21	0.21	0.20	0.10
H/C	1.46	1.46	1.48	1.45	1.48	1.45	0.01
O/C	0.49*	0.63	0.58	0.50*	0.62	0.61	0.06
<i>Proximate composition(wt %)</i>							
EHM	16.35	8.70*	9.28*	18.11	10.96	11.09	3.88
VM ^a	74.71	80.62*	75.31	75.63	83.70*	74.07	3.90
FC ^a	18.12	16.95*	21.23	20.03	14.62*	20.09	2.45
AC ^a	7.17*	2.42*	3.45*	4.33*	1.67*	5.84*	2.08
Silica (% of ash)	0.10	0.10	0.10	0.40*	0.15	0.35*	0.14
<i>Minerals (g kg dry⁻¹)</i>							
Ca	4.65	4.49	6.41	20.96*	6.29	3.73	6.55
Fe	0.18	0.05	0.11	0.57*	0.07	0.24*	0.19
Mn	0.03	0.04	0.02	0.01	0.01	0.03	0.01
Mg	2.05*	1.17	1.68	2.23*	1.07	1.77	0.46
Cu	0.05	0.02	0.04	0.06	0.02	0.04	0.02
K	10.86*	6.74*	7.96*	2.94*	4.06*	12.20*	3.65
Na	1.19*	0.36*	0.69	0.95	0.68	0.73	0.28
Cl	4.36	7.26	6.80	5.98	3.08*	3.16*	1.83
<i>Heating value (MJ kg dry⁻¹)</i>							
HHV	19.45	19.20	19.20	19.20	19.00	18.30*	0.40
NHV	14.68	16.10	15.92	14.11*	15.44	14.81	0.77
<i>Chemical composition (%)</i>							
Extractive	24.72*	13.09	13.95	12.19	10.58	21.95*	5.80
Insoluble Lignin ^b	35.52	26.73	29.32	40.98	27.33	24.52*	6.26
Soluble Lignin ^b	3.59*	3.12*	2.93	2.19	2.24	2.07	0.61
Total Lignin ^b	39.11	29.85*	32.25	43.17	29.57*	26.59*	6.37
AnhydroGlucose ^b	19.65*	33.25	29.05	17.90*	31.65	29.60	6.46
AnhydroXylose ^b	5.30*	11.85	10.30	6.25*	12.20	14.55	3.61
AnhydroGalactose ^b	2.50*	1.15	1.45	1.20	0.90*	1.65	0.56
AnhydroMannose ^b	1.10	2.55*	1.70	0.90	3.30*	1.00	0.97
AnhydroArabinose ^b	4.50	1.55	2.90	4.25	1.35	3.45	1.33
Uronic acids ^b	4.80	3.80	4.70	5.20	3.30	5.50	0.84
Total sugars ^b	37.85*	54.15	50.10	35.70*	52.70	55.75	8.70
Acetyl group ^b	1.00	1.8	1.8	1.00	2.80*	2.85*	0.82
<i>Others^b</i>	14.87	11.78	12.40	15.80	13.26	8.97*	2.42

^adry basis. ^bdry ash free basis. ^cStandard deviation. *nd*-not determined. EHM-Equilibrium Hygroscopic Moisture. VM-Volatile matter. FC-Fixed Carbon. AC-Ash content. HHV-Higher Heating Value. NHV-Net Heating Value.

*significant difference, using a Bonferroni-corrected alpha value (p=0.001)

Table 4. Values of mass loss of biomasses in function of the temperature ranges, in percentage

Biomasses	Temperature rates (°C)						Residual mass (%)
	T _i - 100	100-200	200-300	300-400	400-500	500-600	
	Mass lost (%)						
Leaves	8.04	1.85	16.94	28.08	9.47	3.16	32.46
Primary branch	13.76	0.92	18.68	39.32	6.34	4.90	16.08
Secondary branch	7.63	1.08	19.45	36.54	6.02	3.00	26.26
Stem Bark	9.73	1.49	14.22	31.78	10.17	3.13	29.47
Stem	7.04	0.82	17.66	46.35	6.86	4.99	16.00
Parchment	8.00	4.31	24.80	25.77	7.61	4.44	25.07
SD ^a	2.48	1.31	3.52	7.65	1.71	0.94	6.84

^aStandard deviation

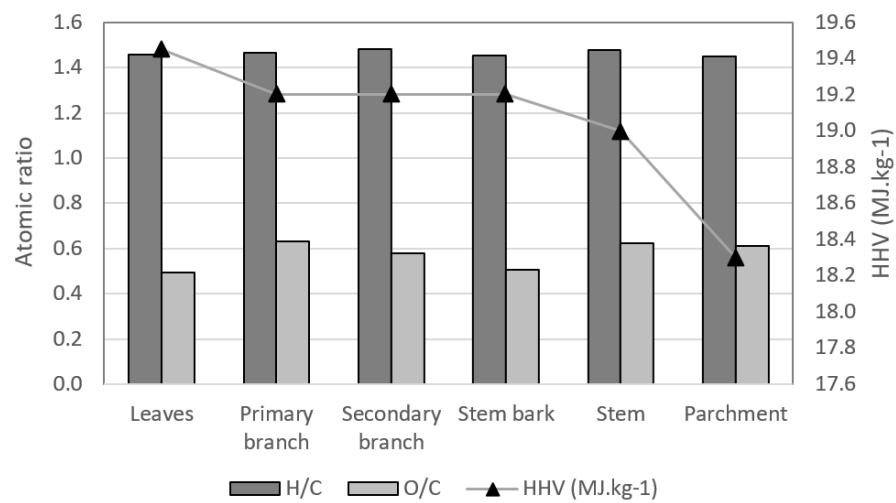


Figure 1. Molar ratios of hydrogen and oxygen to carbon and high heating value for studied residual biomasses from the coffee production chain.

Figure

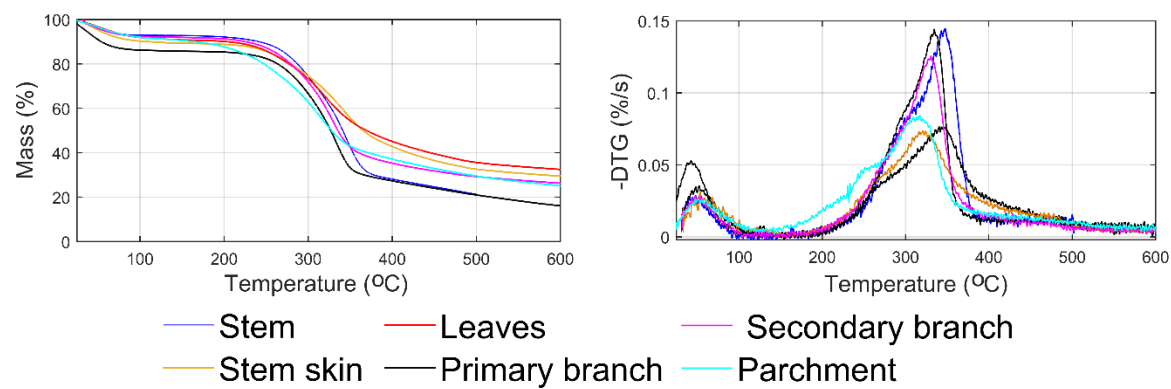


Figure 2. TG and DTG of the residual biomasses of the coffee production chain.