



LUT
Lappeenranta
University of Technology

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

Mendoza Clara Lisseth Martinez, Rocha Elém Patrícia Alves, Carneiro Angélica de Cassia Oliveira, Borges Fernando José Gomes, Ribas Larisse Aparecida Batalha, Vakkilainen Esa, Cardoso Marcelo

This is a Post-print version of a publication

published by Elsevier

in Biomass and Bioenergy

DOI: 10.1016/j.biombioe.2018.11.003

Copyright of the original publication: © 2018 Elsevier Ltd.

Please cite the publication as follows:

Mendoza Clara Lisseth Martinez, Rocha Elém Patrícia Alves, Carneiro Angélica de Cassia Oliveira, Borges Fernando José Gomes, Ribas Larisse Aparecida Batalha, Vakkilainen Esa, Cardoso Marcelo. (2019). Characterization of residual biomasses from the coffee production chain and assessment the potential for energy purposes. Biomass and Bioenergy, Vol 120. p. 68-76. DOI: 10.1016/i.biombioe.2018.11.003



**This is a parallel published version of an original publication.
This version can differ from the original published article.**

1
2
3
4
5
6
7 Characterization of residual biomasses from the coffee production
8
9
10 chain and assessment the potential for energy purposes
11
12

13
14 *Clara Lisseth Mendoza Martinez^{abe*}, Elém Patrícia Alves Rocha^{ac}, Angélica de Cassia*
15
16 *Oliveira Carneiro^b, Fernando José Borges Gomes^d, Larisse Aparecida Ribas Batalha^b, Esa*
17
18 *Vakkilainen^e, Marcelo Cardoso^a*
19
20
21

22 ^aFederal University of Minas Gerais (UFMG), Belo Horizonte, MG Brazil, 31270-901

23
24 ^bFederal University of Viçosa (UFV), Viçosa, MG, Brazil, 36.570-000

25
26 ^cFederal University of Jequitinhonha and Mucuri Valleys (UFVJM), Janaúba, MG, Brazil, 39440-000

27
28 ^dRural Federal University of Rio de Janeiro, Seropédica - RJ, 23890-000

29
30 ^eLappeenranta University of Technology, Skinnarilankatu 34, Fi-53850 Lappeenranta, Finland
31
32

33
34 ABSTRACT – Chemical quantitative characterization of biomass is relevant for waste to
35
36 energy recovery technologies. In the present work, selected agroindustry solid residues
37
38 from coffee crops – parchment and coffee shrub, i.e., stem, branches and leaves – were
39
40 characterized. Properties such proximate, ultimate and biochemical composition, energy
41
42 content, and thermogravimetric analysis, were evaluated. Results showed high values of
43
44 higher heating value and volatile matter content. The silica contents are small for all
45
46 samples. Additionally, the high content of extractives and lignin, reveal that these residual
47
48 biomasses are more suitable for charcoal than cellulose pulp production. The extensive
49
50 residue characterization provided valuable data that helped in outcome of the evaluation of
51
52 different conversion technologies as being an environmentally friendly alternative,
53
54 contributing to sustainable, reliable, carbon-neutral form of modern energy and upgrade the
55
56
57
58
59
60

61 *Corresponding Author at: School of Chemical Engineering, Federal University of Minas Gerais, room 5210, block 2, 6627 Antonio
62 Carlos Road, 31270901, Belo Horizonte, Minas Gerais, Brazil.
63 E-mail address: clara.mendoza.martinez@gmail.com
64
65

1
2
3
4
5 large quantity of waste generated by the coffee industry into energetically valued residues,
6
7
8 by improving their management.
9

10
11 **KEYWORDS:** Chemical characterization; coffee shrub; waste quantification; waste to
12
13 energy
14
15

16 17 18 19 1. INTRODUCTION 20 21

22 Brazil, Vietnam, Colombia and Indonesia are the largest bulk coffee beans
23
24 producers in the world, responsible for more than 50 % of world production. The coffee
25
26 production chain generates a large quantity of residues from the cherries and shrub. Large
27
28 scale around the world. It is estimated that the annual world production of coffee generates
29
30 over ten million tons of residues yearly (solid and liquid). This amount excludes the
31
32 residues of cultivation (pruning leaves) which are difficult to estimate due to the differences
33
34 in agronomic management practices [1]. Organic residues from coffee production represent
35
36 a serious source of environmental concern, if discarded inadequately and with poor
37
38 management.
39
40
41
42
43

44 With exports amounting to 30.2 million bags of 60 kg in 2017, Brazil is the largest
45
46 producer and exporter of bulk coffee beans in the world [2, 3]. The gross amount of bulk
47
48 coffee beans (*Coffea arabica* and *Coffea robusta*) produced in Brazil (2017) was 2.78
49
50 million tons according to [4], and the total area planted in the country with coffee shrubs
51
52 (*Coffea arabica* and *Coffea robusta*) in 2017 was 2.21 million hectares, where 1.86 million
53
54 hectares (84.16 %) were in production [5]. As can be seen in Table 1, Southeastern Brazil,
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
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
7
8 shrub.
9
10

11
12
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]
15

16
17
18
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.
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49

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
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
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].
8
9

10
11
12
13
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.
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53

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
57
58
59
60
61
62
63
64
65

1
2
3
4
5 producers often want to avoid. The thermochemical conversion technologies for recovery
6
7 of energy from wastes can play a vital role in mitigating the problems caused by the large
8
9 amount of residual waste. In this sense, the residues from bulk coffee beans production can
10
11 be used to generate thermal energy to dry agricultural products or to heat animal facilities,
12
13 or as fuel to generate mechanical or electrical energy. However, knowledge of the quantity,
14
15 physical and chemical characteristics and technologies available for use of residues has
16
17 been an hindrance to find an alternative that conserves energy and contributes to
18
19 sustainable development.
20
21
22
23
24

25 The concern with the increase of coffee bean productivity has ignored the changes
26
27 to the characteristics to the residues provided by the coffee production chain, additionally,
28
29 little or partial information exist about its use in the generation of value-added products. In
30
31 order to solve some limitations in relation to the use of bulk residual coffee biomass, such
32
33 as low energetic density, high content of moisture, high heterogeneity that leads to
34
35 difficulties in handling, transport and storage, agricultural / forestry companies and research
36
37 centers, suggests solutions for reducing these problems, trough treatments that produce
38
39 homogeneous, high yielding, high quality and low cost products, such as biodiesel, biogas,
40
41 source of sugars [12], and precursor for production of activated carbon [13, 14].
42
43
44
45
46
47

48 The aim of this study was to present an extensive characterization of residual
49
50 biomasses from the coffee production chain for energy purposes, increasing knowledge
51
52 about the alternatives applicable to the energy matrix of countries where the coffee industry
53
54 is one of the major agricultural activity, through physical and chemical analyzes that
55
56 identify the most important quality indices, the interactions between them, as well as the
57
58
59
60
61
62
63
64
65

1
2
3
4
5 quantification of its importance. An extensive characterization of the residues presented in
6
7 this work is not readily available in the literature and these results are fundamental tools for
8
9 the qualification and quantification of the effects of their properties on conversion
10
11 technologies that include thermochemical processes such as pyrolysis, gasification, and
12
13 combustion, and physical processes such as briquetting and pelletizing.
14
15
16
17

18 2. MATERIALS AND METHODS

19 2.1. *Sampling and preparation for characterization process*

20
21
22
23
24 Residues from coffee shrub (*Coffea arabica* L.) cultivation: parchment, leaves and
25
26 wood, provided by a rural farm in the municipality of Paula Cândido, MG, Brazil
27
28 (20°49'50.0" S 42°55'03.3" W) were used. The plantation was established in 1986, and due
29
30 to low productivity, stumping of new plant formation was required. The wood collected
31
32 was 11 years old (from after the last stumping period), from a 30-years-old plantation.
33
34
35
36

37
38 The biomasses were ground in an industrial mincing Lippel® brand, and posteriorly
39
40 in an electric hammer mill, motor Weg® mark of 10 CV and 3520 rpm, which was coupled
41
42 with a screen opening of 2 mm. For samples intended for chemical analysis it was
43
44 necessary to further reduce the particle size, using a knife mill type Wiley® Mill Model 4.
45
46 The biomasses were finally classified into superposed screen with openings of 40 mesh and
47
48 60 mesh according to the American Society for Testing and Materials (ASTM), 1982.
49
50
51

52
53 The experiment was conducted according to a randomized design with six
54
55 biomasses and two replicates for each characterization. Data were subjected to analysis of
56
57 variance (ANOVA). For the large number of tests and variables involved, Bonferroni-
58
59
60
61
62
63
64
65

1
2
3
4
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,
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

corrected alpha value ($\rho = 0.001$) was employed to reduce the likelihood of spurious correlations. Statistical analyzes were performed on the IBM SPSS® software platform, 2015.

2.2. *Stock estimation of the coffee shrub wood parts.*

The wood samples were previously separated into (I) stem, (II) primary branch and (III) secondary branch according to their diameter, 10 ± 2 cm, 2 ± 1 cm and 1 ± 0.5 cm, respectively, for individual properties analysis and stock estimation.

2.3. *Laboratory procedures for biomass characterization*

An extensive characterization of the solid fuel was performed, evaluating their properties, including proximate and ultimate composition, energy content, several biochemical composition (polysaccharides, lignin, extractives, uronic acids and acetyl group) and thermogravimetric analysis of each residue group.

2.3.1. *Basic density.*

The measurement for basic density of wood sample (stem) was determined according to the Scandinavian Pulp, Paper and Board (SCAN-CM) 43:95 (1995) standard procedures of 25 disks obtained from different cut sections on the main axis of the shrub. The drying analysis of wood parts of the coffee shrub, (stem, primary branch and secondary branch) with dimensions of 30 cm length and variation of the diameter for each wood part, was conduct in a climate-controlled room with temperature ($23\text{ }^{\circ}\text{C}$ – $24\text{ }^{\circ}\text{C}$) and relative humidity (60 %–70 % RH) control. The mass loss of the samples was monitored by periodic weightings until reaching anhydrous mass.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

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

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

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

1
2
3
4
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
7
8 1000 $^\circ\text{C}$.
9

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.
21
22

23
24
25 **Table 2.** Stock estimation of the woods parts (stem, primary branch and secondary branch)
26 in the coffee shrub.
27

28
29
30
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.
34
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
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5 this way, the stem provides more amount of stacked biomass than the branches, as a result
6
7 of the significant difference between the densities.
8
9

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
15
16 production chain.
17
18

19 **Table 3.** Properties of residual biomasses from the coffee production chain.
20
21
22

23 3.2.1 *Basic density of coffee wood.* In the average value of basic density of coffee
24
25 wood (598.7 kg m^{-3}), negligible variations between the base and the top of the stem were
26
27 observed. For energy, high wood density is preferred, resulting in higher mass production
28
29 for a given volume of wood [18]. Operational advantages, such as gains in harvesting and
30
31 forest transport processes can be achieve, due to the fact that larger volumes of harvested
32
33 wood will generate greater specify mass values [19]. According to the measures suggested
34
35 by [20], wood basic density for charcoal production should exceed $500 \text{ kg}\cdot\text{m}^{-3}$. The value
36
37 found for coffee wood is similar to values reported in the literature for *Eucalyptus* wood,
38
39 that presents basic density between 436 and $668 \text{ kg}\cdot\text{m}^{-3}$ for the species *Eucalyptus pellita*,
40
41 *Eucalyptus urophylla* and *Eucalyptus grandis*, traditionally used for energy conversion,
42
43 including firewood and charcoal [21].
44
45
46
47
48
49

50 3.2.2. *Ultimate analysis.* The biomasses collected are basically composed of carbon
51
52 (50.26 \% – 54.41 \% , dry basis), hydrogen (6.13 \% – 6.59 \% , dry basis) and oxygen (35.52
53
54 \% – 42.29 \% , dry basis). Small amounts of nitrogen and sulfur were also observed. Biomass
55
56 with high values of carbon and hydrogen, contributes the most to the calorific value of the
57
58
59
60
61
62
63
64
65

1
2
3
4
5 fuel [22]. The energy generated by thermal reactions is associated with the enthalpy of
6
7 carbon, hydrogen and sulfur [23]. The presence of nitrogen and sulfur in the biomass have a
8
9 direct impact on the environmental pollution, due to the formation of harmful oxides (NO_x ,
10
11 SO_x) from volatile compounds [24]. The content of sulfur observed in the elemental
12
13 composition was low (0.20 %–0.43 %). Generally, the S content in biomass varies in the
14
15 interval of 0.01 %–2.3 % [25].
16
17
18
19
20

21 The coffee shrub is highly N-demanding, the nitrogen requirements increases with
22
23 shrub age especially at the beginning of grain production. If there are not limiting factor,
24
25 the nitrogen will promote rapid plant development specifically through the increase in
26
27 number of plagiotropic branches per shrub, number of nodes per branch, and number of
28
29 fruiting nodes, flowers and leaves per node, which, taken together, are associated with
30
31 higher yields in coffee beans [26, 27]. Hence the coffee shrub presents high potential for
32
33 nitrate assimilation in leaves as well as in roots. That is the reason of the highest levels of
34
35 nitrogen in leaves with significant difference between the other biomasses. The supporting,
36
37 slowly growing parts have the lowest nitrogen content. The nitrogen content in biomasses
38
39 varies in the interval of 0.10 %–12 % [25, 28]. The values of nitrogen and sulfur found in
40
41 this study are similar to other biomasses used for energy, which are environmentally more
42
43 advantageous than other sources of thermal energy such as mineral coal.
44
45
46
47
48
49

50 The molar ratios of oxygen and hydrogen to carbon for the residues studied are
51
52 shown in Figure 1. Oxygen is generally present in plant-based fuels, and its presence
53
54 decreases the calorific value [29]. Therefore, low H/C and O/C ratios are desirable for the
55
56 use of biomass for energy. The samples with low O/C ratio, also have more energetic
57
58
59
60
61
62
63
64
65

1
2
3
4
5 content because C-C bonds have higher chemical energy than C-O bonds [30]. In the
6
7 biomasses collected, higher O/C ratio can be observed in the primary branch (O/C = 0.63)
8
9 with no significant difference among biomasses. In H/C ratio, secondary branch and stem
10
11 have the highest value (H/C = 1.48), no significant difference between the biomasses were
12
13 found for this property. Parchment appears to have a low value for the heating value
14
15 considering the relatively high O/C ratio. This fact may be also associated with high AC.
16
17 According to [22], higher proportion of oxygen, hydrogen and inorganic elements,
18
19 compared with carbon, tend to decrease the HHV of the fuel.
20
21
22
23
24
25

26 *3.2.3. Heating value.* [31], reported that heating value is one of the most important
27
28 parameters for energy modeling and simulation in thermochemical conversion processes.
29
30 For the HHV, Table 3 shows mean values between 18.30–19.45 MJ·kg⁻¹ (dry basis) similar
31
32 values are found in literature (18.60–21 MJ·kg⁻¹, dry basis) for residues from coffee
33
34 production chain and are analogous to biomasses commonly used in energy generation [6,
35
36 32, 33]. NHV shows mean values between 14.11–16.10 MJ kg dry⁻¹. Primary branch has
37
38 the higher value of NHV with no significant difference with the other biomasses, mainly
39
40 due to its low moisture content and its high HHV, influenced by low AC and mineral
41
42 composition. (Table 3).
43
44
45
46
47

48 **Figure 1.** Molar ratios of hydrogen and oxygen to carbon and high heating value for
49
50 studied residual biomasses from the coffee production chain
51
52

53 *3.2.4. Proximate analysis.* The proximate analysis aims to quantify the moisture,
54
55 volatiles (condensable and non-condensable), fixed carbon and ash biomass content. The
56
57 FC content is of special interest since this indicates the potential for charcoal generation
58
59
60
61
62
63
64
65

1
2
3
4
5 from devolatilized biomass. The FC content in the samples varies in the interval of 14.62
6
7
8 %–21.23 %; secondary branch presents the highest values of FC content with no significant
9
10 difference among the biomasses. The biomasses studied presents high values of FC, similar
11
12 to FC content mentioned in the literature for biomasses more commonly used in energy
13
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
19
20 eucalyptus (82.62 %) and bamboo (84.65 %) [36, 37]. Solid fuels with high VM and low
21
22 FC content are more susceptible to thermal degradation [38], requiring less length of time
23
24 on a thermochemical process, making the biomass degradation faster compared to fuels
25
26 with high FC and low VM content.
27
28
29
30
31
32

33 Ash is the inorganic solid residue left after the fuel is completely burned [39]. In the
34
35 data obtained for ash content, it was observed that the residual biomasses from the coffee
36
37 production chain had low ash contents in the range of 1.67 %–4.33 %, except for the
38
39 parchment and leaves, which had higher values of 5.84 % and 7.17 %, respectively.
40
41 According to [40], [41], in the coffee production chain, the residues from the coffee cherry
42
43 typically generate significantly more AC than the coffee woody biomasses, supporting the
44
45 data obtained. Few results of coffee shrub leaves have been reported; however, studies from
46
47 leaves of different species show that ash content is significantly high compared to the tree
48
49 and shrub wood from which it comes: for example [42] reported $16.8 \text{ g}\cdot\text{kg}^{-1}$ - $67.8 \text{ g}\cdot\text{kg}^{-1}$
50
51 AC of leaves in different trees and shrub species.
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
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.

17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
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
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
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
7
8 temperatures pyrolysis by 20 %–50 % or more.
9

10
11
12
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
15
16 temperatures higher than 873°C because of the ash deposition propensity in thermal fuel
17
18 conversion systems. The presence of minerals increase both, the tendency for ash particles
19
20 to stick to heat transfer surfaces and the subsequent rate of strength build-up in ash
21
22 deposits. These operational problems are closely related to the chemical composition of the
23
24 AC. The gasification process requires a feedstock with less than 5 % ash content, preferably
25
26 less the 2 %, in order to prevent the formation of clinkers [62]. To mitigate the negative
27
28 effects of minerals in thermochemical conversion processes, [63] suggested a pre-treatment
29
30 to reduce their concentration in the fuel, e.g. fuel leaching.
31
32
33
34
35
36
37

38
39 *3.2.5. Chemical composition.* Another important characteristic of biomass is the
40
41 composition in terms of the main structural chemical compounds. Data of chemical
42
43 composition is presented in Table 3. The dried biomass is composed mainly of about 40 %
44
45 to 60 % of cellulose (composed of units of Anhydroglucose linked by glycosidic bonds β 1-
46
47 4), 15 % to 30 % of hemicelluloses (matrix polysaccharides) and 4 %–35 % of lignin
48
49 (cross-linked phenolic polymers) [39, 64]. However, residues from coffee production chain
50
51 contain several other components, including lipids, tannin, polyphenols and nitrogenous
52
53 compounds [65-67]. These minor components were not evaluated in this study, but were
54
55 considered in the mass balance presented in the Table 3.
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5 The carbohydrate fraction range for the studied samples were 17.90 %–33.25 %;
6
7 5.30 %–14.55 %; 0.90 %–2.50 %; 0.90 %–3.30 %; 1.35 %–4.50 % for anhydroglucose,
8
9 anhydroxylose, anhydrogalactose, anhydromannose and anhydroarabinose, respectively.
10
11 These values are within in the ranges found in studies carried out for biomasses used in
12
13 energy production, where the anhydroglucose represent, on average, 46.6 % of the chemical
14
15 composition of biomass, varying from 44.5 % to 50 %, the anhydroxylose are the dominant
16
17 fraction of the hemicelluloses and represent 10.8 % to 13.2 %, on average of 12.2 % of the
18
19 biomass. The other carbohydrates (anhydrogalactose, anhydromannose and
20
21 anhydroarabinose) contributed with approximately 0.7 %, 0.6 % and 0.2 %, respectively
22
23 [68].
24
25
26
27
28
29

30 The chemical composition of the biomass exerts a great influence on the results of
31
32 energy conversion, affecting the thermogravimetric performance of the process. The
33
34 hemicelluloses are more susceptible to the reactions of thermal degradation because of the
35
36 presence of hydroxyls connected to its main chain and the absence of crystalline
37
38 agglomerates [69]. The branched chains of the hemicelluloses and cellulose are easily
39
40 degraded at low temperatures, having maximum peaks loss at approximately 275°C for
41
42 hemicelluloses and 350°C for cellulose [70].
43
44
45
46
47

48 For lignin, higher content in biomass leads to more sustainable biofuel production,
49
50 because lignin is the chemical component that has a greater thermal stability due to the C-C
51
52 bonds between monomeric units of phenyl-propane, and consequently has more stability in
53
54 its aromatic matrix contributing for charcoal and products like methanol and bio-oil
55
56 formation [71]. The acid insoluble lignin content of the samples evaluated in this study
57
58
59
60
61
62
63
64
65

1
2
3
4
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
7
8 such *Eucalyptus grandis*, *Eucalyptus globulus*, *Eucalyptus dunnii* and *Eucalyptus urophylla*
9
10 [72], and higher values than those reported in the literature for *Coffea arábica* residues
11
12 [40].
13
14
15
16
17

18 The total extractive content ranged from 10.57 % to 24.72 %. Leaves of the shrub of
19
20 *Coffea arábica* present a total extractive significantly higher than the other lignocellulosic
21
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
25
26 during the milling of the biomass, because the extraction with ethanol / toluene only
27
28 extracts substances such as waxes, fats, resins, phytosterols and non-volatile hydrocarbons
29
30 [73]. The lowest levels of total extractives were found in the samples of the coffee shrub
31
32 wood, corresponding to approximately 50 % of the total extractives verified for the leaves.
33
34 Because of high extractive content its use in processes such as the production of cellulose
35
36 pulp is not attractive due to the increase in the expense of reagents.
37
38
39
40
41
42

43 The extractives play an important role in the use of biomass, because they influence
44
45 the physical and energetic properties. Depending on their thermal stability, these substances
46
47 can contribute to the increase in the yield of charcoal. Some of the extractives are volatile
48
49 and therefore they are important in the direct burning of the biomass, because they react
50
51 faster and help to maintain the combustion flame. For the production of charcoal, the high
52
53 volatile extractive content in the biomass is detrimental because it provides lower
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5 gravimetric yield in charcoal due to the degradation of these substances at low temperatures
6
7
8 [74].
9

10
11 *3.2.6. Thermogravimetric analysis.* Figure 2 shows the thermal behavior of the
12
13 residual biomasses of the coffee production chain by Thermogravimetric analysis (TG) and
14
15 Differential thermogravimetric analysis (DTG).
16
17

18
19 **Figure 2.** TG (a) and DTG (b) of the residual biomasses of the coffee production chain.
20
21

22 It is observed that the thermal degradation profiles of the biomasses were similar,
23
24 with small differences in the temperatures corresponding to the maximum peaks of the
25
26 curve, mainly related to the degradation of the hemicelluloses and cellulose. The
27
28 thermogravimetric data (TG) curves and the first derivate data (DTG) curves, usually show
29
30 three bands of thermal degradation, which the first one is attributed to the drying of the
31
32 biomasses and the other two to the degradation of its main components; it should be
33
34 emphasized that each biomass components degrades in different temperature ranges. The
35
36 second temperature range corresponds mainly to the thermal degradation of the
37
38 hemicelluloses and of cellulose and lignin in smaller proportions. The third thermal
39
40 degradation range was then initiated, this temperature range corresponded mainly to the
41
42 degradation of the cellulose. The loss of mass for the cellulose needs a greater amount of
43
44 energy than the hemicelluloses, due to the depolymerization of the cellulose chain and the
45
46 breakdown of its monomer [75], that is the reason the degradation of the cellulose occurs
47
48 after the degradation of the hemicelluloses. The degradation peak of lignin is absent, due to
49
50 the fact that its thermal decomposition occurs in a wide temperature range [69, 76]. The
51
52 table 4 shows the measurements of the mass losses (%) obtained for each biomass,
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5 according to the temperature ranges from T_i (initial temperature) to 600°C, with intervals of
6
7
8 100°C.
9

10 **Table 4.** Values of mass loss of biomasses in function of the temperature ranges, in
11
12 percentage.
13
14

15
16 As presented in Figure 2, the combustion process of the samples could be divided
17
18 into two stages. The first stage extended from 33°C–127°C; 23°C–105°C; 32°C–107°C;
19
20 31°C–101°C; 27°C–121°C; 25°C–102°C for leaves, primary branch, secondary branch,
21
22 stem, stem bark and parchment, respectively, which represented the dehydration by
23
24 evaporation. The second stage was from 233°C–424°C; 243°C–380°C; 237°C–422°C;
25
26 242°C–384°C; 233°C–464°C; 280°C–364°C for leaves, primary branch, secondary branch,
27
28 stem, stem bark and parchment, respectively, which represent the liberation of the volatile
29
30 compounds. A similar phenomenon was shown in the combustion characteristics of oil
31
32 palm fiber and eucalyptus in torrefaction [77]. From Table 4, the mass loss percentage of
33
34 the first and second stage in the total mass loss was approximately 8.04 % and 45.02 %;
35
36 13.76 % and 58.00 %; 7.63 % and 55.99 %; 9.73 % and 46.00 %; 7.04 % and 64.01 %; 8.00
37
38 % and 50.57 % for leaves, primary branch, secondary branch, stem, stem bark and
39
40 parchment, in the first and second stage, respectively. As coffee shrub residues are
41
42 biomasses, the main composition of the biomasses are cellulose, hemicelluloses and lignin.
43
44 Therefore, the combustion of coffee shrub residues corresponds to the combustion of other
45
46 biomasses. Cellulose rapidly decomposes between 300°C and 350°C; lignin decomposes
47
48 between 410°C and 540°C and hemicelluloses decompose between 198°C and 398°C [76-
49
50 78]. Therefore, the mass loss in the second stage of the thermal degradation samples was
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
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

18
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:
27
28
29
30
31
32
33
34
35
36
37
38

- 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.
44
- 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
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5 primary branch of the coffee shrub, as well as its low percentage of ash compared to the
6
7 other evaluated biomasses make them desirable as feedstock for combustion.
8
9

- 10 • Woody parts of the coffee shrub have high economic potential for energy applications.
11
12 The low moisture content reduces transport and storage costs [81]. Additionally, the
13
14 energy consumption in the drying stage when subjected to processes such as
15
16 gasification, combustion and pyrolysis, decrease.
17
18
- 19 • For the production of bio-oil by fast pyrolysis process, the biomass is subjected to high
20
21 temperatures and short vapor residence time. High ash content generates secondary
22
23 vapor cracking, reducing the bio-oil quality and liquid yield. However, the presence of
24
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.
28
29
- 30 • During the processes of combustion, the sulfur is converted into H₂S and SO₂, which
31
32 are strong sources of contamination. In this sense, leaves of the coffee shrub are the
33
34 least qualified because of the higher content of sulfur. In addition, the sample has the
35
36 highest nitrogen content, resulting in the formation of nitrous oxides.
37
38
- 39 • For the charcoal production, biomass with lower fractions of cellulose and
40
41 hemicelluloses should be preferred. The parchment of coffee cherry, stem, primary and
42
43 secondary branch of coffee shrub experienced a greater thermal degradation than the
44
45 other biomasses at low temperatures, probably, due to the high anhydrosugars content
46
47 in its chemical composition
48
49
- 50 • The high content of cellulose and high calorific value of the parchment of the coffee
51
52 cherry makes it an attractive biomass for use as a direct combustion material.
53
54
55
56
57
58
59
60
61
62
63
64
65

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
- 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.

16
17
18
19
20
21
22
23
24
25

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.

26 27 28

4. CONCLUSIONS

29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50

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

ACKNOWLEDGMENT

54
55
56
57

This work was kindly supported by CNPq

58 59 60 61 62 63 64 65

REFERENCES

- 1
2
3
4
5 [1] M. Echeverria, M. Nuti, Valorisation of the Residues of Coffee Agro-industry:
6 Perspectives and Limitations, The Open Waste Management Journal 10(1) (2017).
7
8
9
10 [2] USDA, UNITED STATES DEPARTMENT OF AGRICULTURE. Coffee: World
11 Markets and trade, 2018/2019 forecast overview, Foreign Agricultural Service, Office of
12 Global Analysis, 2018.
13
14
15 [3] ICO, INTERNATIONAL COFFEE ORGANIZATION. Historical data on the global
16 coffee trade: total production, (2018).
17
18
19 [4] IBGE, Agriculture and Livestock Census 2018, Brazilian Institute of Geography and
20 Statistics , Rio de Janeiro, (2018).
21
22
23 [5] CONAB, Brazilian census monitoring, National Supply Company, Brasília, (2018).
24
25
26 [6] J.L. de Oliveira, J.N. da Silva, E.G. Pereira, D. Oliveira Filho, D.R. Carvalho,
27 Characterization and mapping of waste from coffee and eucalyptus production in Brazil for
28 thermochemical conversion of energy via gasification, Renewable and Sustainable Energy
29 Reviews 21 (2013) 52-58.
30
31
32 [7] F.M. DaMatta, C.P. Ronchi, M. Maestri, R.S. Barros, Ecophysiology of coffee growth
33 and production, Brazilian Journal of Plant Physiology 19(4) (2007) 485-510.
34
35
36 [8] M. Maestri, R. Barros, A. Rena, F. Last, Tree crop ecosystems, Tree crop ecosystems
37 (2001).
38
39
40 [9] M. JB, Conilon Coffee: How to Plant, Treat, Collect, Prepare and Sell, MM Graphic
41 Productions, Rio de Janeiro, 1998.
42
43
44 [10] A.A. Filho, Adensed Coffee: Spaces and care in crop management, BRAZILIAN
45 COFFEE RESEARCH AND DEVELOPMENT CONSORTIUM, AGRONOMIC
46 INSTITUTE OF PARANÁ, LONDRINA, 2002, p. 30.
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

- 1
2
3
4
5 [11] V. Heuzé, G. Tran, Coffee hulls, fruit pulp and by-products Coffee hulls, fruit pulp and
6 by-products, Feedipedia, a programme by INRA, CIRAD, AFZ and FAO, available
7
8 in: <https://feedipedia.org/node/549>, 2015.
9
10
11
12 [12] S.I. Mussatto, L.M. Carneiro, J.P. Silva, I.C. Roberto, J.A. Teixeira, A study on
13 chemical constituents and sugars extraction from spent coffee grounds, Carbohydrate
14 Polymers 83(2) (2011) 368-374.
15
16
17 [13] K. Kante, C. Nieto-Delgado, J.R. Rangel-Mendez, T.J. Bandosz, Spent coffee-based
18 activated carbon: specific surface features and their importance for H₂S separation
19 process, Journal of hazardous materials 201 (2012) 141-147.
20
21
22 [14] P. Pappa, F. Pelleria, E. Gidakos, Characterization of biochar produced from spent
23 coffee waste, 3rd International Conference on Industrial and Hazardous Waste
24 Management, 2012.
25
26
27 [15] R.W. Scott, Colorimetric determination of hexuronic acids in plant materials,
28 Analytical chemistry 51(7) (1979) 936-941.
29
30
31 [16] R. Solar, F. Kacik, I. Melcer, Simple semimicro method for the determination of O-
32 acetyl groups in wood and related materials, Nordic Pulp and Paper Research Journal 2(4)
33 (1987) 139-141.
34
35
36 [17] O. Goldschmid, Ultraviolet spectra. Lignins: Occurrence, Formation, Structure and
37 Reactions, New York, NY: John Wiley and Sons, 1971.
38
39
40 [18] M. TEMMERMAN, Towards a cleaner charcoal production process, Small 2 (2016)
41 3.1.
42
43
44 [19] M. Assis, L. Brancheriau, A. Napoli, P.F. Trugilho, Factors affecting the mechanics of
45 carbonized wood: literature review, Wood science and technology 50(3) (2016) 519-536.
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

- 1
2
3
4
5 [20] J.T. Lima, S.C. Rosado, P.F. Trugilho, Assessment of wood density of seven clones of
6 Eucalyptus grandis, Southern African Forestry Journal 2001(191) (2001) 21-28.
7
8
9
10 [21] F.d.A. RIBEIRO, J. ZANI FILHO, Variation of the basic density of wood in species /
11 provenances of Eucalyptus spp, Institute for Research and Forest Studies, 1993, pp. 76-85.
12
13
14 [22] A. Demirbas, Combustion characteristics of different biomass fuels, Progress in energy
15 and combustion science 30(2) (2004) 219-230.
16
17
18 [23] P. Trugilho, M. Bianchi, S. Rosado, J. Lima, A. Napoli, Elemental analysis of clones
19 of eucalyptus wood, Biomassa & Energia 5(1) (2012) 53-58.
20
21
22 [24] L. Wilson, W. Yang, W. Blasiak, G.R. John, C.F. Mhilu, Thermal characterization of
23 tropical biomass feedstocks, Energy Conversion and Management 52(1) (2011) 191-198.
24
25
26 [25] S.V. Vassilev, D. Baxter, L.K. Andersen, C.G. Vassileva, An overview of the chemical
27 composition of biomass, Fuel 89(5) (2010) 913-933.
28
29
30 [26] R.B. Nazareno, C.A. da Silva Oliveira, C. Sanzonowicz, J.B.R. Sampaio, J.C.P. da
31 Silva, A.F. Guerra, Initial growth of Rubi coffee in response to nitrogen, phosphorus and
32 potassium doses and to water regimes, Brazilian Agricultural Research, 2003, pp. 903-910.
33
34
35 [27] M.L.C. Carelli, J.I. Fahl, J.D.C. Ramalho, Aspects of nitrogen metabolism in coffee
36 plants, Brazilian Journal of Plant Physiology 18(1) (2006) 9-21.
37
38
39 [28] J.J. Manyà, J. Arauzo, An alternative kinetic approach to describe the isothermal
40 pyrolysis of micro-particles of sugar cane bagasse, Chemical Engineering Journal 139(3)
41 (2008) 549-561.
42
43
44 [29] T.d.P. Protásio, L. Bufalino, G. Tonoli, A. Couto, P. Trugilho, J. Guimarães, Relation
45 between higher heating value and elemental and mineral biomass plant components,
46 Pesquisa Florestal Brasileira 31(66) (2011) 113-122.
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

- 1
2
3
4
5 [30] P. McKendry, Energy production from biomass (part 1): overview of biomass,
6 Bioresource technology 83(1) (2002) 37-46.
7
8
9
10 [31] M. Dogru, C. Howarth, G. Akay, B. Keskinler, A. Malik, Gasification of hazelnut
11 shells in a downdraft gasifier, Energy 27(5) (2002) 415-427.
12
13
14
15 [32] T. Keipi, H. Tolvanen, L. Kokko, R. Raiko, The effect of torrefaction on the chlorine
16 content and heating value of eight woody biomass samples, Biomass and Bioenergy 66
17 (2014) 232-239.
18
19
20
21
22 [33] M.E. Doumer, G.G.C. Arízaga, D.A. da Silva, C.I. Yamamoto, E.H. Novotny, J.M.
23 Santos, L.O. dos Santos, A. Wisniewski, J.B. de Andrade, A.S. Mangrich, Slow pyrolysis
24 of different Brazilian waste biomasses as sources of soil conditioners and energy, and for
25 environmental protection, Journal of Analytical and Applied Pyrolysis 113 (2015) 434-443.
26
27
28
29
30 [34] M.L. de Souza-Santos, Solid Fuels Combustion and Gasification: Modeling,
31 Simulation, CRC Press2010.
32
33
34
35
36
37 [35] A. Demirbaş, Relationships between lignin contents and fixed carbon contents of
38 biomass samples, Energy Conversion and Management 44(9) (2003) 1481-1486.
39
40
41
42 [36] C.J. Donahue, E.A. Rais, Proximate analysis of coal, J. Chem. Educ 86(2) (2009) 222.
43
44
45 [37] J. Parikh, S. Channiwala, G. Ghosal, A correlation for calculating elemental
46 composition from proximate analysis of biomass materials, Fuel 86(12) (2007) 1710-1719.
47
48
49 [38] E.R.K. Fernandes, C. Marangoni, O. Souza, N. Sellin, Thermochemical
50 characterization of banana leaves as a potential energy source, Energy conversion and
51 management 75 (2013) 603-608.
52
53
54
55
56 [39] P. Basu, Biomass gasification and pyrolysis: practical design and theory, Academic
57 press2010.
58
59
60
61
62
63
64
65

- 1
2
3
4
5 [40] S.I. Mussatto, E.M. Machado, S. Martins, J.A. Teixeira, Production, composition,
6 and application of coffee and its industrial residues, *Food and Bioprocess Technology* 4(5)
7
8 (2011) 661-672.
9
10
11
12 [41] J. L. de Oliveira, J. N. da Silva, M. A. Martins, E. G. Pereira, and M. da Conceição
13 Trindade Bezerra e Oliveira, Gasification of waste from coffee and eucalyptus production
14 as an alternative source of bioenergy in Brazil, *Sustain. Energy Technol. Assessments*
15 (2018).
16
17
18 [42] C. Petisco, B. García-Criado, B. R. Vázquez de Aldana, A. García-Ciudad, and S.
19 Mediavilla, Ash and Mineral Contents in Leaves of Woody Species: Analysis by
20 Near-Infrared Reflectance Spectroscopy, *Commun. Soil Sci. Plant Anal.* (2008).
21
22
23 [43] X. Ren, R. Sun, H.-H. Chi, X. Meng, Y. Li, Y.A. Levendis, Hydrogen chloride
24 emissions from combustion of raw and torrefied biomass, *Fuel* 200 (2017) 37-46.
25
26
27 [44] Y. Shao, J. Wang, F. Preto, J. Zhu, C. Xu, Ash deposition in biomass combustion or
28 co-firing for power/heat generation, *Energies* 5(12) (2012) 5171-5189.
29
30
31 [45] L. Wang, H. Wu, P.A. Jensen, K. Dam-Johansen, J.E. Hustad, Ash transformation and
32 deposition behavior during co-firing biomass with sewage sludge, *Impact of Fuel Quality*
33 on Power Production & Environment (2012).
34
35
36 [46] C. Bartolomé, A. Gil, Ash deposition and fouling tendency of two energy crops
37 (cynara and poplar) and a forest residue (pine chips) co-fired with coal in a pulverized fuel
38 pilot plant, *Energy & Fuels* 27(10) (2013) 5878-5889.
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

- 1
2
3
4
5
6 [47] L. Wang, J.E. Hustad, Ø. Skreiberg, G. Skjevraak, M. Grønli, A critical review on
7
8 additives to reduce ash related operation problems in biomass combustion applications,
9
10 Energy Procedia 20 (2012) 20-29.
11
12 [48] S.K. Loh, The potential of the Malaysian oil palm biomass as a renewable energy
13
14 source, Energy Conversion and Management 141 (2017) 285-298.
15
16 [49] H.P. Michelsen, F. Frandsen, K. Dam-Johansen, O.H. Larsen, Deposition and high
17
18 temperature corrosion in a 10 MW straw fired boiler, Fuel Processing Technology 54(1)
19
20 (1998) 95-108.
21
22 [50] D.C. Elliott, P. Biller, A.B. Ross, A.J. Schmidt, S.B. Jones, Hydrothermal liquefaction
23
24 of biomass: developments from batch to continuous process, Bioresource technology 178
25
26 (2015) 147-156.
27
28 [51] L.-E. Åmand, B. Leckner, D. Eskilsson, C. Tullin, Deposits on heat transfer tubes
29
30 during co-combustion of biofuels and sewage sludge, Fuel 85(10) (2006) 1313-1322.
31
32 [52] P.A. Jensen, M. Stenholm, P. Hald, Deposition investigation in straw-fired boilers,
33
34 Energy & Fuels 11(5) (1997) 1048-1055.
35
36 [53] Y. Zheng, A.D. Jensen, J.E. Johnsson, Deactivation of V₂O₅-WO₃-TiO₂ SCR
37
38 catalyst at a biomass-fired combined heat and power plant, Applied Catalysis B:
39
40 Environmental 60(3) (2005) 253-264.
41
42 [54] B. Strömberg, F. Zint, Release of chlorine from biomass and model compounds at
43
44 pyrolysis and gasification conditions, Progress in Thermochemical Biomass Conversion
45
46 (2001) 1234-1245.
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

- 1
2
3
4
5 [55] J.T. Hamilton, W.C. McRoberts, F. Keppler, R.M. Kalin, D.B. Harper, Chloride
6 methylation by plant pectin: an efficient environmentally significant process, *Science*
7
8 301(5630) (2003) 206-209.
9
10
11
12 [56] H. Zhao, Q. Song, Q. Yao, HCl Capture by Rice Straw Char and Its Influence on the
13 Transformation of Alkali and Alkaline Earth Metallic Species during Pyrolysis, *Energy &*
14
15 *Fuels* 30(7) (2016) 5854-5861.
16
17
18
19 [57] R. Kaczmarczyk, A. Mlonka-Mędrała, Chloride corrosion in biomass-fired boilers–Fe-
20 O-Cl system thermodynamic analysis, *E3S Web of Conferences*, EDP Sciences, 2016, p.
21 00060.
22
23
24
25
26 [58] Y. Wang, H. Wu, Z. Sárossy, C. Dong, P. Glarborg, Release and transformation of
27 chlorine and potassium during pyrolysis of KCl doped biomass, *Fuel* 197 (2017) 422-432.
28
29
30
31 [59] S.C. Van Lith, V. Alonso-Ramírez, P.A. Jensen, F.J. Frandsen, P. Glarborg, Release to
32 the gas phase of inorganic elements during wood combustion. Part 1: development and
33 evaluation of quantification methods, *Energy & Fuels* 20(3) (2006) 964-978.
34
35
36
37
38 [60] E. Björkman, B. Strömberg, Release of chlorine from biomass at pyrolysis and
39 gasification conditions¹, *Energy & Fuels* 11(5) (1997) 1026-1032.
40
41
42
43 [61] A. Toptas, Y. Yildirim, G. Duman, J. Yanik, Combustion behavior of different kinds
44 of torrefied biomass and their blends with lignite, *Bioresource technology* 177 (2015) 328-
45 336.
46
47
48
49
50 [62] E.P.A. Rocha, F.J.B. Gomes, E. Sermyagina, M. Cardoso, J.L. Colodette, Analysis of
51 Brazilian Biomass Focusing on Thermochemical Conversion for Energy Production,
52 *Energy & Fuels* 29(12) (2015) 7975-7984.
53
54
55
56
57
58
59
60
61
62
63
64
65

- 1
2
3
4
5 [63] I. Obernberger, T. Brunner, G. Bärnthaler, Chemical properties of solid biofuels—
6 significance and impact, *Biomass and Bioenergy* 30(11) (2006) 973-982.
7
8
9
10 [64] E. Sjostrom, *Wood chemistry: fundamentals and applications*, Elsevier 2013.
11
12 [65] A. Farah, Coffee constituents, *Coffee: emerging health effects and disease prevention*
13 1 (2012) 22-58.
14
15
16
17 [66] S. Oestreich-Janzen, *3.25-Chemistry of Coffee*, (2010).
18
19 [67] P.S. Murthy, M.M. Naidu, Sustainable management of coffee industry by-products and
20 value addition-A review, *Resources, Conservation and Recycling*, 2012, pp. 45-58.
21
22
23 [68] J.L. Gomide, J.L. Colodette, R.C.d. Oliveira, C.M. Silva, Technological
24 characterization, for pulp production, of the new generation of Eucalyptus clones from
25 Brazil, 2005.
26
27
28
29
30
31 [69] F. Santos, J. Queiroz, J. Colodette, C. Souza, *Bioenergy and Biorefinery: Sugarcane*
32 and Forest Species, Brazil, 2013.
33
34
35
36 [70] D. Shen, S. Gu, A. Bridgwater, The thermal performance of the polysaccharides
37 extracted from hardwood: cellulose and hemicellulose, *Carbohydrate Polymers* 82(1)
38 (2010) 39-45.
39
40
41
42 [71] S. Sen, S. Patil, D.S. Argyropoulos, Thermal properties of lignin in copolymers,
43 blends, and composites: a review, *Green Chemistry* 17(11) (2015) 4862-4887.
44
45
46
47 [72] F.J.B. Gomes, J.L. Colodette, A. Milanez, J.C. Del Río, M.C. dos Santos Muguet,
48 L.A.R. Batalha, A.d.F.G. Gouvêa, Evaluation of alkaline deconstruction processes for
49 Brazilian new generation of eucalypt clones, *Industrial Crops and Products* 65 (2015) 477-
50 487.
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

- 1
2
3
4
5 [73] R.M. Rowell, R. Pettersen, J.S. Han, J.S. Rowell, M.A. Tshabalala, 3 Cell Wall
6 Chemistry, (2005).
7
8
9
10 [74] R.C. Santos, A.C.O. Carneiro, A.F.M. Castro, R.V.O. Castro, Bianche, J. J., M.T.
11 Cardoso, Correlations of quality parameters of wood and charcoal of clones of eucalyptus,
12 Scientia Forestalis, 2011, pp. 221-230.
13
14
15 [75] Z. Luo, S. Wang, Y. Liao, K. Cen, Mechanism study of cellulose rapid pyrolysis,
16 Industrial & engineering chemistry research 43(18) (2004) 5605-5610.
17
18 [76] H. Yang, R. Yan, H. Chen, D.H. Lee, C. Zheng, Characteristics of hemicellulose,
19 cellulose and lignin pyrolysis, Fuel 86(12) (2007) 1781-1788.
20
21 [77] W.-H. Chen, P.-C. Kuo, S.-H. Liu, W. Wu, Thermal characterization of oil palm fiber
22 and eucalyptus in torrefaction, Energy 71 (2014) 40-48.
23
24 [78] K.-M. Lu, W.-J. Lee, W.-H. Chen, T.-C. Lin, Thermogravimetric analysis and kinetics
25 of co-pyrolysis of raw/torrefied wood and coal blends, Applied Energy 105 (2013) 57-65.
26
27 [79] I. Obernberger and G. Thek, Physical characterisation and chemical composition of
28 densified biomass fuels with regard to their combustion behaviour, Biomass and Bioenergy
29 27 (2004) 653–669.
30
31 [80] M. J. C. van der Stelt, H. Gerhauser, J. H. A. Kiel, and K. J. Ptasinski, Biomass
32 upgrading by torrefaction for the production of biofuels: A review, Biomass and Bioenergy
33 (2011).
34
35 [81] C. N. Hamelinck, R. A. A. Suurs, and A. P. C. Faaij, International bioenergy
36 transport costs and energy balance, Biomass and Bioenergy (2005).
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

[82] I. Obernberger and G. Thek, The pellet handbook: The production and thermal utilisation of biomass pellets. (2010).

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)

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

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

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

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

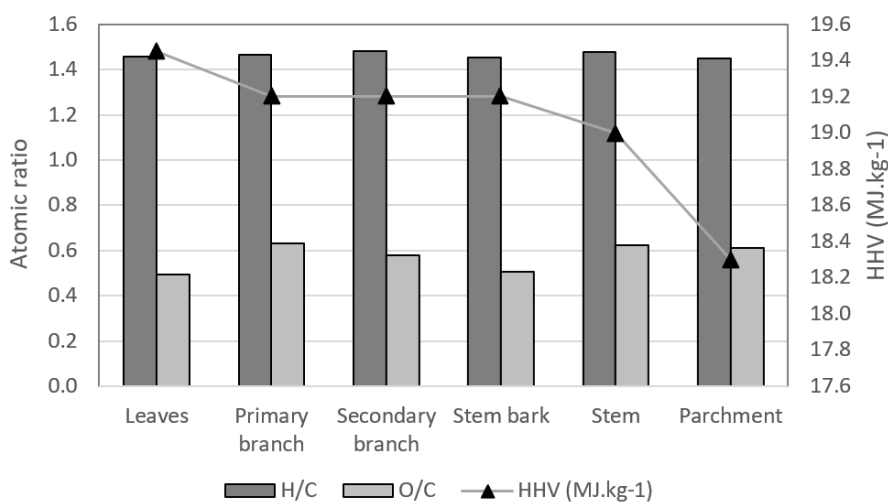


Figure 1. Molar ratios of hydrogen and oxygen to carbon and high heating value for studied residual biomasses from the coffee production chain.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

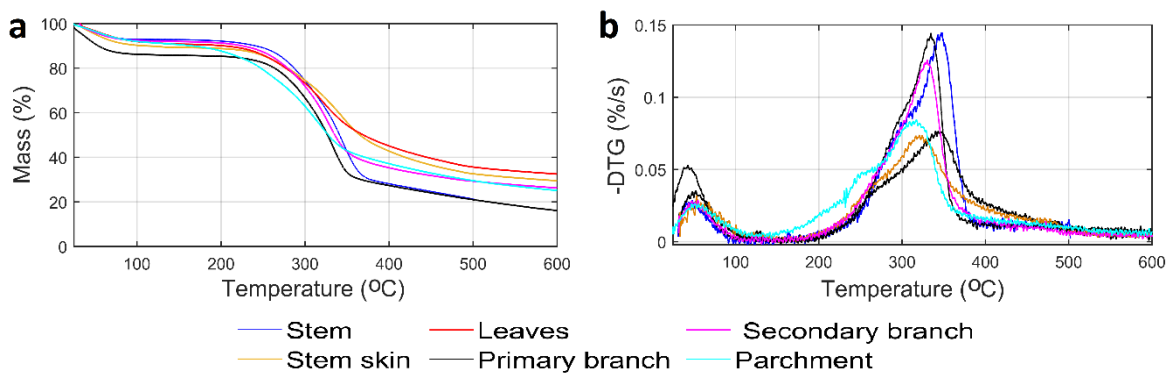


Figure 2. TG (a) and DTG (b) of the residual biomasses of the coffee production chain.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

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

*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

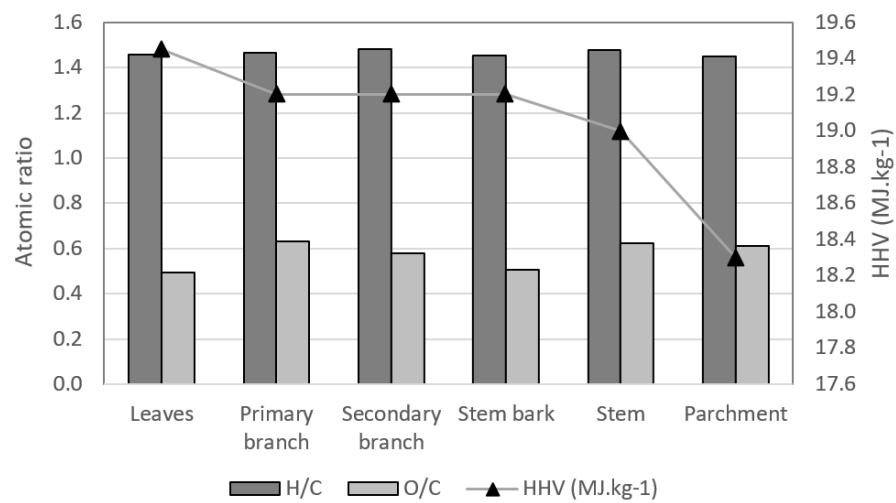


Figure 1. Molar ratios of hydrogen and oxygen to carbon and high heating value for studied residual biomasses from the coffee production chain.

Figure

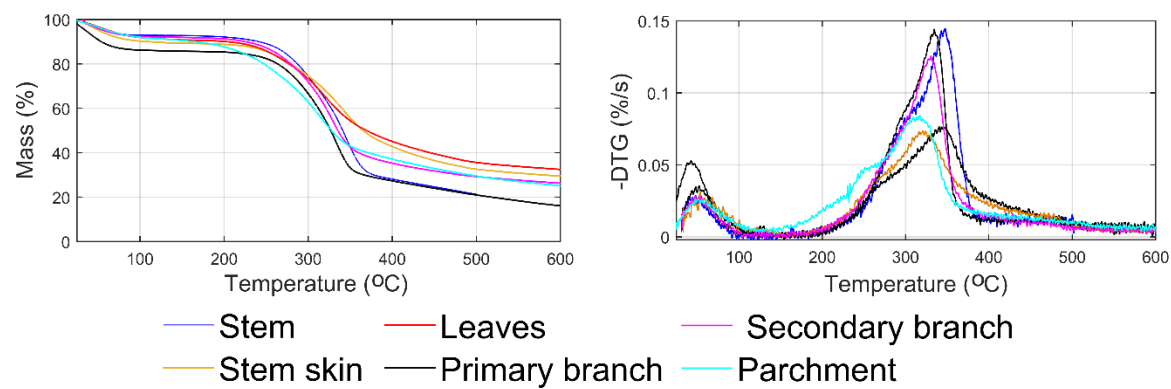


Figure 2. TG and DTG of the residual biomasses of the coffee production chain.