

## **Characterization of residual biomass from the harvest of *Eucalyptus saligna* for thermal conversion processes**

Caracterização da biomassa residual da colheita de *Eucalyptus saligna* para processos de conversão térmica

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### **Abstract**

Considering the increasing need for renewable products, the present work aims to evaluate the physical-chemical properties of the eucalyptus harvest residues and its constituent fractions individually (barks, leaves, and branches), through proximate, ultimate, energetic and thermal analyzes. The biomass studied was *Eucalyptus saligna* species, cultivated mainly for the production of pulp and paper. The proximate analysis of the residue resulted in the moisture content of 10.1%, ash content of 3.9%, volatile materials about 81.1%, and fixed carbon of 15.0%, showing similar values to the constituent fractions. The ultimate analysis of the residue resulted in 46.5% of carbon content, 5.8% of hydrogen, and 43.2% of oxygen. The high heating value (HHV) for the residue is 17.93 MJ/kg, comparable to other biomasses of importance, including eucalyptus wood, the noblest part of the forest cultivation. The thermogravimetric (TGA) and differential thermal analysis (DTA) were carried out and the resulting thermograms show three main ranges of biomass degradation. The first range, from 30 to 150 °C, corresponds to the drying of the material; in the range from 200 to 325 °C hemicelluloses degrade, with partial degradation of lignin and cellulose, and in the range from 325 to 380 °C, the majority of cellulose degradation takes place. The physical-chemical data demonstrate that the eucalyptus residue is an excellent source of biomass for thermal conversion processes. Obtaining products with higher added value from this residue contributes to the implementation of new technological practices that link economic development to environmental responsibility.

**Keywords:** Eucalyptus harvest residue; Physical-chemical characterization; Thermal conversion.

### **Resumo**

Considerando a crescente necessidade de produtos renováveis, o presente trabalho tem como objetivo avaliar as propriedades físico-químicas dos resíduos da colheita do eucalipto e suas frações constituintes individualmente (cascas, folhas e galhos), por meio de análises imediata, elemental, energética e térmica. A biomassa estudada foi a espécie *Eucalyptus saligna*, cultivada principalmente para a produção de celulose e papel. A análise imediata do resíduo resultou em teor de umidade de 10,1%, teor de cinzas de 3,9%, materiais voláteis em torno de 81,1% e carbono fixo de 15,0%, apresentando valores semelhantes entre as frações

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constituintes. A análise elementar do resíduo resultou em 46,5% de teor de carbono, 5,8% de hidrogênio e 43,2% de oxigênio. O poder calorífico superior do resíduo foi determinado em 17,93 MJ/kg, comparável a outras biomassas importantes, incluindo a madeira de eucalipto, a parte mais nobre do cultivo florestal. A análise termogravimétrica (TGA) e térmica diferencial (DTA) foram realizadas e os termogramas resultantes mostram três faixas principais de degradação da biomassa. A primeira faixa, de 30 a 150 °C, corresponde à secagem do material; na faixa de 200 a 325 °C as hemiceluloses degradam, com degradação parcial da lignina e celulose, e na faixa de 325 a 380 °C, ocorre a maior parte da degradação da celulose. Os dados físico-químicos demonstram que o resíduo do eucalipto é uma excelente fonte de biomassa para processos de conversão térmica. A obtenção de produtos de maior valor agregado a partir desse resíduo contribui para a implantação de novas práticas tecnológicas que vinculam o desenvolvimento econômico à responsabilidade ambiental.

**Palavras-Chave:** Resíduo florestal de eucalipto; Caracterização físico-química; Conversão térmica.

## 1 Introduction

The action plan prepared by the United Nations, called Agenda 2030, aims to promote global sustainable development. Among the objectives proposed and related to the environment, it can be highlighted: the encouragement to responsible consumption and production; the promotion of sustainable use of terrestrial ecosystems; the universal access to drinking water and basic sanitation; the promotion of sustainable agriculture; the expansion of clean and affordable energy generation; and the action against global climate change (UN, 2015). In order to meet the goals established in this action plan, the adoption of sustainable practices as a commitment of the whole society must be considered. In this context, industrial development is linked to the adoption of sustainable and socially responsible policies and actions, representing new challenges and opportunities for the different economic actors worldwide.

Agro-industrial residue and by-products can be used as an alternative to minimize environmental impacts. The possibility of applying these residues, both inside and outside the industry of origin could represent a viable and sustainable practice. In the pulp and paper industries, residues generated in harvesting wood from cultivated forests can be used as raw material to obtain products with higher added value. The characterization of the residual biomass from coffee production is an example of a study carried out to evaluate and quantify the properties of residual biomass as shown in (MENDOZA MARTINEZ *et al.*, 2019), where the residue can be viable for thermochemical conversion processes such as pyrolysis, gasification and combustion. Agroforestry and industrial residues have received

increasing attention as a raw material for thermal processes, aiming higher value products, as presented by (FERREIRA *et al.*, 2020), where sugar cane straw is used in pyrolysis processes. Other sources of residual biomasses were recently studied in (BHARATH *et al.*, 2020), where date palm trees from the West Asia region were characterized for the production of biofuels.

Lignocellulosic biomass is a complex mixture of natural polysaccharide polymers known as cellulose and hemicelluloses, apart from lignin and small amounts of other substances, such as extracts and inorganic materials contained in the cell wall of plants. Cellulose is the main constituent of the cell wall of vegetables, representing 40 to 45% of the dry matter of most woods. It is a long and linear polysaccharide, composed of the union of a single monomer (glucose) through  $\beta$ -(1,4) glycosidic bonds. Except for its degree of polymerization, cellulose has the same structure in all types of biomasses (CORTEZ (ORG); LORA (ORG); GÓMEZ (ORG), 2008). The high degree of ordering and crystallinity presented is due to a large number of existing hydrogen bonds, responsible for the relative thermal stability exhibited by the compound. Cellulose decomposes at temperatures ranging from approximately 315 to 400 °C (VIEIRA *et al.*, 2020). Hemicelluloses, on the other hand, comprise the non-cellulosic polysaccharides present in the biomass. They are generally made up of pentoses (xylose, arabinose, galactose, mannose, and rhamnose), have ramifications, are amorphous and much smaller than cellulose (YANG, H. *et al.*, 2007). They represent, on average, 20 to 30% of the dry matter of wood, and its degradation occurs at temperatures ranging from 190 to 360 °C (SHEN; GU; BRIDGWATER, A. V., 2010). The third major component of biomass is lignin, which is also a biopolymer, distinct from cellulose and hemicelluloses. Lignin can be represented by a three-dimensional, amorphous and branched macromolecule, with repetitive phenylpropane structures joined by ether (C-O-C) or carbon-carbon (C-C) bonds. This biopolymer represents, on average, 18 to 35% of the dry matter of wood. Its decomposition occurs over a wide temperature range, from 100 °C to 900 °C (SHEN; GU; BRIDGWATER, A. V., 2010), being responsible for the presence of phenols and other aromatic compounds in bio-oil, also contributing to the formation of biochar (PEREIRA *et al.*, 2013).

Thermochemical processing is considered as one of the technological alternatives to add value to products from agroforestry residues, highlighting pyrolysis as one of the most used methods. Fundamentally, pyrolysis is a physical-chemical process, in which the biomass is heated to temperatures ranging from 300 °C to 800 °C in a non-oxidizing atmosphere. Therefore, under such conditions, the organic matter undergoes decomposition, that is, the macromolecules of the original components of the biomass undergo rupture, resulting in a complex mixture of organic compounds. At the end of the process, three phases are produced: solid phase (also called charcoal or biochar), liquid phase, consisting of condensable vapors (called bio-oil or pyroligneous liquor) and the gas phase, consisting basically of CO, H<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> (non-condensable gases). The liquid and gaseous phases can be used to generate heat and electricity, also they can be converted, through chemical routes, into fuels and chemicals of high industrial demand (BRIDGWATER, T., 2006). Many of the fuels and chemicals obtained from petroleum can also be produced from bio-oil which is also nominated "green oil". The solid phase, in turn, is a source of low-cost carbonaceous material, which has multiple applications: soil fertilizer; bioadsorbent of heavy metals and polluting organic compounds in wastewater treatment plants; air decontamination agent and humidity controller in the construction industry; carbon-based electrodes in electrochemical energy conversion and storage systems such as superconductors and batteries; reducing agent in blast furnaces in the steel industry; and inert additive in the cosmetics and paints industry (FAKAYODE *et al.*, 2020).

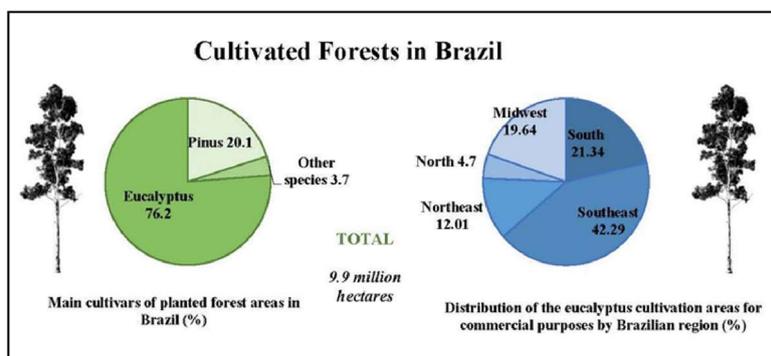
The pyrolysis of biomass is being extensively studied from different vegetable raw materials, such as *Prosopis juliflora* wood (CHANDRASEKARAN; RAMACHANDRAN; SUBBIAH, 2018), poplar wood (DONG *et al.*, 2012), and rice-husk (VIEIRA *et al.*, 2020; ZHANG, Z. *et al.*, 2020). Innovative proposals are presented by (LANGUER *et al.*, 2020), who analyzed the thermal processing of sludge from water and sewage treatment plants, showing potential for obtaining higher value-added products.

Considering the social, environmental, and economic impacts of eucalyptus cultivation, there is a growing concern and market interest in transforming forest residues into renewable products with higher added value. In this way, better use of cultivated forests

and the consolidation of a low carbon economy is achieved (IBA, 2017). The employment of biomass in energy generation processes can be considered a measure to mitigate emissions of greenhouse gases since the amount of CO<sub>2</sub> released during the combustion of biomass is similar to the absorbed during its growth. Thus, considering a cultivated area that will produce energy, the CO<sub>2</sub> balance is virtually zero and biomass can be considered a material with neutral emissions, causing less impact when compared to the burning of fossil origin materials.

According to data collected in the Survey on Vegetable Extraction and Silviculture, a publication from the Brazilian Institute of Geography and Statistics, in 2018 Brazil had 9.9 million hectares of forested area planted for commercial purposes, distributed over 3,488 cities, 76.2% of which corresponding to eucalyptus (IBGE, 2019). Figure 1 shows some information about the planted forest areas in Brazil and the main species cultivated.

Figure 1 – Main cultivated forests in Brazil and distribution of eucalyptus planted area by region in 2018



Source: adapted from IBGE (2019).

The management of soil regarding the eucalyptus forest residue has been widely discussed, taking into account soil conservation, plantation productivity, and the potential of the residue to produce higher added value products. Regarding soil conservation, after harvesting, the decomposition of barks, branches, and leaves contributes to fertilization. Most nutrients are found in barks and leaves, suggesting that the best harvesting practice involves thinning and cleaning the logs at the planting site (RESQUIN *et al.*, 2020). The removal of a portion of these residues does not compromise the nutrient stock in the soil (ROCHA *et al.*, 2016), which is in accordance with (NÚÑEZ-REGUEIRA, 2004) where it is

estimated that to avoid soil impoverishment, approximately 10% of the residues must remain at the plantation site, mainly the barks. Thus, the appropriate management and use of forest harvest residue allow better utilization of the material including energy purposes without compromising the production cycle.

Within the context of using the forest residue from the eucalyptus harvest to obtain products with higher added value, the characterization of the biomass properties presents great relevance, mainly considering applications for thermal conversion. The properties of biomass are reflected in the characteristics and yield of the products obtained, and allow the setup of the operational conditions for thermal conversion processes. The set of properties of biomass will define the applicability of the material, and its knowledge is mandatory to carry out any analysis of technical or economic feasibility.

The present study aims to evaluate the physical-chemical properties of eucalyptus forest residue (*Eucalyptus saligna*) and its fractions (barks, leaves, and branches), employing proximate, ultimate, energetic, and thermal analyzes. With the results obtained, it is possible to evaluate the quality of the residue as a source of biomass for thermal conversion processes as well as the production of biomaterials - biochar or bio-oil. The extensive characterization of this residual biomass is not available in the literature, and the results contribute to the expansion of knowledge of the residue of this important species, making it possible to add value to the residual biomass from the eucalyptus forest industry.

## 2 Materials and Methods

### 2.1 Biomass and preparation of samples

The eucalyptus forest residue used in the present study was obtained from the forest plantation of the company CMPC Celulose Brasil, located in the city called Barra do Ribeiro, in the state of Rio Grande do Sul, in southern Brazil, (30.35 °S, 51.25 °O), characterized by a subtropical climate. The site is the largest of CMPC properties in the Rio Grande do Sul state for the production of eucalyptus. The collected residue corresponds to the *Eucalyptus saligna* species at 7 years old. The appropriate harvest average age is close to 8 years,

considering the optimization of forest resources according to the company management plan (CMPC, 2019). This eucalyptus species is one of the most cultivated in the country, and it is characterized by having smooth bark, erect trunk, and reaching up to 30 meters in height. Figure 2 illustrates one of the *Eucalyptus saligna* planted fields, the remaining residue in the soil after harvest, and the collection of the residual biomass for characterization.

Figure 2 – *Eucalyptus saligna* planted area (left), residue deposited on the soil (center), and collection of the residual biomass (right)



A commercial eucalyptus clone has about 12% of roots, 8% of barks, about 2 to 5% of leaves, and the branches represent 4 to 8% of the tree (FOELKEL, 2010). From the study presented in (GATTO *et al.*, 2014) regarding the planting of *Eucalyptus* spp., the roots represent 9.4% of the tree, followed by 9.0% of branches, 5.6% of barks, and 4.5% of leaves. Regarding the generation of residue after harvest, approximately 23% of a eucalyptus tree becomes waste, with 12% barks, 6% branches, and 5% leaves (SILVA, F. De C. E, 2016).

The residue was collected and part of it divided into three constituent fractions, that is, barks, branches, and leaves. The samples were reduced in size in a knife mill and sieved through a 40-mesh sieve, to uniformize the particle size. The analyzes were performed on the residue as well as on its different fractions, characterizing the forest biomass and its constituents separately, and thus obtaining more comprehensive results.

## 2.2 Proximate analysis

The proximate analysis of a sample provides the content in mass percentage of moisture, ash, volatile materials, and fixed carbon, contributing to the understanding of the material behavior when subjected to a thermal conversion process. The tests were carried out in a 3000 W muffle furnace, equipment developed by the laboratory team (Figure 3) with digital PID temperature control and feature of programming ramps and thermal levels. Porcelain crucibles with lids were used to contain the sample (Figure 3).

Figure 3 – Muffle furnace developed by the research group (left) and crucibles used in the proximate analysis disposed inside the furnace (right)



To determine the moisture content (% U), the samples were dried at a temperature around 104 °C to 110 °C, until constant mass. The moisture content (% U) represents the amount of water present in the biomass and was determined according to Equation 1.

$$\%U = \frac{(A - B)}{A} \times 100 \quad (1)$$

where A = initial mass of the sample; B = final mass of the sample after heating.

The ash content (% AC) represents the mass of biomass that does not undergo combustion, that is, it represents the inorganic residue that remains after the burning of organic matter. It was determined by heating the sample to 750 °C for two hours with semi-capped crucibles. The ash content was calculated according to Equation (2).

$$\%AC = \frac{(C - D)}{A} \times 100 \quad (2)$$

where C = mass of the crucible with lid and ash residue; D = mass of empty crucible with lid; A = initial mass of the sample.

The volatile matter (% VM) represents the fraction of the biomass that is released in the form of gases formed from the exposure of the sample to high temperatures. The volatile fraction was determined by heating the sample in a crucible with a lid for 6 minutes at 950 °C. To determine the volatile matter, the percentage of total mass loss (% ML) in the thermal process was first calculated using Equation (3).

$$\%ML = \frac{(F - G)}{(F - D)} \times 100 \quad (3)$$

where D = mass of the empty crucible with a lid; F = mass of crucible with lid and sample before heating; G = mass crucible with lid and sample after heating.

The percentage of volatile material (% VM) is obtained by Equation (4), where the moisture content initially present in the sample is discounted.

$$\%VM = \%ML - \%U \quad (4)$$

where % ML = mass loss; % U = moisture content of the sample.

The fixed carbon (%FC) was determined by difference using Equation (5) and corresponds to the amount of carbon remaining after discounting moisture, ash content, and volatile matter.

$$\%FC = 100\% - (\%U + \%AC + \%VM) \quad (5)$$

### 2.3 Ultimate analysis

The elemental composition of biomass is an important property that defines the energy content and determines the applicability of a material. It is an assay used to determine the chemical composition of different materials, providing the mass percentages of the elements carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulfur (S) contained in the sample. In addition to the elements mentioned above, the ultimate analysis also provides the ratio between the atomic percentages of hydrogen/carbon (H/C) and oxygen/carbon (O/C). These relationships allow the calculation of the High Heating Value (HHV) and the Low Heating Value (LHV), due to the existence of a correlation between both.

The higher the proportion of oxygen and hydrogen, compared to carbon, the lower the energetic value of a material, due to the lower energy involved in the C – O and C – H bonds than in the C – C bond (MCKENDRY, 2002).

In this work, the elemental composition was determined through the use of empirical correlations based on a large number of data and covering all categories of solid lignocellulosic materials (PARIKH; CHANNIWALA; GHOSAL, 2007). Such correlations use the results previously obtained in the proximate analysis, being a simple, rapid, economic, and efficient method. The values of the ultimate analysis were obtained through Equation 6 (wt% carbon), Equation 7 (wt% hydrogen), and Equation 8 (wt% oxygen), as presented in (PARIKH; CHANNIWALA; GHOSAL, 2007).

$$C(\%) = 0.637(FC) + 0.455(VM) \text{ (wt\%)} \quad (6)$$

$$H(\%) = 0.052(FC) + 0.062(VM) \text{ (wt\%)} \quad (7)$$

$$O(\%) = 0.304(FC) + 0.476(VM) \text{ (wt\%)} \quad (8)$$

where CF = fixed carbon; VM= volatile material.

## 2.4 High heating value

The characterization of the high heating value (HHV) allows the knowledge of the energy efficiency of the material, that is, the amount of energy released in the form of heat during the complete combustion per unit mass of the material, which can be measured in kJ/kg or MJ/kg. The conduction of this assay traditionally requires a bomb calorimeter and gaseous oxygen, among other materials, generating a relatively high cost in the analysis. Without significant loss of quality in the results, empirical equations can be used that define a general correlation between the HHV (on a dry basis) and the values obtained in the proximate analysis. The use of validated empirical correlations enables a quick and efficient assessment of the energy performance of fuels and biomasses, in general. The HHV is calculated using equation (9), presented by (PARIKH; CHANNIWALA; GHOSAL, 2005).

$$HHV = 0.3536(\%FC) + 0.1559(\%VM) - 0.0078(\%AC) \text{ (MJ/kg)} \quad (9)$$

where: % FC = fixed carbon (wt%); %VM = volatile material (wt%); %AC = ash content (wt%).

## 2.5 Thermal analysis

The thermal analysis comprises several techniques that relate the physical-chemical properties of a sample over a temperature range. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) show the mass loss and the derivative of mass loss with temperature, respectively. They were carried out to verify the thermal degradation kinetics of the samples and to support pyrolysis tests since the stages observed in the curves are directly related to the thermal degradation of hemicelluloses, cellulose, and lignin. Samples of approximately 20 mg were used, in platinum crucible, in a TGA equipment, brand TA Instruments, model SDT Q600 V20.9 Build 20, shown in Figure 4. The assays are performed under inert atmosphere (N<sub>2</sub>) with 100 mL/min flow rate and heating rate of 30 °C/min, and temperature ranging from 25 to 450 °C.

Figure 4 – TGA equipment model SDT Q600 (left) and crucible used to perform the thermal analysis (right)



## 3 Results and Discussion

### 3.1 Proximate Analysis

The results of the proximate analysis of the forest residue from the eucalyptus harvest and its fractions separately are shown in Table 1. The amount of water present in the biomass impacts on the physical-chemical properties of the material, highlighting the low heating value (LHV), which is strongly influenced, both being inversely proportional, that is, the LHV decreases with the moisture content. About volatile content, higher percentages favor the formation of the liquid phase (bio-oil), while smaller percentages favor the formation of the solid phase (biochar). Besides, the higher the volatile content, the greater the reactivity of the material, and the faster it will burn. The ash content reflects the non-combustible content of the material, that is, minerals and inorganic compounds, such as oxides of calcium, magnesium, potassium, sodium, silicon, iron, and phosphorus. The ash content constitutes on average less than 1% by mass of the materials of lignocellulosic origin. A high ash content reduces the HHV and LHV and represents impurities that must be reduced for better thermal conversion of the biomass, without causing damage to the reactor. The gravimetric yield of biomass, in terms of biochar, is directly proportional to the fixed carbon content and can be considered an important factor in the energy qualification of the final product, as it is directly related to the heating values and the lignin content (PEREIRA *et al.*, 2013).

Table 1 – Proximate analysis results for the biomass and its different components

Sample	% U	% AC	% VM	% FC
Residue	10.1	3.9	81.1	15.0
Barks	10.2	6.2	79.9	13.9
Leaves	9.1	3.7	81.0	15.3
Branches	10.4	1.9	85.1	13.0

When observing the results presented in Table 1, it can be seen that the values found are similar to those reported by (SILVA, F. T. M.; ATAÍDE, 2019), who have analyzed wood from a different species of eucalyptus (*Eucalyptus urograndis*), in carbonization studies, and obtained values of 7.6%, 0.46%, 87.95% and 11.59% for moisture, ashes, volatiles, and fixed carbon, respectively. The ash content of the residue is higher than that of wood, a more noble part, and is mainly due to the contribution of barks. The results found in (ALMEIDA;

BRITO; PERRÉ, 2010) for bark samples of *Eucalyptus saligna* are similar to those found in the present study, recording the following values for ash content, volatile materials, and fixed carbon, in the order: 6.20%, 81.60% and 12.20%. The same authors found for the barks of *Eucalyptus grandis* 5.50% for ash content, 60.00% for volatile material, and 34.50% for fixed carbon. It is important to note in the present study the characterization of the eucalyptus harvest residue and its other components, such as leaves and branches, not extensively reported in the literature, increasing the knowledge about alternatives applicable to the countries that have eucalyptus cultivations.

The water content found is consistent with that expected for vegetable materials and comparable to that found in the literature for eucalyptus wood, although it may vary with the time of harvest. From an energetic point of view, the recommended values must be below 30%, since a higher moisture percentage leads to a decrease in LHV and a consequent decrease in the efficiency of the thermal conversion processes (IGNACIO; SANTOS, P. E. De A.; DUARTE, 2019). Biomasses with low moisture content (less than 10%) are desirable due to their higher energetic efficiencies and improved rate of thermal processes (FERMANELLI *et al.*, 2020; SHER *et al.*, 2020).

The most pronounced difference to the results of the residual biomass and the values presented in the literature for eucalyptus wood is the ash content. However, according to (IGNACIO; SANTOS, P. E. De A.; DUARTE, 2019) the ash content can be divided into two parts: the natural ash from the mineral composition of the material itself and the ash from cutting and transporting biomass, which is a consequence of the adhesion of particles such as soil, sand, stones and the bark itself. It can be seen that the ash content of the residue (3.9%) is very similar to that of leaves (3.7%), with the highest content in the bark (6.3%) and the lowest in the branches (1.9%). The ash content of the eucalyptus residue (3.9%) is comparable to the one found from the dry coffee husk, which is also lignocellulosic biomass, that contains 3.55% ash, which is a low value compared to other agriculture residues (SETTER *et al.*, 2020). High ash concentrations are not favorable for thermal conversion, since they decrease the burning yield, in addition to causing problems in the reactor structure, such as scale, corrosion, and slag formation.

It is also noted, through the data in Table 1, the high content of volatile material (81.1%) and fixed carbon (15.0%) for the residue. Compared with data from the literature (FERMANELLI *et al.*, 2020) for three other biomass residues, the following values are found for volatile matter and fixed carbon respectively: 53.80% and 17.01% for rice husk, 70.03% and 23.18% for peanut shell, 64.47% and 16.54% for wheat straw. Thus, it can be seen that the data obtained in the present study demonstrate the feasibility of the residual biomass from the eucalyptus harvest to the thermal conversion processes.

### 3.2 Ultimate Analysis

The ultimate analysis provides the proportion of C, H, O, N, and S. For energy purposes, in general, biomasses with a high content of carbon and low content of oxygen are preferred. Table 2 shows the results obtained for the elemental composition of the residue and its fractions separately (barks, branches, and leaves), in the percentage of carbon (C), hydrogen (H), and oxygen (O). According to the data in Table 2, the samples studied have similar values in terms of C, H, and O, being around 46%, 5%, and 43%, respectively. As a comparison, lignocellulosic biomasses have an average elemental composition of 51% carbon and 42% oxygen in mass (ZHANG, L.; XU, C. (Charles); CHAMPAGNE, 2010). The results presented by (CARDONA *et al.*, 2019) show the elemental composition of *Eucalyptus* spp. with 46.5% (C), 5.1% (H), and 47.6% (O), values very similar to the residue studied in this work.

Table 2 – Data obtained in the ultimate analysis for the studied biomass and its different components

Sample	% C	% H	% O
Residue	46.5	5.8	43.2
Barks	45.2	5.7	42.2
Leaves	46.6	5.8	43.2
Branches	47.0	5.9	44.5

### 3.3 High heating value

The elemental composition is directly related to the heating values, since it provides the mass percentages of the main elements forming the biomass and thus it is possible to relate to the amount of energy released in the breaking of the chemical bonds of these elements. The results of the HHV are shown in Table 3.

Table 3 – High heating values for the studied biomass and its different components

	<b>Residue</b>	<b>Barks</b>	<b>Leaves</b>	<b>Branches</b>
HHV (MJ/kg)	17.93	17.31	17.99	17.87

When comparing the data in tables 1, 2, and 3, it can be seen that barks with a higher percentage of ash have lower energy efficiency. Similar values were found by (SILVA, F. T. M.; ATAÍDE, 2019), who analyzed samples of *Eucalyptus urograndis* wood already used in the Brazilian energy matrix. The analysis of the barks indicates that even though the material is less noble because it contains the lowest levels of carbon, and higher ash content, it is still somewhat comparable to the other constituent fractions in terms of releasing energy by combustion.

Table 4 shows the values of ultimate analysis and HHV reported in the literature for some sources of biomass with the purpose of comparison with the residual biomass studied in this work. A general analysis of Table 4 shows that all the biomasses listed have C, H, and O contents in the 40 to 50%, 5 to 7%, and 35 to 53% ranges, respectively. Eucalyptus residue shows values very similar to those of eucalyptus wood itself with sometimes a higher carbon and lower oxygen content, thus giving to this residue a non-negligible energetic value compared to other biomasses currently studied.

When analyzing the HHV for several biomasses (residual and non-residual) of eucalyptus (Table 4), it can be observed the proximity among them, which vary about 15 and 20 MJ/kg. There is no significant difference between the values presented by the wood and the residue, confirming the potential of residual biomass from eucalyptus for application in energy processes.

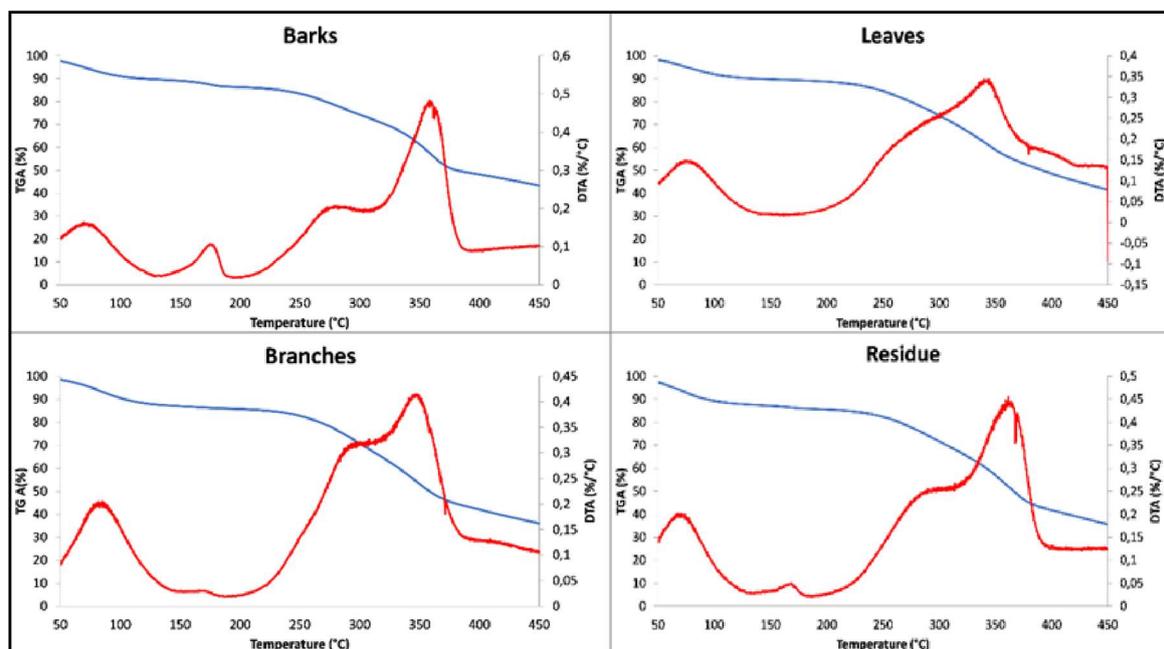
Table 4 – Ultimate and energetic analyzes data for different biomasses

Biomass	% C	% H	% O	HHV (MJ/kg)	Reference
Residue from <i>Eucalyptus saligna</i>	46.5	5.8	43.2	17.93	Present study
<i>Eucalyptus urosemante</i>	-	-	-	18.60	(IGNACIO; SANTOS, P. E. De A.; DUARTE, 2019)
Wood - <i>Eucalyptus urograndi</i>	46.13	5.90	47.83	20.25	(SILVA, F. T. M.; ATAÍDE, 2019)
Bark - <i>Eucalyptus saligna</i>	-	-	-	17.10	(IGNACIO; SANTOS, P. E. De A.; DUARTE, 2019)
Wood - <i>Eucalyptus saligna</i>	-	-	-	19.90	(IGNACIO; SANTOS, P. E. De A.; DUARTE, 2019)
Bark - <i>Eucalyptus grandis</i>	-	-	-	16.90	(IGNACIO; SANTOS, P. E. De A.; DUARTE, 2019)
Wood - <i>Eucalyptus grandis</i>	-	-	-	20.00	(IGNACIO; SANTOS, P. E. De A.; DUARTE, 2019)
Raw bark - <i>Eucalyptus</i> spp.	40.39	5.49	35.5	-	(MARTINI; AFROZE; AHMAD RONI, 2020)
<i>Eucalyptus tereticornis</i> debarked	50.83	5.86	43.22	-	(WU <i>et al.</i> , 2019)
Raw biomass <i>Eucalyptus</i> spp.	46.5	5.1	47.6	18.10	(CARDONA <i>et al.</i> , 2019)
Rice husk	45.09	6.62	47.78	17.94	(FERMANELLI <i>et al.</i> , 2020)
Rice husk	31.39	3.39	43.40	15.77	(VIEIRA <i>et al.</i> , 2020)
Peanut shell	50.64	6.86	41.32	20.60	(FERMANELLI <i>et al.</i> , 2020)
Wheat straw	43.09	7.28	47.02	17.35	(FERMANELLI <i>et al.</i> , 2020)
Wheat straw	41.32	5.69	51.81	15.56	(SHER <i>et al.</i> , 2020)
Barley straw	40.87	5.78	52.80	15.46	(SHER <i>et al.</i> , 2020)
Coffee husk (dry)	46.41	6.33	44.51	18.50	(SETTER <i>et al.</i> , 2020)

### 3.4 Thermal Analysis

Thermogravimetric analysis is a high-precision analytical technique that can be used to support the study of pyrolysis at low heating rates, being able to provide relevant information on the kinetics of the reaction processes. In Figure 5, the resulting thermograms exhibit the mass loss (TGA) and the derivative curves with temperature (DTA). Both results show the mass loss, where can be identified the changes undergone by the material over a controlled temperature range.

Figure 5 – TGA and DTA curves of eucalyptus harvest residue and its components: barks, leaves, branches, and residue



The thermal analysis of the residue and its fractions did not show significant differences, presenting three ranges of degradation. The first range, from room temperature to about 100 °C, is attributed to the drying of the material, i.e. evaporation of water and the loss of some volatile components that are present in the sample, with an average value of 10% of mass loss (Table 5). It was also observed, from 100 to 200 °C, an average loss of mass that varied from 3.25 to 4.80% (Table 5). This is considered a zone of thermal stability, where temperature higher than 200 °C usually determine the beginning of the degradation of the lignocellulosic biomass components. The biomass is thermally stable below this temperature range as long as it is not subjected to prolonged periods (RANDRIAMANANTENA *et al.*, 2009).

The second range, from 200 to 325 °C, corresponds to the major degradation of hemicelluloses (SILVA, C. M. S. DA *et al.*, 2017). Hemicelluloses are less thermally stable, due to their structural characteristics (YANG, H. *et al.*, 2007). In this range, there is also degradation of lignin and cellulose, but at a lower rate. The third and last range, from approximately 325 to 380 °C, is attributed to cellulose degradation (SILVA, C. M. S. DA *et al.*, 2017). Cellulose is more resistant to thermal degradation and is responsible for about half

of the dry biomass composition, which explains the higher peak intensity in the DTA graph about 350 °C (YANG, H. *et al.*, 2007). The absence of a specific peak for lignin may be related to the fact that this biopolymer undergoes slow degradation over a wide temperature range, which varies from 150 to 900 °C, as a result of its high thermochemical stability (FERMANELLI *et al.*, 2020; YANG, H. *et al.*, 2007). Also, the low rate of mass loss of lignin normally results in a high yield of solid products from the pyrolysis process (QUAN; GAO; SONG, 2016). Furthermore, the temperature of the analysis did not exceed 450 °C, since this range is suitable for the efficiency of the slow pyrolysis process when the solid phase (biochar) is targeted. Beyond that temperature, it is expected that there will be no further degradation of hemicelluloses and cellulose, and the residual mass can be attributed almost entirely to lignin (FERMANELLI *et al.*, 2020). Results for thermal degradation of wood from four eucalyptus hybrids reported in (SANTOS, R. C. DOS *et al.*, 2012) are similar to that of the residue and its fractions analyzed in this work.

In Table 5, mass loss and residual mass are presented as a function of different temperature ranges, obtained from the thermogravimetric analysis, to assess the thermal stability of each of the samples studied.

Table 5 – Values of mass loss and residual mass as a function of temperature ranges (in percentage) for the biomass studied and its different constituents

Sample	room temp. – 100 °C	100 – 200 °C	200 – 300 °C	300 – 400 °C	400 – 450 °C	Residual mass (%)
Barks (%)	8.92	4.75	29.30	26.13	4.83	26.07
Leaves (%)	8.07	3.25	14.75	25.37	7.13	41.43
Branches (%)	9.48	4.80	15.00	28.69	5.95	36.08
Residue (%)	10.70	3.76	13.85	29.89	6.26	35.54

Table 5 shows that leaves were the material that had the highest residual mass and consequently the lowest mass loss (about 59%) throughout the thermogravimetric analysis, and can be considered the most thermally stable. The barks showed the highest overall mass loss (about 74%) and are considered the least stable up to the employed temperature

of 450 °C. In general, a more thermally stable material corresponds to higher solid phase yield, that is, a greater amount of biochar is produced during the pyrolysis process.

According to the result found, it is expected that the residue from the eucalyptus harvest produces around 35% of the solid product and 65% of liquid and gaseous products in thermal processing up to 450 °C. As reported in the thermogravimetric analysis (SANTOS, R. C. DOS *et al.*, 2012) for the wood of four eucalyptus hybrids, significantly lower values were found for the residual mass. Investigating thermal degradation up to a maximum temperature of 500 °C, they found values between 4 to 11% for the solid phase yield. On the other hand, as reported by (PEREIRA *et al.*, 2013) when studying clones of *Eucalyptus* spp., mean residual masses that varied from 25.4 to 27.6% were found, values closer to those from the present study. Therefore, comparing the results, the residual biomass from the harvest of the *Eucalyptus saligna* presents appreciable thermal stability, which must be considered when the objective is the production of the solid phase. The higher values found for the residual mass are due to the chemical composition of this material, especially the lignin content. The higher the lignin content, the greater the thermal resistance of the biomass, and the conversion to the solid phase (VIEIRA *et al.*, 2020). The proportion of products obtained through thermal conversion depends on the biomass characteristics, temperature, and heating rate, among other operational parameters.

A more detailed analysis of Table 5 reveals that the highest thermal degradation of biomass occurred in the temperature range from 300 to 400 °C, in which losses of around 25 to 30% by weight were obtained. This temperature range is normally attributed to cellulose degradation. Similar results to those obtained in the present work are found in the literature for varied sources of biomass (FERMANELLI *et al.*, 2020; SANTOS, R. C. DOS *et al.*, 2012). The use of the eucalyptus harvest residue is still a source of biomass to be better explored. It shows potential for biochar production, with yield in the range of 30 - 35%. For energetic applications, the HHV in the range of 17 ~ 18 MJ/kg is also comparable to traditional biomass.

## 4 Conclusions

The study of the residual biomass from *Eucalyptus saligna* carried out through proximate, ultimate, energetic, and thermal analyzes shows that thermal conversion processes through pyrolysis is a viable technological alternative to add value to this material. Based on the results of thermal analysis, the expected yield for the biochar produced is approximately 35%. The results of characterizations carried out can be used to manage the operational conditions for the processing of pyrolysis. The findings also encourage the best use of cultivated forests, through obtaining bioproducts with superior quality and a higher added value from harvest residues, since part of them can be removed from the soil without compromising nutrient content.

Compared with other biomasses (residual or not), the residue from the harvest of *Eucalyptus saligna* has physical-chemical properties that render an excellent source of biomass for thermal conversion processing. Obtaining new products from the eucalyptus harvest residue can foment practices that combine profitability and sustainability, leading a positive return for the agroforestry area.

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