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WOOD QUALITY OF TEN CLONAL PROGENIES OF RUBBER TREE AS RAW MATERIAL FOR BIOENERGY

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ABSTRACT

The use of wood as a bioenergetic source requires knowledge of its technical properties. The rubber tree *Hevea brasiliensis* has an economic life cycle of 25 to 30 years in Brazil. It is used for extracting rubber and generating residual wood for fuel. Our goal was to characterize the wood quality of 10 clonal progenies as a source of raw material for bioenergy. Ten clonal progenies of 12-year-old *Hevea brasiliensis* from an experimental planting in Selvíria municipality were evaluated. Three trees per clone were evaluated for individual properties of Higher Heating Value, immediate chemical analysis, chemical composition, fiber di-

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mensions, thermogravimetric analysis of wood under nitrogen atmosphere and Fourier Transform Infrared Spectroscopy analysis. We highlight clone IAC 311 for fuel because it presents elevated Higher Heating Value and fixed carbon and less volatile material. However, the other genetic materials studied also meet the specifications for energy use and can be highly viable given their physical, chemical, energy, and thermal properties.

Keywords: Raw material, bioenergy, chemical composition, *Hevea brasiliensis*, Fourier Transform Infrared Spectroscopy, thermogravimetric biomass, wood density.

INTRODUCTION

The reduction of fossil fuels, especially oil, natural gas and coal, was discussed by Gonçalves *et al*. (2015), while their substitution by renewable energy sources was suggested by Mehmood *et al*. (2017). The generation of energy through wood can be a good alternative to replace the energy generated by fossil fuels, since it emits less greenhouse gases in the combustion process, considering that the use of fossil fuels leads to numerous problems to the environment, which is caused by excess CO_2 in the atmosphere, including: acid rain, caused by the reaction between pollutants and water vapor in the atmosphere; gradual decrease of the ozone layer and water contamination (Skeva *et al*. 2014). Vegetal biomass can be used to obtain the most varied forms of energy, whether by direct or indirect conversion. The advantages of using this material as a substitute for fossil fuels include less atmospheric pollution and the stability of the carbon cycle. Compared to other types of renewable energy, vegetable biomass stands out for its high energy density and the ease of storage, conversion, and transport of this material (Saccol *et al.* 2020).

The internal supply of energy in Brazil consists of 43,5 % of renewable sources, of which biomass corresponds to 9,8 % Empresa de Pesquisa Energética-EPE (2022). According to data from Brazilian tree industry (2023), areas with forests planted for industrial purposes in Brazil totaled 9,9 million in 2022 and contributed 91 % of all wood produced for industrial purposes.

Species and clones of *Eucalyptus* and *Corymbia* are widely used as sources of biomass in Brazil (Tenorio and Moya 2013). However, knowledge of other forest species and clonal progenies, such as *Hevea brasiliensis*, can be an alternative to increase the use of forest biomass and reduce dependence on fossil fuels in the energy matrix, thus contributing to the country's economic development.

Hevea brasiliensis is an important forest species because its main output is latex, which is responsible for the fabrication of several synthetic products for industrial use. However, when rubber trees no longer reach acceptable levels of latex production, which varies between 25 and 30 years of age (Lima *et al*. 2020), their exploitation becomes economically unfeasible. Consequently, these trees are felled for reformulation of planting, and, in general, the wood does not have an adequate destination, other than use as firewood in small rural locations. No thought has been given to its energetic characteristics for industrial use (Ramos *et al*. 2016).

Since 1995, the Brazilian State of São Paulo has established itself as the main rubber producer, representing half of the country's production (Brioschi *et al*. 2010). The planted area in Brazil has been increasing significantly, from 159,500 ha to 218,307 ha in 2022 alone (IBÁ 2023). This increase in the cultivable areas of the species in Brazil, was due to the potential of the rubber tree species in capturing CO_2 and other gases harmful to the environment and the use of the species in agroforestry systems (Satakhun *et al*. 2019). Thus, the species has potential for latex extraction, helps to balance the environment, and is a source of renewable biomass for clean energy production.

According to Ratnasingam *et al.* (2009), aside from latex, *H. brasiliensis* produces a large amount of biomass, an estimated 2,1 m^3 from each tree at 25 years old with a tree diameter of 40 cm and 20 m in height. Therefore, it is well past time to consider identifying alternative uses of this biomass, as well as study of this waste to produce energy, which would help reduce dependence on fossil fuels with implications for the environment Bersch *et al*. (2017).

Wood quality evaluation for energy purposes aims to measure and classify the superior characteristics of clonal progenies because such evaluation is essential to decision-making in the implementation of reforestation projects aimed at the use of biomass as an energy source. Wood characteristics provide a way to differentiate among different clone types (Lima *et al*. 2011). According to Protásio *et al*. (2019), the main wood properties for the selection of energy species are basic density, higher heating value, lignin content, ash contents, fiber

wood anatomy and thermal behavior.

Among wood properties, basic density is considered one of the most important parameters among physical wood properties, as it affects most other properties. Its effects, however, are interactive and difficult to assess in isolation, requiring knowledge of other quality wood properties for the selection of superior clonal genotypes (Pereira *et al*. 2016). According to Purba *et al.* (2021), forest biomass quality for energy production varies among genetic materials between and within wood, thus it is important to evaluate wood quality to validate its suitability for use. Scriba *et al.* (2021), cite that the study of wood properties among clones with potential employment in the forestry market is important for the selection and recombination of superior genetic material from the best individuals with the best quality of the desired technological properties for the establishment of better-quality plantations for the desired use.

Chemical and anatomical composition of wood is also relevant for energy use. Specifically, when wood is thermally degraded, it undergoes a transformation process whereby all its primary components, including cellulose, hemicellulose, and lignin, are drastically altered, in turn affecting its energetic properties (Yu *et al*. 2017).

The immediate chemical analysis of an energy source provides a profile of volatile material contents, fixed carbon, and ash (residual material), all of which influence the properties of burning fuel because volatile constituents burn quickly, and fixed carbon burns slowly (Fernandes *et al*. 2013). The content of volatile materials and fixed carbon is causally related to calorific value, increasing the burning time of the energy source. The content of volatile materials and fixed carbon in wood are interdependent properties since the percentage of ash thereof is generally low (Silva *et al*. 2020).

Thermal stability is an essential consideration when selecting biomass with energy potential. Techniques, such as thermogravimetric analysis (TGA), make it possible to understand biomass decomposition as a function of heating in thermochemical conversion processes. Thermogravimetric analysis consists of analyzing variation of sample mass using a system with controlled temperature and atmosphere. In addition to obtaining information on composition and thermal stability, this analysis provides an assessment of temperature ranges at which decomposition is most pronounced (Yeo *et al*. 2019). The evaluation of energy properties and efficiency of material allows the selection of more competitive materials compared to other energy sources.

In this context, our objective was to characterize the quality of the wood from 10 clones of *Hevea brasiliensis,* as a source of raw material for bioenergy through the characterization of the anatomical properties of fiber length and width, physical property basic density of the wood: energy properties through the characterization of the higher heating value, immediate analysis through the contents of extractives, lignin and holocellulose. We also evaluated the chemical characterization of the main chemical groups of wood through FTIR- Fourier Transform Infrared Spectroscopy, and biomass characterization through thermal degradation by thermogravimetric (TGA) analysis.

MATERIALS AND METHODS

Selection of species and planting

Wood samples were collected from 30 with 12-year-old rubber *Hevea brasiliensis* (Willd. ex Juss.) Muell. Arg. trees (Table 1), three of each clonal progeny, in the municipality of Selvíria, Mato Grosso do Sul State (20°20′S, 51°24′W, elevation 350 m). The trial plantation was established in 2006 at a spacing of 3 m × 3 m from seeds of 10 free-pollinated clones (IAC 40ill., IAC 41ill., IAC 326ill., IAC 311ill., IAC 301ill., IAN 873ill., GT1ill, PB 330ill., Fx 2261ill., and RRIM 725ill.). Soil in the experimental area was classified as Red Latosol with clayey texture (Santos *et al*. 2006). In 2018, three selected trees of clonal progenies were felled, and discs 10 cm in thickness from each tree at breast height (1,30 m from the ground) were cut from each tree. From each disc, samples close to the bark were used to determine HHV, chemical constituents, wood density, fiber dimensions, thermogravimetric parameters, and properties under Fourier-Transform Infrared Spectroscopy- FTIR.

Table 1: Improved population consisting of ten open-pollination progenies.

Clonal progenies	Parental
IAC 40ill.	RRIM 608 x AVROS 1279.
IAC 41ill.	RRIM 608 (AVROS 33 x Tjir 1) x AVROS 1279 (AVROS 256 x AVROS 374)
IAC 326ill.	RRIM 623 (PB 49 $_X$ Pil B 84) x Fx 25 (F351 X AVROS 49)
IAC 311ill.	AVROS 509 (Pil A 44 x Lun N) x Fx 2 5 (F351 x AVROS 49)
IAC 301ill.	RRIM 605 x AVROS 1518.
IAN 873ill.	PB 86 x FB 1717.
GT1ill.	Primary clone
PB 330ill.	PB 5/51 x PB 32/36
Fx 2261ill.	F 1619 x AVROS 183.
RRIM 725ill.	Fx25 (F351 x AVROS 49)ill.

ill.= illegitimate (progenies obtained from a free-pollination clone).

Determination of chemical and energy properties

Wood was ground in a Wiley knife mill, of metallic steel type, manufactured by the Marconi-materials company, with the company located in the municipality of Piracicaba, in the state of São Paulo, Brazil, transformed into sawdust, and then sieved with 40-60 mesh to later characterize its chemical and energetic properties.

Higher heating value

Samples were fragmented into smaller pieces with a hammer and chisel and milled in a micro mill. The samples, before the determination of the Higher Heating Value (HHV), were dried in greenhouses to determine the moisture content. To perform the analysis, the isoperibolic method was used with an IKA C200, calorimeter of the type coated plastic from the company Biovera-Laboratory Equipment and Technical Assistance, with its company based in Rio de Janeiro, in the state of Rio de Janeiro, Brazil. the methodology adopted for the determination of the HHV, according to ASTM D5865-98 (2004).

Proximate analysis

Prior to these analyses, the biomasses (all treatments) were dried in an oven at 100 °C for 10 minutes to get the moisture to 0 %. The determination of ash content was performed according to the standard ASTM D1102-84 (2013), and the volatile content was determined according to ASTM E872 (1982). Both tests were done in triplicate. Both standards were adopted, as all material was used for the calculation. The fixed carbon content was calculated according to Equation 1.

$$FCC = 100 - \left(AC + VC \right) \quad (1)$$

Where: FCC= Fixed Carbon Content (%); AC= Ash Content (%); VC= Volatile Content (%).

Chemical assays

To determine extractives (EX) and lignin (LI) contents, TAPPI T204 (2001) and TAPPI T22 (2011) were used, respectively. The samples were fragmented into smaller pieces with a hammer and chisel and milled in a micro mill. The resulting powder was sieved through 40 mesh and 60 mesh screens, and the material retained on the last sieve was used for analysis. The analyses were sequential such that the extractives were

first removed, then lignin by acid treatment, with holocellulose (HO) content finally calculated. For extractive contents, extractions were performed in solutions of toluene: alcohol (2:1v:v) and alcohol, at times exceeding 12 h in a Soxhlet extractor. For lignin, extractive-free powder was prepared in several stages with 72 % sulfuric acid to obtain insoluble and soluble lignin (Cary 100 UV-visible spectrophotometer). Finally, the two lignin values were added. The content of insoluble lignin (IL) was determined according to Equation 2.

$$IL = \left(\frac{DWlig}{DW} \right) x\ 100 \quad (2)$$

Where: DW=dry sawdust weight, and DWlig=dry weight of insoluble lignin. Soluble lignin (SL) filtrates and the blank were read at two wavelengths (215 nm and 280 nm), respectively, using quartz cuvettes.

The soluble lignin (SL) content was determined according to Equation 3.

$$SL = \frac{\left(4,53\left(L215 - blank\right) - L280 - blank\right)}{\left(300DW\right)} x\ 100 \quad (3)$$

Where: DW=dry sawdust weight. Ex and Li were expressed as a percentage (%) of oven-dried weight of unextracted wood.

After determining the levels of extractives, soluble and insoluble lignin, the holocellulose (HO) content was calculated according to Equation 4.

$$HO = \left(100 - \left(Ex + Li\right)\right) \quad (4)$$

Where: Ex=Extractives and Li=Lignin.

To determine each variable, a triplicate was used for each clone of *Hevea brasiliensis*.

Wood density

Wood density was determined by the ratio between dry mass and saturated volume, according to Brazilian standard ABNT NBR-11941 (2003).

Fiber analysis

Small pieces were cut from the side of samples, and macerations were prepared according to the modified Franklin method (Berlyn and Miksche 1976). Modifications resulted from the differences caused by the higher concentration of hydrogen peroxide used in our study. Macerations were stained with alcoholic safranin and mounted in a solution of water and glycerin (1:1). Fiber measurements were performed on an Olympus CX 31 microscope equipped with a camera (Olympus Evolt E330) and a computer with image analyzer software (Image-Pro 6.3). Terminology followed the IAWA list (1989). Fiber length (FL) and fiber wall thickness (FWT) were evaluated.

Thermogravimetric analysis (TGA)

Sieved samples consisted of remnants retained in the 30-mesh sieve. Approximately 20 mg of clonal material from each progeny was heated from 0 **ºC** to 700 **ºC** at 20 **ºC**/min^{-1} under nitrogen atmosphere, using TGA 55 equipment. The degradation analysis was performed for each thermogravimetric event of rubber tree clones.

From TG curves, mass loss calculations were performed in the following temperature ranges: 50 ºC - 100 °C, 100 ºC - 250 °C, 250 ºC - 400 °C, 400 ºC - 600 °C and 600 ºC - 700 °C. The residual mass at 700 °C was also calculated for each clonal progeny of *Hevea brasiliensis*.

Fourier transform infrared spectroscopy (FTIR)

Sieved samples consisted of remnants retained in the 30-mesh sieve. Approximately 10 mg of the material were used to read the absorbance spectra using a Perkin Elmer model Spectrum 65 spectrometer in the region from 500 cm^{-1} to 4000 cm^{-1}, spectral resolution of 4 cm^{-1} and 32 scans.

Data analysis

Tests of homogeneity and analysis of variance (ANOVA) were performed, and when significant difference was detected between treatments, the Tukey test was used, at 1 % significance. The data were analyzed with the statistical software SigmaPlot version 12.

RESULTS AND DISCUSSION

Chemical and energetic properties, basic density and fiber analysis

Table 2 shows the values for the energetic properties for each of 10 rubber clonal progenies. The values of HHV ranged from18357 kJ·kg^{-1} (IAC-301ill.) to 19070 kJ·kg^{-1} (IAC-311ill.), fixed carbon from 15,16 % (IAC-40ill.) to 15,72 % (IAC-311ill.), volatile material from 82,79 % (IAC-311ill.) to 83,92 % (IAC-301ill.), and ash content from 0,42 % (IAC-311ill.) to 1,49 % (IAC-301ill.). The values oscillated among the different rubber tree clonal progenies, presenting different values in their energetic and chemical properties.

The values of energy and chemical characteristics, wood density and wood fiber of rubber tree clonal progenies showed different behaviors. Progenies IAC 311ill., PB 330ill., IAC 41ill., IAC 301ill., and IAN 873ill. presented higher lignin and fixed carbon levels that contributed to HHV (Table 2), thus presenting superior energy performance compared to other clones. According to Trugilho and Silva (2001), these differences in energy properties can be associated with chemical composition that can affect the energy characteristics of biomass.

However, Muzel *et al*. (2014) reported Brazilian forest species that presented higher HHV and were, therefore, widely used for energy generation, as noted by the author above. Studying the wood of clones of *Eucalyptus grandis* and *H. brasiliensis,* Telmo and Lousada (2011) reported HHV of 17895 kJ·kg^{-1} and 17897 kJ·kg^{-1}. Such similarity between these species highlights the wide use of *Eucalyptus* in Brazil for the generation of energy.

Table 2: Comparison among ten 12-year-old rubber tree clonal progenies, according to energetic properties, chemicals, wood density and fiber analysis.

Clonal progenies/ Properties	IAC 40ill.	IAC 41ill.	IAC 326ill.	AC 311ill.	AC 301ill.	IAN 873ill.	GT1ill.	PB 330ill.	Fx 2261ill.	RRIM 725ill.
HHV ($kJ \cdot kg^{-1}$)	18895 ab	18827 ab	18770 abc	19070 a	18357 c	18729 abc	18791 abc	18895 ab	18524 bc	18867 abc
CC (%)	15,16c	15,70 a	15,42 bc	15,72a	15,66ab	15,25c	15,39bc	15,61ab	15,27c	15,56ab
VMC (%)	83,75ab	83,44cd	83,39d	82,79e	83,92a	83,67b	83,23d	83,55d	83,65bc	83,69b
AC (%)	1,08b	0,87cd	0,86cd	1,49e	0,42a	1,08b	1,38e	1,03bc	0,74d	0,75d
EC (%)	8,0a	5,9bc	4,8c	7,1ab	6,6b	6,6b	6,8b	7,1ab	6,3b	6,9ab
LC (%)	23,4 abcd	24,0 ab	23,1 abcd	24,5 a	23,9 abc	23,8 abc	22,5 cd	24,1 ab	21,9 d	22,9 bcd
HC (%)	68,6 bc	70,1 abc	72,1 a	68,4 c	69,56 bc	69,6 bc	70,7 ab	68,8 c	71,8 abc	70,3 bc
ρ bas ($g \cdot cm^{-3}$)	0,423bc	0,440b	0,495a	0,429bc	0,404c	0,422bc	0,447b	0,448b	0,452b	0,452b
FL (µm)	1025 bc	992 c	1024 c	1077 abc	981 c	1165 a	1139 a	1115 ab	1051 abc	1069 abc
FWT (µm)	3,0 bcd	3,5 abc	3,0 cd	3,7 abc	2,7 d	4,3 a	3,7 abc	3,2 bcd	3,2 bcd	3,8 ab

ill. = illegitimate (progenies obtained from a free-pollination clone); HHV= Higher heating value; CC = carbon content; VMC = volatile matter content; AC = ash content; EC = extractives content; LC = lignin content; HC = holocellulose content; ρbas = Wood density; FL= fiber length; FWT = fiber wall thickness. Distinct letters in rows differ statistically (P<0,001) by Tukey's test.

For decades, HHV of wood for power generation was considered 18830 $kJ \cdot kg^{-1}$. HHV differences between clones observed in this study can be explained by the ecological group of the wood (Tan 1989). Among hardwoods, rubber tree clones have expected HHV of 19089 $kJ \cdot kg^{-1}$. This value was observed in the present study, which reported values ranging from 18357 $kJ \cdot kg^{-1}$ (IAC 301ill.) to 19070 $kJ \cdot kg^{-1}$ (IAC 311ill.). Werther *et al*. (2000) report an HHV for rubber tree residues of 18410 $kJ \cdot kg^{-1}$. In Brazil, values between 16500 $kJ \cdot kg^{-1}$ and 18000 $kJ \cdot kg^{-1}$ are approved for commercial energy uses.

Clones with higher volatile and ash contents had lower HHV, including IAC 301ill. (83,92 %), IAC 40ill. (83,75 %), RRIM 725ill. (83,69 %), IAN 873ill. (83,67 %), Fx 2261ill. (83,65 %), PB 330ill. (83,55 %), GT1ill. (83,23 %), IAC 41ill. (83,44 %), and IAC 311ill. (82,79 %), consequently reducing the energy potential of the fuel. However, fixed carbon content is directly related to calorific power, meaning that a higher fixed carbon content implies greater resistance to thermal degradation of biomass within the burning apparatus for power generation (Arantes *et al*. 2013).

The highest contents of fixed carbon were found for clonal progenies IAC 311ill. (15,72 %) and IAC 41ill. (15,70 %). It is said that the percentage of fixed carbon refers to the fraction of coal that burns in the solid state. Therefore, fuels with high levels of fixed carbon in both clonal progenies are preferable for steel use, owing to thermal stability and high energy power (Neves *et al*. 2011).

Ash content should be in the range of 1 % - 3 % for good energy performance (Schoninger and Zinelli 2012). Thus, the values for this energetic characteristic are within the expected pattern for good energy yield since ash values ranged from 0,42 % (IAC 301ill.) to 1,49 % (IAC 311ill.).

In Brazil, species of *Eucalyptus* are widely used for energy production because of their rapid growth and energetic properties (Jesus *et al*. 2017). However, recent studies show similarity in energetic properties between rubber tree clones. Bersh et al. (2018b) characterized *Eucalyptus* and reported HHV values between 13970 $kJ \cdot kg^{-1}$ and 14250 $kJ \cdot kg^{-1}$, volatile materials of 83,17 % - 86,16 %, ash content of 0,57 % - 0,60 %, and 13,27 % - 14,25 % of fixed carbon content. These values show that rubber tree clones share similar and superior energetic properties, highlighting their use for bioenergy production when compared to *Eucalyptus* wood.

According to Paula (2003), wood from clones has higher fiber wall thickness and length, as well as higher lignin and extractive content. Consequently, this wood is increasingly recommended for energy production for its biomass production, resulting in a greater amount of mass per unit of volume and, consequently, greater energy release capacity. Wood with high lignin content contributes to high gravimetric yield and gives greater resistance to charcoal thermal degradation since this wood has more condensed structures that degrade at higher temperatures (Castro *et al*. 2013, Oliveira *et al*. 2010).

In this context, clones of higher basic densities present larger dimensions in their anatomical constitution. This characteristic is not true across the clonal spectrum as clone IAC 301ill. presented lower density and smaller fiber dimensions. The increase in wood density is followed by an increase of fiber wall thickness and length (Oliveira *et al*. 2010), but this was not observed in the present study. IAN 873ill. was taller and wider, but still had lower density than other clones.

As lignin and extractive content increase, density increases proportionally. Thus, we find an increase in the energy yield of fixed carbon content and HHV (Dias-Junior *et al*. 2015). This premise was not observed for rubber tree clones IAN 873ill. and IAC 40ill. in that they presented lower wood density, even while their HHV and fixed carbon content were higher than those values in other clones. The lower wood density and HHV value of IAC 301ill. may be related to the age of the tree and anatomical characteristics of the species itself (Protásio *et al*. 2014).

Basic density is an important property of wood and should be considered for energy use of a given biomass since that characteristic is causally related to energy production. That is, the higher the density, the greater the amount of energy stocked per unit volume (Queiroz *et al*. 2004). It is recommended that wood used as an energy source should present values above 0,40 kg/cm^3 of wood density (Alzate *et al*. 2005), which is confirmed for all clones listed in Table 2.

The differences found in energetic properties of wood among *H. brasiliensis* clones result from the chemical composition values, fiber dimensions and wood density of the biomass. Studies on other species report that HHV is mainly dependent on lignin and extractive content. High levels of lignin favor the energetic properties of fixed carbon and HHV, which can be attributed to carbon-carbon bonds between monomeric phenyl-propane units present in lignin, which hinder their decomposition, and to the higher content of carbon of this molecular component of biomass (Bufalino *et al*. 2012, Dietenberger and Hausburg 2016).

Holocellulose is considered the most abundant component of the cell wall. However, it is amorphous and offers no resistance to high temperatures of thermal degradation, hampering its use in energy production because of its negative interference in biomass energy, HHV and physics properties (Tan and Largervist 2011). Clones with higher holocellulose levels present lower HHV, specifically IAC 326ill., Fx 2261ill., IAC 41ill., and GT1ill.

Energy from biomass is usually obtained through thermochemical technologies, especially combustion. High ash content is disadvantageous because it decreases the transfer of heat in fuel and increases corrosion of the equipment used in the process. It also decreases the HHV of biomass (Protásio *et al*. 2014, Soares *et al*. 2014).

Only a few studies have reported on the characteristics of wood for energy purposes. For example, Menucelli *et al*. (2019) studied 10 clonal progenies of rubber tree and reported characteristics superior to clones evaluated in the present study, such as fiber length between 1189 μm - 1097 μm, fiber wall thickness of 4,55 μm - 5,13 μm, extractive contents between 12,42 % - 16,34 %, lignin content between 27,51 % - 22,47 %, and wood density from 0,57 kg/cm^{-3} to 0,66 kg/cm^{-3}. These wood characteristics promoted higher HHV content between 18592 kJ·kg^{-1} and 19757 kJ·kg^{-1}, values that could be attributed to differences in genetic material (Soares *et al*. 2014).

Fourier transform infrared spectroscopy (FTIR)

Table 3 summarizes the main chemical and functional groups found in the wood of *H. brasiliensis* clones according to Tyutkova *et al*. (2019), being identified by the number of waves of the carboxylic groups: = C-H (902 cm^{-1}), C-O-O (1114 cm^{-1}), - C-H (1464 cm^{-1}), C = O (1743 cm $^{-1}$), C-H (2924 cm $^{-1}$) and O-H (3370 cm $^{-1}$).

Table 3: Characteristic bands of infrared spectra (FTIR) for *Hevea brasiliensis* clones and their respective functional groups.

Wavenumber (cm^{-1})	Functional group	Chemical group
902	=C-H	Bond oscillation cellulose
1114	C-O-C	Bond oscillation cellulose
1464	C-H	Bond oscillation in lignin
1743	C=O	Unconjugated Keto group xylan
2924	C-H	Bond symmetric oscillation in aromatic methoxyl, and methylene groups of side chains
3370	O-H	Valence oscillation in bond water

One can observe that all clones have a strong absorption band at 1114 cm^{-1} where the lignin present in wood is located (Schuerch 1989). However, clones IAC 40, GT1, PB 330, IAC 41, RRIM 725, and IAN 873 had higher wavelengths in this spectrum. This could be explained by the chemical structure of wood because these clones have higher levels of lignin (Table 2) and, hence, higher resistance to thermal degradation of the material, as characterized by the stretch mode of the O-H combination.

According to Figure 1, the group found at 1743 cm^{-1} can be attributed to C=O, indicating the presence of an acetyl or carboxylic acid group derived from lignin. The high proportion of these chemical groups indicates an increase in HHV (Table 1). The same behavior was reported by Schuerch (1989).

It was possible to notice a strong striation between bands 1743 cm^{-1} and 2924 cm^{-1}, larger than the other spectral bands reported. The bands are characterized by strong bonding between hemicellulose and lignin, which is characterized mainly by C-H, N-H and O-H that are desirable for energy production (Popescu *et al.* 2011).

At band 3370 cm^{-1}, the phenolic groups bonded to hydrogen formed O-H chemical groups (Pandey and Pitman 2003). This group is responsible for high degradation resistance of the wood, which is dependent on lignin content, as was possible to observe in this study. Clones with higher lignin levels present higher absorption spectra, namely IAC 40 and GT1, in the present study (Figure 1).

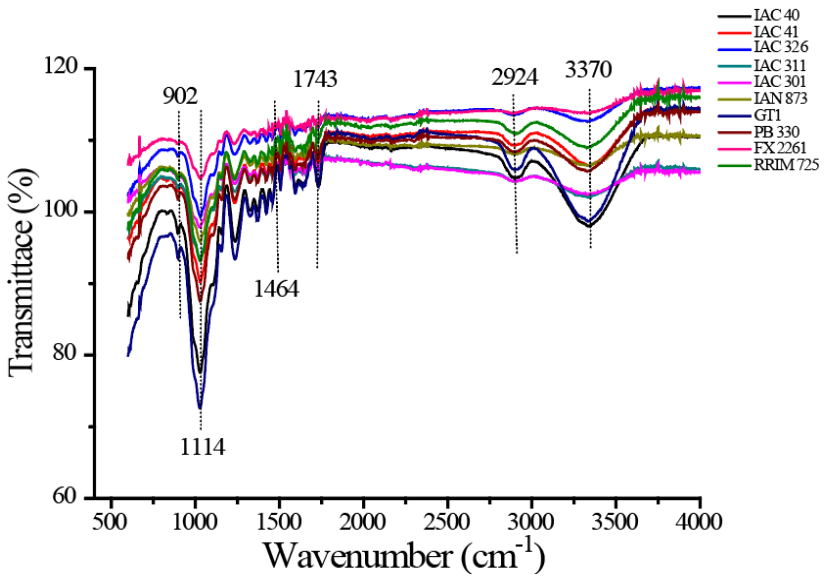

Figure 1: Main spectra obtained for *Hevea brasiliensis* wood clone.

Thermogravimetric analysis (TGA)

Table 4 shows averages of mass loss of different clonal progenies of *Hevea brasiliensis*, as a function of temperature ranges from 50 ºC to 700 ºC.

Table 4: Mean values of mass loss (%) of different clonal progenies of *Hevea brasiliensis* as a function of temperature ranges.

Clonal progenies	50-100 (ºC)	100-250 (ºC)	250-400 (ºC)	400-600 (ºC)	600-700 (ºC)	Residual mass *
IAC 40ill.	1,55	3,02	64,22	5,90	1,35	23,96
IAC 41ill.	1,16	2,86	71,39	4,95	1,19	18,45
IAC 326ill.	1,55	2,57	64,56	5,68	1,15	24,49
IAC 311ill.	1,71	2,68	66,13	5,62	1,12	22,74
IAC 301ill.	1,80	3,45	62,12	6,27	1,37	24,99
IAN 873ill.	1,44	2,65	66,42	5,87	1,67	21,95
GT1ill.	1,91	2,83	64,29	5,96	1,46	23,55
PB 330ill.	2,37	3,19	63,60	6,66	1,84	22,34
Fx 2261ill.	1,61	2,81	65,30	6,28	1,91	22,09
RRIM 725ill.	1,66	3,93	63,14	6,12	1,63	23,52
Mean	1,68	3,00	65,11	5,94	1,47	22,80

* Residual mass, considering the mass of wood absolutely dry (s).

The first two temperature ranges, 50 ºC - 100 ºC and 100 ºC - 250 ºC, correspond to drying of wood (Vieira 2019), making an average total of 4,68 % of initial average total loss for clonal progenies of *Hevea brasiliensis*.

Between 250 ºC and 400 ºC, an average loss in biomass of 65,11 % was verified. It can be inferred that most of this lost mass results from degradation of hemicellulose, cellulose, and volatile emissions, as well as the start of partial lignin decomposition (López-González *et al*. 2013). The maximum rate observed among clonal progenies of *Hevea brasiliensis* in this range of degradation refers to the maximum degradation of cellulose, as this constituent corresponds to 40 % - 45 % of the wood (Pereira *et al*. 2013). According to Figure 2, it is possible to observe the mass losses of *Hevea brasiliensis* clones at different temperatures.

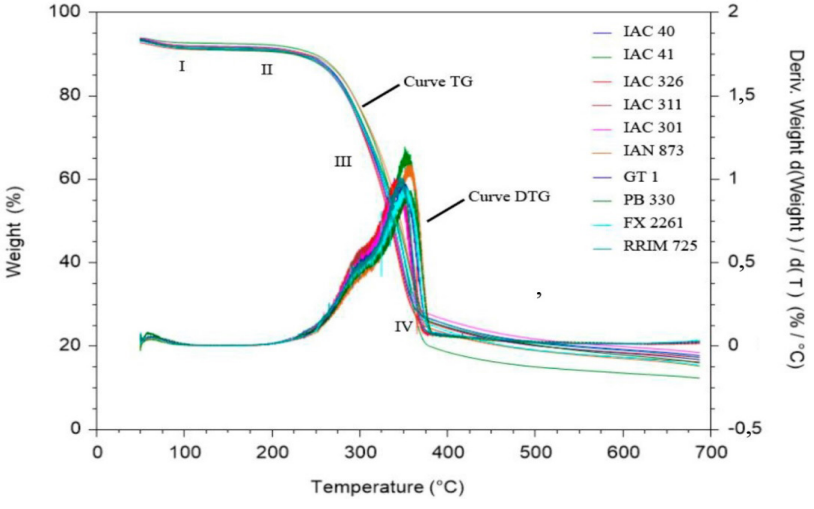

Figure 2: TG and DTG curves of mass losses for *Hevea brasiliensis* clones.

Between 400 and 600 ºC, the average mass loss was 5,94 %. According to Shen *et al*. (2010) for this temperature range, wood thermal degradation of 5 % to 10 % can be expected, as was observed in *Hevea brasiliensis*.

The general average mass loss observed in the 600 ºC to 700 ºC range was 1,47 %, showing that hemicelluloses and celluloses were totally degraded and that the observed mass loss refers to lignin in small proportion since it is a more thermally stable wood component. The absence of a peak of degradation related to lignin likely results from the fact that its thermal decomposition occurs over a wide temperature range, emphasizing that only a fraction decomposes at temperatures below 450 ºC, as mentioned by Huang *et al*. (2009).

The residual mass refers to total wood that is converted into charcoal at the end of the carbonization process. Lower residual masses were observed for clones IAC 41ill. (18,45 %) and IAN 873ill. (21,95 %), but higher residual masses for IAC 326ill. (24,99 %) and IAC 301ill. (24,49 %). The values for other clonal progenies were close. These differences between residual masses can be explained by the clonal effect of the species (Vieira 2019).

In Brazil, *Eucalyptus* clones are widely cultivated for energy production (Ferreira *et al*. 2017). However, it was found that clonal progenies of *Hevea brasiliensis* are more thermally resistant than 12 *Eucalyptus* clones studied by Vieira (2019), which obtained an average residual mass of 22,03 %. On the other hand, they are less thermally resistant to *Eucalyptus* clones studied by Pereira *et al*. (2013), who report residual masses at 7,5 years with values of 25,11 %, these differences being attributed to wood chemical constitution.

CONCLUSIONS

The results found in this work corroborate those of *Eucalyptus* species used in the generation of energy. However, clonal progeny IAC 311iil. presented superior characteristics with higher values of calorific value, fixed carbon and lower content of volatile material.

Through the analysis of wood quality, we identified which programs cloned with lower densities presented smaller HHV and smaller fiber components, as specifically observed in clonal progeny IAC 301.

FTIR showed functional groups characteristic of wood, including =C-H, C-O-O, -C-H, C=O and O-H. They are part of the chemical composition of wood and are suitable for energy production.

Wood thermogravimetric analyses did not show significant variations between clonal progenies since we were able to distinguish the stages of thermal degradation, especially those associated with hemicelluloses and cellulose in the range of 250 ºC - 400 ºC. We observed satisfactory residual mass values for the conversion of wood to charcoal.

In general, the ten genetic materials of *Hevea brasiliensis* have biomass suitable for commercial energetic use and are highly viable owing to their physical, chemical, energy and thermal characteristics.

AUTHORSHIP CONTRIBUTIONS

E. P. A.: Conceptualization, Resources, Data Curation, Funding aquisition, Investigation, Methodology, Validation, Writing- review & editing; E. L. L.: Conceptualization, Validation, Writing-Original draft, Data Curation, Software; M. L. M. F.s: Conceptualization, Resources; F. M. Y.i: Conceptualization, Resources; F. G. D. S. J.: Conceptualization, Resources; M. A. D. M.: Conceptualization; J. C.: Conceptualization; M. L. T. D. M.: Conceptualization; P. D. S. G.: Conceptualization

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