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Impact of Chemical Composition on *Eucalyptus* Wood Clones for Sustainable Energy Production

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Abstract: The energy potential of wood biomass is significantly shaped by its chemical composition. Analyzing the chemical composition of wood biomass and understanding the correlations between these parameters and wood combustibility are essential stages in the selection process of *Eucalyptus* clones tailored for firewood production and energy generation. In this study, we aimed to evaluate the impact of chemical composition on the direct combustibility of *Eucalyptus* clones. We examined the structural chemical composition and conducted proximate analysis, including fixed carbon, volatile material, and ash, to investigate the relationship between proximate composition and wood combustibility parameters. Our findings revealed significant correlations between wood chemical composition and combustibility parameters. In particular, lignin content, ethanol-soluble extractives, and xylose demonstrated inverse relationships with the parameters of maximum combustion rate, combustion characteristic index, and ignition index. Conversely, holocellulose content, cold-water-soluble extractives, and glucose exhibited direct correlations with the same combustibility parameters. Furthermore, fixed carbon and volatile matter contents demonstrated direct and inverse correlations, respectively, with ignition temperature. These findings have significant implications for enhancing the efficiency and sustainability of biomass energy production.

Keywords: bioenergy; biomass; combustion; sustainability



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1. Introduction

The global energy landscape is predominantly dependent on non-renewable sources, which release greenhouse gases such as carbon dioxide (CO₂), carbon monoxide (CO), and methane (CH₄), exacerbating the impacts of climate change [1]. To address this challenge, the current energy transition plan has embraced biomass as a promising alternative to achieve the 2050 carbon neutrality goals [2]. The utilization of wood biomass for energy production not only offers notable environmental and economic benefits but also advances energy independence and the decentralization of energy systems [3].

Firewood plays a significant socio-economic role globally, providing cooking fuel for economically vulnerable populations; heating residences, restaurants, small-to-medium-sized enterprises; or being used in large industrial boilers for heat and power generation [4].

Firewood has long played a significant role in Brazil's energy landscape [5]. Brazil, as the largest country within the Latin American territory, exhibits a remarkable geographical and demographic diversity. Notably, exclusive dependence on firewood for energy is most common in economically disadvantaged regions, notably Northeast Region and the arid areas of northern Minas Gerais [6]. In these regions, significant amounts of firewood are harvested, often in an unsustainable way [7]. Illegal firewood collection for residential and industrial purposes has extensively degraded the Caatinga biome, a cornerstone of northwestern Brazilian territory [8]. Financial constraints among the local population primarily drive their use of firewood, rendering other, more expensive energy sources impractical. This creates a dual challenge by intertwining environmental damage and economic constraints in these regions [9].

Eucalyptus stands as the genus of choice for Brazil's reforestation programs, serving the needs of diverse forest-based industries. This preference is driven by a combination of factors, including favorable soil and climate conditions, land ownership structures, and significant historical investments in research and development. Brazil has 7.4 million hectares of planted forests with the *Eucalyptus* genus, with a key utilization being energy generation through direct combustion or charcoal production [10]. *Eucalyptus* offers the nation a comparative advantage in producing raw materials from planted forests, thanks to its wood quality, advancements in silviculture practices, improved forest management, and genetic enhancements. The adaptation of *Eucalyptus* through breeding programs and workforce training has continually improved this scenario. The production within planted forests can help meet the demand for wood and alleviate pressure on native forest ecosystems [11].

Wood biomass stands out as the most extensively utilized resource, finding applications across a wide spectrum of technological domains. To harness forest resources effectively while promoting sustainability, a comprehensive understanding of the composition and structural attributes of timber is imperative. Moreover, one promising solution lies in tapping into forest biomass as a sustainable energy reservoir, suitable for combustion or other forms of energy production [12,13]. Furthermore, the direct combustion of *Eucalyptus* wood for energy generation requires an understanding of its chemical composition [14] to select the best strategies to increase resource uses.

Significant variations in chemical composition are discernible not only among different wood species but also within the same species. These variations primarily arise from factors such as age, genetic diversity, and environmental influences. Furthermore, even within a single species, pronounced disparities manifest along the vertical axis and from the pith to the bark [15]. Distinctions also emerge between heartwood and sapwood, as well as between wood harvested at the beginning and end of the growing season, and even at the level of individual cells [3].

The careful evaluation of wood quality and composition has garnered significant attention in numerous research activities [2,3]. This consideration is rooted in the profound influence exerted by the raw material on the ultimate characteristics of the end product. In this regard, the wood's chemical composition is an important indicator for addressing its use, such as the production of pulp, paper, or energy.

Understanding the interplay between the structural and chemical characteristics of wood, and its ignition and combustion properties can lead to the selection of clones that maximize energy output while minimizing emissions and waste. Furthermore, the investigation of wood combustibility in the context of *Eucalyptus* sp. clones proves to be one of the alternatives to optimize energy production processes and minimizing environmental and socio-economic impacts.

In a previous study [16], we evaluated the chemical composition of *Eucalyptus* sp. clones grown for cellulosic pulp production, providing essential insights into their quality as raw materials for the industry. In this study, the authors observed that glucose and xylose were the main wood monosaccharides present in the biomass and that steroids, fatty acids and aromatics were the most abundant compounds in all clones, followed by smaller

amounts of substituted alkanolic acids, fatty alcohols, glycerol derivatives, and triterpenes. Building upon that knowledge, the present study focuses on assessing how the structural (cellulose, hemicellulose, and lignin) and immediate (volatile material, fixed carbon, and ashes) chemical composition, along with the monomeric composition of polysaccharides, impact the combustibility of wood from *Eucalyptus* sp. clones, which is a critical aspect in selecting appropriate clones for direct combustion in energy generation.

2. Materials and Methods

Ten six-year-old *Eucalyptus* sp. clones (detailed in Table 1) were selected for this study. The material was sourced from a clonal test, which was established in Itama-randiba, Minas Gerais, Brazil, with spacing of 6 × 1 m (17.86° S latitude and 42.86° W longitude). This region experiences a Cfa tropical highland climate (according to the Koppen classification), meaning a region with a temperate climate, with distinct wet and dry seasons; significant precipitation throughout the year, where the annual average precipitation ranges from 1150 to 1450 mm; and hot summers, with temperature averages around 20.1 °C. The prevalent soil types in the area are Ferric Luvisols and Arenosols [17].

Table 1. Evaluation of genetic materials of *Eucalyptus camaldulensis*, *Eucalyptus grandis*, and *Eucalyptus urophylla*, and their tree growth characteristics.

Clone	Origin	DBH (cm)	Height (m)		
			Total	Commercial	
1	<i>E. camaldulensis</i> × <i>E. grandis</i>	<i>E. urophylla</i> × <i>E. grandis</i>	13.39	23.07	21.40
2	<i>E. urophylla</i> × <i>E. grandis</i>	<i>E. camaldulensis</i> × <i>E. grandis</i>	16.55	26.06	24.54
3	<i>E. camaldulensis</i> × <i>E. grandis</i>	<i>E. urophylla</i> × <i>E. grandis</i>	15.25	25.40	23.72
4	<i>E. urophylla</i> × <i>E. grandis</i>	<i>E. camaldulensis</i> × <i>E. grandis</i>	15.25	25.37	22.87
5	<i>E. urophylla</i> × <i>E. grandis</i>	<i>E. camaldulensis</i> × <i>E. grandis</i>	15.39	23.63	21.03
6	<i>E. urophylla</i> × <i>E. grandis</i>	<i>E. pelita</i>	14.67	22.60	21.37
7	<i>E. urophylla</i> × <i>E. grandis</i>	<i>E. camaldulensis</i> × <i>E. grandis</i>	15.84	24.30	22.10
8	<i>E. urophylla</i> × <i>E. grandis</i>	<i>E. pelita</i>	15.07	24.30	22.52
9	<i>E. camaldulensis</i> × <i>E. grandis</i>	<i>E. urophylla</i> × <i>E. grandis</i>	13.20	23.03	21.23
10	<i>E. grandis</i>	<i>E. urophylla</i> × <i>E. grandis</i>	14.92	22.70	20.64

DBH = diameter at breast height. Commercial height corresponds to up to 4 cm in diameter.

Five carefully selected trees per clone were chosen based on their diameters and heights, which closely matched the population mean. The population mean refers to the reference values at the age when the plant materials marketed by the company were collected. These trees were located within the designated plot and displayed no signs of diseases or pests. Following the harvesting process, samples with a thickness of 2.5 cm were extracted at seven longitudinal positions relative to the commercial height, specifically at 0%, 2%, 10%, 30%, 50%, 70%, and 100%.

For ease of analysis, the harvested tree discs were divided into four parts, all intersecting through the pith. Among these parts, two opposing ones were specifically allocated to perform chemical and thermogravimetric assessments of the wood (Figure 1).

Wood chemical characterization was conducted following the guidelines of the Technical Association of the Pulp and Paper Industry—TAPPI—and the American Society for Testing and Materials—ASTM. The wood disk samples were ground with a Wiley mill and subsequently blended. The fraction retained on 40–60-mesh sieves was selected for chemical analysis. For ash content analysis, five grams of sieved material was subjected to treatments in an oven at 600 °C, following the guidelines outlined in the TAPPI T 211 om-16 standard [18]. To determine extractive content, wood sawdust was utilized. Two grams of the sample was exposed to different solvents (dichloromethane, ethanol, and water). The extraction setup allowed for 6 h of contact between the sample and the solvent. Extractive content was calculated based on the difference in mass of the wood before and after solvent interaction, following the TAPPI T 207 CM standard [19]. Klason lignin content

was determined using the TAPPI T 222 standard test method [20], while acid-soluble lignin was measured according to the TAPPI UM 250 standard [21]. Total lignin content was obtained as the sum of both measurements.

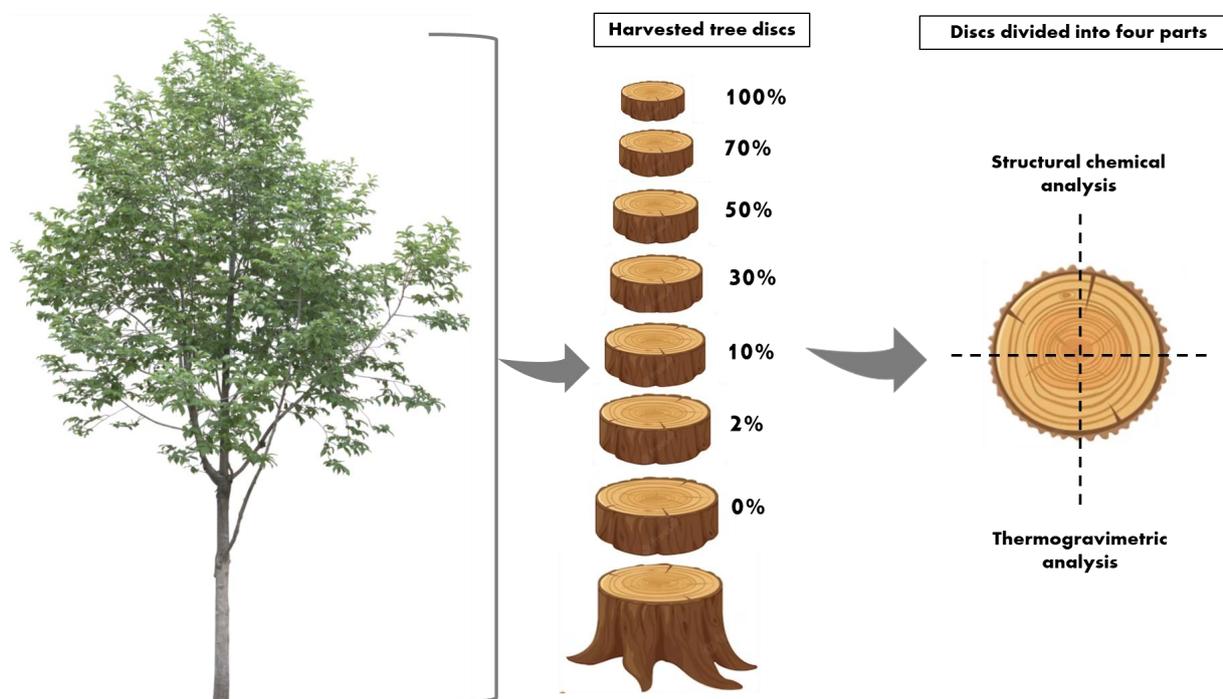


Figure 1. Schematic representation of tree sampling for obtaining the evaluated materials (adapted from Vieira et al. (2021) [16]).

Furthermore, the holocellulose content was determined by subtracting the sum of total lignin content, total extractives, and ash content from 100%. The quantification of monosaccharide content, specifically arabinose, galactose, glucose, mannose, rhamnose, and xylose, was conducted with gas-liquid chromatography (GLC) following the TAPPI T 249 cm-21 test method [22]. Furthermore, a proximate analysis, including fixed carbon, volatile material, and ash, was conducted following the standards set by the American Society for Testing Materials—ASTM [23].

2.1. Wood Combustibility Parameters

The thermogravimetric analysis of wood was conducted using a Setaram LABSYS Evo TG-DSC 1600 °C apparatus (São Paulo, SP, Brazil) in an oxygen atmosphere (flow rate: 50 mL·min⁻¹). The tests were carried out on sawdust samples comprising all longitudinal sampling positions per tree. Consequently, sawdust from all the cross-sectional discs obtained per tree was combined, creating a single sample representing the thermogravimetric behavior of a specific tree. Given that 5 trees were sampled per clone, a total of 50 TGA experiments were conducted (5 trees per clone, with triplicates for 10 clones). Each wood sample, approximately 4 mg in weight and previously oven-dried at 103 ± 2 °C, underwent a temperature gradient ranging from room temperature (±20 °C) to 550 °C, with a heating rate of 5 °C·min⁻¹, while monitoring the mass loss throughout the process.

The evaluation of the combustion of the *Eucalyptus* clones considered the following parameters: ignition temperature (T_i), burnout temperature (T_f), combustion index (C), ignition index (I_i), time corresponding to the maximum combustion rate (t_c), ignition time (t_i), maximum combustion rate, and average combustion rate.

T_i and T_f were determined as the points where the combustion rate increased and decreased by 1% min⁻¹, respectively [24–26].

To calculate the characteristic C and I_i , we used Equations (1) and (2), respectively [26].

$$C = \frac{\left(\frac{dm}{dt}\right)_{\max} \times \left(\frac{dm}{dt}\right)_{\text{med}}}{T_i^2 \times T_f} \quad (1)$$

$$I_i = \frac{\left(\frac{dm}{dt}\right)_{\max}}{t_c \times t_i} \quad (2)$$

where $(dm/dt)_{\max}$ represents the maximum combustion rate ($\% \text{ min}^{-1}$), $(dm/dt)_{\text{med}}$ denotes the average combustion rate, T_i is the ignition temperature ($^{\circ}\text{C}$), T_f is the burnout temperature ($^{\circ}\text{C}$), and T_c is the time corresponding to the maximum combustion rate (min).

2.2. Statistical Analysis

Prior to conducting the analysis of variance, homogeneity-of-variance tests (Bartlett's test at a significance level of 5%) and normality tests (Shapiro–Wilk test at a significance level of 5%) were performed to ensure data validity. To compare the means of the treatments, the Scott–Knott test was applied at a significance level of 5%. The relationships between chemical properties and wood combustibility parameters were examined using Pearson's correlation coefficient. For significant correlations, simple linear regression models were generated to further explore the associations.

3. Results

3.1. Chemical Characterization of Wood

A notable contrast existed among the average values of all parameters (Figure 2), showing the significance of assessing the relationships between chemical composition and direct burning parameters. Across all clones, the levels of polar extractives (soluble in water or ethanol) were consistently higher than those of lipophilic extractives (soluble in dichloromethane). Lignin content ranged from 25.9% to 29.4%, while carbohydrates presented higher proportions of glucose and xylose.

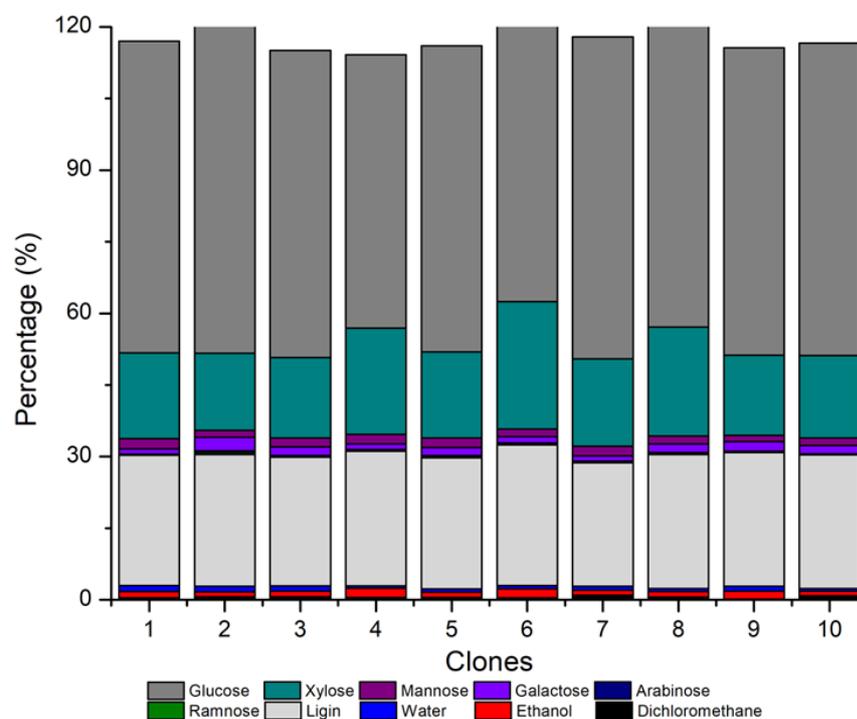


Figure 2. Amounts (%) of dichloromethane, ethanol, water extractives, lignin, and carbohydrates (arabinose, galactose, glucose, mannose, rhamnose, and xylose) in *Eucalyptus* wood.

The volatile matter, fixed carbon, and ash contents displayed variations ranging from 82.05% to 84.47%, 15.42% to 17.19%, and 0.11% to 0.21%, respectively (Figure 3). These values were found to be comparable to those reported for *Eucalyptus grandis* × *Eucalyptus urophylla*, which were 87.95%, 11.59%, and 0.46%, respectively [27]. Regarding the higher and lower calorific values, they fell within the ranges of 19.43 to 20.28 and 18.13 to 18.84 kJ/kg, respectively, resembling those typically observed for hardwood [28], although lower than those found in softwoods [29]. The relatively lower calorific value of hardwoods can be attributed to the structure of lignin, where the presence of syringyl units increases the number of ether bonds, leading to a less condensed structure [29,30]. Conversely, the higher resin content in softwoods contributes to their higher calorific value [31].

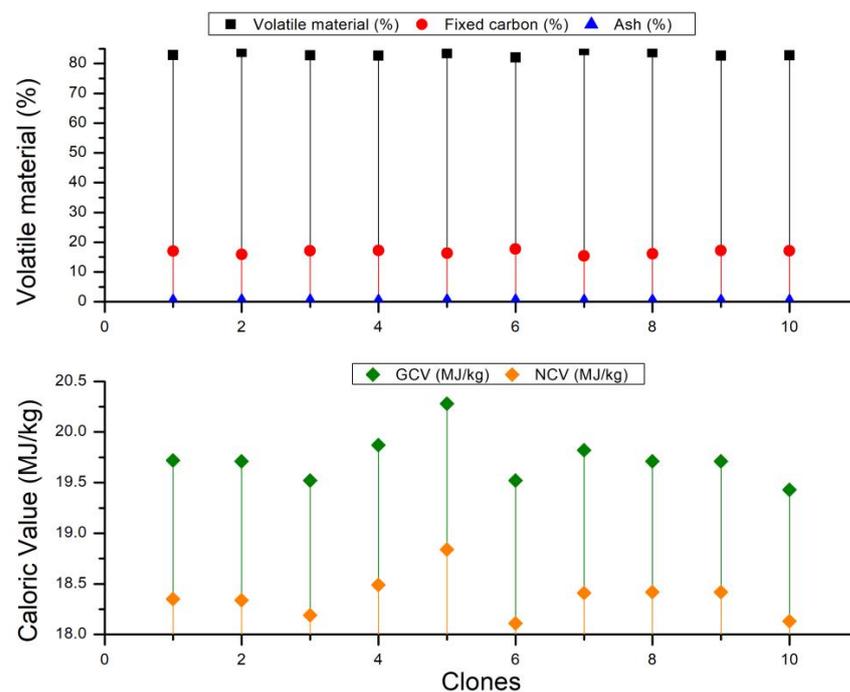


Figure 3. Volatile material, fixed carbon, ash, gross calorific value (GCV), and net calorific value (NCV) of wood from *Eucalyptus* clones.

3.2. Wood Combustibility

Among the *Eucalyptus* clones, wood combustibility parameters, characteristic combustion index, and ignition index displayed the highest coefficients of variation, with values of 11.72, 9.28, and 9.58, respectively. In contrast, the coefficients of variation for ignition temperature and time corresponding to the maximum combustion rate were the lowest, with values of 1.07% and 0.30%, respectively (Table 2).

3.3. Relationships between Wood Chemistry and Combustibility

Wood chemistry revealed significant correlations with combustibility parameters (Table 3). Cold-water extractives showed the most substantial relationships, being directly proportional to six evaluated combustibility parameters, including the maximum mass loss rate, characteristic combustion index, and ignition index, while being inversely proportional to ignition temperature, temperature at the end of combustion, and time corresponding to the maximum combustion rate. Moreover, the total lignin content exhibited inverse relationships with the maximum mass loss rate, characteristic C index, and ignition index. However, the contents of arabinose, mannose, and galactose did not show any significant relationship with any of the evaluated combustibility parameters.

Table 2. Combustibility parameters of wood of *Eucalyptus* spp.

Clone	T _i (°C)	T _f (°C)	(dm/dt) _{max} (% min ⁻¹)	t _c (min)	t _i (min)	C × 10 ⁷ (% ² min ⁻² °C ⁻³)	I _i × 10 ³ (% min ⁻³)
1	234.31	434.82	10.78	52.92	42.08	4.15	4.84
2	232.21	430.74	10.36	52.79	41.66	4.19	4.71
3	232.22	437.57	10.14	53.16	41.66	4.04	4.58
4	236.26	434.02	6.67	53.24	41.47	2.62	3.02
5	235.90	434.77	9.23	53.28	41.73	3.6	4.15
6	239.35	451.38	8.47	53.23	42.09	2.98	3.78
7	232.14	437.97	9.92	53.15	41.31	4.07	4.53
8	237.07	456.03	7.86	53.06	41.63	2.99	3.56
9	234.44	427.1	8.37	53.28	41.11	3.44	3.82
10	236.53	438.01	8.89	53.42	41.52	3.36	4.0
Mean	235.04	438.24	9.07	53.15	41.63	3.54	4.1
SD	2.41	8.89	1.27	0.19	0.30	0.56	0.58
CV (%)	1.07	2.00	9.58	0.30	0.99	11.72	9.28

T_i = ignition temperature; T_f = final combustion temperature; (dm/dt)_{max} = maximum combustion rate; t_c = time corresponding to the maximum combustion rate; t_i = ignition time; C = combustion index; I_i = ignition index. SD = standard deviation. CV = coefficient of variation.

Table 3. Linear correlations between wood chemistry, and T_i, T_f, t_c, t_i, (dm/dt)_{max}, C, and I_i of *Eucalyptus* wood.

Compound (%)	T _i (°C)	T _f (°C)	t _c (min)	t _i (min)	(dm/dt) _{max} (% min ⁻¹)	C × 10 ⁷ % ² / (min ² °C ³)	I _i × 10 ³ (% min ⁻³)
Total lignin	0.44 (0.20)	0.27 (0.46)	0.10 (0.79)	−0.23 (0.53)	−0.80 (0.01)	−0.72 (0.02)	−0.79 (0.01)
Dichloromethane *	−0.32 (0.37)	0.16 (0.66)	−0.01 (0.97)	−0.12 (0.74)	0.29 (0.42)	0.30 (0.40)	0.30 (0.40)
Ethanol *	0.53 (0.12)	0.08 (0.84)	0.26 (0.47)	0.09 (0.81)	−0.64 (0.05)	−0.67 (0.03)	−0.66 (0.04)
Cold water *	−0.67 (0.03)	−0.46 (0.18)	−0.65 (0.04)	0.16 (0.66)	0.75 (0.01)	0.78 (0.01)	0.75 (0.01)
Holocellulose	−0.20 (0.59)	0.02 (0.97)	0.00 (0.99)	0.20 (0.59)	0.58 (0.08)	0.49 (0.15)	0.57 (0.09)
Rhamnose	−0.14 (0.69)	0.11 (0.76)	−0.52 (0.12)	0.17 (0.64)	0.14 (0.71)	0.15 (0.69)	0.14 (0.69)
Arabinose	−0.27 (0.45)	−0.09 (0.81)	−0.43 (0.22)	−0.08 (0.83)	0.20 (0.59)	0.25 (0.49)	0.22 (0.55)
Xylose	0.80 (0.01)	0.76 (0.01)	0.18 (0.63)	0.40 (0.25)	−0.61 (0.06)	−0.74 (0.01)	−0.63 (0.05)
Mannose	−0.11 (0.76)	0.09 (0.81)	−0.07 (0.85)	0.37 (0.29)	0.23 (0.52)	0.19 (0.61)	0.21 (0.55)
Galactose	−0.30 (0.39)	−0.25 (0.50)	−0.39 (0.26)	−0.20 (0.59)	0.18 (0.62)	0.25 (0.48)	0.20 (0.58)
Glucose	−0.71 (0.02)	−0.33 (0.35)	−0.52 (0.13)	−0.17 (0.64)	0.76 (0.01)	0.83 (0.00)	0.78 (0.01)

* Extractive values obtained from treatment with these solvents. T_i = ignition temperature; T_f = final combustion temperature; (dm/dt)_{max} = maximum combustion rate; t_c = time corresponding to the maximum combustion rate; t_i = ignition time; C = combustion index; I_i = ignition index. Significant correlations are represented by values in bold. Values in parentheses indicate the *t*-test *p*-value.

The proximate analysis (including fixed carbon, volatile material, and ash) revealed significant correlations with wood combustibility in the evaluated clones (Table 4).

Table 4. Linear correlations between proximate analysis (fixed carbon, volatile material and ash) and wood combustibility parameters.

(%)	T_i (°C)	T_f (°C)	t_c (min)	t_i (min)	$(dm/dt)_{max}$ (% min ⁻¹)	$C \times 10^7\%^2/(min^2 \text{ } ^\circ C^3)$	$I_i \times 10^3$ (% min ⁻³)
Volatile materials	-0.54 (0.11)	-0.03 (0.93)	-0.42 (0.23)	-0.32 (0.37)	0.33 (0.36)	0.45 (0.19)	0.36 (0.31)
Ashes	0.17 (0.63)	0.13 (0.73)	-0.09 (0.80)	0.28 (0.44)	-0.14 (0.71)	-0.18 (0.63)	-0.15 (0.68)
Fixed carbon	0.54 (0.11)	0.03 (0.94)	0.43 (0.22)	0.31 (0.39)	-0.32 (0.36)	-0.45 (0.20)	-0.36 (0.31)

T_i = ignition temperature; T_f = final combustion temperature; $(dm/dt)_{max}$ = maximum combustion rate; t_c = time corresponding to the maximum combustion rate; t_i = ignition time; C = combustion index; I_i = ignition index. Significant correlations are represented by values in bold. Values in parentheses indicate the t -test p -value.

4. Discussion

4.1. Wood Chemical Characterization

The average contents of compounds soluble in ethanol (1.33%) and cold water (0.845%) were found to be higher than those soluble in dichloromethane (0.57%). Extractives in hardwoods such as *Eucalyptus* are typically rich in polyphenolic compounds while scarce in lipophilic extractives. A higher amount of polar extractives has also been reported for *Eucalyptus camaldulensis* wood [32]. It is worth noting that lipophilic extractives enhance the calorific value of the material [31] due to their high resistance to high temperatures, strong connection between the atoms of the molecule, and high carbon content [33], while polar extractives, rich in oxygen, have little influence on this parameter.

The average lignin content in the clones was 29.15%, which is satisfactory for energy generation. Lignin has a high carbon content and chemical bonds that resist against high temperatures, positively contributing to the calorific value of the material and charcoal production [33,34]. Therefore, the selection of eucalyptus materials for energy generation should aim for high lignin content, which contributes to increased calorific value and yield in bioenergy generation.

Holocellulose content was above 57% in all evaluated clones, representing the sum of cellulose and hemicelluloses contents. Glucose and xylose accounted for the major portions of carbohydrates in hardwoods, being the primary monomers of cellulose, the most abundant organic compound in the world, and hemicelluloses, respectively. However, holocellulose has high oxygen content, which reduces the calorific value of the material and generates instability at high temperatures. During the carbonization process, it degrades, contributing little to the process yield, thus negatively impacting material quality for energy generation [35].

Fixed carbon content, volatile matter, and ash content ranged from 15.42% to 17.19%, 82.05% to 84.47%, and 0.11% to 0.21%, respectively. The fixed carbon content is positively related to wood quality for energy generation, as it facilitates more continuous combustion [36]. Increasing the temperature releases volatile materials, which combust in a gaseous form, resulting in rapid ignition and combustion, but they are unable to provide energy for longer periods [27]. It is also desirable to have low ash content, since it does not contribute to combustion and can impede equipment operation, hindering the wood-burning process [37].

4.2. Wood Combustibility

The average values for the maximum combustion rate, combustion index, and ignition index were 9.07% min⁻¹, 3.54%² min⁻² °C⁻³, and 4.1% min⁻³, respectively. A study by Protásio et al. (2021) [3] observed similar average values for wood combustibility parameters in *Eucalyptus* clones, where the maximum combustion rate, characteristic combustion index, and ignition index were 7.8% min⁻¹, 2.8%² min⁻² °C⁻³, and 3.75% min⁻³, respectively.

The combustion index (C) expresses the intensity of wood combustion and is positively related to its performance during burning [37,38]. On the other hand, I_i expresses the ease with which the fuel ignites, so lignocellulosic biomass with a higher value ignites more easily [26]. Genetic materials 1, 2, 3, and 7 had higher ignition rates, making them suitable to be used for the initial heating of the boiler, while materials 1 and 2 had higher combustion rates, making them the most suitable for maintaining a long and continuous burn, desired in boiler operation. The ignition of materials is linked to volatile materials, while prolonged burning is linked to the fixed carbon content in the material.

4.3. Relationship between Wood Chemistry and Combustibility

The total lignin content displayed linear correlations of -0.8 , -0.72 , and -0.79 with the maximum mass loss rate, characteristic combustion index (C), and ignition index, respectively. Lignins are components with high carbon content and strong chemical bonds between their monomers, providing high thermal resistance. Consequently, they are directly proportional to the calorific value and carbonization yield, resulting in lower mass loss with the increase in temperature, hence exhibiting a lower maximum mass loss rate [39]. Due to the high energy required for their breakdown, lignins have low ignition rate and characteristic combustion index. Therefore, other components of the wood must guarantee the ignition of the material, while lignin assures continuous and prolonged burning.

Cold-water soluble extractives showed positive linear correlations with the maximum mass loss rate, characteristic combustion index, and ignition index, and negative correlations with the ignition temperature, temperature at the end of combustion, and time corresponding to the maximum combustion rate. In hardwoods, cold-water-soluble extractives primarily consist of phenolic compounds, which can be degraded at lower temperatures, explaining these results [3]. The increase in ethanol-soluble extractives reduces wood ignition and reactivity. This is associated with the ability of ethanol to solubilize molecules that are more resistant to thermal degradation, such as phenolic substances. On the other hand, dichloromethane extractives showed no relationship with wood combustibility indices. Although these extractives are resistant to high temperatures and have high carbon content [40], they are less present in hardwood and thus did not show relationships with the evaluated combustibility parameters [41].

High holocellulose content promotes greater volatilization and thermal decomposition of wood at lower temperatures, consequently increasing the combustion intensity due to the higher release of volatile materials [42]. The ignition of the material is important for burning and generating energy; in this context, holocellulose and extractives showed greater potential for this purpose.

Considering the proximate analysis (fixed carbon, volatile material, and ash), significant correlations were found between ignition temperature, and volatile matter and fixed carbon contents. The ignition temperature of the wood was negatively correlated with volatile matter content and positively correlated with fixed carbon content. The higher the volatile matter/fixed carbon ratio, the greater the combustion intensity, the lower the ignition temperature, the shorter the oxidation time, and the higher the biomass combustibility [42,43]. The fixed carbon content in the material is related to the lignin content, while volatile materials are associated with extractives and hemicellulose, justifying the relationships between fixed carbon content and volatile materials, and ignition temperature.

5. Conclusions

In this study, we observed that *Eucalyptus* clones exhibiting higher levels of lignin and ethanol-soluble extractives displayed inverse correlations with maximum combustion rate, characteristic combustion index, and ignition index, showing linear correlation coefficients of -0.80 , -0.72 , -0.79 , and -0.64 , -0.67 , -0.66 , respectively. In contrast, clones rich in cold-water-soluble extractives and holocellulose showed positive correlations with these same combustibility parameters, showing linear correlation coefficients of 0.75 , 0.78 , 0.75 , and 0.58 , 0.49 , 0.57 , respectively. Interestingly, when comparing these parameters, the

contents of xylose and glucose demonstrated negative correlations with combustibility. Considering the proximate analysis, volatile materials and fixed carbon showed linear correlation coefficients of -0.54 and 0.54 with ignition temperature, respectively; the other comparisons between the proximate analysis and the combustibility parameters did not present significant values.

The insights derived from understanding the correlation between chemical composition and combustibility can be regarded as crucial factors in guiding the development of novel clones within breeding programs. Furthermore, this information can serve as a valuable tool for assessing potential clones targeted for sustainable energy production, aligning with climate-oriented objectives.

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References

1. Bustos-Vanegas, J.D.; Martins, M.A.; Freitas, A.G.; Mellmann, J. Experimental Characterization of Self-Heating Behavior of Charcoal from Eucalyptus Wood. *Fuel* **2019**, *244*, 412–418. [CrossRef]
2. De Protásio, T.P.; Lima, M.D.R.; Teixeira, R.A.C.; do Rosário, F.S.; de Araújo, A.C.C.; de Assis, M.R.; Hein, P.R.G.; Trugilho, P.F. Influence of Extractives Content and Lignin Quality of Eucalyptus Wood in the Mass Balance of Pyrolysis Process. *Bioenergy Res.* **2021**, *14*, 175–189. [CrossRef]
3. De Protásio, T.P.; Lima, M.D.R.; Scatolino, M.V.; Silva, A.B.; Rodrigues de Figueiredo, I.C.; Gherardi Hein, P.R.; Trugilho, P.F. Charcoal Productivity and Quality Parameters for Reliable Classification of Eucalyptus Clones from Brazilian Energy Forests. *Renew. Energy* **2021**, *164*, 34–45. [CrossRef]
4. Nishiguchi, S.; Tabata, T. Assessment of Social, Economic, and Environmental Aspects of Woody Biomass Energy Utilization: Direct Burning and Wood Pellets. *Renew. Sustain. Energy Rev.* **2016**, *57*, 1279–1286. [CrossRef]
5. Travassos, I.S.; De Souza, B.I. Os Negócios Da Lenha: Indústria, Desmatamento e Desertificação No Cariri Paraibano. *GEOUSP Espaço. Tempo* **2014**, *18*, 329. [CrossRef]
6. De Oliveira, A.U. *Lenha e Carvão Vegetal No Brasil: Balanço Oferta-Demanda e Métodos Para a Estimativa Do Consumo*; Universidade de São Paulo: São Paulo, Brazil, 2008.
7. Ribeiro, E.M.S.; Santos, B.A.; Arroyo-Rodríguez, V.; Tabarelli, M.; Souza, G.; Leal, I.R. Phylogenetic Impoverishment of Plant Communities Following Chronic Human Disturbances in the Brazilian Caatinga. *Ecology* **2016**, *97*, 1583–1592. [CrossRef] [PubMed]
8. Ministério do Meio Ambiente, M. Caatinga. Available online: <https://antigo.mma.gov.br/biomas/caatinga.html> (accessed on 9 November 2023).
9. Gioda, A. Residential Fuelwood Consumption in Brazil: Environmental and Social Implications. *Biomass Bioenergy* **2019**, *120*, 367–375. [CrossRef]
10. IBÁ. *Indústria Brasileira de Árvores Relatório Anual*; IBÁ: Brasília, Brazil, 2017; p. 80.
11. Bockerhoff, E.G.; Jactel, H.; Parrotta, J.A.; Ferraz, S.F.B. Role of Eucalypt and Other Planted Forests in Biodiversity Conservation and the Provision of Biodiversity-Related Ecosystem Services. *For. Ecol. Manag.* **2013**, *301*, 43–50. [CrossRef]
12. Borges, A.C.P.; Onwudili, J.A.; Andrade, H.; Alves, C.; Ingram, A.; de Melo, S.V.; Torres, E. Catalytic Properties and Recycling of NiFe₂O₄ Catalyst for Hydrogen Production by Supercritical Water Gasification of Eucalyptus Wood Chips. *Energies* **2020**, *13*, 4553. [CrossRef]

13. Penín, L.; López, M.; Santos, V.; Alonso, J.L.; Parajó, J.C. Technologies for Eucalyptus Wood Processing in the Scope of Biorefineries: A Comprehensive Review. *Bioresour. Technol.* **2020**, *311*, 123528. [[CrossRef](#)]
14. Dufourny, A.; Van De Steene, L.; Humbert, G.; Guibal, D.; Martin, L.; Blin, J. Influence of Pyrolysis Conditions and the Nature of the Wood on the Quality of Charcoal as a Reducing Agent. *J. Anal. Appl. Pyrolysis* **2019**, *137*, 1–13. [[CrossRef](#)]
15. Terzopoulou, P.; Kamperidou, V. Chemical Characterization of Wood and Bark Biomass of the Invasive Species of Tree-of-Heaven (*Ailanthus Altissima* (Mill.) Swingle), Focusing on Its Chemical Composition Horizontal Variability Assessment. *Wood Mater. Sci. Eng.* **2022**, *17*, 469–477. [[CrossRef](#)]
16. Vieira, T.A.S.; Arriel, T.G.; Zanoncio, A.J.V.; Carvalho, A.G.; Branco-Vieira, M.; Carabineiro, S.A.C.; Trugilho, P.F. Determination of the Chemical Composition of Eucalyptus Spp. For Cellulosic Pulp Production. *Forests* **2021**, *12*, 649. [[CrossRef](#)]
17. Alvares, C.A.; Stape, J.L.; Sentelhas, P.C.; De Moraes Gonçalves, J.L.; Sparovek, G. Köppen's Climate Classification Map for Brazil. *Meteorol. Z.* **2013**, *22*, 711–728. [[CrossRef](#)] [[PubMed](#)]
18. TAPPI T 211 Om-16; Ash in Wood, Pulp, Paper, and Paperboard: Combustion at 525 °C. Technical Association of Pulp and Paper Industry: Peachtree Corners, GA, USA, 2016.
19. TAPPI T 207 CM; Water Solubility of Wood and Pulp. Technical Association of Pulp and Paper Industry: Peachtree Corners, GA, USA, 2008; p. 3.
20. TAPPI T 222; Acid-Insoluble Lignin in Wood and Pulp. Technical Association of Pulp and Paper Industry: Peachtree Corners, GA, USA, 2002; p. 5.
21. TAPPI UM 250; Acid-Soluble Lignin in Wood and Pulp. Technical Association of Pulp and Paper Industry: Peachtree Corners, GA, USA, 2000.
22. TAPPI 249 CM-21; Carbohydrate Ition of Extractive-Free Wood and Wood Pulp by Gas-Liquid Chromatography. Technical Association of the Pulp and Paper Industry: Peachtree Corners, GA, USA, 2021.
23. ASTM D 1762-84; Standard Method for Chemical Analyses of Wood Charcoal. American Society for Testing Materials: West Conshohocken, PA, USA, 2007; p. 2.
24. Sahu, S.G.; Sarkar, P.; Chakraborty, N.; Adak, A.K. Thermogravimetric Assessment of Combustion Characteristics of Blends of a Coal with Different Biomass Chars. *Fuel Process. Technol.* **2010**, *91*, 369–378. [[CrossRef](#)]
25. Wang, C.A.; Liu, Y.; Zhang, X.; Che, D. A Study on Coal Properties and Combustion Characteristics of Blended Coals in Northwestern China. *Energy Fuels* **2011**, *25*, 3634–3645. [[CrossRef](#)]
26. Moon, C.; Sung, Y.; Ahn, S.; Kim, T.; Choi, G.; Kim, D. Effect of Blending Ratio on Combustion Performance in Blends of Biomass and Coals of Different Ranks. *Exp. Therm. Fluid Sci.* **2013**, *47*, 232–240. [[CrossRef](#)]
27. Silva, F.T.M.; Ataíde, C.H. Valoriza—Tion of Eucalyptus Urograndis Wood via Carbonization: Product Yields and Characterization. *Energy* **2019**, *172*, 509–516. [[CrossRef](#)]
28. Sseremba, O.E.; Mugabi, P.; Banana, A.Y.; Wessels, B.C.; Plessis, M. Variation of Basic Density, Calorific Value and Volumetric Shrinkage within Tree Height and Tree Age of Ugandan Grown Eucalyptus Grandis Wood. *J. For. Res.* **2021**, *32*, 503–512. [[CrossRef](#)]
29. Ramírez-Ramírez, M.A.; Carrillo-Parra, A.; Ruíz-Aquino, F.; Pintor-Ibarra, L.F.; González-Ortega, N.; Orihuela-Equihua, R.; Carrillo-ávila, N.; Luján-álvarez, C.; Rutiaga-Quiñones, J.G. Valorization of Briquettes Fuel Using Pinus Spp. Sawdust from Five Regions of Mexico. *BioResources* **2021**, *16*, 2249–2263. [[CrossRef](#)]
30. Ponnusamy, V.K.; Nguyen, D.D.; Dharmaraja, J.; Shobana, S.; Banu, J.R.; Saratale, R.G.; Chang, S.W.; Kumar, G. A Review on Lignin Structure, Pretreatments, Fermentation Reactions and Biorefinery Potential. *Bioresour. Technol.* **2019**, *271*, 462–472. [[CrossRef](#)]
31. Zanoncio, A.J.V.; Carvalho, A.G.; Trugilho, P.F.; Monteiro, T.C. Extractives and Energetic Properties of Wood and Charcoal. *Rev. Árvore* **2014**, *38*, 369–374. [[CrossRef](#)]
32. Benouadah, N.; Pranovich, A.; Aliouche, D.; Hemming, J.; Smeds, A.; Willför, S. Analysis of Extractives from Pinus Halepensis and Eucalyptus Camaldulensis as Predominant Trees in Algeria. *Holzforschung* **2018**, *72*, 97–104. [[CrossRef](#)]
33. Mészáros, E.; Jakab, E.; Várhegyi, G. TG/MS, Py-GC/MS and THM-GC/MS Study of the Composition and Thermal Behavior of Extractive Components of Robinia Pseudoacacia. *J. Anal. Appl. Pyrolysis* **2007**, *79*, 61–70. [[CrossRef](#)]
34. Farrokh, N.T.; Suopajarvi, H.; Sulasalmi, P.; Fabritius, T. A Thermogravimetric Analysis of Lignin Char Combustion. *Energy Procedia* **2019**, *158*, 1241–1248. [[CrossRef](#)]
35. Yeo, J.Y.; Chin, B.L.F.; Tan, J.K.; Loh, Y.S. Comparative Studies on the Pyrolysis of Cellulose, Hemicellulose, and Lignin Based on Combined Kinetics. *J. Energy Inst.* **2019**, *92*, 27–37. [[CrossRef](#)]
36. Ignacio, L.H.D.S.; Santos, P.E.d.A.; Duarte, C.A.R. An Experimental Assessment of Eucalyptus Urosemente Energy Potential for Biomass Production in Brazil. *Renew. Sustain. Energy Rev.* **2019**, *103*, 361–369. [[CrossRef](#)]
37. Dias, A.F., Jr.; Suuchi, M.A.; Sant'Anna Neto, A.; da Silva, J.G.M.; da Silva, Á.M.; de Souza, N.D.; Protásio, T.D.P.; Brito, J.O. Blends of Charcoal Fines and Wood Improve the Combustibility and Quality of the Solid Biofuels. *Bioenergy Res.* **2021**, *14*, 344–354. [[CrossRef](#)]
38. Xiong, S.; Zhang, S.; Wu, Q.; Guo, X.; Dong, A.; Chen, C. Investigation on Cotton Stalk and Bamboo Sawdust Carbonization for Barbecue Charcoal Preparation. *Bioresour. Technol.* **2014**, *152*, 86–92. [[CrossRef](#)]

39. de Souza, H.J.P.L.; Arantes, M.D.C.; Vidaurre, G.B.; Andrade, C.R.; Carneiro, A.D.C.O.; de Souza, D.P.L.; Protásio, T.D.P. Pelletization of Eucalyptus Wood and Coffee Growing Wastes: Strategies for Biomass Valorization and Sustainable Bioenergy Production. *Renew. Energy* **2020**, *149*, 128–140. [[CrossRef](#)]
40. Cavinato, C.D.; Poletto, M. Kinetic Analysis Of Thermal Degradation Of Cedrela Odorata, Marmaroxylon Racemosum And Tectona Grandis From Timber Industry. *Maderas Cienc. Tecnol.* **2021**, *23*, 1–10. [[CrossRef](#)]
41. Gominho, J.; Lourenço, A.; Marques, A.V.; Pereira, H. An Extensive Study on the Chemical Diversity of Lipophilic Extractives from Eucalyptus Globulus Wood. *Phytochemistry* **2020**, *180*, 112520. [[CrossRef](#)] [[PubMed](#)]
42. Wang, J.; Minami, E.; Asmadi, M.; Kawamoto, H. Effect of Delignification on Thermal Degradation Reactivities of Hemicellulose and Cellulose in Wood Cell Walls. *J. Wood Sci.* **2021**, *67*, 19. [[CrossRef](#)]
43. Chaturvedi, S.; Singh, S.V.; Dhyani, V.C.; Govindaraju, K.; Vinu, R.; Mandal, S. Characterization, Bioenergy Value, and Thermal Stability of Biochars Derived from Diverse Agriculture and Forestry Lignocellulosic Wastes. *Biomass Convers. Biorefin.* **2023**, *13*, 879–892. [[CrossRef](#)]

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