




Article

Influence of Non-Lignocellulosic Elements on the Combustion of Treated Wood and Wooden Panel

João Otávio Poletto Tomeleri ^{1,*} , Luciano Donizeti Varanda ², Leonardo Machado Pitombo ³ ,
Fabio Minoru Yamaji ⁴ and Franciane Andrade de Pádua ⁴ 

¹ Center for Sciences and Technology for Sustainability—CCTS, Postgraduate Program in Planning and Use of Renewable Resources, Federal University of São Carlos, Sorocaba, São Paulo 18052-780, Brazil

² Department of Product-Oriented Materials, SENAI Institute of Innovation in Biomass, Três Lagoas, Mato Grosso do Sul 79640-250, Brazil; lu.varanda@hotmail.com

³ Department of Environmental Sciences, Federal University of São Carlos, Sorocaba, São Paulo 18052-780, Brazil; lpitombo@hotmail.com

⁴ Center for Sciences and Technology for Sustainability—CCTS, Federal University of São Carlos, Sorocaba, São Paulo 18052-780, Brazil; fmyamaji@ufscar.br (F.M.Y.); franciane@ufscar.br (F.A.d.P.)

* Correspondence: tomelerijp@gmail.com

Abstract: Brazil stands out internationally in the production and commercialization of wood products. Although the external and internal demand for these products is met by the Brazilian forestry sector, challenges related to the internal management of lignocellulosic waste are evident, as the country has structural difficulties in the sector of solid waste management. Therefore, the objective was to comparatively analyze the performance of the most abundant lignocellulosic materials in the Brazilian market, regarding energy recovery at the end of their life cycles. Pine wood treated with chromed copper arsenate (CCA), untreated pine wood, eucalypt wood treated with CCA, untreated eucalypt wood, uncoated medium density fiberboard panel (MDF), and MDF panel with melamine coating were sampled. The characterization included thermogravimetric analysis (TGA), scanning electron microscopy (SEM) with energy-dispersive x-ray spectroscopy (EDXA), and elementary analysis (EA). The presence of the CCA salts and the melamine coating reduced the energy potential of the biomass, altering the burning behavior and significantly increasing the amount of generated ashes. They also caused an increase in the concentrations of copper (Cu), chromium (Cr), arsenic (As), and cadmium (Cd) in the wood ashes as well as lead (Pb) and chromium in the panel ashes.

Keywords: energy recovery from biomass; urban solid waste; treated wood; wood panels



Citation: Tomeleri, J.O.P.; Varanda, L.D.; Pitombo, L.M.; Yamaji, F.M.; Pádua, F.A.d. Influence of Non-Lignocellulosic Elements on the Combustion of Treated Wood and Wooden Panel. *Sustainability* **2021**, *13*, 5161. <https://doi.org/10.3390/su13095161>

Academic Editor: Mariusz Maminski

Received: 25 February 2021

Accepted: 30 April 2021

Published: 5 May 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

As a world leader in wood productivity, Brazil is a major producer, consumer, and generator of wood waste. It is possible to see that in Brazil, despite the slowdown in the market, the domestic consumption of timber products is still significantly higher than the amount exported. Eighty-four percent of the production of reconstituted panels and 90% of the production of sawn wood were utilized by the domestic market [1]. With regard to treated wood products, in 2012, in the Latin American scenario, Brazil was already a leader in consumption, with approximately 700 thousand m³·year^{−1}. The treated wood from the eucalypts (93.5%) and pine (6.5%) forests was intended to produce fence posts (62%), posts (30%), sleepers (5%), and products of civil construction (3%) [2].

Due to the wide development of the wood product markets, it is possible to infer how significant these materials are for the fulfillment of the established objectives for a more efficient management of solid waste in the country. Therefore, the great participation of these wood products in the composition of the residues, be they urban or industrial waste, is clear. However, for a long time, legislative gaps related to waste management produced a context whereby regulation was not sufficient to guarantee an efficient environmental management process.

This fact, in addition to resulting in an environment impact, created a scenario where the immediate implementation of measures that met the new legislation were overly complex and, in many cases, economically unviable [3]. This is particularly reflected in the difficulties that several municipalities currently encounter to comply with the guidelines described in the legislation despite its recognized importance for accurate waste management.

According to the data from the Panorama of Solid Waste in Brazil, from the Brazilian Association of Public Cleaning and Special Waste Companies—ABRELPE, in 2019, out of a total of 79 million tons, 6.3 million tons of waste were not collected and, thus, had an improper destination. Of the amount collected, only 59.5% of the solid urban waste was sent to landfills, which represented 43.3 million tons. These inadequate destinations were a reality for 3001 municipalities, responsible for 40.5% of the waste, or 29.5 million tons, which went to dumps or landfills that did not guarantee a set of systems and measures to mitigate the potential environmental impacts [4].

In the Brazilian forestry sector, waste management is based on cogeneration of energy for production processes. In 2019, 67% of the waste generated by companies in the forestry sector was used for energy [1]. Therefore, one of the possible destinations for residual wood found in solid waste is in combustion, which is greatly influenced by the advanced establishment of industrial practices that use energy from biomass. However, post-use wood residues are not always found in their natural form; on the contrary, products that contain wood in their composition come mixed with a wide variety of materials. Residual wood is often accompanied by contaminants, such as metal parts, nails, screws, staples, and plastic parts, which can easily be removed by magnetic or manual separation, as well as chemical contaminants derived from wood treatment, such as varnishes, glues, paints, preservative substances, and other products used for finishing, which, due to the difficulty of removal, tend to accompany the wood through the burning process [5].

Being aware of the need for the responsible reuse of waste materials, in the present study, we aimed to characterize the wood that constitutes urban and industrial solid waste, to verify its applicability in the direct combustion energy sector. This analysis sought to consider the technical aspects, to identify the factors influencing the energy conversion process, and also to evaluate the burning performance of wood residues containing chromed copper arsenate (CCA) and medium density fiberboard panels (MDF), as well as the chemical and structural composition of their ashes.

2. Materials and Methods

2.1. Material

The study was conducted with new, unused materials, obtained directly from the timber market. This decision was made in order to collect materials already processed by the industry, reduce the influence of storage time and the association with contaminants on the evaluated chemical parameters.

The treatments were characterized by materials commonly found on the market for timber products and derivatives, such as untreated (virgin) pine wood; pine wood impregnated with CCA; untreated (virgin) eucalypt wood; eucalypt wood impregnated with CCA; uncoated MDF panels; MDF panels with melamine coating; and a mix, which consisted of a mixture of all materials in equal proportions.

2.2. Methods

Sampling

The sampling was intensive to solve the possible variability found among the botanical genera. The collection of materials damaged by weathering and the use of alternative treatments such as painting and varnish was avoided. Nine samples were collected per treatment, for a total of 54 samples, with approximately 60 kg of material per treatment. After the first sample preparation process 7 kg of material were obtained per treatment. For treated and untreated pine wood, sawn wood with 2 m long and 0.5 m wide were collected.

For treated and untreated eucalyptus, logs of up to 1.5 m were collected. The panels were collected on boards 1 m long by 0.5 m wide.

All the raw material was processed in particulate matter of approximately 50×30 mm and homogenized to constitute a sample weighing 4.5 kg, for each treatment, as shown in Figure 1. Subsequently, the entire quantity was ground until a particulate material, with dimensions between 3 and 5 mm, was obtained. Of this total, 100 g were ground in a Marconi MA 340 knife Wiley mill, using a fixed speed of 1750 rpm, and run through a 30-mesh sieve, for laboratory analysis. The weight reduction for the physical–chemical analyses was carried out in accordance with the standard for sample preparation of solid fuels, CEN/TS 14780: 2005 [6].

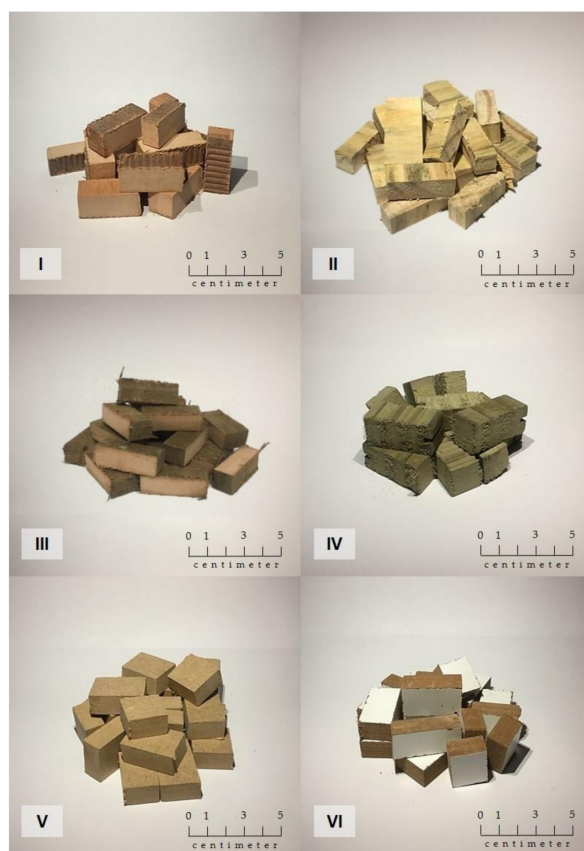


Figure 1. Result of standardization of lignocellulosic materials after first sample preparation procedure. Item I—Untreated eucalypt; Item II—Untreated pine; Item III—Treated eucalypt; Item IV—Treated pine; Item V—Uncoated panel; Item VI—Coated panel. Source: Own elaboration.

2.3. Elementary Analysis of Wood

Sample preparation was performed using the wet digestion method, according to the United States Environmental Protection Agency [7], with the inclusion of an additional digestion cycle for all materials. Samples of particulate matter, smaller than 30 mesh (5 g), were placed in 200 mL Erlenmeyer flasks, containing 15 mL of HNO_3 65%, for 24 h. At the end of this period, an additional 10 mL of HNO_3 65% was added to the flasks, which was followed by a heating mantle for the reflux process for 6 h at a temperature of 55°C .

At the end of the process, the need to apply an additional 10 mL of HNO_3 65% and additional reflux for the completeness of digestion was verified. After cooling the samples, 20 mL of H_2O_2 65% was added, following which the flasks were returned to the heating mantle for another two hours. In addition to the samples, a set of three Erlenmeyer flasks containing only the reagents was established as a blank analytical control. For reading on the equipment, the resulting solutions were filtered and diluted to 100 mL, using deionized water.

Elementary analyses were conducted using Atomic Emission Spectrometry (ICP-AES) technique, to determine the following inorganic elements: Zinc (Zn); Cadmium (Cd); Copper (Cu); Nickel (Ni); Arsenic (As); Lead (Pb); Manganese (Mn); and Chromium (Cr).

2.4. Thermogravimetric Analysis

The analysis of the thermic degradation of the material was carried out in a Perkin Elmer, model Pyris 1 TGA. For the test, synthetic air atmosphere was used, with a flow of $20 \text{ mL} \cdot \text{min}^{-1}$ and a heating rate of $20 \text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$ to $750 \text{ }^{\circ}\text{C}$. Before the tests, the samples were oven dried.

Particles with a particle size of less than 30 mesh (0.59 mm) and an initial mass of 15 mg were used. The collected data were processed to generate graphs for the mass loss curve in addition to the derivative.

2.5. Scanning Electron Microscopy (SEM)

The material of the ash residue obtained after combustion of the muffle furnace at $600 \text{ }^{\circ}\text{C}$ was analyzed through scanning electron microscopy (SEM) for a structural and semi-quantitative characterization of the chemical elements present in the samples.

The tests were conducted using a Hitachi scanning electron microscope, model TM3000, coupled with an energy dispersion spectroscopy (EDS) probe, responsible for obtaining elementary microanalyses. The samples were fixed on a metallic support, on a double-sided carbon adhesive tape. The applied acceleration voltage was 15 kV.

The identification of the elements in the graphics, originating from the EDS was made following a pre-stipulated standard for the intensity. Only peaks greater than or equal to the 0.4 cps/ev count (counts per second per electron volt) were considered across the spectrum from 0 to 10 keV (kilo-electron volt). Values lower than this intensity parameter were not considered despite the presence of these elements in the samples.

2.6. Statistical Analysis

The experimental design was completely randomized, with seven treatments. The data obtained from the immediate and elementary analysis were subjected to analysis of variance (ANOVA) and to the Tukey test (with 5% significance). All tests were processed using the software R version 3.1.3 [8].

3. Results

3.1. Elementary Wood Analysis

The results of the elementary characterization of the wood products and derivatives are presented in Table 1.

Table 1. Elementary chemical composition of the wood products and derivatives, in $\text{mg} \cdot \text{kg}^{-1}$ of dry mass.

	Untreated Pine	Treated Pine	Untreated Eucalypt	Treated Eucalypt	Uncoated Panel	Coated Panel	Mix
Zn	5.61 ± 0.42^c	48.99 ± 1.39^f	2.14 ± 0.33^a	12.90 ± 0.57^d	4.37 ± 0.18^b	6.16 ± 0.14^c	24.57 ± 3.57^e
Cd	0.04 ± 0.001^c	136.39 ± 5.70^e	0.08 ± 0.02^{bc}	28.21 ± 0.36^d	0.15 ± 0.08^{ab}	0.22 ± 0.01^a	-
Cu	1.39 ± 0.05^a	3877.46 ± 460.72^e	1.79 ± 0.50^a	538.91 ± 2.50^c	1.88 ± 0.20^a	8.88 ± 0.30^b	771.29 ± 23.15^d
Ni	0.76 ± 0.13^a	0.93 ± 0.16^a	0.58 ± 0.27^a	1.53 ± 0.13^b	0.62 ± 0.18^a	0.95 ± 0.08^a	0.71 ± 0.13^a
As	2.15 ± 0.25^{ab}	6694.49 ± 378.26^f	4.42 ± 1.35^b	1191.35 ± 7.39^d	1.14 ± 0.36^a	7.98 ± 1.32^c	1336.23 ± 38.12^e
Pb	1.51 ± 0.19^a	10.65 ± 0.25^c	1.36 ± 0.36^a	5.91 ± 0.32^b	1.35 ± 0.37^a	12.90 ± 4.29^c	1.69 ± 0.21^a
Mn	55.90 ± 1.46^b	51.65 ± 2.58^c	17.10 ± 1.00^d	48.21 ± 0.50^c	66.50 ± 1.07^a	57.86 ± 0.64^b	0.49 ± 0.28^e
Cr	0.61 ± 0.04^a	4037.83 ± 153.48^e	1.85 ± 1.30^a	1103.49 ± 26.02^c	0.92 ± 0.12^a	12.22 ± 0.65^b	1180.67 ± 32.63^d

^{a,b,c,d,e,f} Means followed by the same letter do not differ at 5% significance by the Tukey test. Source: Own elaboration.

Untreated biomasses are within the limits established by CEN/TS 14961:2005 [9], for five microelements of coniferous and hardwood. The reference concentration for these elements, expressed in $\text{mg} \cdot \text{kg}^{-1}$, are: Cadmium (<0.05 to 0.50); chromium (0.2 to 10); copper (0.5 to 10); nickel (<0.1 to 10); and zinc (5 to 100) [9].

The results were also similar to the average concentrations obtained by Telmo, Lou-sada, and Moreira [10] for manganese ($45.83 \pm 24.9 \text{ mg} \cdot \text{kg}^{-1}$ and $54.64 \pm 76.1 \text{ mg} \cdot \text{kg}^{-1}$),

chromium ($0.55 \pm 0.35 \text{ mg}\cdot\text{kg}^{-1}$ and $0.53 \pm 0.3 \text{ mg}\cdot\text{kg}^{-1}$), and cadmium ($0.01 \pm 0.35 \text{ mg}\cdot\text{kg}^{-1}$ and $0.03 \pm 0.6 \text{ mg}\cdot\text{kg}^{-1}$), determined for conifers and hardwoods, respectively. The values determined for lead and arsenic, however, were higher than those obtained by Tafur-Marinos et al. [11], who were studying commercial wood chips, used for pyrolysis and gasification. They obtained values of $0.077 \text{ mg}\cdot\text{kg}^{-1}$ for arsenic and $0.74 \text{ mg}\cdot\text{kg}^{-1}$ for lead.

The concentrations for treated wood were higher than those obtained by Junges [12] for arsenic ($1480 \pm 64 \text{ mg}\cdot\text{kg}^{-1}$), chromium ($1900 \pm 7 \text{ mg}\cdot\text{kg}^{-1}$), and copper ($1263 \pm 35 \text{ mg}\cdot\text{kg}^{-1}$) in the samples from the outer portion of used eucalypt posts and lower than the $16,300 \text{ mg}\cdot\text{kg}^{-1}$ (As), $7100 \text{ mg}\cdot\text{kg}^{-1}$ (Cu), and $19,100 \text{ mg}\cdot\text{kg}^{-1}$ (Cr), determined by Helsen and Van den Bulck [13], for pine woods impregnated with a preservative solution containing 32.6% arsenic pentoxide, 49.2% chromium trioxide, and 18.2% copper oxide, treated under laboratory conditions.

An important aspect was the lower concentrations obtained for chromium, copper, and arsenic in treated eucalypt wood, when compared to treated pine. An explanation is based on the different anatomical aspects between conifers and hardwoods, which influenced the permeability and penetration of salts, such as the higher density and presence of conduction vessels in the hardwoods with different sizes, frequencies, and distribution [14]. In addition, chromium forms hexavalent complexes with lignin, particularly the guaiacyl type [15,16]. Conifer lignin is formed due to the predominance of guaiacyl units; therefore, there may be a greater formation of more stable complexes with chromium in pine wood.

The melamine coating contributed to an increase in the concentrations of all the considered elements, with the exception of manganese, nickel and cadmium. Major differences were observed for lead, chromium, copper, and arsenic. These results corroborate with observations made in the literature regarding the presence of surface treatments of wood, such as paints and coatings in general, as these tend to increase the concentration of zinc, cadmium, lead, copper, chromium, and mercury, due to the presence of compounds for pigmentation, drying, and biocides [17]. However, the values obtained for the coated panel were lower than the estimated concentrations for chromium ($19 \text{ mg}\cdot\text{kg}^{-1}$), lead ($182 \text{ mg}\cdot\text{kg}^{-1}$), zinc ($2070 \text{ mg}\cdot\text{kg}^{-1}$), and cadmium ($0.7 \text{ mg}\cdot\text{kg}^{-1}$) for superficially treated wood used for combustion in the energy generation processes in Sweden together with other wood residues [17].

The mixture of all biomasses had an attenuating effect on the concentration of contaminants. This is possibly the effect observed during the processing of large heterogeneous amounts of biomass for energy generation, particularly from solid waste. According to Edo et al. [5], for urban solid waste in Sweden, considerable variation was seen in the concentrations of As ($0.10\text{--}270 \text{ mg}\cdot\text{kg}^{-1}$), Pb ($1.80\text{--}2900 \text{ mg}\cdot\text{kg}^{-1}$), Cu ($3.6\text{--}3200 \text{ mg}\cdot\text{kg}^{-1}$), and Cr ($1.5\text{--}313 \text{ mg}\cdot\text{kg}^{-1}$), in different batches between the years 2004 and 2013.

The concentrations of the elements, identified as contaminants, indicated that, for the best use of wood residues for energy generation, it is necessary to accurately classify each constituent of the set to be processed, as the materials have significant concentrations of potentially toxic elements. These results are in agreement with those obtained by Krook et al. [18], who indicated that, without the correct destination, a high rate of energy recovery from these lignocellulosic residues can cause the generation of pollution problems in the future.

3.2. Thermogravimetric Analysis

To study the burning behavior of materials from residual wood, thermogravimetry tests were performed according to the differences related to the botanical genus and the type of association with non-lignocellulosic elements. Figure 2 shows the thermal degradation of untreated and CCA-treated pine in an oxidizing atmosphere of synthetic air.

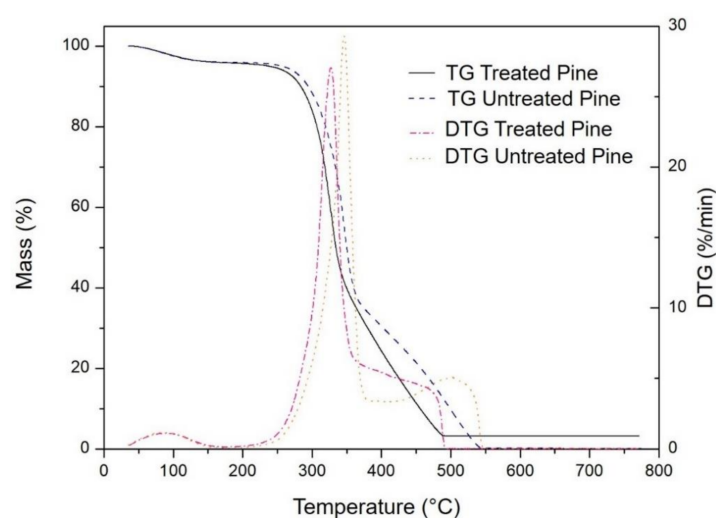


Figure 2. Thermogravimetry curve (TG) and degradation rate (DTG) of untreated and treated pine. Source: Pyris 1TGA, Perkin Elmer.

In general, as expected, all the analyzed materials showed a standard behavior based on the four degradation events, with variations occurring only in the reference temperature parameters and percentage of mass loss that initiated the events.

The second event, which is characterized by the effective start of degradation, had its early start in the treated pine sample, indicating an anticipation of the burning process (Figure 2). This behavior remained throughout the process culminating in the early termination of degradation of treated pine at a temperature of 489 °C, whereas for the untreated pine, this temperature was 544 °C.

Despite the early onset of degradation, the treated pine showed a lower maximum degradation rate of $27\% \cdot \text{min}^{-1}$ at 329 °C, against values of $30\% \cdot \text{min}^{-1}$ at 347 °C for untreated pine. These results demonstrate that the treatment made the pine wood more reactive. However, a slower rate of degradation indicates the direct influence of the CCA salts, decreasing the amount of flammable compounds and resulting in greater ash generation at the end of the process.

According to Helsen et al. [19], the release of chromium, copper, and arsenic is directly related to the increase in temperature and the duration of the exposure to these variations during the pyrolysis process of treated wood. The influence of both parameters is the same for chromium, copper, and arsenic. However, arsenic is characterized as the most volatile compound among the three, resulting in less retention of this element in the waste at the end of the thermal degradation process [19].

Helsen et al. [19], studying the behavior of *Pinus sylvestris* wood, concluded that the CCA treatment influenced a decrease in the onset pyrolysis temperature as well as the peak temperature of maximum degradation in addition to identifying a higher charcoal yield. However, the authors obtained a higher rate of mass loss compared to untreated wood. In general, the CCA salts present acted as catalysts for the decomposition of hemicellulose, resulting in a greater conversion to volatiles at low temperatures [19].

In addition to the displacement of the TG curve toward a faster process of thermal degradation, we observed that, for a biomass containing CCA, the degradation rates remained higher when the wood reached the third burning phase, demonstrating a less noticeable transition compared to those for the untreated biomass (Figure 2). At this stage, the treated pine maintained a higher rate of degradation at temperatures close to 350 °C, which occurred for untreated pine after 500 °C.

The highest degradation rates observed for pine containing CCA in the third event, continued until the abrupt end of the degradation process at 486 °C, indicating that there was an interruption in the degradation of the more thermally resistant compounds. Thus, the start of the fourth event was anticipated, indicating that the compounds with greater

resistance were partially decomposed, as was detected by Fu et al. [20] and Richards and Zheng [21], and also as later observed with SEM on the ashes of this material. As a result, the treated pine produced almost ten times as much ash as untreated pine as a result of less efficient burning.

Under analysis of the same parameters, the behavior of the eucalypt samples were analyzed throughout the combustion process in an oxidizing atmosphere of synthetic air. The results are shown in Figure 3.

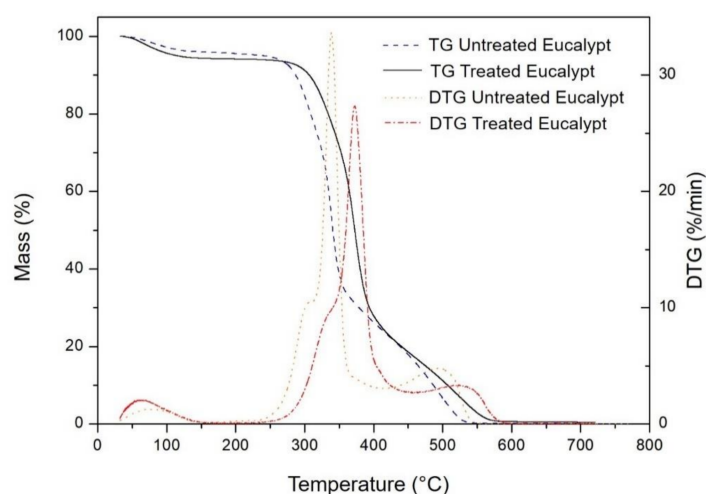


Figure 3. Thermogravimetry curve (TG) and degradation rate (DTG) of eucalypt wood. Source: Pyris 1TGA, Perkin Elmer.

We observed the occurrence of a shoulder at the beginning of event II at 302 °C for untreated eucalypt and at 331 °C for treated eucalypt. According to Sebio-Puñal et al. [22], this peak refers to the transition from the degradation of hemicellulose to cellulose, partially superimposed with lignin.

In addition, in contrast to what occurred with pine wood, the presence of CCA salts significantly delayed the process from the beginning of the decomposition of the hemicelluloses to the end with the degradation of the more thermally resistant compounds. This effect caused the treated eucalypt to present lower degradation rates in all the considered events, in addition to the displacement of the thermodegradation curve (TG), indicating that the compounds decomposed at higher reference temperatures.

The burning of treated eucalypt started at higher temperatures and occurred in a more concentrated manner, with 66.4% of the degraded material at the end of the second stage, while the untreated eucalypt presented values of 62.1%. In event III, this relation was reversed, with the treated eucalypt degrading 7% less of its thermally more-resistant compounds, such as lignin. In addition, there was a greater formation of residues from treated eucalypt, with 1.6% of ash generated against 0.6% from untreated eucalypt in a similar manner as observed by Poletto et al. [23].

These results indicate that the volatilization of arsenic at low temperatures did not cause effects similar to those observed for pine wood. Similarly, the reduction in the speed of degradation from the third event did not generate an abrupt interruption of the process for the more thermally resistant compounds as observed for coniferous wood. The presence of CCA in eucalypt only slowed the whole process, requiring a higher temperature to proceed with the decomposition of the wood.

The lower concentration of CCA for eucalypt, as shown at Table 1, not only minimized the effects of accelerated degradation, but also altered the behavior completely, slowing down the process, increasing the reference temperatures and making the compounds more thermally resistant.

In general, wood that underwent the CCA impregnation process tended to generate greater amounts of waste at the end of combustion, and its thermal degradation was catalyzed by the volatilization of metals. This last factor, however, was variable and could be directly related to the concentration of these metals in association with the lignocellulosic material.

To characterize the burning behavior of coated and uncoated MDF panels, their thermal degradation curves in an oxidizing atmosphere of synthetic air are shown in Figure 4.

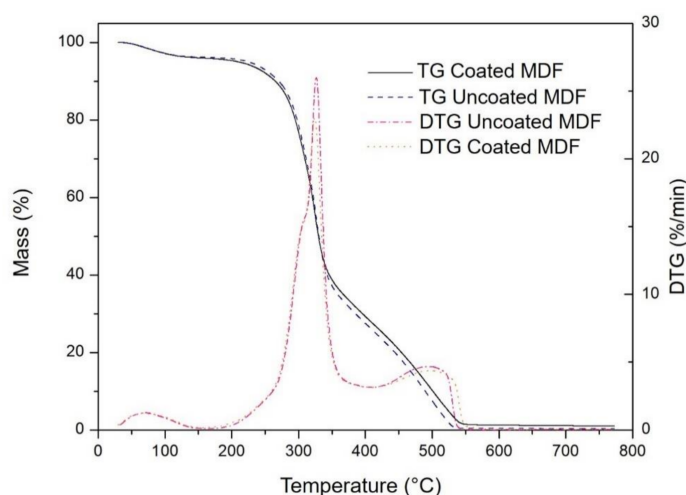


Figure 4. Thermogravimetry curve (TG) and degradation rate (DTG) of MDF panels. Source: Pyris 1TGA, Perkin Elmer.

In general, it was only after the third event, at 350 °C, that the coated panel presented a differentiation in relation to the degradation of the uncoated panel, when it was possible to verify a displacement in the TG curve, resulting from the degradation of more thermally resistant compounds. The decrease in the degradation rate (DTG), and the consequent delay at the end of the process, with a greater generation of residues, indicated a possible interference of the melamine coating, extending the third degradation event by 10 °C.

The coated panel showed a maximum degradation of 23.5% at 325 °C, against 26.5% at 327 °C for the uncoated panel, indicating that the presence of the coating was responsible for displacing the degradation curve and reducing the percentage of mass loss. The melamine coating was responsible for extending the burning process by 10 °C, concentrating the degradation of its compounds at the end of combustion and producing a greater amount of ashes.

To better understand the effect of the coating on the panel thermal degradation process, the thermogravimetry of the isolated material is shown in Figure 5.

The coating degradation occurred mainly in three peaks, with the largest one occurring in the temperature range between 300 °C and 400 °C, exactly at the same range of occurrence of the main peak of degradation for the panel as a whole. However, due to the low proportion represented by the coating in relation to the entire panel, the decomposition that reached the maximum values of 18% at 352 °C had little influence on the total degradation of the coated panel.

The main interference was the decrease in the degradation rate as a whole, even for the degradation events for less thermally resistant compounds. Another important aspect that was verified in the results is that, even after 800 °C, the coating contained more than 20% of its initial mass, indicating that, for the considered temperature range, the coating presents a high contribution to the coated panel ash.

Therefore, the coating contributes to a decrease in the rate of degradation, and to a greater generation of flammable waste, resulting in less efficient burning.

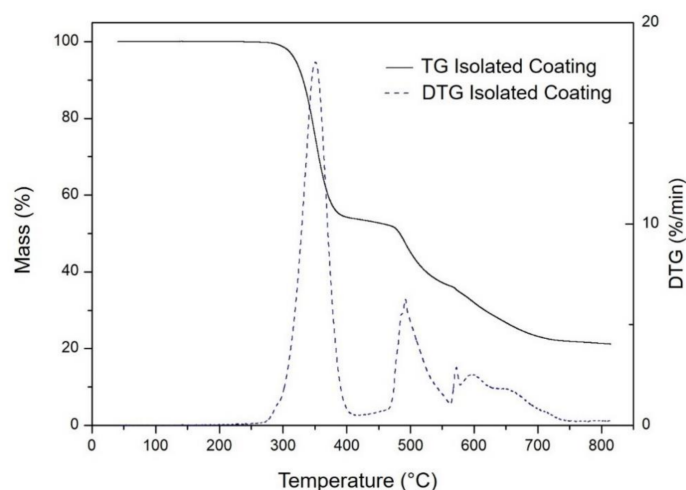


Figure 5. Thermogravimetry curve (TG) and degradation rate (DTG) of the isolated coating. Source: Pyris 1TGA, Perkin Elmer.

The burning behavior of all biomasses processed together was analyzed, composing a mix. The thermal degradation curve and its derivatives are shown in Figure 6.

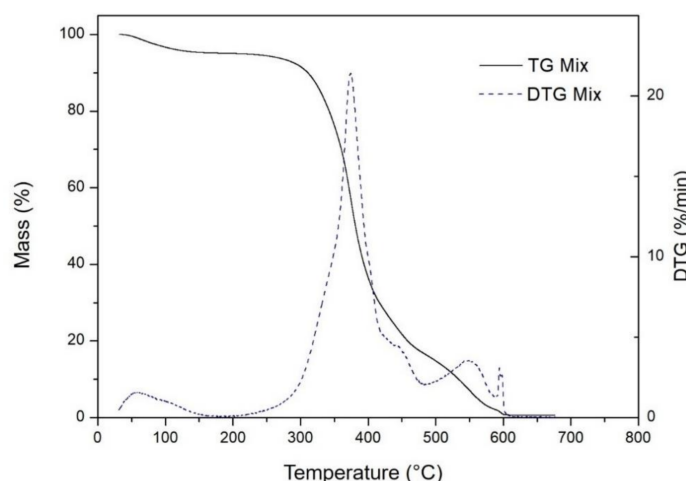


Figure 6. Thermogravimetry curve (TG) and degradation rate (DTG) of the biomass mix composed of equal parts of untreated pine, pine with CCA, untreated eucalypt, eucalypt with CCA, uncoated MDF panel, and coated MDF panel. Source: Pyris 1TGA, Perkin Elmer.

The mix made the whole process more complex, with new peaks and variations not previously detected, in addition to smoothing out other peaks that were previously more accentuated. A previously unidentified peak among the other biomass samples was obtained at a temperature of 440 °C, which according to Sebío-Puñal et al. [22], could be interpreted as the result of overlapping degradation of some by-product of lignin.

In general, compared to the results obtained individually for each biomass, in addition to the decrease in the rate of degradation, there was a delay in the process, which reached completion at temperatures close to 600 °C, with a displacement of all the reference temperatures to values higher than those previously obtained.

The thermal degradation of the mix was similar to that obtained individually for the treated eucalypt. The rise in reference temperatures was possibly enhanced by the low concentrations of CCA salts, and by the presence of the panel coating. The latter was responsible for the peak of degradation observed at 600 °C, similar to that obtained for the isolated material (Figure 5). In addition, the reduction in the maximum process

degradation rate was similar to biomasses containing CCA and melamine coating, with a maximum peak of 21.8%, occurring at 376 °C.

We concluded, therefore, that the mixture of diverse biomasses with different characteristics and components produced a retarding effect in the process of thermal degradation when compared to the individual analysis. This behavior reveals a description of what possibly occurs in recycled biomass processing plants, as burning likely will not happen separately.

3.3. Ash Analysis by SEM and EDX

Figure 7 presents the images obtained by scanning electron microscopy and X-ray dispersive energy spectroscopy for the ashes of untreated pine wood.

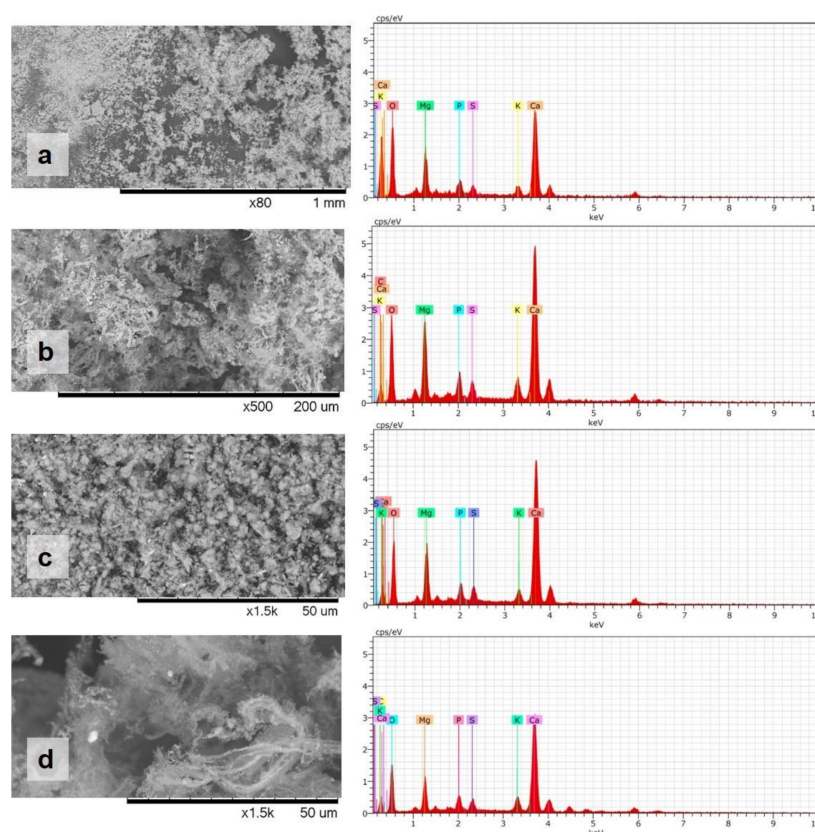


Figure 7. Photomicrography and X-ray Dispersive Energy Spectroscopy (EDX) of untreated pine ash. Figures (a–d) correspond to different magnifications, in different areas of ash analysis. Source: Hitachi TM3000 Scanning Electron Microscope.

The ash structure of untreated pine wood, in general, was homogeneous, consisting of amorphous, irregular, and small-sized particles of approximately 200 μm in size (Figure 7a,b), similar to the coal fly ash mentioned in the literature, which ranges from 1 to 200 μm [24,25]. There was little occurrence of amorphous particles with a vitreous aspect, as identified separately in Figure 7c. This was characterized by the complete absence of porous structures typical of partial burning, indicating agreement with the low ash content values determined for this material in the thermogravimetric analysis.

In general, the chemical elements present in the pine sample were in agreement with the ones expected for uncontaminated biomasses [26], which presented a satisfactory yield of the burning process, resulting in a low total ash content, composed mainly of inorganic elements, similar to those identified in the literature for this biomass.

Figure 8 presents the images and X-ray dispersive energy spectroscopy of the ashes originating from the combustion of pine wood treated with CCA.

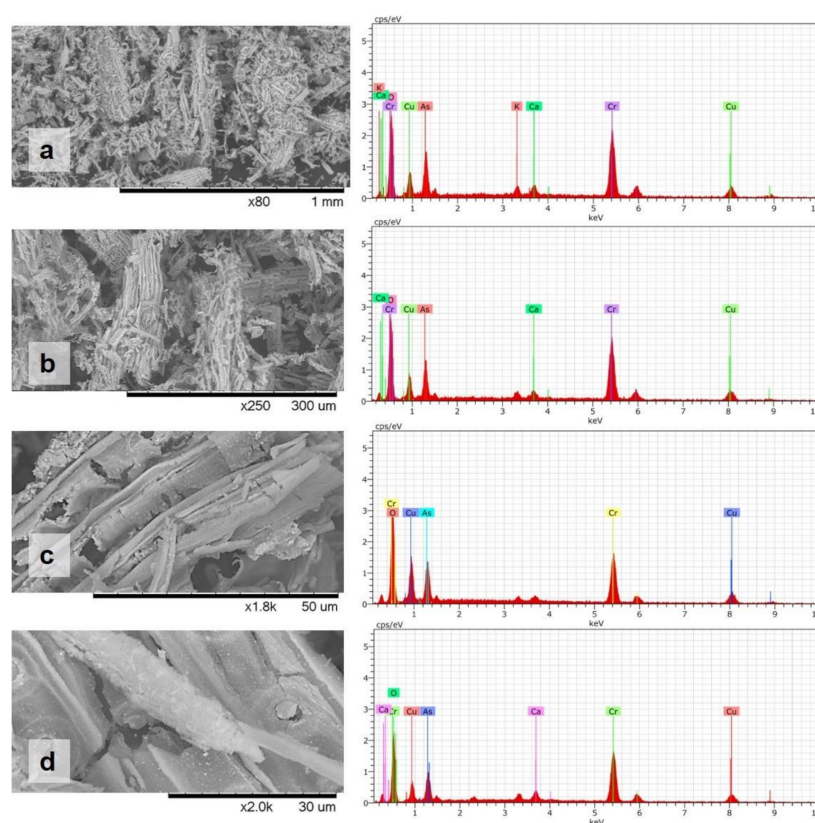


Figure 8. Photomicrography and X-ray Dispersive Energy Spectroscopy of the treated pine ash. Figures (a–d) correspond to different magnifications, in different areas of ash analysis. Source: Hitachi TM3000 Scanning Electron Microscope.

The treated pine ashes were composed predominantly of amorphous, porous, and larger particles, with some reaching lengths above 1 mm (Figure 8a,b). These fragments resembled the organic partial-burning particles obtained by Nortey Yeboah et al. [25], as a result of the combustion of charcoal, with large dimensions, above 200 μm , fibrous, and with a woody aspect.

The CCA salts incorporated into the wood delay the burning process in the decomposition phase of the more thermally resistant compounds. Analyzing the ashes of the treated pine, the structural difference presented by the residual particles was visible, and it was even possible to identify the remnants of the anatomical elements of the wood, such as the tracheids as shown in Figure 8d.

In all the images, there was a predominance of the elements chromium, oxygen, copper, arsenic, and calcium. In addition to oxygen, chromium was the element with the highest intensity of identification, indicating that, among the elements that comprised the treatment salts, it was the one that showed the greatest permanence in the combustion residues, being less influenced by factors, such as volatilization.

The concentrations previously discussed and presented in Table 1 indicated that for pine wood, arsenic was the most predominant element among the components of the CCA. After burning, this relation changed. Several authors reported that the arsenic behavior was similar to that of other volatile species, which ends up directly influencing the enrichment of the fly ash fraction, making the less volatile elements, such as copper and chromium, remain as solids in the bottom ash [27].

In treated wood, arsenic is predominantly associated with chromium, forming chromium arsenate (CrAsO_4) fixed in lignin, in CrAsO_4 –lignin compounds, or precipitated as CrAsO_4 in an inorganic form on cellulose [28]. After burning, this element is commonly observed in the ashes to be associated with calcium (e.g., calcium arsenate complexes), which have a higher boiling point than other compounds containing arsenic. As soon as the wood is burned,

the arsenic volatilizes and returns to the ashes through the association of steam with compounds of fly ash containing calcium [27,29–32]. Moreover, according to Jerzak [32], at temperatures below 1000 °C, arsenic and chromium can be complexed with other elements present in fly ash, such as potassium, in solid complexes of K_3AsO_4 and K_2CrO_4 .

Therefore, under the burning conditions in industries, it is expected that the wood treated with CCA will produce ashes with high levels of these elements. In cases of incineration, in firing devices that do not have conditions for cooling the gases or even filters, part of the arsenic tends to be released together with the combustion vapors.

Figure 9 presents images of the X-ray dispersive energy spectroscopy of untreated eucalypt ash obtained through scanning electron microscopy.

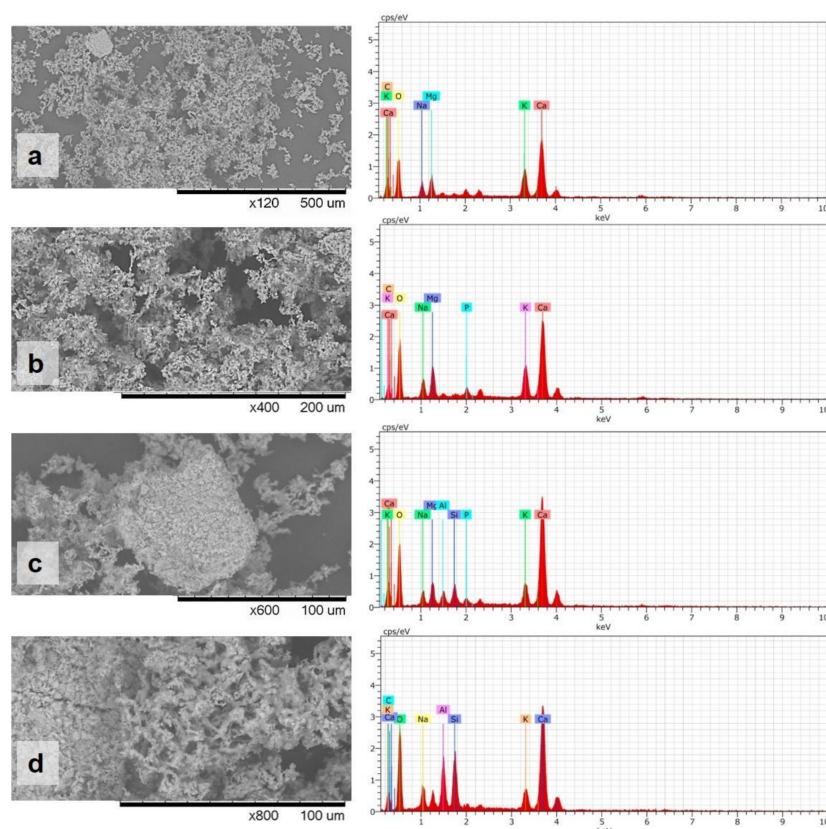


Figure 9. Photomicrography and X-ray Dispersive Energy Spectroscopy of untreated eucalypt ash. Figures (a–d) correspond to different magnifications, in different areas of ash analysis. Source: Hitachi TM3000 Scanning Electron Microscope.

To untreated eucalypt it was possible to characterize the predominance of amorphous, irregular, and small-sized particles that form almost all the ash. There was a predominance of the elements calcium, oxygen, carbon, potassium, magnesium, and sodium, while silica and aluminum occur in a smaller proportion.

Considering the subsequent use of ash in other industrial processes, the low occurrence of silica for untreated eucalypt compromises its use as a sand substitute for the civil construction sector. According to Cacuro and Waldman [33], the applications of sugarcane ash as an increase in cement properties would be justified by the binding properties present in siliceous particles, which in an aqueous medium reacts with calcium hydroxide to form compounds with cementitious properties. However, the absence of toxic elements such as heavy metals and the abundance of calcium, potassium, magnesium, sodium, and even aluminum, would justify the application of ash in agriculture to correct the soil pH, due to the release of Ca^+ , Na^+ ions, Al^+ , and OH^- , and for the improvement of the water retention capacity due to the increased microporosity [33].

Figure 10 presents the images of the X-ray dispersive energy spectroscopy of treated eucalypt ash obtained through scanning electron microscopy.

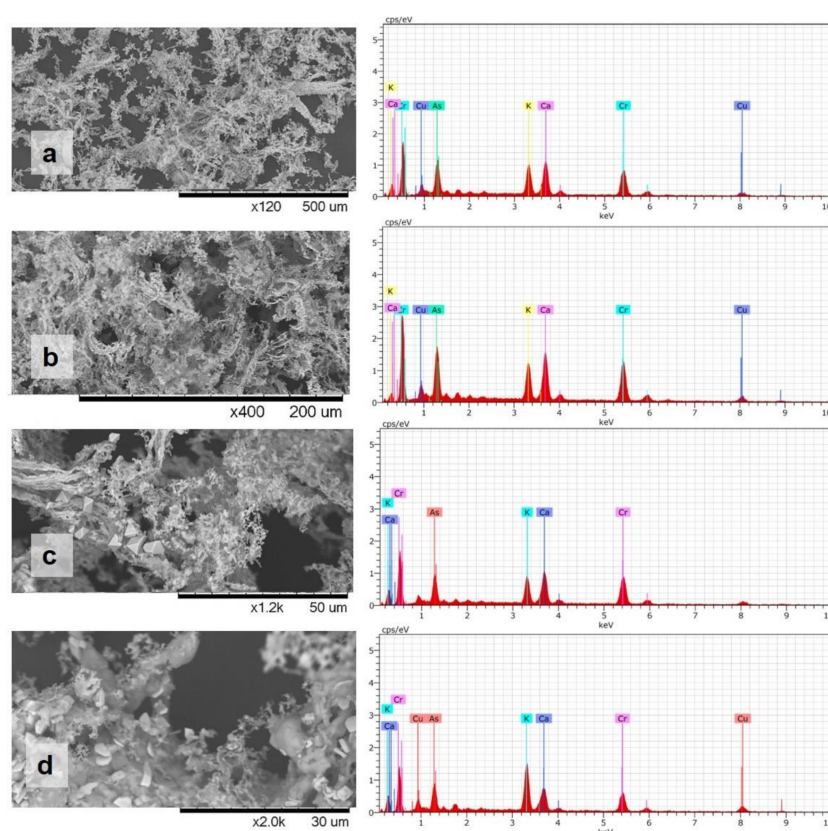


Figure 10. Photomicrography and X-ray Dispersive Energy Spectroscopy obtained by SEM of treated eucalypt ash. Figures (a–d) correspond to different magnifications, in different areas of ash analysis. Source: Hitachi TM3000 Scanning Electron Microscope.

In comparison with the untreated biomass, the ashes of the treated eucalypt are characterized by the presence of less homogeneous and larger structures. In addition, the visualization of particles from 40 to 50 μm , prismatic in shape and associated with the structures that make up the ash matrix, was exclusive to the CCA wood (Figure 10c,d).

In all the analyzed samples, chromium, copper, and arsenic were the most abundant elements, in addition to calcium and potassium, indicating that even after the process of burning the biomass, heavy metals remained in the ashes. Moreover, the different sampling points, as well as the variations in magnification, did not significantly interfere with the intensity patterns for the peaks of each element, indicating that the elements in the residues did not have predetermined distribution patterns.

In all samples analyzed for the treated wood, both pine and eucalypt presented chromium as the element of greatest determination intensity, indicating that there was less release of this element, to the detriment of the others considered, in agreement with Helsén et al. [19], who identified arsenic as the most volatile and least retained species in the burning residues.

Figure 11 shows the images of the spectroscopy of the X-ray dispersive energy from the ashes originating from the combustion of the uncoated MDF panel, analyzed by scanning electron microscopy.

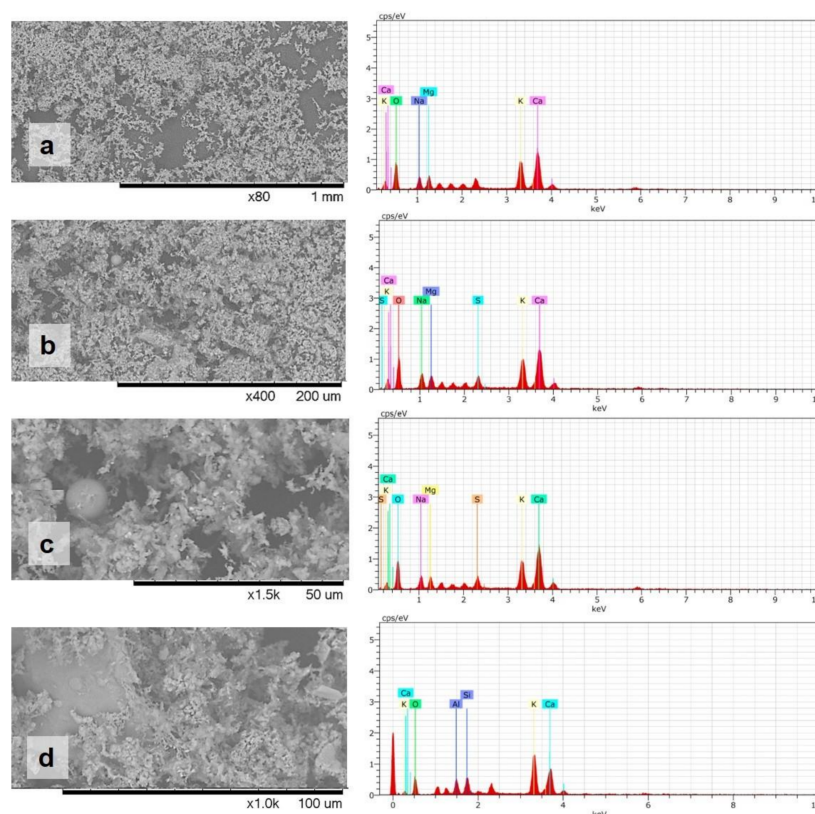


Figure 11. Photomicrography and X-ray Dispersive Energy Spectroscopy obtained by SEM from uncoated MDF panel ash. Figures (a–d) correspond to different magnifications, in different areas of ash analysis. Source: Hitachi TM3000 Scanning Electron Microscope.

The ashes of uncoated panel were similar to those produced by the untreated eucalypt, with the absence of partial burning elements and the predominance of small, amorphous inorganic particles, smaller than 200 μm (Figure 11a,b).

The low ash contents determined by the thermogravimetric analysis combined with the presented pattern indicate an efficient burning. In general, the chemical composition of the uncoated MDF ashes was marked by the predominance of calcium, oxygen, potassium, sodium, sulfur, and magnesium, and lower proportions of silica and aluminum.

The absence of potentially toxic elements, which may originate from the industrial process of manufacturing the panels, indicates that there are no reasons for restrictions on the use of the ashes of these materials, when they are processed in conjunction with virgin wood.

Figure 12 shows the images and the dispersive energy X-ray spectroscopy of the ashes originating from the combustion of coated MDF panels.

The main differentiating factor from the uncoated panel was the abundant presence of amorphous residual structures, large in size, and easy to identify (Figure 12a,b).

The presence of the coating residues significantly altered the chemical composition of the ashes. The main differences between the identification of elements, such as calcium, sodium, potassium, magnesium, and aluminum, were the presence of elements, such as titanium and chlorine. Unlike titanium, the abundance of chlorine elements did not change among the different particles analyzed. The highest intensity of titanium determination occurred mainly when considering the residual coating surface, as seen in Figure 12c.

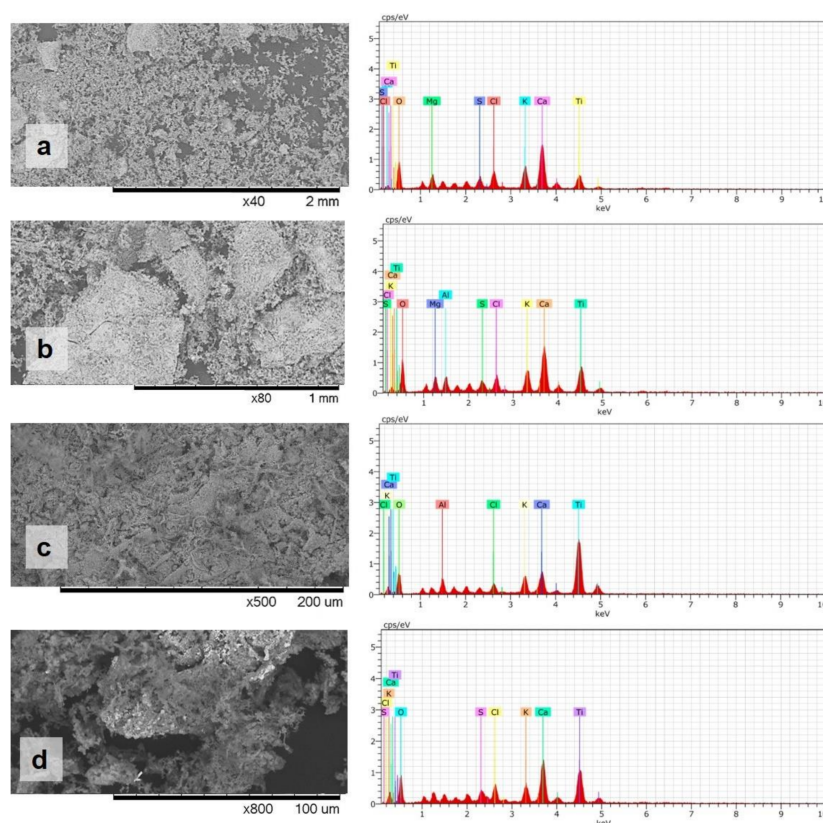


Figure 12. Photomicrography and X-ray Dispersive Energy Spectroscopy of coated MDF panel ash. Figures (a–d) correspond to different magnifications, in different areas of ash analysis. Source: Hitachi TM3000 Scanning Electron Microscope.

Titanium dioxide is used specifically in the plastics industry for its resistance to degradation by ultraviolet light, high levels of refraction, and chemical inertia [34].

The presence of chlorine in the ash composition of the coated panel indicates the possibility of the formation of chlorinated compounds during the burning process. Although most of the chlorine is retained in the ashes as a compound with less toxicity and risk to the environment, its presence does not eliminate the concern of the corrosive action that this element has. Despite the difficulty in predicting the behavior of residues as sources of corrosive materials for combustion processes, according to Hamaguchi and Vakkilainen [35], the most severe problems of corrosion in boilers that burn biofuels are expected in processes involving the deposition of chlorine-rich materials.

Therefore, from a technological point of view, the presence of the coating material was responsible for increasing the volume of ash produced and changing its chemical composition, compared to the uncoated MDF panel. This interfered negatively in the combustion process, forcing the handling of larger amounts of waste, and possibly increasing the need for maintenance in the burning apparatus.

To analyze the structures formed by burning the mixture of biomasses, Figure 13 presents the images of the X-ray dispersive energy spectroscopy of the ashes.

In general, as expected, the mixing of the materials produced a more heterogeneous residue, with a predominance of particles produced by biomasses that had a greater influence of non-lignocellulosic elements in their composition, such as the chemical treatment salts and melamine coating. As observed in the structural analysis of the ashes, the elemental composition of the samples was highly heterogeneous, with its distribution determined mainly by the origin of the analyzed particle.

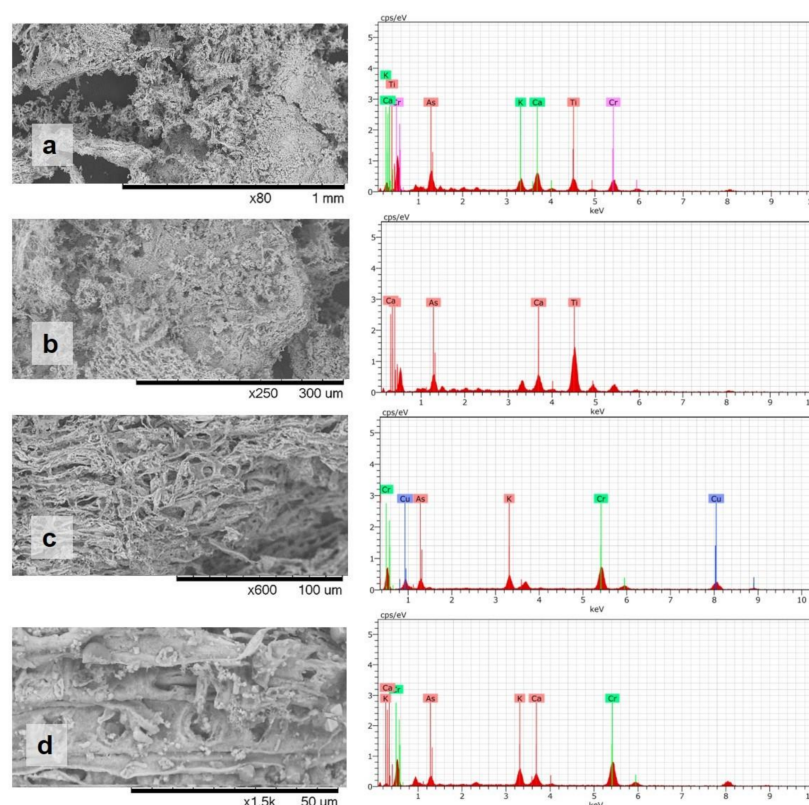


Figure 13. Photomicrography and X-ray Dispersive Energy Spectroscopy of the ashes of the biomass mix. Figures (a–d) correspond to different magnifications, in different areas of ash analysis. Source: Hitachi TM3000 Scanning Electron Microscope.

Therefore, even with the mixture, the behavior of the biomass residues did not change in comparison with the results obtained for the individual burning of materials. From the morphology of the particles to the distribution of the elements, they were restricted to the conditions observed individually for each biomass.

Ash is one of the main by-products that discourage the energetic application of urban solid waste, as several studies indicate the presence of toxic elements in both fly and bottom ash. However, waste incineration has been the most viable technique for application in solid waste management large scale plants [36].

The permanence of toxic elements in the ashes of the treated materials clearly expresses the main risks that the energy use of these residues represent. The results obtained by Edo et al. [5], established that, “There is an urgent need to adapt the pretreatment techniques applied to waste, so as not to compromise on its quality as a fuel and minimize dangerous emissions to the environment”.

Therefore, the data presented reinforce that the characterization of the materials and the correct handling of the generated ashes are essential processes in the management of solid waste.

4. Conclusions

The association of wood with CCA salts and the MDF panel with a melamine coating reduced the energy potential of the biomass, changing the burning behavior, and significantly increasing the amount of waste generated. The treated pine wood had the highest ash content among the tested materials, followed by the coated panel, the mix, and the treated eucalypt.

The preservation salts changed the burning behavior of pine and eucalypt woods in a different manner, possibly by the different observed concentrations of copper, chromium, and arsenic for these materials. The decrease in the maximum rate of degradation and the high

production of ash, containing partially burned particles, were the only negative aspects common to both species of treated wood.

The elementary analysis showed that the materials had significant variations in the concentrations of the considered elements. Among the treated woods, pine had the highest concentrations of copper, chromium, arsenic, and cadmium. In the panels, it was possible to observe a significant increase in the concentrations of lead and chromium, considering the presence of the melamine coating. The mixture of the biomasses produced a dilution effect on the concentration of the elements, in comparison with the analyses made individually for each material. However, considering the EN ISO 17225-1 [37] and EN 15359 [38] standards of environmental control, this mixture would still be prevented from being used for energy generation.

The identification of potentially toxic elements in the ashes of the treated pine and eucalypt, such as chromium, copper, and arsenic, demonstrate the need to develop practices associated with the use of energy that guarantee the mitigation of the environmental pollution risks, associated with the disposal of ashes. These practices must consider the urgency of reducing the waste volume deposited in landfills while seeking to enhance the energy potential presented by these materials.

In Brazil, discussions regarding the promotion of recycling as a tool to reduce the volume of waste going into landfills, and the generation of the economic value at the end of the product's useful life must take place in multiple approaches regarding the issue of reuse. In addition to the guidelines that classify and restrict the final disposal of solid waste, initiatives are needed to build a marketing vision for these materials, encouraging recycling processes. In the case of energy applications, actions aimed at the classification of these residues are essential to obtain high-quality and environmentally safe fuels.

Author Contributions: Conceptualization, F.A.d.P., L.D.V., and J.O.P.T.; methodology, F.A.d.P., J.O.P.T., and L.M.P.; writing—original draft preparation, J.O.P.T.; writing—review and editing, J.O.P.T.; supervision, F.A.d.P. and F.M.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior—BRASIL (CAPES)—Finance Code 001.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are available from the corresponding author upon request.

Acknowledgments: The authors would like to thank the Coordination of Superior Level Staff Improvement—CAPES for financing the study and the Biomass and Bioenergy Laboratory of the Federal University of São Carlos for providing the laboratory resources to the study.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. IBÁ—Indústria Brasileira de Árvores. *Relatório Anual 2020*; Indústria Brasileira de Árvores: São Paulo, Brazil, 2020; p. 66.
2. Ferrarini, S.F.; Santos, H.S.; Miranda, L.G.; Azevedo, C.M.N.; Pires, M.J.R.; Maia, S.M. Classificação de resíduos de madeira tratada com preservativos à base de arseniato de cobre cromatado e de boro/flúor. *Quím. Nova* **2012**, *35*, 1767–1771. [[CrossRef](#)]
3. Nascimento Neto, P.N.; Moreira, T.A. Política Nacional de Resíduos Sólidos: Reflexões acerca do novo marco regulatório nacional. *Rev. Bras. Ciênc. Ambient.* **2010**, *15*, 10–19.
4. ABRELPE—Associação Brasileira de Empresas de Limpeza Pública e Resíduos Especiais. *Panorama dos Resíduos Sólidos no Brasil, Relatório Técnico 2020*; ABRELPE: São Paulo, Brazil, 2020; p. 52.
5. Edo, M.; Björn, E.; Persson, P.-E.; Jansson, S. Assessment of chemical and material contamination in waste wood fuels—A case study ranging over nine years. *Waste Manag.* **2016**, *49*, 311–319. [[CrossRef](#)] [[PubMed](#)]
6. European Committee for Standardization. *CEN/TS 14780: Solid Biofuels—Methods for Sample Preparation*; European Committee for Standardization: Brussels, Belgium, 2005; p. 46.
7. United States Environmental Protection Agency—EPA. *Method 3050B: Acid Digestion of Sediments, Sludges, and Soils*; United States Environmental Protection Agency: Washington, DC, USA, 1996.

8. R Core Team. *R: A Language and Environment for Statistical Computing*; Version 3.1.3; R Foundation for Statistical Computing: Vienna, Austria, 2015.
9. European Committee for Standardization. *CEN/TS 14961: Solid Biofuels. Fuel Specifications and Classes*; European Committee for Standardization: Brussels, Belgium, 2005; p. 22.
10. Telmo, C.; Lousada, J.; Moreira, N. Proximate analysis, backwards stepwise regression between gross calorific value, ultimate and chemical analysis of wood. *Bioresour. Technol.* **2010**, *101*, 3808–3815. [\[CrossRef\]](#)
11. Tafur-Marinos, J.A.; Ginepro, M.; Pastero, L.; Zelano, V. Digestion Procedures for the elemental analysis of wood by inductively coupled plasma-optical emission spectrometry. *Anal. Lett.* **2016**, *49*, 1722–1733. [\[CrossRef\]](#)
12. Junges, J. Pyrolysis of Wood Treated with CCA in a Fixed Bed Reactor. Master's Thesis, University of Caxias do Sul, Caxias do Sul, Brazil, 2015.
13. Helsen, L.; Van Den Bulck, E. Kinetics of the low-temperature pyrolysis of chromated copper arsenate-treated wood. *J. Anal. Appl. Pyrolysis* **2000**, *53*, 51–79. [\[CrossRef\]](#)
14. Amaral, L.S. Preservation Penetration and Retention in Eucalyptus with Different Diameters. Master's Thesis, Federal University of Lavras, Lavras, Brazil, 2012.
15. Pizzi, A. The chemistry and kinetic behavior of Cu-Cr-As/B wood preservatives. IV. Fixation of CCA to wood. *J. Polym. Sci. Polym. Chem. Ed.* **1982**, *20*, 739–764. [\[CrossRef\]](#)
16. Lepage, E. *Destinação Final de Madeira Tratada com CCA. Informativo Técnico*; Montana Química—Divisão Osmose: São Paulo, Brazil, 2010; p. 5.
17. Krook, J.; Mårtensson, A.; Eklund, M. Sources of heavy metal contamination in Swedish wood waste used for combustion. *Waste Manag.* **2006**, *26*, 158–166. [\[CrossRef\]](#)
18. Krook, J.; Mårtensson, A.; Eklund, M.; Libiseller, C. Swedish recovered wood waste: Linking regulation and contamination. *Waste Manag.* **2008**, *28*, 638–648. [\[CrossRef\]](#)
19. Helsen, L.; Bulck, E.V.D.; Mullens, S. Low-temperature pyrolysis of CCA-treated wood: Thermogravimetric analysis. *J. Anal. Appl. Pyrolysis* **1999**, *52*, 65–86. [\[CrossRef\]](#)
20. Fu, Q.; Argyropoulos, D.S.; Tilotta, D.C.; Lucia, L.A. Understanding the pyrolysis of CCA-treated wood: Part I. Effect of metal ions. *J. Anal. Appl. Pyrolysis* **2008**, *81*, 60–64. [\[CrossRef\]](#)
21. Richards, G.N.; Zheng, G. Influence of metal ions and salts on products from pyrolysis of wood: Application to thermo-chemical processing of newsprint and biomass. *J. Anal. Appl. Pyrolysis* **1991**, *21*, 133–146.
22. Sebio-Puñal, T.; Naya, S.; López-Beceiro, J.; Tarrio-Saavedra, J.; Artiaga, R. Thermogravimetric analysis of wood, holocellulose, and lignin from five wood species. *J. Therm. Anal. Calorim.* **2012**, *109*, 1163–1167. [\[CrossRef\]](#)
23. Poletto, M.; Zattera, A.J.; Santana, R.M. Thermal decomposition of wood: Kinetics and degradation mechanisms. *Bioresour. Technol.* **2012**, *126*, 7–12. [\[CrossRef\]](#)
24. Hemmings, R.; Berry, E. On the Glass in Coal Fly Ashes: Recent Advances. In *Symposium Q—Fly Ash and Coal Conversion By-Products IV. Materials Research Society Proceedings*; Cambridge University Press: Cambridge, UK, 1987; Volume 113.
25. Yeboah, N.N.; Shearer, C.R.; Burns, S.E.; Kurtis, K.E. Characterization of biomass and high carbon content coal ash for productive reuse applications. *Fuel* **2014**, *116*, 438–447. [\[CrossRef\]](#)
26. Vamvuka, D.; Karakas, E. Ash properties and environmental impact of various biomass and coal fuels and their blends. *Fuel Process. Technol.* **2011**, *92*, 570–581. [\[CrossRef\]](#)
27. Pedersen, A.J.; Ottosen, L.M.; Damø, A.J. Elemental analysis of ash residue from combustion of CCA treated wood waste before and after electrodialytic extraction. *Chemosphere* **2006**, *65*, 110–116. [\[CrossRef\]](#)
28. Rowell, R. The Chemistry of Solid Wood. In *Advances in Chemistry Series*, 1st ed.; American Chemical Society: Washington, DC, USA, 1984; p. 614.
29. Lindroos, L. *Balance of arsenic and recycling. Doc. No. IRG/WP 02-50189*; International Research Group on Wood Preservation, IRG Secretariat: Stockholm, Sweden, 2002.
30. Sterling, R.O.; Helble, J.J. Reaction of arsenic vapour species with fly ash compounds: Kinetics and speciation of the reaction with calcium silicates. *Chemosphere* **2003**, *51*, 1111–1119.
31. Jerzak, W. Effect of Pine Bark Combustion Temperature on Content of Major, Minor, and Trace Elements in Ashes: Experimental Study and Thermodynamic Equilibrium Calculations. *J. Energy Eng.* **2020**, *146*, 04019031. [\[CrossRef\]](#)
32. Jerzak, W. Experimental and Thermodynamic Analyses of Trace Element Speciation during the Combustion of Ground Cedar Nut Shells. *Energy Fuels* **2017**, *31*, 1969–1979. [\[CrossRef\]](#)
33. Cacuro, T.A.; Waldman, W.R. Cinzas da queima de biomassa: Aplicações e potencialidades. *Rev. Virtual Quím.* **2015**, *7*, 2154–2165. [\[CrossRef\]](#)
34. da Luz, A.B.; Lins, F.A.F. Minerais de Titânio. In *Rochas & Minerais Industriais*; da Luz, A.B., Lins, F.A.F., Eds.; Centro de Tecnologia Mineral Ministério da Ciência e Tecnologia: Rio de Janeiro, Brazil, 2005; p. 867.
35. Hamaguchi, M.; Vakkilainen, E. Corrosão em tubos de superaquecedor de caldeiras de recuperação: Um desafio. *O Papel* **2010**, *71*, 57–71.
36. Al-Ghouti, M.A.; Khan, M.; Nasser, M.S.; Al-Saad, K.; Heng, O.E. Recent advances and applications of municipal solid wastes bottom and fly ashes: Insights into sustainable management and conservation of resources. *Environ. Technol. Innov.* **2021**, *21*, 101267. [\[CrossRef\]](#)

-
37. International Organization for Standardization. *ISO 17225-1: Solid Biofuels. Fuel Specifications and Classes—Part 01: General Requirements*; International Organization for Standardization: Brussels, Belgium, 2005; p. 56.
 38. International Organization for Standardization. *ISO 15359: Solid Recovered Fuels. Specifications and Classes*; International Organization for Standardization: Brussels, Belgium, 2005; p. 28.