

Article

Densified and Carbonized Fuel Derived from Biomass and Municipal Solid Waste as a Vector for Energy Transition from Coal in Brazil

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Abstract

The transition to a low-carbon economy requires sustainable alternatives to fossil fuels. Up-recycling municipal solid waste and forestry biomass into solid biofuels presents a promising waste-to-energy strategy. This study aimed to develop a high-calorific, highly durable hybrid solid fuel without synthetic binders, utilizing the natural interlocking of lignocellulosic and plastic matrices under mild slow pyrolysis. Blends of Eucalyptus sawdust and municipal solid waste rejects (40 wt%) were densified with and without a glycerol binder. The optimal binder-free blend underwent slow pyrolysis at 400 °C and 500 °C to evaluate energy up-grading. Results showed that the binder-free formulation achieved mechanical durability of 99.67%, whereas glycerol severely compromised the dimensional stability of the pellets. Mild pyrolysis (400 °C, 30 min) increased the higher heating value to 27.75 MJ/kg—significantly outperforming local coal (18.3 MJ/kg)—while maintaining trace chloride levels, confirming the production of an environmentally safe, premium-grade energy vector.

Keywords: biomass; waste disposal; residues; renewable energy; alternative fuel



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1. Introduction

The global transition to a low-carbon future and the urgent need for sustainable municipal solid waste (MSW) management have driven the development of waste-to-energy technologies [1–5]. Various processing methods, including biochemical (such as hydrolysis and anaerobic digestion) and thermochemical routes (such as gasification, pyrolysis, and incineration), are employed to convert biomass and waste into valuable gaseous, liquid, and solid

products [5–8]. Among these, pyrolysis stands out as one of the most promising directions for biowaste processing [5,7,8]. While gasification aims primarily at syngas production and biochemical methods require long residence times and specific feedstock conditions, slow pyrolysis is uniquely optimized for maximizing the yield and quality of carbon-rich solid products [9]. As recently highlighted in the literature, the up-recycling of biomass waste into biochar and carbonized fuels through pyrolysis provides an exceptionally versatile material [7]. This solid product has widespread applications across various technologies and industries, serving as an environmental sorbent, a catalyst support, an agricultural soil amendment, and a high-calorific alternative to traditional fossil fuels [5,8,10].

In developing countries like Brazil, integrating diverse waste streams into the energy matrix is crucial to address both waste disposal challenges and industrial energy demands [11]. The Brazilian energy scenario currently faces a strategic shift due to the Just Energy Transition Program (Law 14,299/2022) [12], which mandates a managed transition away from coal. Consequently, the industrial sector, which still heavily relies on coal [13], requires renewable solid fuel alternatives. Simultaneously, Brazil is a global reference in the forest industry, generating massive amounts of Eucalyptus and Pine residues. Blending these abundant lignocellulosic residues with the non-recyclable, plastic-rich fraction of MSW presents a significant opportunity to produce premium-grade refuse-derived fuels (RDF) and bio-coal [4,14,15].

Despite the advances in RDF production and biomass densification, significant research gaps remain. Current studies often rely on energy-intensive pre-treatments or the addition of costly synthetic binders to achieve adequate mechanical durability [4,16,17]. Furthermore, the energetic valorization of hybrid blends combining specific MSW fractions with distinct forestry residues under mild slow pyrolysis is still underexplored [4,5]. The novelty of this study lies in addressing these gaps by developing a high-calorific, highly durable hybrid solid fuel without the use of additional binders, leveraging the natural interlocking of the plastic and lignocellulosic matrices.

Based on these identified gaps, the purpose of this work was to: (i) produce densified fuels from mixtures of *Pinus* spp./*Eucalyptus* spp. and MSW; (ii) characterize their physico-chemical properties; and (iii) evaluate the potential of slow pyrolysis as an energy upgrading route for this fuel for applications in industry for energy generation and thermoelectric power plants.

2. Materials and Methods

The general structure and the experimental steps of this research were illustrated in Figure 1.

2.1. Fuel Samples Origin and Preparation

Forest biomass resources available in the southern region of Brazil—untreated *Pinus* spp. sawdust (P) and *Eucalyptus* spp. sawdust (E)—provided by timber processing companies, and samples of MSW sorting rejects (MSWr) collected at a MSW processing and recycling center were applied to make up the composition of the alternative densified fuel (DF). The gravimetric composition of the MSWr was previously determined based on the methodology of [18]: paper/cardboard (PC)—78.6 wt%; low density plastic (LP)—18.4 wt%; closed-cell expanded polystyrene foam (EPS)—3.0 wt%. The P, E and MSWr samples were crushed into particles smaller than 3.0 mm using a household blender and a knife mill (CIENLAB Super Macro, Campinas, Brazil) and sent for characterization tests. Methods for pre-treating and preparing mixtures of P, E and MSWr were tested. The base sample of DF was represented by the exclusive composition of biomass (100% P, 50% P and 50% E, and 100% E). MSWr was incorporated into the biomass mixture at mass fractions of 0 and 40%

relative to the total mass of DF. This specific 40 wt% MSWr proportion was selected based on preliminary studies conducted by our research group, which indicated that it provides an optimal balance for the densification process [19].

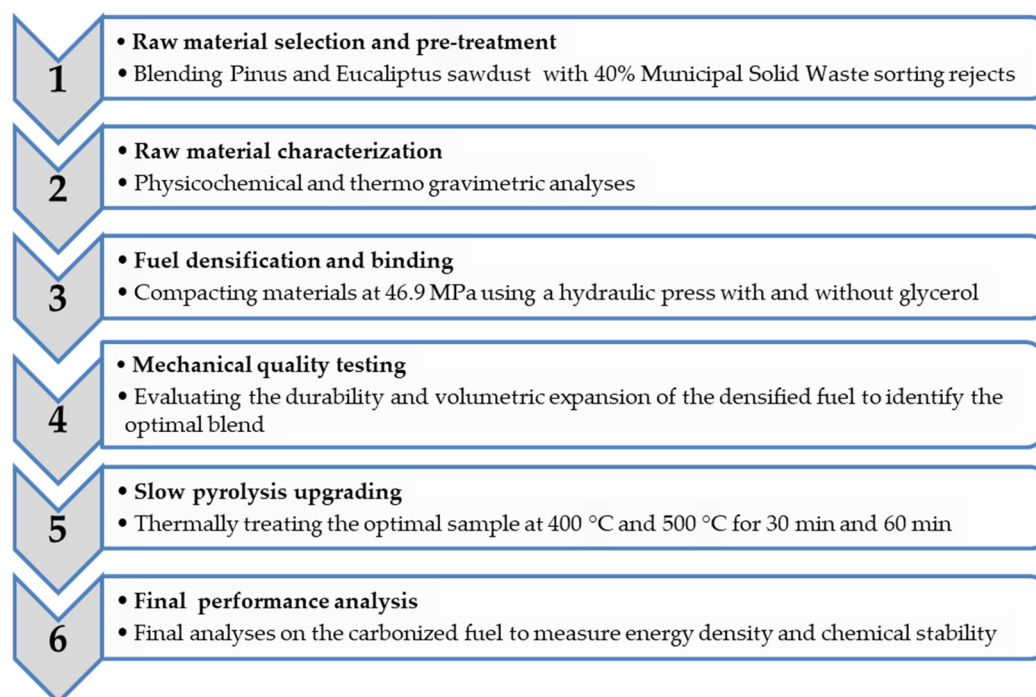


Figure 1. General structure of the research.

The DF samples were prepared under two conditions: with and without a binder (PA-grade glycerin, Neon, G). The mass of the binder-free DF samples was 2.5 g, and the mass of the samples with binder (5 wt% or 0.125 mL) was 2.625 g. The mixtures were prepared individually using a scale (Marte AD330L, São Paulo, Brazil, precision of 0.001 g), according to the proportions of biomass and the components of the MSWr as presented in Table 1. For sample identification, the nomenclature X-Y-Z was applied, where X represents the mass percentage of MSWr, Y the type of biomass used, and Z the presence of G.

Table 1. Composition of the DF samples.

DF Sample	MSWr Fractions (wt%)			Biomass (wt%)		G (wt%)
	PC	LP	EPS	P	E	
0-P-0	0	0	0	100	0	0
0-E-0	0	0	0	0	100	0
0-PE-0	0	0	0	50	50	0
40-E-0	31.44	7.36	1.2	0	60	0
40-PE-0	31.44	7.36	1.2	30	30	0
0-P-G	0	0	0	100	0	4.76
0-E-G	0	0	0	0	100	4.76
0-PE-G	0	0	0	50	50	4.76
40-E-G	29.94	7.01	1.14	0	57.15	4.76
40-PE-G	29.94	7.01	1.14	28.57	28.57	4.76

2.2. Fuels Characterization

The proximate analysis of the fuel samples was performed using a thermo-gravimetric analyzer (Leco TGA 701, St. Joseph, MI, USA), following ASTM D7582-15 [20] for analyzing hygroscopic humidity (HH), combined with ASTM D3174-12 [21] for ash and ASTM D3175-

20 [22] for volatile matter determinations. The fixed carbon content was obtained by difference based on ASTM D3172-13 [23]. The ultimate analysis was performed using an analyzer Leco 628 Series Sulfur (St. Joseph, MI, USA) following ASTM D5373-16 [24] for CHNO and ASTM D4239-18 [25] for S. The analysis of each sample was performed in triplicate. The Higher Heating Value (HHV) was determined by the experimental method using a Leco AC-500 calorimeter (St. Joseph, MI, USA) and an IKA C 200 calorimeter (Staufen im Breisgau, Germany) following ASTM D5865-19 [26]. The Lower Heating Value (LHV) was calculated according to Equation (1).

$$LHV = [HHV - 2.43(9H + U)], \quad (1)$$

where HHV is the Higher Heating Value (MJ/kg, d.b.); H is the hydrogen content in the fuel (kg/kg, d.b.); U is the moisture content in the fuel (kg of water per kg of fuel); and the LHV is obtained in MJ/kg (d.b.).

The trace element analyses were performed for Al, Ba, Ca, Co, Cd, Cr, Cu, Fe, Mn, Sb, Se, Sn, Zn, Pb, Hg, Ni, Te, Tl, and V. The samples were digested to remove organic components following the ASTM D5258-02 [27] and SMWW method 3120 B [28]. This process involves acid extraction of elements from sediments through microwave heating in a closed vessel. The quantification of trace elements was performed using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The samples were also analyzed in terms of chloride content using the soluble salts method ABNT NBR 9917:2009 [29] and SMWW method 4500-Cl B [30], with determination by ion chromatography, which ensures high precision and accuracy for trace anion quantification. The determination of the major elements contained in the ashes was carried out using an Energy Dispersive X-ray Fluorescence Spectrometer (EDXRF) (Shimadzu EDX 7000, Kyoto, Japan), following the semi-quantitative method for solid or powder samples. The calibration was performed using known oxide standards, allowing for accurate estimation of the elemental composition in the sample. Matrix correction was automatically applied, adjusting for absorption and secondary fluorescence effects. The loss on ignition was determined following ASTM D7348-07 [31]. Two ash fusibility indexes were applied to the results. One was the $B/A_{(+P)}$ proposed by [32] and described by Equation (2), and the other was $R_{S(+P)}$ described by [33] through Equation (3).

$$B/A_{(+P)} = \frac{(Fe_2O_3 + CaO + MgO + Na_2O + K_2O + P_2O_5)}{(SiO_2 + Al_2O_3 + TiO_2)} \quad (2)$$

A $B/A_{(+P)} < 0.5$ represents a low slagging tendency, $0.5 < B/A_{(+P)} < 1$ corresponds to a moderate slagging tendency and $B/A_{(+P)} > 1$ represents a high slagging tendency.

$$R_{S(+P)} = \left(B/A_{(+P)} \right) \cdot S_d, \quad (3)$$

where S_d is the percentage of S in dry fuel. If $R_{S(+P)} < 0.6$, the slagging inclination is low; $R_{S(+P)} = 0.6$ – 2.0 , medium; $R_{S(+P)} = 2.0$ – 2.6 , high; $R_{S(+P)} > 2.6$, extremely high. These ash fusibility indexes were calculated from the results of the ash chemical composition determination.

Thermo-Gravimetric Analysis (TGA) was conducted in an inert (N_2) atmosphere on samples of each component of DF (PC, LP, EPS, P, and E), and their selected mixtures (0-PE-0, 40-PE-0, and 40-E-0). Analysis was performed using an SDT650 analyzer (TA Instruments, New Castle, DE, USA) equipped with TRIOS software (version 5.1.1.46572). The temperatures ranged from ambient to 1000°C at a heating rate of $10^\circ\text{C}/\text{min}$ and a gas flow rate of $100\text{ mL}/\text{min}$. Although evaluating multiple heating rates is essential for comprehensive kinetic studies, estimating kinetic parameters (activation energy and pre-exponential factor) by isoconversional methods was beyond the scope of this study. The

TGA aimed exclusively to delineate the thermal degradation profiles, structural stability, and residual volatile matter of the samples. For these purposes, a single, low heating rate was deliberately selected based on [5] to ensure a high-resolution separation of the degradation peaks of the different matrix components, as well as to minimize thermal lag and temperature gradients, thereby ensuring complete degradation. The binder sample (G) was also analyzed to determine the onset temperature (T_{onset}) of thermal decomposition and the optimal DF compaction temperature.

2.3. Densified Fuel Preparation and Characterization

The selected blends were compacted in a bench-scale hydraulic press developed on the basis of the work by [34] using a load cell (Enerpac LH50, Milwaukee, WI, USA) with capacity of 4.5 t, reading of 500 kg and accuracy of $\pm 2\%$ in triplicate (Figure 2).



Figure 2. Scheme of the bench-scale set-up.

The compaction pressure applied was 46.9 MPa, defined on the basis of the literature [35–38]. Each alternative fuel composition was initially weighed and inserted into the press cylindrical mold made of SAE 1045 steel (internal diameter of 17.5 mm and height of 90 mm) along with a thermocouple (Akso AK892, São Leopoldo, Brazil) to determine the sample's compaction temperature, which was previously heated in a laboratory oven with forced air circulation. When the desired temperature was reached ($\pm 5^\circ\text{C}$), the heating of the mold was stopped and it was positioned in the press, with the material kept under pressure for around 5 min based on the average time applied by [6,35]. The compaction temperature tested was 100°C , the onset temperature of thermal decomposition of the binder G. The moisture content of the material to be compacted adopted in this study was 10 wt% based on the range of 10 wt% to 15 wt% indicated by [39]. The density (D) of the DF samples was determined using a stereometric method, following [40], according to Equation (4).

$$D = \frac{m}{V}, \quad (4)$$

where m represents the mass and V is the volume of the sample. The volume of the DF samples was calculated after measuring the diameter and height of each cylindrical sample 24 h after compaction using a digital caliper with an accuracy of 0.01 mm. The mass was obtained using an analytical balance (Katashi, China) with an accuracy of 0.0001 g. Additionally, the relaxation (expansion) coefficient (R) was determined, as per [41] using Equation (5) to assess the volumetric behavior of the compacts after densification.

$$R = \left(\frac{h_{24} - h_0}{h_0} \right), \quad (5)$$

where h_0 is the height of the DF immediately after compaction, h_{24} is the height measured 24 h after compaction, and R is the expansion coefficient expressed as a percentage. High R values indicate greater material elasticity, whereas lower values suggest greater rigidity and stronger bonding forces between particles. The method cited by [42] was adopted to

determine the mechanical durability (*DR*) of the compacted fuels during transportation, handling, and storage operations. The DF samples were subjected to four consecutive free drops from a height of 1850 mm onto a flat steel plate. The *DR* was calculated as the ratio between the final mass (m_f) and the initial mass (m_i) of the DF, according to Equation (6).

$$DR = \left(\frac{m_f}{m_i} \right) \times 100 \quad (6)$$

Following the test, samples that exhibited a mass loss exceeding 10% (durability less than 90%) were classified as having low durability. The stability of the DF against moisture exposure (Water Uptake, W_U) was evaluated using the water absorption test, which was performed based on the procedure of [41] and Equation (7).

$$W_U = \frac{W_t - W_i}{W_i} \times 100, \quad (7)$$

where W_u is the water content in the sample (wt%), W_t is the wet weight of sample at time t and W_i is the initial weight of sample before placing in water. Three DF units of each condition were tested, and the average value was obtained, with standard deviations representing the experimental error. This assay allows for the assessment of the material's physical and mechanical resistance when in contact with water. The weathering and moisture resistance test was conducted according to [6], in which the compacts were exposed to external environmental conditions without any type of cover or protection for 14 days to determine the increase in DF thickness (Δ_h , also named resistance to humidity) through Equation (8) and the increase in weight (R_m) through Equation (9).

$$\Delta_h = \frac{h_i - h_o}{h_o} \times 100\%, \quad (8)$$

$$R_m = \frac{m_i - m_o}{m_o} \times 100\%, \quad (9)$$

where h_o and h_i represent the thickness of DF before and after tests; m_o and m_i represent the mass of DF before and after tests, respectively. Three DF units were tested for samples prepared under each condition. To prevent rainwater from accumulating, the compacts were maintained in a container with a porous base throughout the test.

2.4. Densified Fuel Pyrolysis and Characterization

Amongst the ten samples listed in Table 1, sample 40-E-0 exhibited the best physical quality as a DF and was selected for pyrolysis tests (duplicate). For this purpose, a muffle furnace (Quimis, Diadema, Brazil) was utilized for heating at 30 °C/min from ambient temperature up to two final temperatures: 400 °C and 500 °C. The thermal treatment exposure times applied were 30 min and 60 min. The pyrolysis temperatures of 400 °C and 500 °C were chosen based on the thermal degradation behavior of similar mixed feedstocks [5]. These temperatures encompass the active pyrolysis zones, specifically 240–360 °C for hemicellulose and cellulose degradation, and 350–500 °C for plastics and remaining cellulose, which was also confirmed by the preliminary TG and DTG profiles of the individual DF components. The heating rate of 30 °C/min was applied to efficiently reach the target temperatures, while the residence times of 30 and 60 min were selected to evaluate the effect of thermal severity and ensure the complete devolatilization of the carbonaceous matrix. The runs were identified by “40-E-0_Temperature_time” and the average pyrolysis yield (*PY*) was reported. The pyrolysis products were characterized in terms of dimensions (thickness and diameter) for volume and density calculation, *HHV* and quality parameters by applying the same tests applied for the non-pyrolyzed DF samples

and subjected to TGA in both inert and oxidizing atmospheres. Finally, the experimental data were analyzed according to the availability of replication. For *HHV*, *PY*, and *D*, a 2×2 factorial Analysis of Variance (ANOVA) was performed to evaluate the isolated and interactive effects of the pyrolysis temperature (400 °C and 500 °C) and residence time (30 min and 60 min), considering a 5% significance level ($\alpha = 0.05$).

3. Results and Discussion

3.1. Fuels Composition

Table 2 presents the results for proximate and ultimate analyses, and heating values determinations.

Table 2. Results for proximate and ultimate analyses and heating values.

Parameter	MSWr Fractions			Biomass			Blends	
	PC	LP	EPS	P (0-P-0)	E (0-E-0)	0-PE-0	40-E-0	40-PE-0
Proximate analysis								
HH ¹ (wt%)	8.54	3.31	1.91	7.41	11.90	9.66	10.09	8.74
A ² (wt%, d.b. ³)	5.70	0.74	0.42	0.32	1.18	0.75	2.56	2.30
VM ⁴ (wt%, d.b.)	85.21	98.51	99.58	85.29	82.63	83.96	84.81	85.61
FC ⁵ (wt%, d.b.)	9.09	0.75	n.d. ⁶	14.39	16.19	15.29	12.63	12.09
Ultimate analysis (wt%, d.b.)								
C	53.18	85.60 ⁷	91.57 ⁷	48.38	46.47	47.43	52.00	52.57
H	8.17	13.40 ⁷	7.80 ⁷	6.83	6.76	6.80	7.70	7.73
N	0.24	0.26 ⁷	0.15 ⁷	0.23	0.24	0.24	0.24	0.24
O	32.49	0.00 ⁷	0.00 ⁷	44.23	45.27	44.75	37.38	37.06
S	0.14	0.00 ⁷	0.04 ⁷	0.01	0.02	0.02	0.06	0.05
Cl [−]	0.08	<0.01	0.02	<0.01	0.06	0.03	0.06	0.04
Heating Value (MJ/kg, d.b.)								
HHV	19.53	38.67	49.70	19.69	19.66	19.68	21.38	21.39
LHV	17.74	35.66	47.95	18.20	18.18	18.19	19.69	19.69

¹ Hygroscopic humidity; ² dry basis; ³ ashes; ⁴ volatile matter; ⁵ fixed carbon; ⁶ not determined; ⁷ data from [43].

The composition of the blends was calculated through mass balance considering a homogenous mixture. Table 2 shows that C and O are the main components of the biomasses P and E, and also of PC, a renewable MSWr fraction. According to [43], the two other MSWr fractions (LP and EPS) present mainly C and H, which explains why their *HHV* was much higher (38.67 MJ/kg and 49.70 MJ/kg, d.b., respectively) compared to the other fuels (17.74–19.69 MJ/kg, d.b.). The *HHV* of G was in this range as well. The incorporation of 40% MSWr to wood biomass (40-PE-0 and 40-E-0) yielded an *HHV* approximately 9% superior to pure wood biomass (P and E) and approximately 27% superior to local coal (18.3 MJ/kg, d.b.), besides the low chloride content. These results show the potentiality and benefits of incorporating MSWr into industrial pyrolysis processes for energy generation, such as demonstrated by [34]. The non-renewable fuels (LP and EPS) presented higher VM contents, while for the renewable ones (PC, P, E and 0-PE-0) and the blends (40-PE-0 and 40-E-0), it varied between 82.63 wt% and 85.61 wt% (d.b.). Furthermore, N, S, and Cl[−]—three undesirable elements in solid fuels—were found in exceptionally low concentrations in the optimal 40-E-0 formulation (0.24 wt%, 0.02 wt%, and 0.06 wt%, respectively). As reported by [5], these reduced levels of N and S indicate a very low probability of forming harmful gaseous pollutants, such as NO_x and SO_x, during large-scale combustion. Additionally, keeping the chloride content at trace levels is a critical environmental and operational advantage. As highlighted by [4,10], low chloride concentrations not only minimize the potential for chloride-induced equipment corrosion but also prevent the formation of highly toxic polychlorinated dioxins and furans, confirming that the proposed fuel is environmen-

tally safe for energy generation. Nevertheless, it is important to emphasize that MSWr is an intrinsically heterogeneous material, and its composition can vary significantly depending on regional and seasonal factors. Therefore, continuous evaluation and monitoring of the MSWr fraction's physicochemical characteristics are essential in scaled-up operations to prevent fluctuations in the hybrid fuel's composition and to ensure that potential pollutant emissions consistently remain within safe environmental limits. The results for ash chemical composition and fusibility indexes determinations were presented in Table 3.

Table 3. Results for ash composition determination and fusibility indexes.

Parameter	MSWr Fractions			Biomass		Blends			Man1/ Man2 ¹
	PC	LP	EPS	P (0-P-0)	E (0-E-0)	0-PE-0	40-E-0	40-PE-0	
Ash composition (wt%, d.b. ²)									
Fe ₂ O ₃	0.95	0.08	n.d. ³	2.88	1.77	2.33	1.37	1.70	3.2/2.0
CaO	58.11	56.41	n.d.	33.67	30.99	32.33	41.01	41.82	n.a. ⁴
MgO	0.62	2.91	n.d.	12.47	0.00	6.23	0.41	4.15	n.a.
Na ₂ O	0.00	0.00	n.d.	0.00	0.00	0.00	0.00	0.00	0.48/0.41
K ₂ O	0.36	0.28	n.d.	2.46	4.08	3.27	2.58	2.10	5.7/6.5
P ₂ O ₅	0.00	0.00	n.d.	6.33	4.30	5.31	2.58	3.19	n.a.
SiO ₂	1.42	2.07	n.d.	12.85	33.43	23.14	20.66	14.48	19/21
Al ₂ O ₃	0.00	0.00	n.d.	2.28	0.86	1.57	0.51	0.94	4.6/12.0
TiO ₂	0.00	7.51	n.d.	0.00	0.00	0.00	0.55	0.55	n.a.
MnO	0.00	0.00	n.d.	3.99	0.82	2.40	0.49	1.44	n.a.
SrO	0.00	0.02	n.d.	0.00	0.18	0.09	0.11	0.05	n.a.
Cr ₂ O ₃	0.00	0.00	n.d.	0.03	0.03	0.03	0.02	0.02	n.a.
Rb ₂ O	0.00	0.00	n.d.	0.03	0.02	0.03	0.01	0.02	n.a.
ZnO	0.03	0.22	n.d.	0.00	0.04	0.02	0.05	0.04	n.a.
BaO	0.00	0.00	n.d.	0.38	0.00	0.19	0.00	0.11	n.a.
SO ₃	0.32	0.46	n.d.	0.00	0.00	0.00	0.13	0.13	n.a.
CuO	0.00	0.00	n.d.	0.00	0.00	0.00	0.00	0.00	n.a.
LOI ⁵	38.01	30.04	n.d.	18.78	14.23	16.51	22.70	24.06	n.a.
Ash fusibility indexes									
<i>B/A</i> _(+P)	42.25	6.23	n.d.	3.82	1.20	2.00	2.21	3.31	n.a.
<i>R</i> _{S(+P)}	5.92	0.00	n.d.	0.04	0.02	0.03	0.12	0.18	n.a.

¹ Manufacturer 1/manufacturer 2; ² dry basis; ³ not determined; ⁴ not applicable; ⁵ loss on ignition.

Even though the low ash content found in all fuel samples, it is well known that the combination of alkali metals and sulfur in these residues can promote ash fouling and slagging in the conversion systems. The presence of P₂O₅, which is typical of biomass, is also related to these problems. The biomass fuels P and E and the blends presented concentrations of P₂O₅ in the range of 2.58–6.33 wt% (d.b.). Ref. [44] found 3.77 wt% of P₂O₅ in P. PC, the second major constituent of the DF samples, presented 42.25 for B/A_(+P) and 5.92 for R_{S(+P)}. This might be attributed to the high concentration of CaO found in the PC ashes, primarily because calcium carbonate (CaCO₃) is extensively incorporated as a mineral filler and pigment during the manufacturing process of these materials [45], as it can be seen by the high concentration of Ca in the dry sample (20,832.45 mg/kg), and ends up as the main constituent of the ash (58.11 wt%). In addition to CaCO₃, kaolinite (Al₂O₃·2SiO₂·2H₂O) and talc (3MgO·4SiO₂·H₂O) are other common fillers used in cardboard manufacturing. These compounds may occur in the presence of Al (192.27 mg/kg) and of Mg (4.97 wt%). Both undergo dehydroxylation reactions and release water vapor at 450–700 °C and at 800 °C, respectively. Such peaks were not observed for the PC sample in these temperature regions in Figure 3 given the very little concentrations of Al₂O₃ and MgO found in the PC ash sample (0.00 and 0.62 wt%, respectively). CaO was also found in higher amount in LP sample compared to P and E. The high loss on ignition determined for this and

the other ash samples may be attributed to the decomposition of ash minerals, such as carbonates or sulfates, which break down into volatile components like CO_2 or SO_2 and result in mass loss at elevated temperatures. The dominant features of wood ash are its higher CaO content and the absence of sulfur [14,33]. Additionally, it is rich in acid oxides (SiO_2 , Al_2O_3), which makes the values of the $B/A_{(+P)}$ index low, and near zero for the value for $R_{S(+P)}$, indicating that the melting temperature of these biomass ashes is high, as previously reported by [46]. Even if formed on radiation surfaces, the deposits will be loose [32]. The presence of P_2O_5 in P ash sample was not considered by [15], but they found 2.99 for the $B/A_{(+P)}$ index. Reference values for fuel composition were adopted from the recommendations of two major biomass boiler manufacturers operating in Brazil (Manufacturer 1 and Manufacturer 2). The parameters and respective reference limits considered in these recommendations were the concentrations of Na_2O , K_2O , SiO_2 , Fe_2O_3 , and Al_2O_3 in the fuels' ash (Table 4), as well as the chloride content in the dry fuel samples (lower than or equal to 0.12 wt% and 0.17 wt%, respectively). Upon analyzing the results for the studied blends (0-PE-0, 40-E-0, and 40-PE-0), it was verified that all of them meet these compositional parameters. Only biomass E exhibited a SiO_2 concentration greater than the reference value (33.43 wt%), which is known to be abrasive to the feeding system and is consequently prone to negatively impact the service life of boiler components [47]. To complement the physicochemical characterization of the fuels, the trace element results (Table 4) were analyzed based on the Resolution of the State Environmental Council of Santa Catarina, Brazil, CONSEMA 190/2022—Section II, Subsection XVIII—Articles 52 and 53 [48].

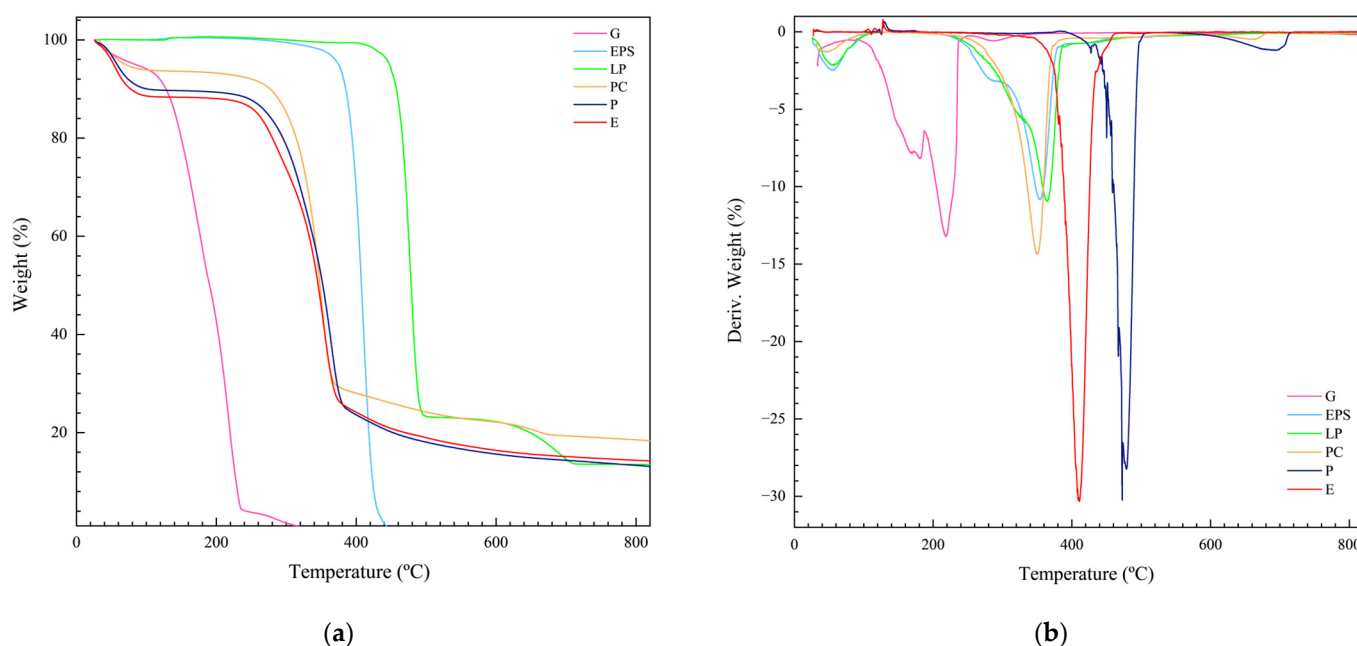


Figure 3. TG (a) and DTG (b) profiles of the DF components (PC, LP, EPS, P, and E) and the binder (G) in N_2 and at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$.

The measured concentrations of As, Cd, Co, Hg, Pb, Ni, Se, Te, and Tl in all samples were within the maximum limit established and provided in Table 4. Therefore, there would be no environmental restrictions related to the concentration of each of these elements for the application of the fuels evaluated in this study. Ref. [44] found Cr, Cu, Pb, Ni, and Zn in concentrations 200, 1000, 4, 4, and 5.5 times higher than the concentrations found in this study, respectively.

Table 4. Results for trace elements analysis.

Parameter	MSWr Fractions			Biomass		Blends			CONSEMA 190/2022 [48]
	PC	LP	EPS	P (0-P-0)	E (0-E-0)	0-PE-0	40-E-0	40-PE-0	
Trace elements (mg/kg, d.b. ¹)									
Al	192.27	452.62	<0.10	10.27	58.81	34.54	129.05	114.49	n.a. ²
As	<0.01	<0.01	<0.01	<0.01	1.08	0.54	0.65	0.32	1.0
Ba	<0.10	34.38	<0.10	14.64	<250	7.32	2.53	6.92	n.a.
Ca	20,832.45	686.66	1027.40	498.05	716.18	607.12	7042.30	6976.86	n.a.
Cd	<0.001	<0.001	<0.001	<0.001	<0.5	n.d.	0.00	0.00	0.5
Co	<0.01	<0.01	<0.01	<0.01	<1	n.d.	0.00	0.00	1.0
Cr	<0.01	<0.01	<0.01	<0.01	<50	n.d.	0.00	0.00	n.a.
Cu	2.01	18.22	<0.01	<0.01	<50	n.d.	1.97	1.97	n.a.
Fe	50.39	49.33	76.44	10.27	<50	5.14	20.39	23.47	n.a.
Hg	<0.05	<0.05	n.d	<0.05	<0.05	n.d.	0.00	0.00	0.5
Mg	4.97	1.64	<0.10	79.94	<50	39.97	1.68	25.67	n.a.
Ni	1.18	<1	1.06	<1	<1	n.d.	0.38	0.38	1.0
Pb	<1	1.61	<1	<1	<1	n.d	0.12	0.12	1.0
Sb	<0.005	1.94	0.01	<0.005	<5	n.d. ³	0.14	0.14	n.a.
Se	2.85	<0.10	<0.01	<0.05	<1	n.d.	0.90	0.90	1.0
Sn	<0.10	<0.10	<0.10	<0.10	<50	n.d.	0.00	0.00	n.a.
Te	<1	<1	<1	<1	<1	n.d.	0.00	0.00	1.0
Tl	<0.5	<0.5	<0.5	<0.5	<0.5	n.d.	0.00	0.00	0.5
Va	<50	<50	<50	<50	<50	n.d.	0.00	0.00	n.a.
Zn	72.26	32.64	105.29	4.37	<50	2.19	26.38	27.70	n.a.

¹ Dry basis; ² not applicable; ³ not determined.

3.2. Thermo-Gravimetric Profiles of the Fuels

The total mass loss (TG) and mass loss rate (DTG) curves obtained for the binder G, and the fuels P, E, PC, PL and EPS were presented in Figure 3, and Figure 4 presents the ones for DF samples without G.

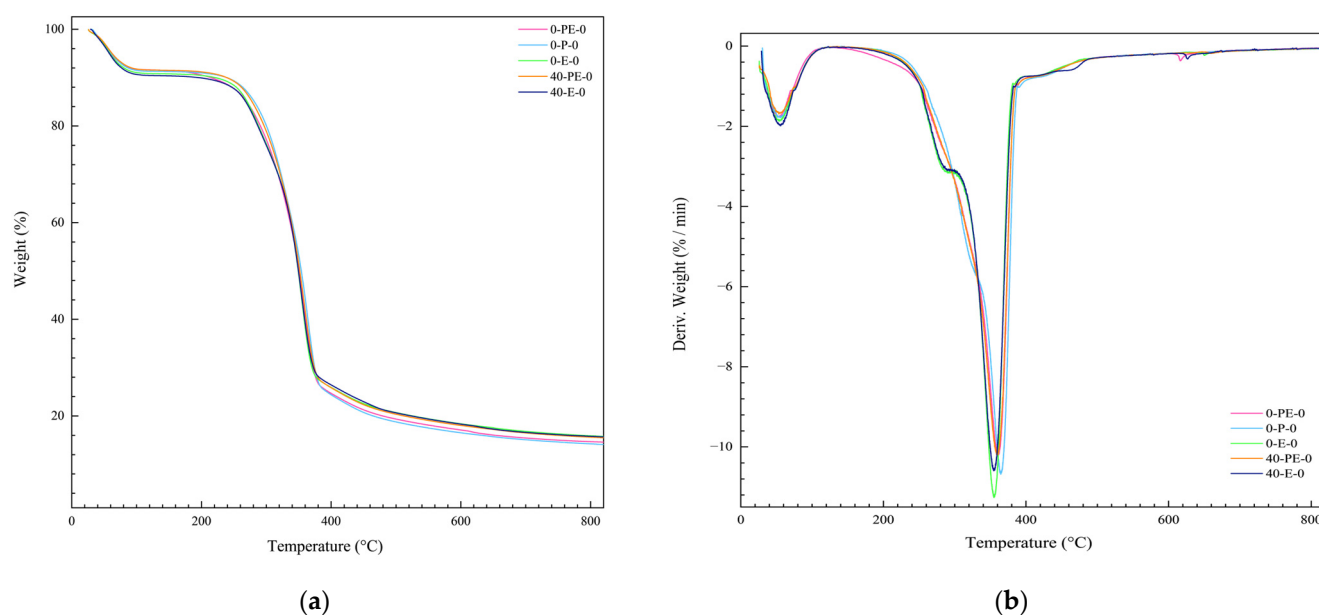


Figure 4. TG (a) and DTG (b) profiles of the DF samples without binder G (0-PE-0, 0-P-0, 0-E-0, 40-PE-0 and 40-E-0) in N₂ and at a heating rate of 10 °C/min.

It can be observed in Figure 3 that the G curve profile showed a small moisture volatilization range up to approximately 100 °C, followed by the onset of the main thermal

degradation between 140 °C and 240 °C, indicating a process that occurred in more than one stage. Regarding the DTG curve profile, it exhibited multiple small and broad peaks, suggesting more than one mass-loss event and a relatively low degradation rate when compared to the literature. Studies with pure G showed a decomposition process that occurs approximately between 150 °C and 325 °C, with degradation peaks associated with parallel reactions and the formation of intermediate by-products. These data suggest that G exhibits variable thermal behavior depending on its degree of purity [49,50]. Concerning the biomasses—P, E, and PC—, they are lignocellulosic materials with complex decomposition profiles, presenting similar and characteristic thermal-degradation curves [51,52]. As pointed out by [53] in their study on the thermal decomposition of biomasses, the degradation of lignocellulosic materials occurs in three well-defined stages. The first stage begins with a curve that includes a small and steady intermediate region associated with moisture removal, between approximately 100 °C and 300 °C. As for the second stage, between 300 °C and 400 °C, the decomposition of hemicellulose and cellulose takes place. At temperatures above 400 °C, the third stage occurs, in which the curve indicates continuous and gradual lignin degradation, concluding with char formation, characteristic behavior of lignocellulosic matrices [53]. As for the EPS and PL, the TG analyses showed that the curves of these materials exhibited the expected and characteristic behavior of polymeric materials, presenting a single main degradation step. The initial mass-loss temperature for the PL was approximately 450 °C, and the dominant degradation stage extended up to 500 °C. When analyzing the degradation curve of EPS, it is observed that the initial mass-loss temperature was approximately 325 °C, and the process was completed around 450 °C, occurring in a single stage. In the DTG graph of Figure 3, the EPS presented a single, intense and narrow peak around 400 °C, indicating a synchronized breakdown of the polymer chains. The plastic showed a less symmetrical peak in a broader range, around 470 °C, indicating a higher thermal stability of the material. A slight asymmetry can also be observed along the PL peak, caused by its more complex degradation process, which leads to the formation of the residue observed in the TG analysis.

In Figure 4, the TG profiles of the DF samples without the binder were quite similar, following the same behavioral pattern: moisture removal, main degradation, and degradation of higher-molecular weight material accompanied by char formation.

In the DTG analysis, the profiles of the mixtures remained similar; however, 0-E-0 and 40-E-0 exhibited a ‘shoulder’ in the degradation peak, indicating that the process occurred in more than one stage. Figure 5 presents the TG and DTG profiles for DF samples containing G: 0-PE-G, 0-P-G, 0-E-G, 40-PE-G, 40-E-G.

It exhibited curves that were similar to one another, but with some noticeable variations. Amongst these mixtures, 0-P-G and 40-E-G showed the greatest differences in mass loss compared to the others, with 0-P-G presenting the lowest mass loss and 40-E-G showing the highest mass loss around 200 °C and 300 °C. The curve profiles of the G-containing mixtures do not display a pronounced main degradation step, instead, a slight drop was observed after the initial moisture removal stage. The 40-E-G sample also differed from the expected behavior in the final stage of the process, forming a small intermediate by-product (between 380 °C and 480 °C) before completing combustion. Overall, in the DTG curves shown in Figure 5, the same behavior was observed. The materials exhibited similar profiles, with 40-E-G showing an additional peak, which may indicate the presence of more than one type of organic matter. Table 5 presents the degradation peaks of the groups of pure materials, DF samples with and without G.

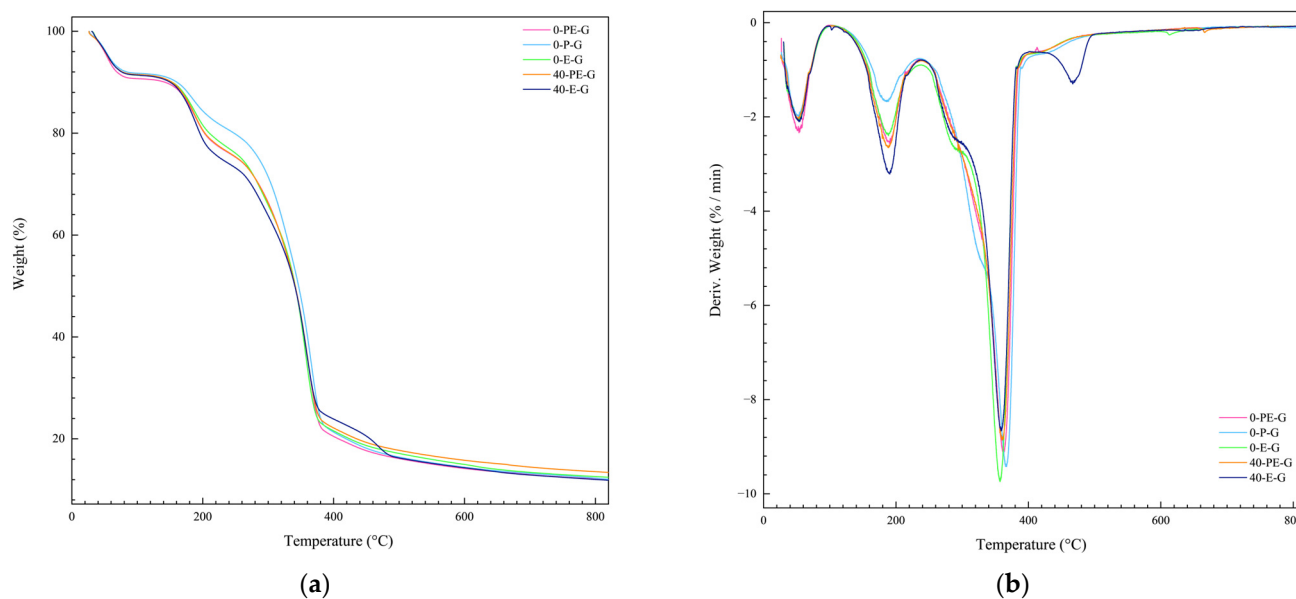


Figure 5. TG (a) and DTG (b) profiles of the DF samples with binder G (0-PE-G, 0-P-G, 0-E-G, 40-PE-G and 40-E-G) in N₂ and at a heating rate of 10 °C/min.

Table 5. Degradation peaks of the pure material and DF samples.

Sample		T_{max} (°C)			
		Peak 1	Peak 2	Peak 3	Peak 4
Pure materials	G	160	180	220	-
	E	60	350	-	-
	P	60	360	-	-
	PC	45	350	-	-
	PL	475	-	-	-
	EPS	410	-	-	-
DF without G	0-P-0	40	365	-	-
	0-E-0	40	355	-	-
	0-PE-0	40	360	-	-
	40-PE-0	40	360	-	-
	40-E-0	40	355	-	-
DF with G	0-P-0	50	180	365	-
	0-E-0	50	185	355	-
	0-PE-0	50	185	360	-
	40-PE-0	50	185	360	-
	40-E-0	50	190	355	470

It can be inferred from this that the presence of G did not alter the main degradation stage but only delayed the onset of the thermal event [54]. The DF samples—whether with or without G—showed very similar peak ranges. It was observed that the T_{max} (°C) values of the main peaks (peak 2 for the DF without G and peak 3 for those with G) followed the same trend and fell within the same temperature range, around 360 °C. However, the onset (T_{onset}) and final (T_{final}) temperatures of the thermal events differ between the two DF groups, as shown in Figure 5. Ref. [54] explained the variations in T_{onset} and T_{final} between the DF groups by stating that the absence of G makes the matrix more susceptible to the onset of degradation and less thermally stable, which may indicate lower molecular cohesion in the mixture without plasticizer.

3.3. Densified Fuels Quality

Table 6 shows the quality aspects of the non-pyrolyzed and pyrolyzed DF samples.

Table 6. Pyrolysis yield and quality test results of non-pyrolyzed and pyrolyzed DF.

DF Sample	PY ¹ (wt%)	D ² (g/cm ³)	DR ³ (%)	R _m ⁴ (wt%)	Δ _h ⁵ (mm)	R ⁶ (%)
40-E-0_400_30	43.375 ± 4.59	0.506 ± 0.054	98.997	1.075	−1.17	n.a. ⁷
40-E-0_400_60	32.66 ± 0.18	0.400 ± 0.027	94.568	3.03	−2.439	n.a.
40-E-0_500_30	31.21 ± 0.23	0.437 ± 0.003	97.594	2.298	3.06	n.a.
40-E-0_500_60	21.51 ± 1.84	0.737 ± 0.039	93.227	−26.667	−33.389	n.a.
0-PE-0	n.a.	0.519 ± 0.030	n.d. ⁸	n.d.	n.d.	4.022
0-E-0	n.a.	0.847 ± 0.027	n.d.	n.d.	n.d.	1.507
0-P-0	n.a.	0.526 ± 0.030	n.d.	n.d.	n.d.	2.420
40-PE-0	n.a.	0.538 ± 0.034	n.d.	n.d.	n.d.	4.022
40-E-0	n.a.	0.726 ± 0.026	99.669	n.d.	n.d.	3.125
0-PE-G	n.a.	0.927 ± 0.030	n.d.	n.d.	n.d.	12.400
0-E-G	n.a.	0.531 ± 0.088	n.d.	n.d.	n.d.	10.680
0-P-G	n.a.	0.535 ± 0.010	n.d.	n.d.	n.d.	10.578
40-PE-G	n.a.	0.974 ± 0.030	n.d.	n.d.	n.d.	14.400
40-E-G	n.a.	0.974 ± 0.036	92.467	n.d.	n.d.	12.000

¹ Pyrolysis Yield; ² density; ³ durability; ⁴ increase in weight; ⁵ increase in thickness; ⁶ expansion coefficient; ⁷ not applicable; ⁸ not determined.

The quality test results demonstrate the decisive influence of composition and thermal processing on the properties of the DF. A clear trend of increasing density was observed in the formulations containing G, with the highest values recorded for the 40-PE-G and 40-E-G. The presence of 40% MSWr also lead to density increase, although less pronouncedly, possibly due to the greater heterogeneity and cohesion of the particles, which promotes additional contact points during compaction. The incorporation of G favored the initial densification of some formulations, but this effect did not translate into greater stability after the compaction load was removed. The lower dimensional stability of the glycerol-containing formulations can be mainly attributed to the combined effect of interparticle lubrication and the matrix's increased affinity for moisture. During compaction, G reduces friction between particles and the mold wall, facilitating flow and load rearrangement. Although this behavior may improve initial void filling, it also reduces frictional resistance and limits the effective solid–solid contact responsible for compact consolidation. Ref. [55] observed a similar response in the pelletization of agro-industrial biomasses, where G acted as a lubricant that weakened solid–solid interactions, thereby increasing porosity and water susceptibility. This mechanism aligns with the higher expansion values (relaxation factor, *R*) observed in the present study, which varied up to 14.400% for the G-containing samples. The rearrangement promoted by G during pressure application was not accompanied by the formation of sufficiently stable contacts to preserve the compact's geometry after unloading. Furthermore, G's highly polar and hygroscopic nature, containing three hydroxyl groups, likely intensified this instability by retaining moisture, which promotes the swelling of the lignocellulosic fraction and the widening of discontinuities formed during the post-compaction relaxation [56,57]. The durability was evaluated only for the formulations considered the most promising based on initial density and dimensional stability, namely 40-E-0 and 40-E-G. Despite the experimental limitation, the results were sufficient to identify clear trends related to the presence of MSWr and G. Samples 40-E-0 and 40-E-G exhibited durability of 99.670% and 91.085%, respectively. Both contained 40% MSWr, suggesting that this component favored structural interlocking and mechanical resistance. The reduction in durability in the presence of G is consistent with its plasticizing effect, which increases expansion and reduces internal rigidity, as also discussed

by [58]. The water uptake test was not conclusive due to the rapid disintegration of all samples when immersed in water. This behavior aligns with [38,59], who also observed low resistance of DF in water immersion tests. Furthermore, it was not possible to conclude the weathering resistance test because intense and continuous rainfall occurred during the experimental period, leading to the complete disaggregation of the DF samples (G-free and G-containing formulations) after only a few days of exposure. The pyrolysis samples (40-E-0_400_30, 40-E-0_400_60, 40-E-0_500_30, and 40-E-0_500_60) exhibited densities lower than or similar to 40-E-0 sample. The largest density reduction occurred to 400 °C and 60 min, reinforcing the importance of longer residence time in devolatilization and the formation of more porous structures, a phenomenon widely documented in biochar studies [60]. This is widely documented and attributed to the thermal degradation of lignocellulosic components (hemicelluloses, cellulose, and lignin), which releases volatiles and results in a carbonaceous matrix with lower specific mass and higher porosity [61]. Studies involving heterogeneous wastes such as RDF also report the formation of chars with a larger surface area and lower density in the 400–500 °C range [10,62]. Additionally, ash-rich components present in MSWr can catalyze carbonization, further contributing to less dense structures [63]. The pyrolysis samples demonstrated high durability, ranging between 93.227% and 98.997%. These results confirm that pyrolysis at 400–500 °C favored the formation of a more stable carbonaceous matrix, reducing the material's susceptibility to mechanical degradation compared to the 40-E-G sample. A slight reduction in durability was observed with increasing residence time at 400 °C, decreasing from 98.997% (30 min) to 94.568 (60 min). This reduction is possibly related to the partial destruction of the carbonaceous matrix under prolonged exposure to the applied temperature. Despite that, the values remained high, indicating good stability for potential product applications. The durability assessment demonstrated that 40-E-0 exhibited a notable performance (99.669%) considering the absence of a binder and thermal treatment. This superior performance indicates that the combination of Eucalyptus biomass and MSWr was able to develop a cohesive structure on its own. Unlike the G formulations, the absence of a liquid lubricating phase preserved direct contact and sliding resistance between particles during pressing, favoring the interlocking of the fibrous fraction and geometric retention upon load removal. The hybrid composition of 40-E-0 also played a crucial role in this mechanism. The combined presence of eucalyptus fibers, paper, and cardboard enhanced mechanical interlocking and the formation of a continuous fibrous network. Additionally, the flexible plastic and expanded polystyrene fractions likely contributed to void filling and increased contact areas within the heated matrix during compaction. This structural rearrangement, involving elastic and plastic deformations, creates short-distance bonding forces (molecular, electrostatic, and magnetic) [55,56]. However, as the interfaces were not examined using microstructural techniques, the specific internal contribution of the MSWr plastics should be considered a highly plausible hypothesis compatible with the excellent physical results obtained. The authors also reported that the presence of moisture increased interfacial forces and capillary pressure, generating greater cohesion between particles, in addition to the formation of solid bridges resulting from the softening and diffusion of molecules between particles and the solidification of components that act as natural binders, such as lignin, proteins, and carbohydrates. Similar results were discussed by [42]. These mechanisms explain the high mechanical resistance observed in the 40-E-0 sample, indicating that, in certain formulations, pyrolysis may be unnecessary, thereby reducing the energy consumption of the production process. On the other hand, the sample 40-E-G showed a lower durability of 92.467%. Although this value is still considered acceptable for solid fuels, the reduction compared to the binder-free formulation (99.669%) confirms the detrimental effect of glycerol in this specific blend. While some studies in the literature,

such as [16,42], report that natural additives like glycerol can improve mechanical strength and water resistance by increasing interparticle cohesion, our results demonstrate the opposite for the MSWr-biomass blend. As previously discussed, the excessive lubrication provided by the additive hindered the necessary solid–solid interlocking, resulting in a less durable compact. The pyrolysis samples exhibited distinct behaviors against moisture when exposed to environmental conditions, demonstrating a strong dependence on the temperature and residence time of the applied thermal treatment. Under mild pyrolysis conditions (400 °C/30 min), sample 40-E-0_400_30 showed minimal changes in thickness (Δ_t of -1.17 mm) and a discreet mass gain (R_m of $+1.07$ wt%), indicating good physico-structural stability and a hygroscopic behavior compatible with the residual porosity of the carbonized matrix. For (40-E-0_400_60, a more expressive mass gain was observed (R_m of $+3.03$ wt%), possibly associated with greater porosity development due to prolonged thermal degradation. This moderate water absorption is consistent with the hydrophilic nature of lignocellulosic constituents, whose hydroxyl groups interact with water molecules [64].

For the properties of water uptake, mechanical durability, and weathering stability (mass and thickness variations), the absence of experimental replicates precluded the application of hypothesis tests. Thus, these results were evaluated through an exploratory analysis. The conditions of 400 °C/30 min, 400 °C/60 min, and 500 °C/30 min presented similar behavior, with water uptake between 20.08% and 22.75%, elevated durability (94.5% to 98.9%), and minor variations in mass and thickness after the weathering test. In contrast, the 500 °C/60 min condition exhibited a clearly distinct behavior, characterized by a massive water uptake (53.15%), lower durability (93.2%), and expressive reductions in mass (-26.67%) and thickness (-33.39%) after weathering. The convergence of these results indicates a consistent trend: the most severe pyrolysis condition simultaneously concentrated the highest water absorption, lowest durability, and highest physical degradation. This suggests that the temperature increase associated with a longer residence time favored the development of a more porous and mechanically less stable structure. Ultimately, the 400 °C/30 min condition presented the best balance between dimensional stability, low water uptake, and high mechanical strength, standing out as the most promising configuration. The HHV of 40-E-0_400_30 was 27.75 ± 0.57 MJ/kg, very similar to the one obtained for 40-E-0_400_60 (26.57 ± 0.75), but 29.79% higher when compared to 40-E-0, showing that the pyrolysis improved the fuel quality. For the pyrolysis at 500 °C, the HHV of the samples was also similar, 23.50 ± 2.21 MJ/kg (30 min) and 24.59 ± 0.75 MJ/kg (60 min). The increase in temperature from 400 °C to 500 °C resulted in a drop of 11.46% in the HHV of the pyrolysis product. Although the energy content in this study was determined experimentally, evaluating the fuel quality of solid alternative fuels can also be efficiently achieved through predictive modeling. As demonstrated in the literature, predicting the HHV of raw materials and biochars—typically based on their proximate or ultimate composition—is highly feasible and serves as a reliable main indicator of fuel quality [65]. This predictive approach is particularly advantageous for large-scale operations and routine quality control, as it provides a rapid and cost-effective energy estimation without the need for continuous calorimetric testing. The 2×2 factorial ANOVA ($\alpha = 0.05$) demonstrated that the effects of temperature and residence time depended on the evaluated property. For the HHV, only the temperature presented a significant effect ($p = 0.0249$), indicating that raising the pyrolysis temperature altered the energy content of the char, while the residence time had no statistically significant influence ($p = 0.9589$). For the PY, both temperature and time exhibited significant effects ($p < 0.05$), evidencing that the increase in pyrolysis severity promoted a reduction in the solid mass recovered. Regarding D , only the residence time showed a significant effect ($p = 0.0278$), suggesting that longer carbonization periods favored the reduction in the material's apparent specific mass. In

all cases, no significant interaction between temperature and time was observed ($p > 0.05$), indicating that the effects of these factors occurred independently. When compared to the recent literature on waste-derived fuels, the performance of the proposed 40-E-0 formulation stands out. While recent studies on the co-pelletization of biomass and plastic wastes report substantial improvements in energy density—such as the hybrid biofuels developed by [4] that reached 22.6 MJ/kg, the densified RDFs evaluated by [5] with heating values around 24 MJ/kg, or the briquettes by [6] that achieved heating values comparable to coal—the pyrolyzed 40-E-0 fuel achieved an exceptional *HHV* of 27.75 MJ/kg. This value significantly surpasses the local coal (18.3 MJ/kg) and is highly competitive with the current state-of-the-art. Furthermore, regarding physical stability, the unpyrolyzed 40-E-0 blend achieved a mechanical durability of 99.67% without the need for additional binders, while its mildly pyrolyzed counterpart (400 °C/30 min) maintained an excellent durability of 99.0%. This performance exceeds the durability typically observed for pure biomass pellets and matches the high stability reported by recent studies that utilized specific binders, thermoplastics, or required multiple densification cycles at elevated temperatures to stabilize the matrix [4–6,16]. Figure 6 shows the thermal degradation curves in an inert atmosphere (N_2) and Figure 7 under synthetic air for the chars produced from 40-E-0 under the pyrolysis conditions applied.

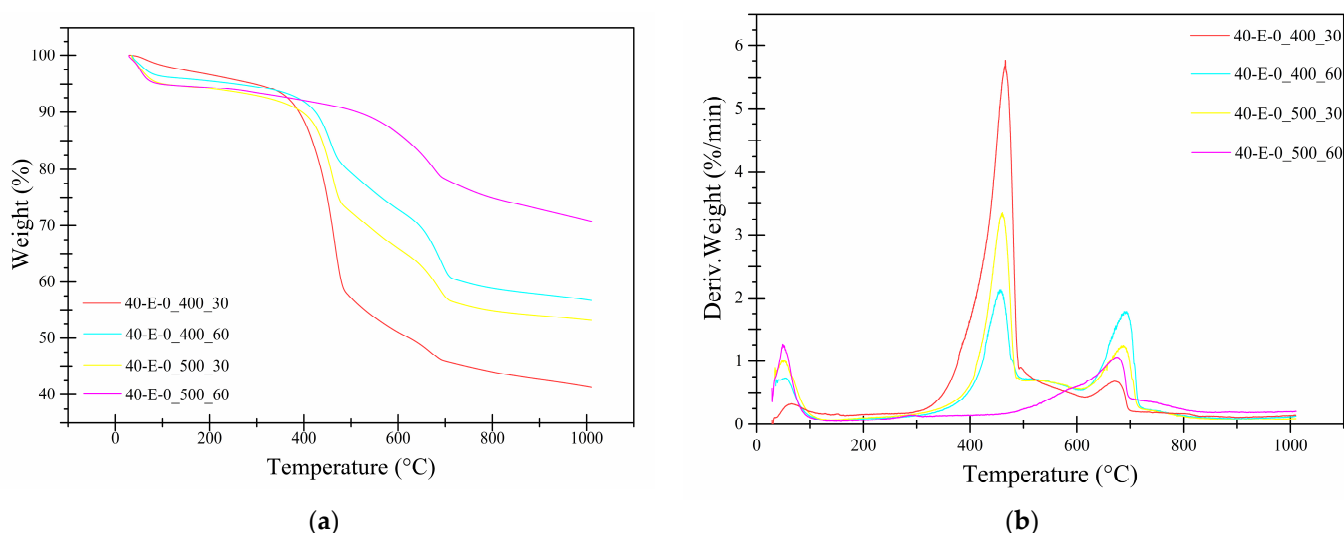


Figure 6. TG (a) and DTG (b) profiles of the 40-E-0 chars under N_2 and at a heating rate of 10 °C/min.

It can be observed in Figure 6 that all chars began their first degradation event with higher thermal degradation peaks in the range of 400–600 °C. However, the sample 40-E-0_400_30 exhibited the greatest mass loss, possibly due to residual organic matter that continued to form char as the temperature increased. Figure 7 reveals three main degradation stages.

The initial stage occurs at temperatures up to approximately 250 °C, characterized by moisture loss and the release of light volatile compounds, before the main degradation stage begins. Around 280–300 °C, the major mass-loss stage begins and continues up to approximately 500 °C, indicating the degradation of hemicellulose and cellulose [66]. At temperatures above 500 °C, the final stage is observed, corresponding to the oxidation of the remaining carbonaceous material, a behavior consistent with that expected in oxidizing atmospheres during thermal analyses, considering that pyrolysis involves both decomposition and partial oxidation of the solid fuels [67]. Furthermore, a deeper analysis of the TG curves in inert atmosphere (Figure 6) highlights the enhanced thermal stability of the chars produced at 500 °C. These samples exhibited a significantly flatter TG profile with

minimal mass loss at higher temperatures, confirming that the severe pyrolysis successfully devolatilized the labile organic matter, leaving a highly recalcitrant carbon matrix. Under oxidizing conditions (Figure 7), the combustion behavior is also strongly influenced by pyrolysis severity. The chars produced at 500 °C exhibit a delayed onset of the main degradation stage compared to those produced at 400 °C. This lower initial reactivity is attributed to the prior removal of easily ignitable volatiles, meaning the remaining fixed carbon requires higher temperatures to ignite. However, once ignition occurs, the oxidation is intense and concentrated, as evidenced by the sharper DTG peaks, particularly for those subjected to longer residence times, indicating greater thermal severity. Finally, the terminal plateau of the TG curves in synthetic air reveals the proportional concentration of ashes, which is naturally higher in the 500 °C samples due to the extensive volatilization of the organic mass. When examining the samples treated at 400 °C, it becomes evident that extending the residence time to 60 min did not result in a significant reduction in the residual mass, suggesting that the temperature was not sufficient to promote further degradation of the more resistant lignocellulosic structures. These findings corroborate specific trends reported in the recent literature. For instance, Refs. [60,68] observed that increasing the pyrolysis temperature significantly reduces the char yield and promotes deep devolatilization, whereas extending the residence time at a fixed temperature produces only marginal changes in mass loss and physicochemical properties. Similarly, regarding mixed waste, Ref. [5] demonstrated that the thermal severity driven by the final temperature is the primary factor dictating the degradation of densified refuse-derived fuels. Together, these studies confirm that residence time plays a secondary role when compared with the dominant thermal effect of temperature.

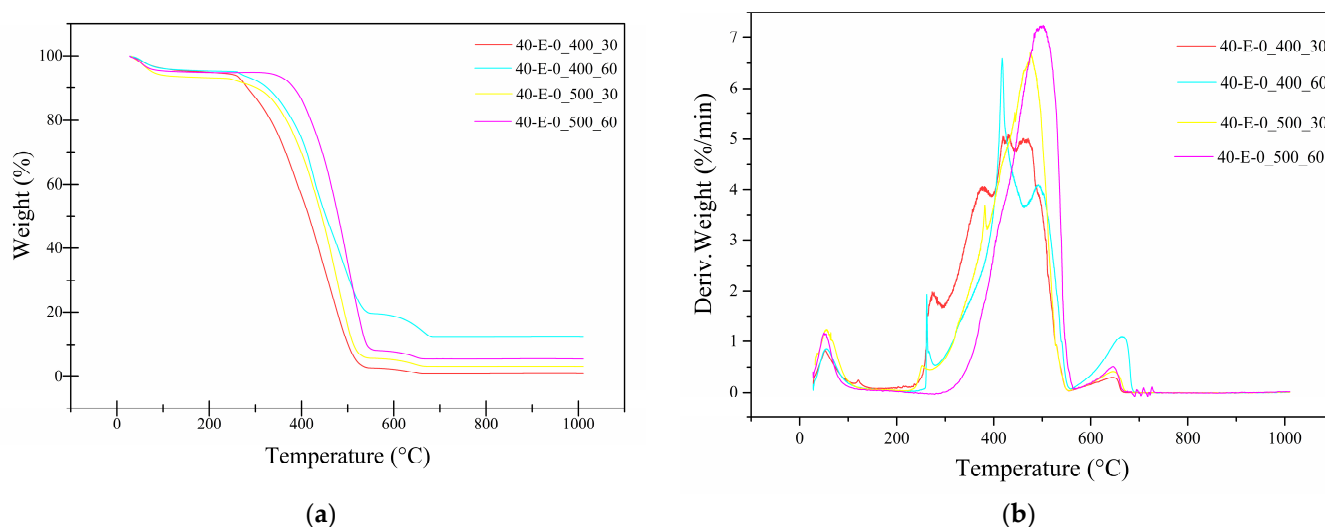


Figure 7. TG (a) and DTG (b) profiles of the 40-E-0 chars under synthetic air and at a heating rate of 10 °C/min.

4. Conclusions

This study evaluated the physicochemical properties, densification, and pyrolysis upgrading of hybrid solid fuels derived from forestry biomass (Pinus and Eucalyptus) and municipal solid waste rejects (MSWr). The results highlight the potential of using these waste streams as a sustainable vector for energy transition from coal. The key findings of this research are summarized as follows:

- **Optimal Formulation without Binders:** The incorporation of 40 wt% MSWr into Eucalyptus sawdust without the addition of glycerol (sample 40-E-0) yielded the best physical quality. It achieved an exceptional mechanical durability of 99.67%

and low volumetric expansion (3.12%), proving that the natural interlocking of the matrices is superior to the use of a glycerol binder, which severely compromised dimensional stability.

- **Energy Upgrading via Mild Pyrolysis:** Slow pyrolysis significantly improved fuel quality. The optimal thermal treatment at 400 °C for 30 min increased the Higher Heating Value (HHV) of the 40-E-0 blend to 27.75 MJ/kg—an increase of nearly 30% compared to the raw blend, and significantly surpassing the energy content of the local coal (18.3 MJ/kg).
- **High Physical Stability after Carbonization:** Even after mild pyrolysis, the carbonized fuel maintained an excellent durability of 99.0% and demonstrated good physico-structural stability with minimal water absorption, making it suitable for transport and storage.
- **Environmental Compliance:** The optimal formulation exhibited trace levels of chloride (0.06 wt%), nitrogen, and sulfur, meeting strict quality standards and indicating a significantly reduced risk of generating toxic pollutants (such as dioxins/furans) or causing equipment corrosion.

Despite these highly promising results, this study presents certain limitations. The fuel production and quality assessments were conducted at a bench scale, which restricted the ability to perform extensive experimental replicates for some physical tests. Therefore, future work should focus on pilot-scale validation to assess the impacts of the intrinsic seasonal heterogeneity of MSWr on fuel quality. Additionally, investigating long-term combustion performance in actual boilers—specifically regarding real-time gaseous emissions and slagging/fouling behavior—along with comprehensive economic feasibility analyses, will be essential steps toward the industrial-scale waste-to-energy implementation of this hybrid biofuel.

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Abbreviations

The following abbreviations are used in this manuscript:

A	Ash
$B/A_{(+P)}$	Ash fusibility correlation 1
d.b.	Dry basis
D	Density
DF	Densified fuel
DR	Mechanical durability
DTG	Mass loss rate
E	<i>Eucalyptus</i> spp. sawdust
EDXRF	Energy dispersive X-ray fluorescence spectrometer
EPS	Closed-cell expanded polystyrene foam
FC	Fixed carbon
G	Glycerol
HH	Hygroscopic humidity
HHV	Higher heating value
ICP-OES	Inductively coupled plasma optical emission spectrometry
LHV	Lower heating value
LP	Low density plastic
MSW	Municipal solid waste
MSWr	Municipal solid waste sorting rejects
n.a.	Not applicable
n.d.	Not determined
P	<i>Pinus</i> spp. sawdust
PC	Paper/cardboard
PY	Pyrolysis yield
R	Relaxation (expansion) coefficient
RDF	Refuse-derived fuel
$R_{S(+P)}$	Ash fusibility correlation 2
R_m	Increase in weight
TG	Total mass loss
TGA	Thermo-gravimetric analysis
VM	Volatile matter
W_U	Water uptake
Δ_h	Resistance to humidity

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