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TGA1: IRON- AND STEELMAKING PROCESSES

BIOmass for COkemaking DEcarbonization

Project Deliverable Report

D2.2

Biomass and biochar selection and characterization

Public

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1 Summary

The growing concern over climate change and the need to reduce greenhouse gas emissions have driven both industry and research towards sustainable solutions for energy and materials production. This report describes research activities aimed at identifying, selecting, and characterizing biomass within the European RFCS BioCoDe project. Project partners include RINA-CSM, Thyssenkrupp Steel Europe (Germany), and Paul Wurth Italia.

The project aims to replace a portion of the fossil carbon currently used in steel coke production with biomass (carbon-neutral), sourced and available in Europe, particularly in Mediterranean regions. In the context of decarbonizing integrated steelmaking processes, BioCoDe aims to demonstrate the industrial feasibility of this substitution to reduce CO_2 emissions from the coking process, while ensuring the final coke maintains the best metallurgical characteristics. To this end, the research activities described here focus on the characterization and physicochemical analysis of ten different types of biomasses available in the Mediterranean area of Europe, which were identified before the activities outlined in this report.

2 Introduction

The underlying idea of the European RFCS BioCoDe project is to decarbonize the production process of steel coke by partially replacing fossil carbon with a carbon-neutral source, such as biomass of plant origin, which emits no fossil CO_2 during combustion. When introducing such biomass as a substitute for the current coal used, it mustn't alter the final properties of the coke produced. Therefore, before conducting the analyses and characterizations detailed in the following report, a study was conducted on the most readily available biomass in the Mediterranean area of Europe, particularly in Italy. Subsequently, ten biomass types most abundant in Apulia near the steel plant in Taranto were selected. The study considered their availability, annual production quantity, and proximity to the production point near the plant. In selecting these biomasses as partial substitutes for coking coal, they must adhere to certain typical coal parameters. Their substitution should not compromise the quality, yield, or safety of the coking process. Consequently, the focus was on analyzing specific characteristics essential for a coking material. To be suitable, these biomasses must exhibit a high carbon content and low levels of sulfur, phosphorus, and alkalis. From a process yield perspective, it is important that they have low moisture and volatile substance content.

3 Selection and pretreatment of biomasses

The selection of biomasses is a crucial step for several reasons, including availability, accessibility, and, importantly, suitability of raw materials for the cokemaking process requirements. The first two aspects can vary significantly depending on the geographical region. While some biomasses, such as agricultural or forestry residues, may be abundant in certain areas, others might be more challenging to source or have higher costs. Biomass prices can be influenced by factors such as local supply and demand dynamics, production and transportation costs, as well as governmental policies and regulations. Biomasses competing with other applications, such as the energy or food sectors, may command higher prices and limited availability. This poses challenges for projects heavily reliant on biomass as energy sources or raw materials.

Within the context of the BioCoDe project, biomass selection took these considerations into account, aiming to maximize the use of locally available resources, which vary in accessibility. Regarding suitability, as previously mentioned, it's crucial to note that biomasses differ significantly in terms of chemical composition, energy content, and physicochemical properties. These factors impact the yield and quality of the final product. In the BioCoDe project, the selected biomasses were identified through an upstream study before the experimentation phase. They were deemed suitable based on their availability in the Apulia region and proximity to the supply point near the Taranto production site. The selected biomasses were collected, identified with a unique code, and pre-treated by initial chipping using a sharp-milling process to reduce their size. The biomasses considered in the experiment are listed in Table 1. It is worth noting that eucalyptus, despite not being widely available locally, was included for comparison purposes due to its extensive literature presence in studies.

Identification code	**Biomass**	**Type of residue**
202348/1	Pallet	Industrial
202348/2	Pine	Agro-forestry
202348/3	Eucalyptus	Agro-forestry
208448/4	Olive branches	Agro-forestry
208448/5	Olive trunks	Agro-forestry
208448/6	Boxes with plywood bottom	Industrial
208448/7	Boxes with chipboard bottom	Industrial
208448/8	Olive pomace	Industrial
208448/9	Vine	Agro-forestry
208448/10	Straw	Agro-forestry

Table 1: Selected biomasses for the experimentation

The figures below show the biomasses used in the experimentation before and after the chipping treatment, except for samples 208448/8 (olive pomace) and 208448/10 (straw), which did not undergo this pretreatment.

Figure 1: Sample 202348/1 – Pallet wood before and after chipping

Figure 2: Sample 202348/2 – Pine wood before and after chipping

Figure 3: Sample 202348/3 – Eucalyptus wood before and after chipping

Figure 4: Sample 202348/4 – Olive branches before and after chipping

Figure 5: Sample 202348/5 – Olive trunks before and after chipping

Figure 6: Sample 202348/6 – Boxes with plywood bottom before and after chipping

Figure 7: Sample 202348/7 – Boxes with chipboard bottom before and after chipping

Figure 8: Sample 202348/8 – Olive pomace

Figure 9: Sample 202348/9 – Vine shoots before and after chipping

Figure 10: Sample 202348/10 – Straw

4 Biomass characterization

The biomasses were characterized through chemical, physical, and technological analyses, and the results were compared with the corresponding characterizations performed on a typical coking blend and a high volatile coking blend used as a baseline for the technological test. This comparison will aid in selecting the most promising biomasses to advance to the next phase of pilot experimentation.

4.1 Mass determination of moisture

For each sample, the moisture percentage was determined, a characteristic that directly affects the pyrolysis efficiency. Except for samples 202348/8 and 202348/10, which were used as-is, the moisture determination was carried out on the chipped biomasses. The results are shown in Table 2 and Figure 11.

Identification code	Biomass	Moisture (%m/m)
202348/1	Pallet	9.89
202348/2	Pine	28.98
202348/3	Eucalyptus	28.61
202348/4	Olive branches	33.62
202348/5	Olive trunks	15.52
202348/6	Boxes with plywood bottom	12.21
202348/7	Boxes with chipboard bottom	11.81
202348/8	Olive pomace	56.05
202348/9	Vine	41.33
202348/10	Straw	12.20
202337/7	Standard mixture	7.81
202337/10	Technological test mixture	7.10

Table 2: Moisture content of samples obtained through mass determination

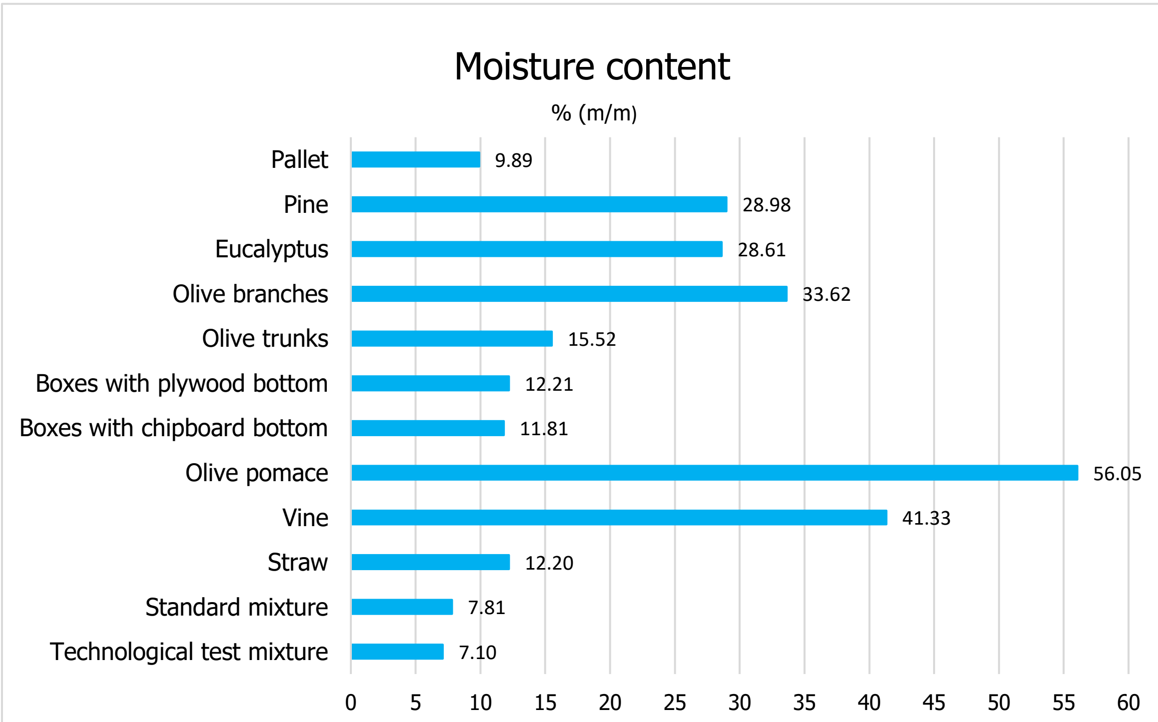

Figure 11: Graphical representation of the moisture content of samples obtained through mass determination

The moisture content determined from the analyzed biomass samples widely varies and, in all cases, is higher than the reference cokemaking blend. Specifically, olive pomace shows the highest moisture content at 56%; lower values could likely have been obtained using less recently produced olive pomace. Significantly lower and closer to the moisture content of the coal blend are the moisture levels found in pallet wood and crate wood, as these are already aged woods. Similar moisture levels are also found in the straw. Regarding the biomass obtained from pruning residues, the moisture content is heavily influenced by the time of year when the pruning took place and the time elapsed between pruning and analysis. For instance, the vine pruning residues analyzed were pruned approximately a month before testing, whereas the pruning residues from pine, eucalyptus, and olive trees were from earlier pruning seasons.

4.2 Mass determination of ash

The amount of ash is crucial for evaluating the quality of the coke produced. The ash quantity is reported in Table 3 and graphically represented in Figure 12.

Identification code	Biomass	Ash content (%m/m)
202348/1	Pallet	0.33
202348/2	Pine	0.76
202348/3	Eucalyptus	1.72
202348/4	Olive branches	3.69
202348/5	Olive trunks	2.96
202348/6	Boxes with plywood bottom	1.19
202348/7	Boxes with chipboard bottom	4.76
202348/8	Olive pomace	3.10
202348/9	Vine	2.72
202348/10	Straw	8.74
202337/7	Standard mixture	8.77
202337/10	Technological test mixture	8.52

Table 3: Ash content of samples obtained through mass determination

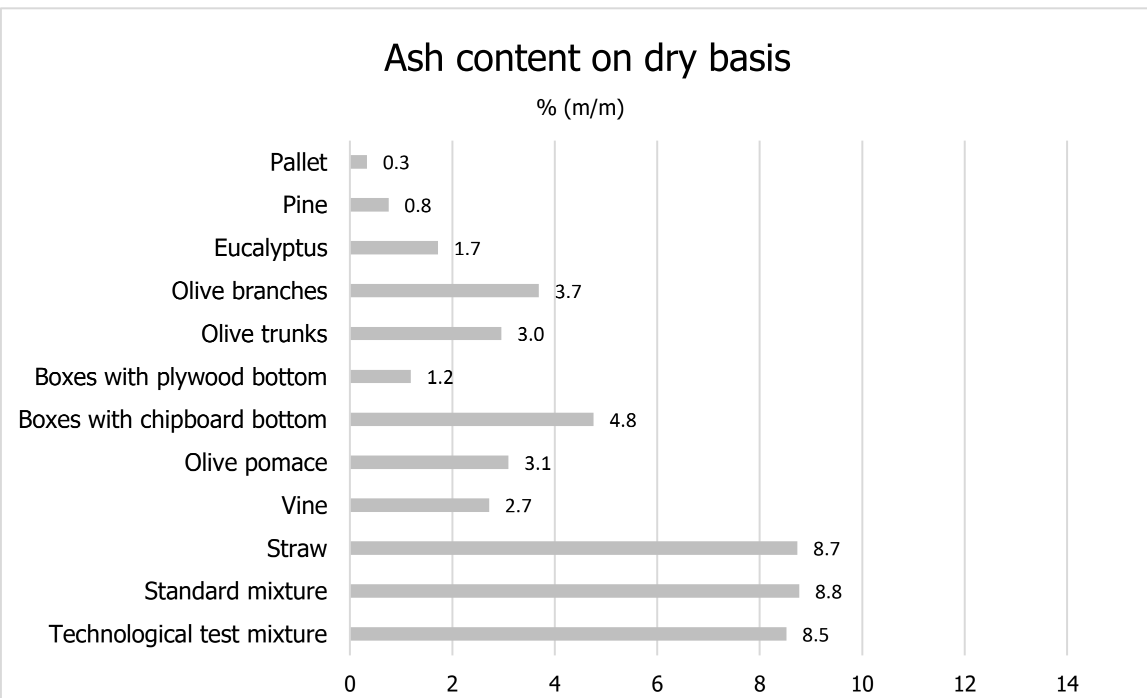

Figure 12: Graphical representation of the ash content of samples obtained through mass determination

The ash content varies considerably depending on the type of biomass analyzed and, except for straw, is significantly lower than that of the fossil blend. Samples from pallets, pine, and crates with plywood bottoms have the lowest ash content. Regarding olive wood, branches have slightly higher ash content compared to trunks, possibly due to the presence of soil or other inert material deposited on the surface of leaves and twigs during collection. Of particular interest is the higher ash content in boxes with chipboard bottom compared to those entirely made of plywood, suggesting the presence of inert material within the chipboard mix. As mentioned, straw has the highest ash content among the biomasses, equivalent to that characterizing the coal blend. Unlike other biomasses, straw also exhibits compact ashes rather than powdery ones, indicative of their fusion during the incineration process (Figure 13). This characteristic is due to its high SiO_2 content and low CaO content, which allows the ashes to melt at relatively low temperatures. However, while this property poses a significant challenge for using straw in waste-to-energy processes for steam and/or electricity production due to the formation of boiler pipe fouling, it is not an issue when used for biocoke production.

Figure 13: Ashes from straw (left) and coal (right) obtained from the same initial quantity of material

4.3 Proximate analysis

The proximate analysis was conducted using thermogravimetric analysis (TGA). Table 4 presents the results of the analysis, including moisture and ash contents, volatile matter (V.M.) produced from the thermal degradation of coal, and fixed carbon (F.C.), which is calculated as the difference between the dry mass of the sample and the sum of volatile matter and ash content.

Identification code	Biomass	Moisture (%m/m)	Ash* (%m/m)	V.M.* (%m/m)	F.C.* (%m/m)
202348/1	Pallet	7.95	0.42	80.89	18.69
202348/2	Pine	20.90	1.37	65.24	33.39
202348/3	Eucalyptus	20.55	1.61	65.43	32.96
202348/4	Olive branches	4.78	4.32	77.30	18.38
202348/5	Olive trunks	10.88	3.18	72.02	24.80
202348/6	Boxes with plywood bottom	9.55	0.93	78.26	20.81
202348/7	Boxes with chipboard bottom	9.76	1.40	77.39	21.21
202348/8	Olive pomace	0.18	3.13	81.55	15.32
202348/9	Vine	5.12	3.00	77.00	20.00
202348/10	Straw	6.21	9.13	72.10	18.77
202337/7	Standard mixture	0.94	10.22	21.41	68.37
202337/10	Technological test mixture	0.98	8.74	26.78	63.76

Table 4: Proximate analysis results (values on a dry basis)

The moisture values reported in the table differ from those obtained through mass characterization, with the former significantly lower than the latter. This is primarily due to the different quantities and preparation methods required for the two analyses. During the preliminary grinding step for TGA analysis, biomass samples lose a considerable amount of moisture. It should also be noted that for olive pomace, the sample analyzed using TGA had already been oven-dried before grinding to facilitate the process. However, determining the moisture content is necessary to express the other values on a dry basis, thereby eliminating an additional variable during comparison. Regarding ash content, the results from TGA analysis align entirely with those obtained through mass analysis. The only exception is sample 202348/7 (chipboard boxes), which showed an ash content of 4.76% by mass determination and 1.40% by TGA analysis, likely due to the presence of metallic fragments in the former case. Volatile matter in coking coals represents the component that, during heating in the absence of oxygen, transforms into gases and oils/tars at various condensation temperatures. Similarly, this occurs with biomasses. In the coking process, the gas produced, known as coke gas, is a significant energy source for the facility, primarily composed of hydrogen, methane, and carbon monoxide. Although valuable, a high quantity of volatile matter implies a reduction in coke yield, making it an important consideration when formulating fossil blend mixes and selecting biomass types to replace them. Fixed carbon, closely related to coke formation yield, represents the residual carbon in biomass after the pyrolysis phase in the absence of oxygen. Higher fixed carbon content results in higher biomass coke yield, and consequently, lower volatile matter produced. Figures 14 and 15 depict graphical representations of volatile matter and fixed carbon content for the analyzed biomasses.

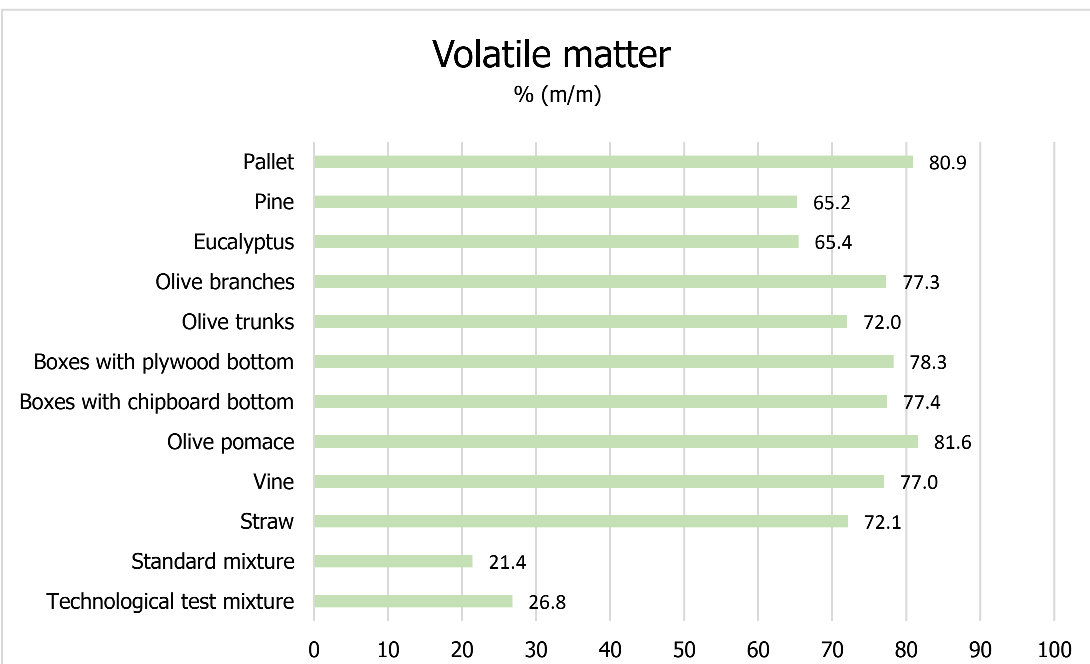

Figure 14: Graphical representation of volatile matter content from proximate analysis (values on a dry basis)

The fraction of volatile matter of the biomasses varies from 65.2% in pine to 81.6% in olive pomace, values significantly higher than those of fossil coals (21.4% in the example fossil blend). Conversely, among the analyzed biomasses, fixed carbon content is highest in pine (33.4%) and lowest in olive pomace (15.3%). The fossil blend, on the other hand, exhibits a much higher fixed carbon content (68.4%). Substituting biomass in its natural state (or at most dried) for fossil coals results in a reduction in coke formation yield by 3 to 4 times for an equivalent amount replaced. However, it's important to consider the biomass's effect on increasing coke gas production, a byproduct crucial for steelmaking facilities as mentioned earlier. An all-encompassing graphical representation of the results from the proximate analysis is shown in Figure 16.

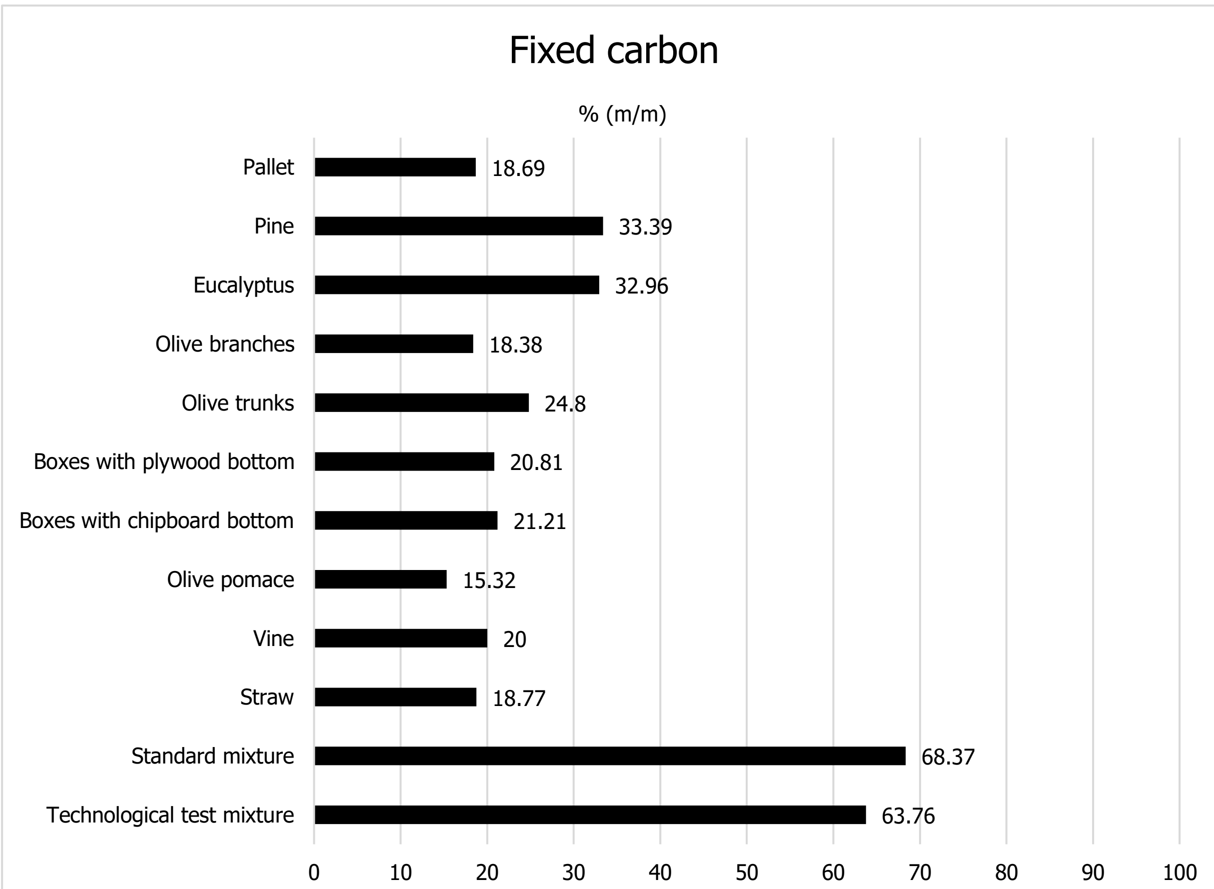

Figure 15: Graphical representation of fixed carbon content from proximate analysis (values on a dry basis)

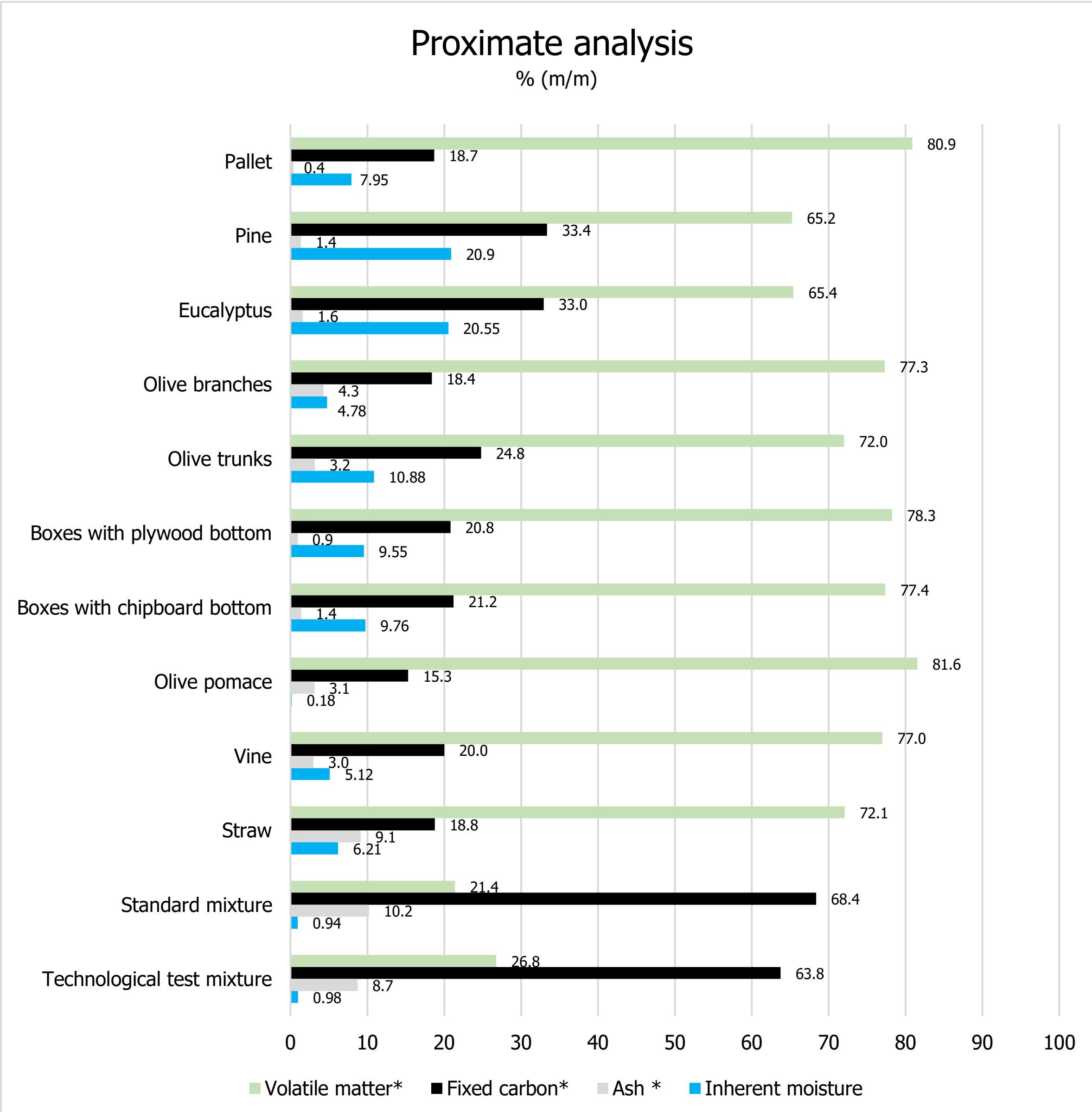

*Figure 16: Graphical representation of the results from proximate analysis (*values on dry basis)*

Below are the trends obtained from the thermogravimetric analysis of each biomass, while Table 5 provides an overview of the results of this analysis, summarizing the main data.

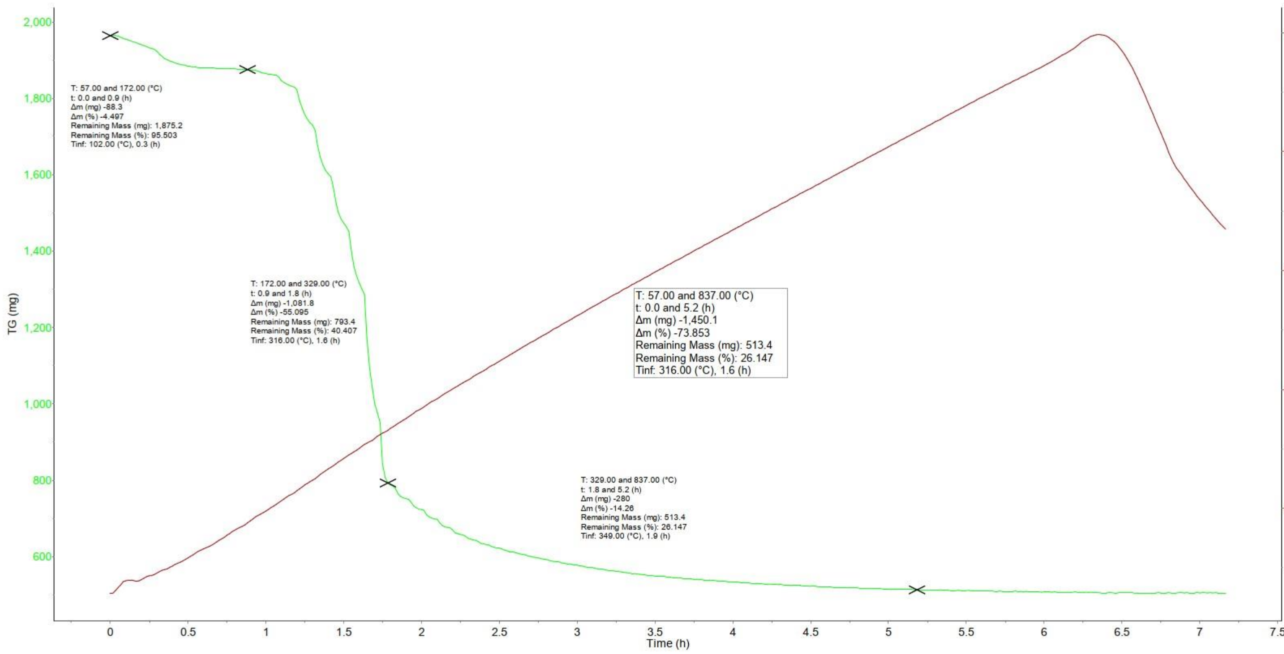

Figure 17: TG pallet

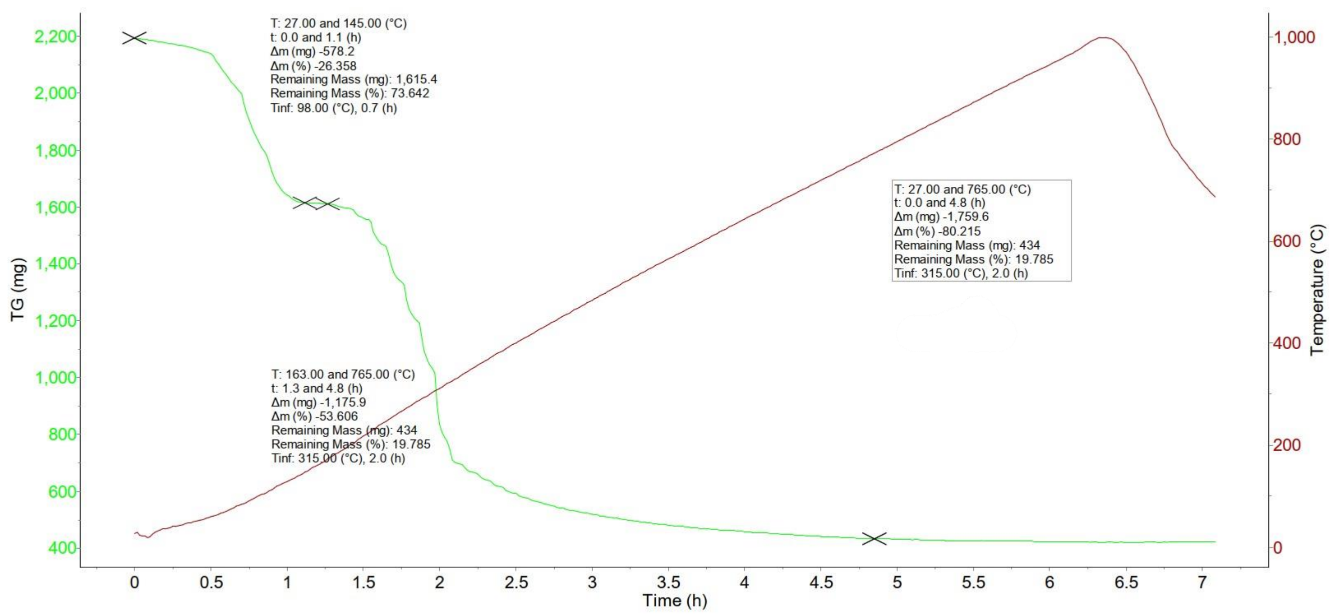

Figure 18: TG pine

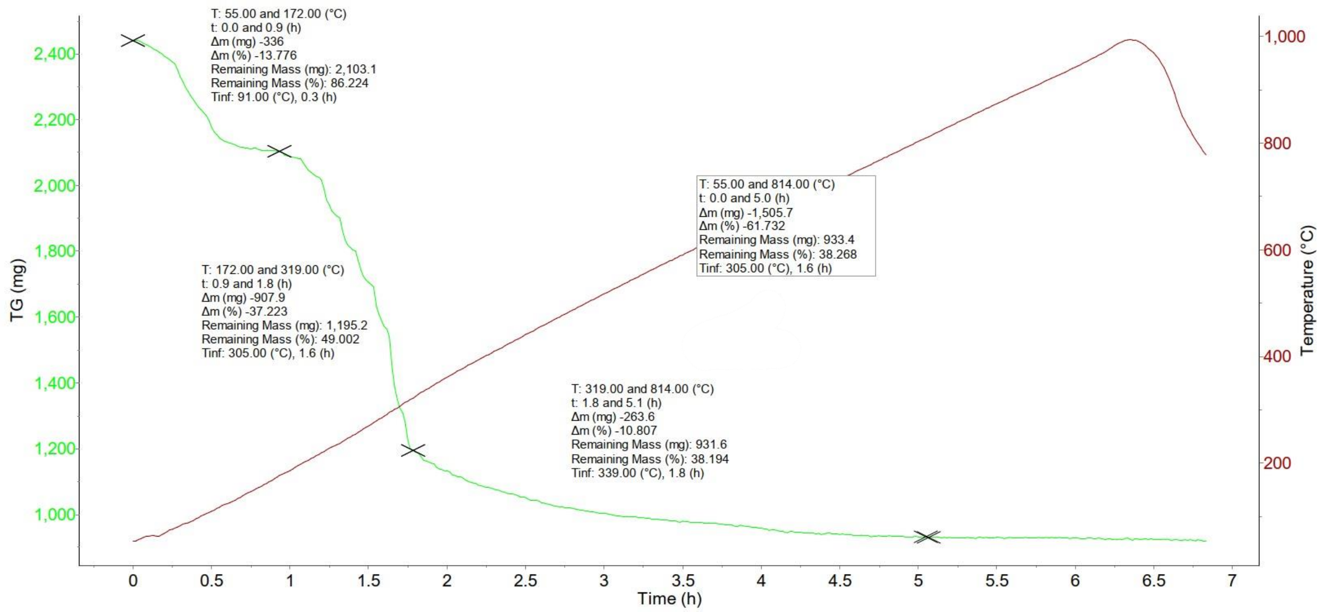

Figure 19: TG eucalyptus

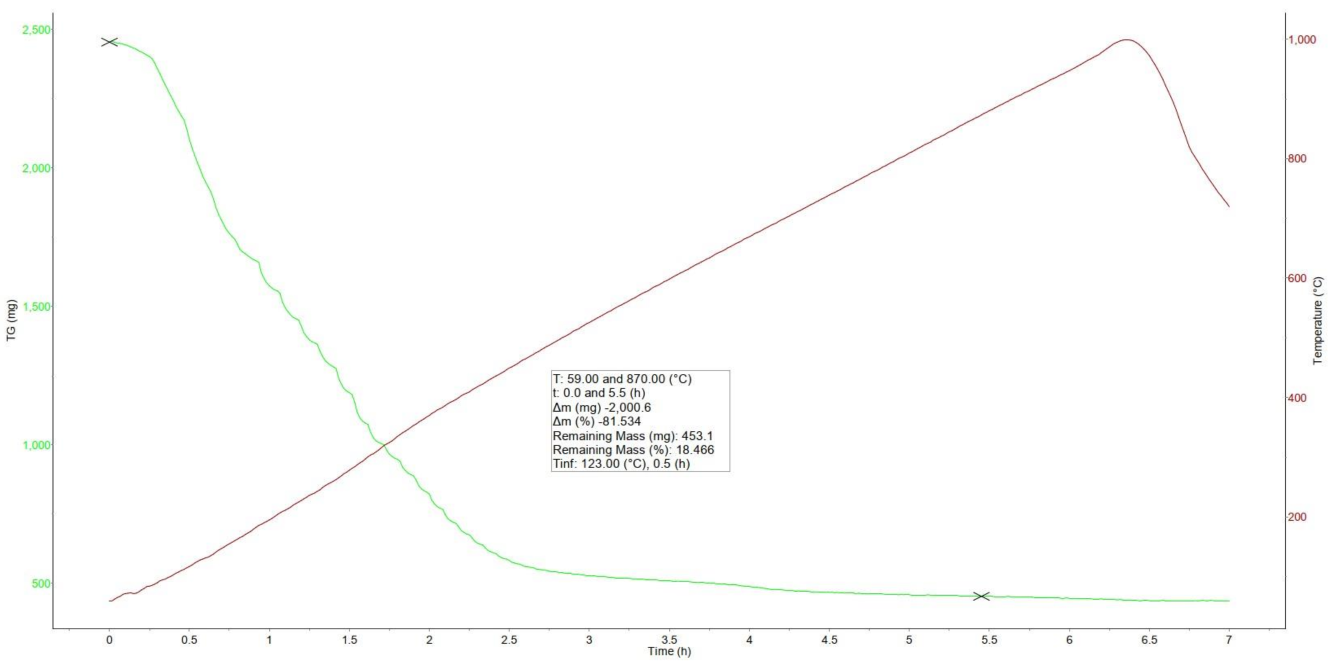

Figure 20: TG olive brunches

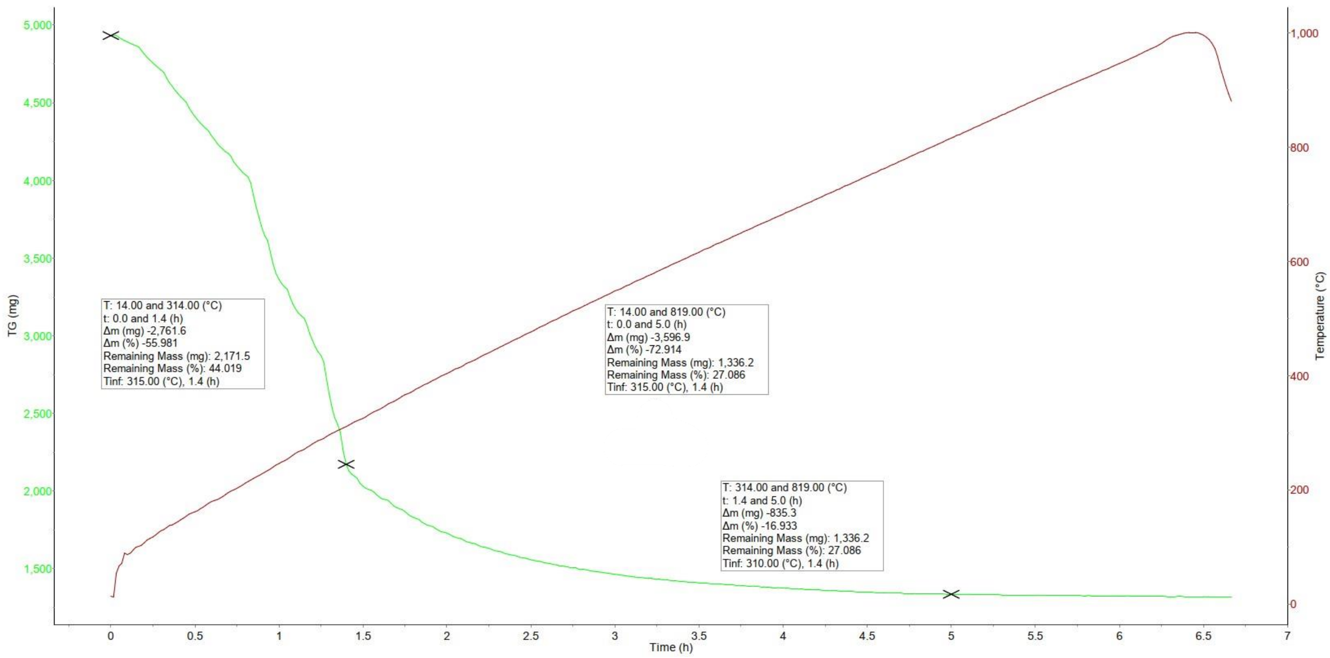

Figure 21: TG olive trunks

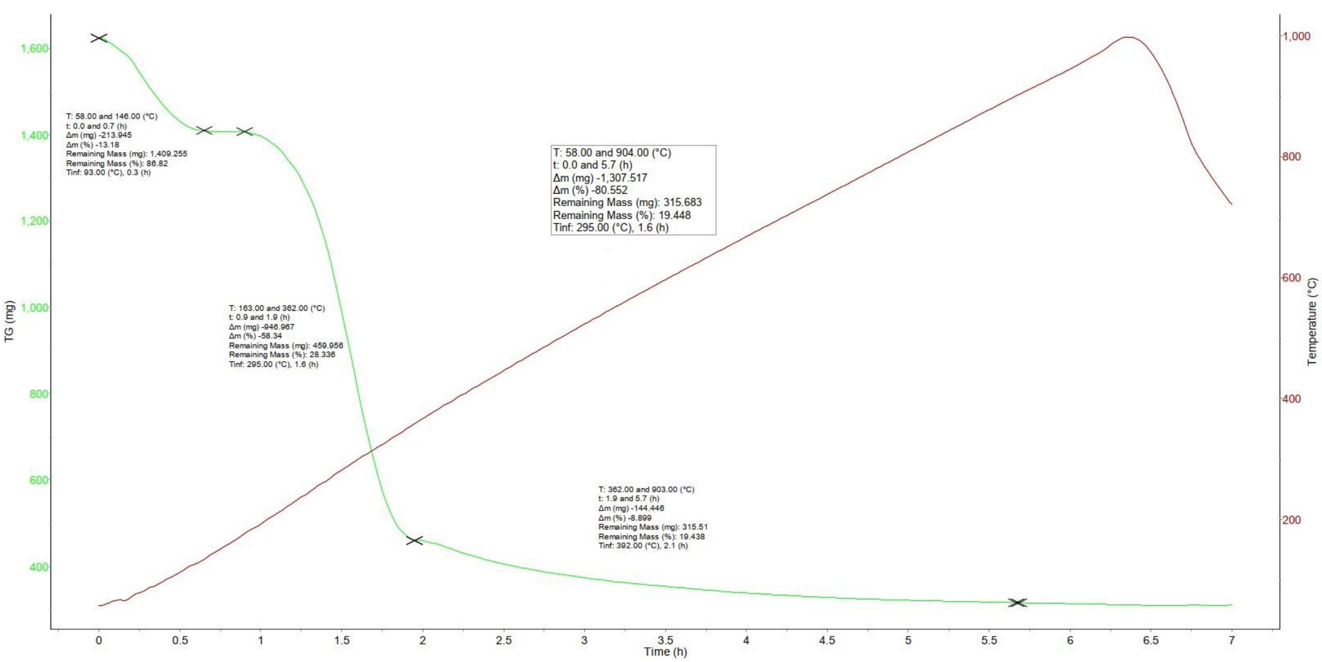

Figure 22: TG boxes with plywood bottom

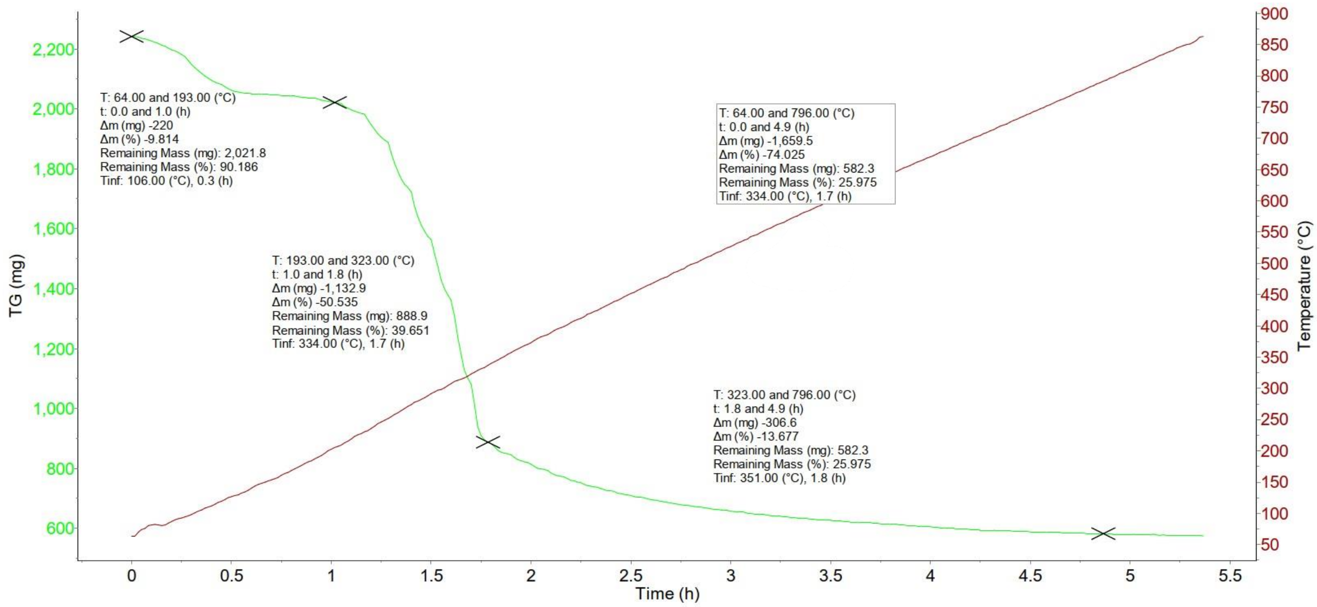

Figure 23: TG boxes with chipboard bottom

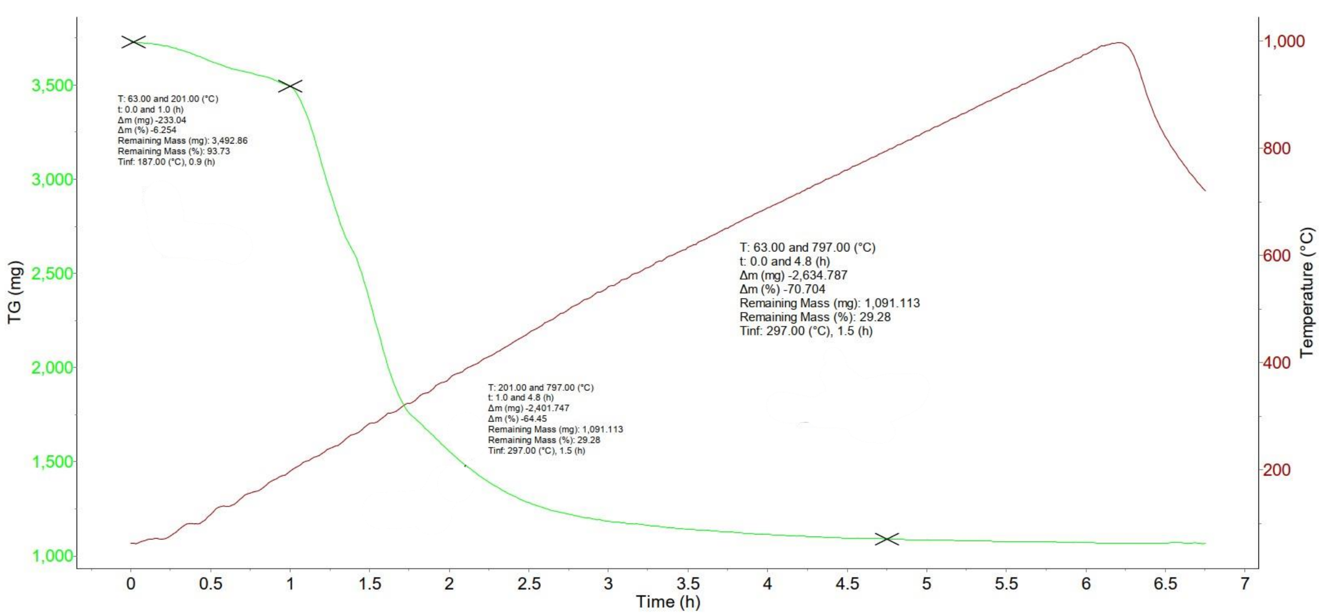

Figure 24: TG olive pomace

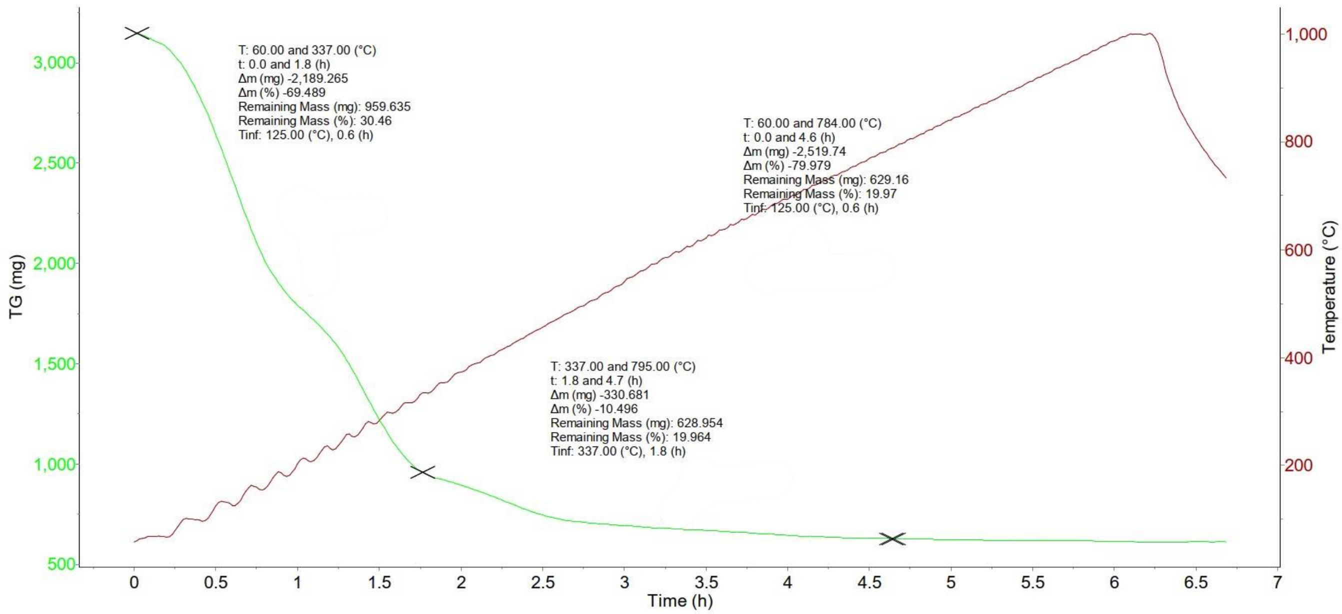

Figure 25: TG vine

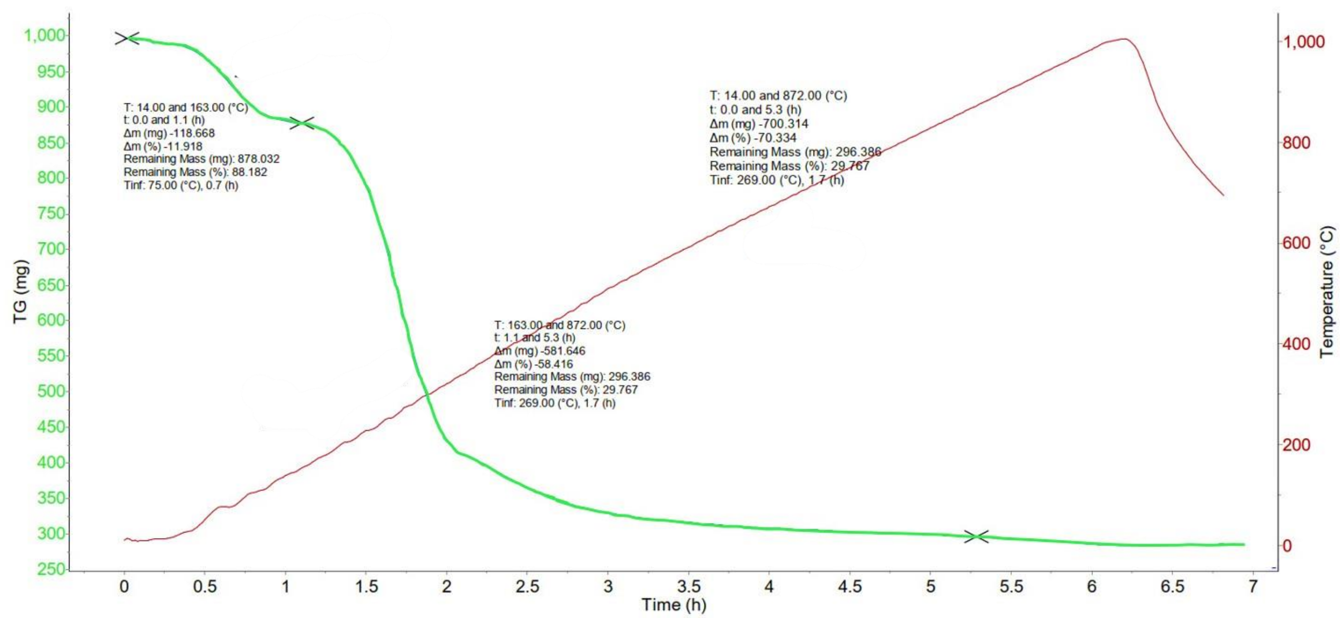

Figure 26: TG straw

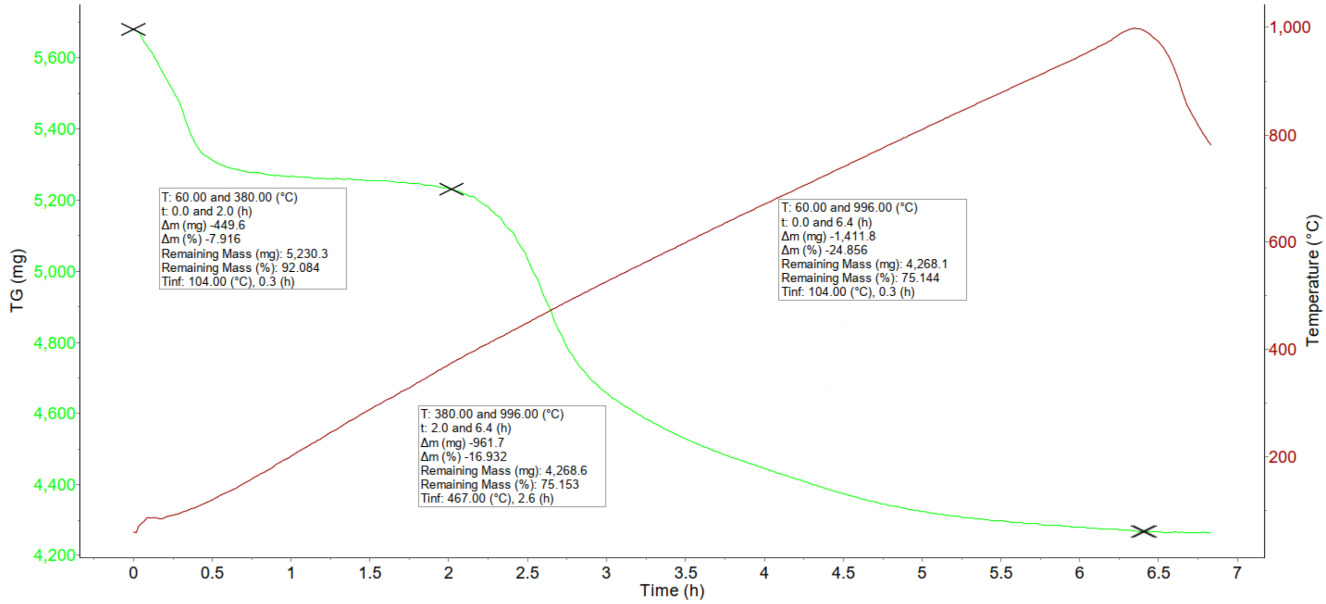

Figure 27: TG carbon mixture

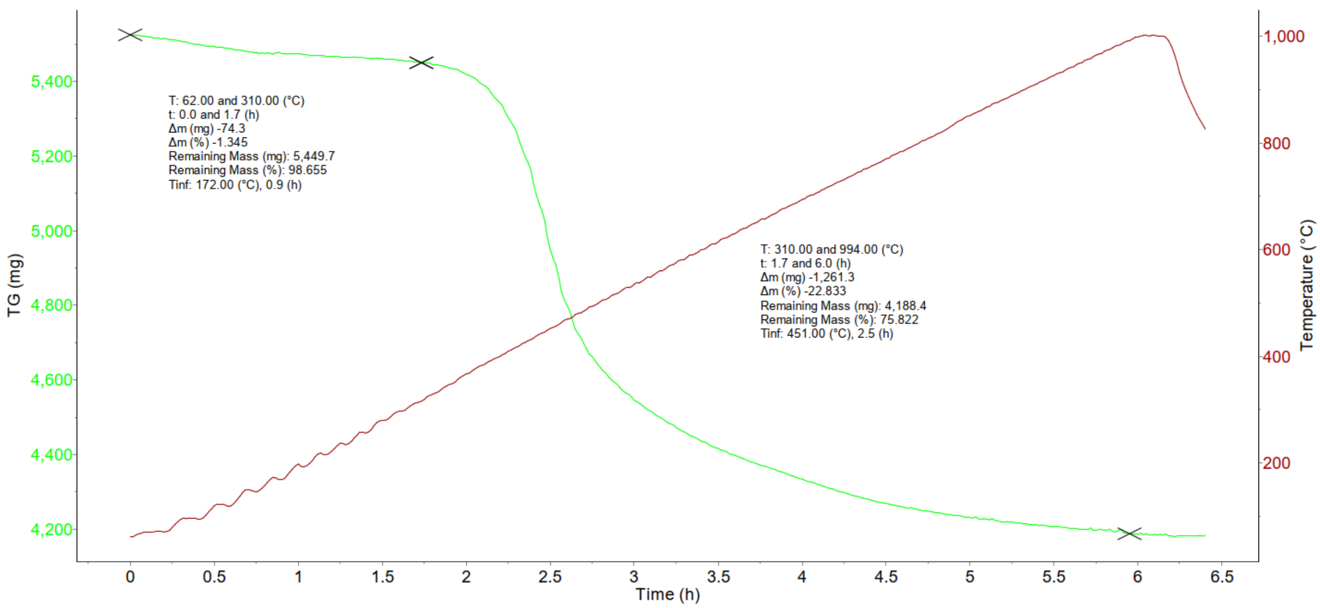

Figure 28: TG technological test mixture

Identification code	Biomass	$T_{i,loss}$ [°C]	$T_{f,loss}$ [°C]	Initial weight [g]	Final weight [g]	Weight loss [g]	Percentage loss [%]
202348/1	Pallet	57	837	1.963	0.513	1.45	73.9
202348/2	Pine	27	765	2.194	0.434	1.76	80.2
202348/3	Eucalyptus	55	814	2.439	0.933	1.506	61.7
202348/4	Olive branches	59	870	2.453	0.453	2	81.5
202348/5	Olive trunks	14	819	4.933	1.336	3.597	72.9
202348/6	Boxes with plywood bottom	58	904	1.623	0.315	1.308	80.5
202348/7	Boxes with chipboard bottom	64	796	2.242	0.582	1.66	74.0
202348/8	Olive pomace	63	797	3.727	1.091	2.636	70.7
202348/9	Vine	60	784	3.151	0.629	2.522	80.0
202348/10	Straw	14	872	0.996	0.296	0.7	70.3
202337/7	Standard mixture	60	996	5.680	4.268	1.412	24.9
202337/10	Technological test mixture	310	994	5.524	4.188	1.335	23.0

Table 5: TG summary

The thermogravimetric analyses of the ten biomasses, intended for use in the coking plant as substitutes for coal, show a variety of thermal behaviors and decomposition characteristics. Key trends emerge from the data. Woody biomasses like pine and eucalyptus tend to show a more gradual decomposition compared to more fibrous materials like straw and olive branches, which decompose at lower temperatures and at a faster rate. Olive pomace and vine residues display decomposition profiles that indicate a significant presence of volatile materials. The last two thermogravimetric analyses are related to mixtures of fossil coals. The first fossil coal mixture and the second, a technological test mix, show greater thermal stability compared to the biomasses, with decomposition occurring at higher temperatures. This suggests that while biomasses are viable substitutes for coal, they exhibit different combustion and decomposition characteristics that must be considered to optimize the coking process.

4.4 Ultimate and calorimetric analysis

Through LECO analysis, the chemical analysis of biomass was conducted to determine the content of carbon, sulphur, nitrogen, oxygen, and hydrogen. The results are reported in Table 6.

Ultimate analysis [m%]											
	Pallet	Pine	Eucalyptus	Olive branches	Olive trunks	Boxes with plywood bottom	Boxes with chipboard bottom	Olive pomace	Vine	Straw	Standard mixture
S	0.04	0.03	0.05	0.07	0.14	0.07	0.04	0.06	0.08	0.13	0.66
C	51.91	51.70	43.47	47.82	53.49	49.99	50.72	59.03	46.08	49.08	74.98
H	3.96	6.42	3.03	4.74	4.64	4.68	5.34	6.57	4.06	5.60	4.10
O	42.93	39.00	47.71	41.71	37.63	43.65	41.31	29.47	45.76	33.63	9.96
N	0.75	1.43	0.63	1.17	0.81	0.69	1.16	1.7	0.99	2.05	1.55
Cl	0.01	0.02	0.08	0.2	0.09	0.02	0.03	0.08	0.03	0.41	0.06

Atomic ratio											
H/C	0.92	1.49	0.84	1.19	1.04	1.12	1.26	1.34	1.06	1.37	0.66
O/C	0.62	0.57	1.10	0.65	0.53	0.65	0.61	0.37	0.74	0.51	0.10
C/N	80.75	42.18	69	47.68	77.04	84.52	51.01	40.51	54.30	27.93	56.43

Table 6: Ultimate analysis results

Carbon, hydrogen, and oxygen are the main components, of cellulose, hemicellulose, and lignin. Olive pomace and straw, the only two non-wood biomass types, show lower oxygen and higher nitrogen values compared to all others. Particularly for straw, it exhibits the lowest C/N ratio among all, a parameter in ecology used to measure sample biodegradability; a lower ratio indicates greater degradability. This aligns with the fact that straw degrades more easily than typical wood biomass. High O/C and H/C ratios, however, imply reduced material reactivity and lower calorific power. Thus, a thermal pretreatment to decrease oxygen and hydrogen content before biomass use is beneficial. A low sulphur content is advantageous for biomass, typically an order of magnitude lower than fossil carbons. Chlorine levels are generally non-critical, slightly above reference values in a few cases. Focusing on biomass carbon content, it notably ranges between 46.08% and 59.03%, compared to 74.98% in the carbon mix. Unlike fossil carbons, biomass doesn't show a direct correlation between elemental carbon and fixed carbon yield. Olive pomace, with the highest elemental carbon but lowest fixed carbon among studied biomass, exemplifies this. Oxygen and hydrogen presence in biomass likely causes more carbon to volatilize as carbon monoxide or methane, reducing fixed carbon. Undesirable sulphur in coke carbons is removed during cokemaking, as it contaminates cast iron, reducing quality. Biomass sulphur content is extremely low compared to the carbon mix, an undeniable advantage. Highest values slightly exceed 0.1%, versus 0.66% in fossil mix. Heating value is crucial for cokemaking process energy; Table 7 show biomass calorimetric analysis results.

Identification code	Biomass	Higher heating value [Kcal/kg]	Carbon content [%]
202348/1	Pallet	4500	51.91
202348/2	Pine	4700	51.70
202348/3	Eucalyptus	4200	43.47
202348/4	Olive branches	4900	47.82
202348/5	Olive trunks	4700	53.49
202348/6	Boxes with plywood bottom	4600	50.00
202348/7	Boxes with chipboard bottom	4600	50.72
202348/8	Olive pomace	4700	59.03
202348/9	Vine	4500	46.08
202348/10	Straw	4200	49.08
202337/7	Standard mixture	7711	74.98
202337/10	Technological test mixture	7800	80.09

Table 7: Calorimetric analysis results

As evidenced by the results of calorimetric analysis, the higher heating value is largely correlated with the carbon content found in biomass. Indeed, all biomass samples showed a lower heating value compared to the carbon mix, which is about 7711 kcal/kg and characterized by a carbon content of

74.98%. Olive brunches exhibit the highest heating value among the biomass types, followed by olive wood, olive pomace, and pine. Straw and eucalyptus have the lowest heating values among the biomass types. However, all biomass samples fall within a heating value range of 4200 kcal/kg to 4900 kcal/kg.

4.5 XRF analysis on ash

After determining the ash content of each sample, they were analyzed using XRF analysis to investigate their composition. The results are reported in Table 8.

Biomass	SiO_2	CaO	Al_2O_3	MgO	Fe_2O_3	P_2O_5	Na_2O	K_2O	TiO_2	MnO	SO_3
	% (m/m)										
Pallet	8.07	39.2	4.82	8.51	28.55	2.261	2.82	3.64	0.83	0.94	0.03
Pine	9.42	58.18	3.58	6.65	9.07	2.37	3.1	3.85	0.08	0.29	2.95
Eucalyptus	6.96	61.05	2.48	8.1	3.97	4.02	2.89	6.57	0.04	0.48	2.6
Olive branches	10.67	49	3.51	4.53	11.46	4.47	4.69	6.77	0.11	0.26	0.07
Olive trunks	13.45	44.46	4.5	2.59	24.04	0.828	3.32	4.1	0.15	0.49	1.95
Boxes with plywood bottom	9.41	28.06	2.82	7.64	40.96	1.957	3.22	3.61	0.26	0.89	0.57
Boxes with chipboard bottom	12.87	43.68	11.88	5.01	12.64	1.122	2.54	4.91	3.44	0.71	0.03
Olive pomace	31.4	12.84	9.78	3.03	3.7	7.17	1.25	29.81	0.35	0.16	0.03
Vine	6.89	51.07	2.59	13.64	2.58	13.32	2.98	5.64	0.06	0.68	0.03
Straw	65.05	7.44	3	2.12	0.78	2.252	1.9	14.85	0.03	0.13	0.22
Standard mixture	50.43	1.80	31.44	1.16	6.36	0.49	0.21	2.52	1.80	0.06	1.38
Technological test mixture	51.07	1.67	29.60	1.10	9.72	0.461	0.48	2.72	1.54	0.03	1.01

Table 8: XRF analysis on ash

The ashes resulting from the complete oxidation of biomass are characterized by various metal oxides whose concentration varies depending on the type of biomass. For instance, biomasses such as pine, eucalyptus, and vine have more than half of their ash content composed of calcium oxide, specifically 58%, 61%, and 51%, respectively. On the other hand, straw has approximately 65% of its ash content consisting of silicon dioxide, which explains its low melting point ash, as previously mentioned. Sulfur and phosphorus are undesirable elements in coke carbons, and thus in biomass, due to their negative impact on cast iron quality. As seen in the elemental analysis of raw biomass, XRF analysis of ashes also confirms that the sulphur content in biomass is significantly lower compared to that in carbons. Olive trunks, eucalyptus, and pine are exceptions, with pine showing the highest sulphur content at 2.95%. Conversely, phosphorus levels in biomass are much higher compared to fossils, peaking at around 13% for vine. Olive trunks have phosphorus content closest to fossil mix, specifically 0.83% compared to the fossil mix 0.49%.

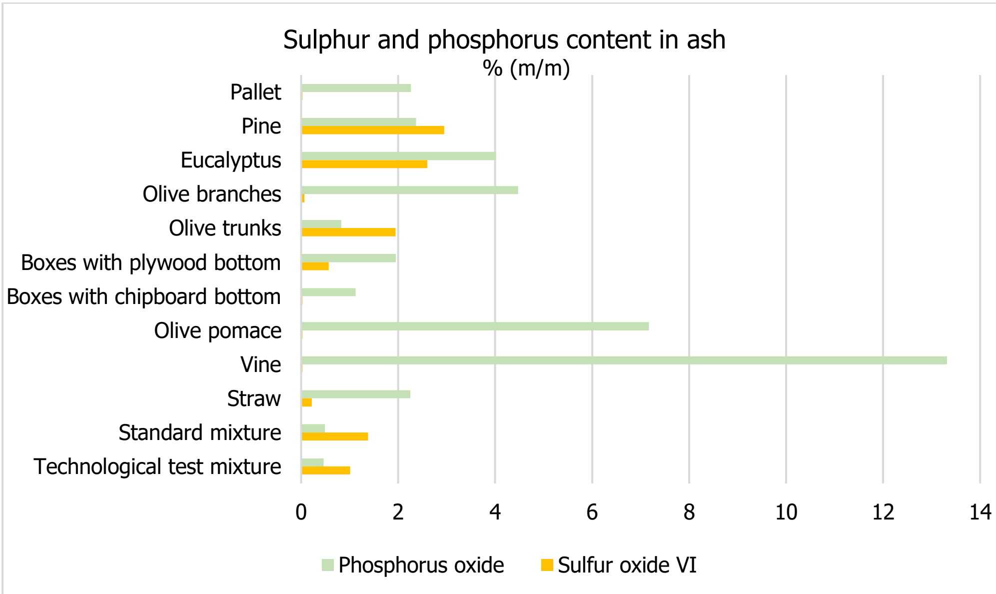

Figure 29: Sulphur and phosphorus content in ash

Other elements of concern are alkalis, particularly sodium and potassium, and alkaline earth elements like calcium and magnesium. These elements negatively impact coke quality by increasing its reactivity and simultaneously reducing its strength. In blast furnaces, this would result in higher coke consumption and reduced coke size, leading to decreased permeability of the blast furnace bed. Below in Table 8 and in Figures 30 and 31, the values of alkali and alkaline earth elements found in the ashes of the analyzed biomass are presented.

		ALKALI			**ALKALI EARTH**		
		Na2O	K2O	(Na2O+K2O)	CaO	MgO	(CaO+MgO)
Sample	**Biomass**	%(m/m)					
202348/1	Pallet	2.82	3.64	6.46	39.2	8.51	47.71
202348/2	Pine	3.1	3.85	6.95	58.18	6.65	64.83
202348/3	Eucalyptus	2.89	6.57	9.46	61.05	8.1	69.15
202348/4	Olive branches	4.69	6.77	11.46	49	4.53	53.53
202348/5	Olive trunks	3.32	4.1	7.42	44.46	2.59	47.05
202348/6	Boxes with plywood bottom	3.22	3.61	6.83	28.06	7.64	35.7
202348/7	Boxes with chipboard bottom	2.54	4.91	7.45	43.68	5.01	48.69
202348/8	Olive pomace	1.25	29.81	30.16	12.84	3.03	15.87
202348/9	Vine	2.98	5.64	8.62	51.07	13.64	64.71
202348/10	Straw	1.9	14.85	16.75	7.44	2.12	9.56
202337/7	Standard mixture	0.21	2.52	2.73	1.80	1.16	2.96

202337/10	Technological test mixture	0.48	2.72	3.20	1.67	1.10	2.77

Table 9: Content of alkali and alkaline earth elements in biomass ash

All biomass samples exhibit higher quantities of alkali oxides compared to the fossil mix used as a reference. The highest amount of sodium oxide was found in olive brunches (4.7%), while olive pomace had the highest potassium oxide content (29.8%). Olive pomace, characterized by the highest total alkali content, is followed by straw. Among the analyzed samples, pallet wood shows the lowest alkali metal content with 2.8% sodium oxide and 3.6% potassium oxide. Slightly higher quantities were observed in the ashes of pine, plywood boxes, and chipboard boxes. These findings suggest that the analyzed biomass could degrade coke quality by increasing reactivity in blast furnaces. Therefore, careful attention and selection of biomass are crucial considering these factors.

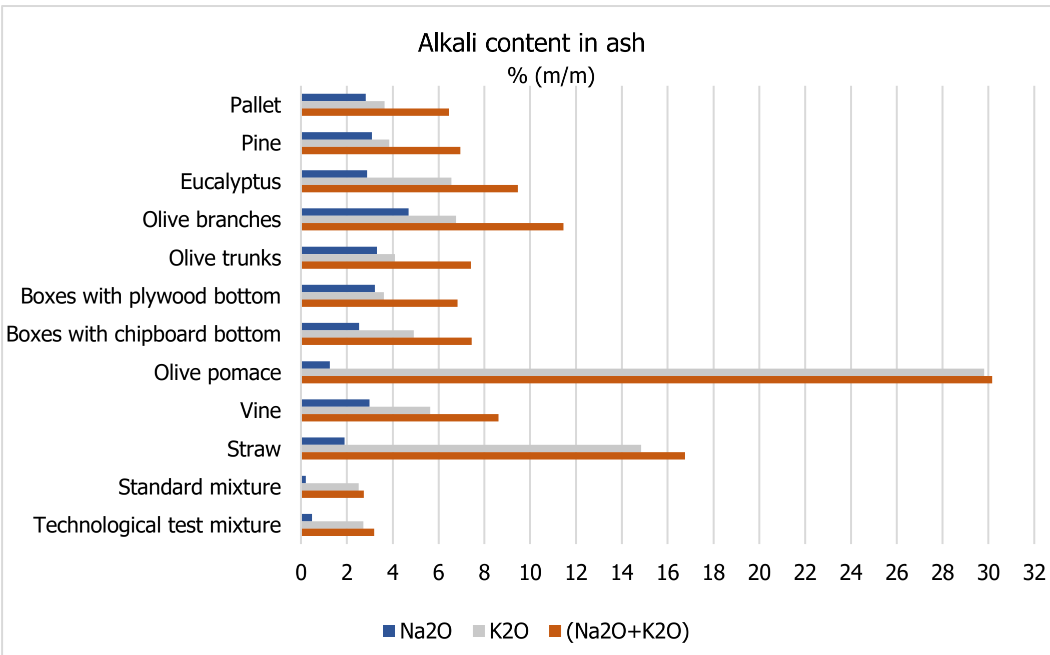

Figure 30: Alkali content in ash

Regarding alkaline earth metals as well, biomass exhibits significantly higher contents compared to fossil carbons, particularly in terms of calcium oxide rather than magnesium. The highest values of alkaline earth metals are found in pine (64.8%), eucalyptus (69.2%), and vine (64.7%), while the lowest are in olive pomace and straw, the latter showing a complete contrast to the other biomass samples.

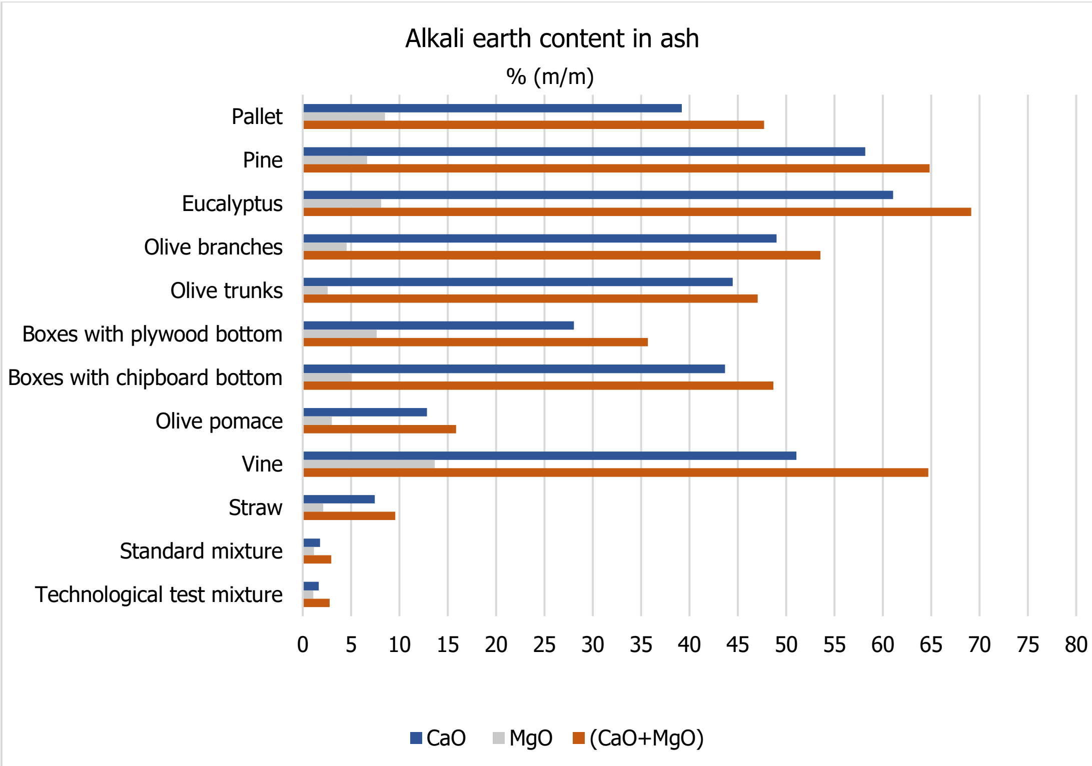

Figure 31: Alkali earth content in ash

4.6 Technological tests

Finally, technological tests for cokemaking coals were conducted, namely fluidity and dilation determinations. These tests are crucial in industrial practice to assess the rheological properties of carbons during coke transformation.

They analyze the temperature at which the coal exhibits maximum contraction and dilation, evaluating the fluidity window width and maximum fluidity value achieved. Greater coal dilation implies stronger pressure on coke oven walls. To counteract this negative effect, low-volatile coals are blended with certain quantities of high-volatile coals, known for high fluidity. In selecting these, fluidity window breadth is paramount, ideally encompassing the maximum dilation range of low-volatile coals. Biomass does not exhibit fluidity and dilation values; hence these tests cannot be directly conducted on it. Therefore, the impact of adding a specific biomass fraction on the technological properties of a reference cokemaking blend was evaluated.

Given the temperature-sensitive nature of these tests and to eliminate moisture variability, which affects biomass reactivity, all samples were pre-dried. Additionally, they were ground to a particle size finer than 212 µm, suitable for dilation tests but finer than the 425 µm required for fluidity tests. Figure 19 illustrates these biomass samples prepared for use in technological tests.

Figure 32: Biomass samples after fine grinding and drying

4.6.1 Fluidity test

During the cokemaking process, bitumen is distilled from coal, and the mixture goes through a plastic phase. As the temperature increases, bitumen loses hydrogen and solidifies into carbon grains that cement together, giving coke its structure.

The formation of the plastic phase and solidification are critical stages in coke production, significantly influencing product quality. The plasticity of the coal blend determines adhesion during coke production and, consequently, its mechanical properties. Fluidity is a measure of coal's ability to form a plastic phase and produce quality coke. Below in Table 9 are the results of fluidity tests conducted on a reference fossil blend with the addition of 3% biomass. This blend was specifically prepared for the tests, using 40% low-volatile coal and 60% high-volatile coal, resulting in a reference fluidity value just under 3000 ddpm.

Another crucial aspect in selecting coal for cokemaking blends is the initial softening temperature. Regarding high-volatile coals, it's crucial that their initial softening temperature is lower than the initial dilation temperature of low-volatile coals. This is because coal fluidity is closely monitored in industrial practice, as it helps mitigate the effects of dilation, which can lead to pressure on coke oven walls.

Therefore, the temperature range in which coal maintains its plastic state is highly important. The maximum temperature at which coal loses its fluidity is known as the solidification temperature, corresponding to the temperature at which semicoke forms. Understanding this range allows for predicting the behavior of the blend inside the coke oven during distillation. The most promising biomasses are those that minimally affect the maximum fluidity value of the fossil blend and, at the same time, do not excessively reduce its plasticity range.

Identification code	**Description**	**Initial softening temperature (°C)**	**Max fluidity temperature (°C)**	**Solidification temperature (°C)**	**Plastic range (°C)**	**Max fluidity (ddpm)**	**Log_{10} maximum fluidity**
202348/1	Pallet	398	450	486	88	288	2.46
202348/2	Pine	401	449	486	85	363	2.56
202348/3	Eucalyptus	401	449	485	84	545	2.74
202348/4	Olive branches	404	449	488	84	619	2.79
202348/5	Olive trunks	398	447	488	90	447	2.65
202348/6	Boxes with plywood bottom	410	449	485	75	369	2.57
202348/7	Boxes with chipboard bottom	398	446	485	87	386	2.59
202348/8	Olive pomace	400	445	484	84	778	2.89
202348/9	Vine	399	447	486	87	682	2.83
202348/10	Straw	399	447	483	84	463	2.67
202337/7	Standard mixture	417	462	492	75	159	2.2
202337/10	Technological test mixture	399	447	489	90	2991	3.48

Table 10: Fluidity test results

As shown in the table and graphical representation in Figure 33, even a small addition of biomass results in a marked reduction of fluidity values in the reference blend, decreasing from 2991 ddpm to 288 ddpm in the case of pallet wood. Olive pomace shows the least impact among the biomasses, although still significant, with a fluidity value of 778 ddpm. This is followed by vine at 682 ddpm and olive brunches at 619 ddpm.

Regarding the plasticity range, there were no substantial variations compared to the reference blend, except for boxes, which shifted from an initial value of 90 °C to 75 °C. For boxes, there was a delay in fluidity development, shifting from 399°C to 410°C. The solidification temperature remained essentially unchanged for all biomasses.

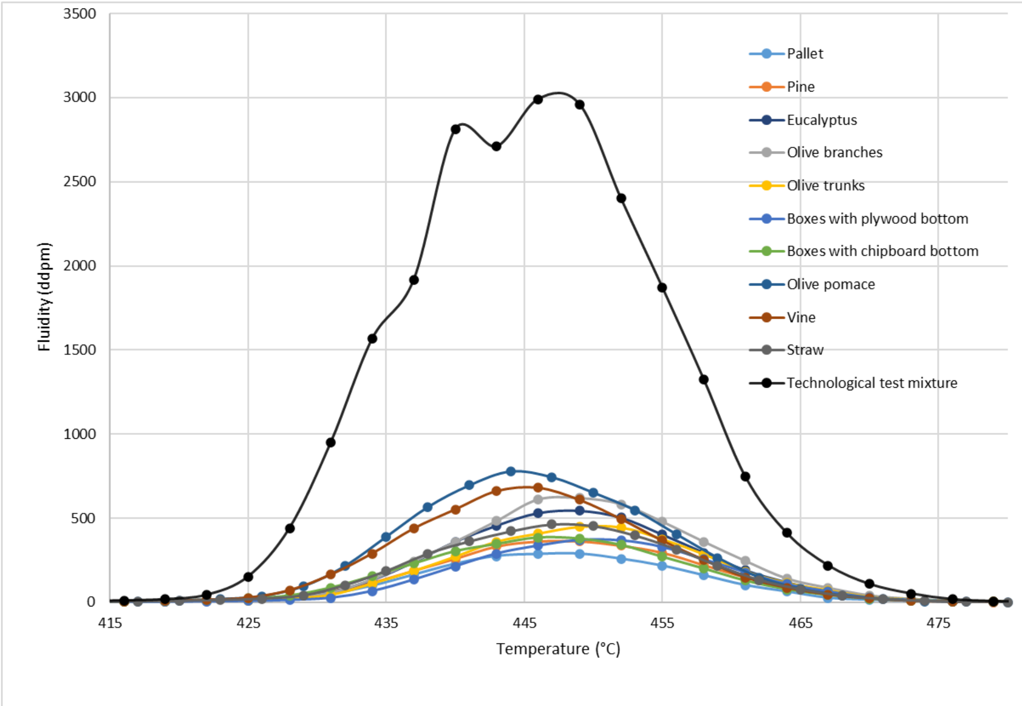

Figure 33: Graphical representation of fluidity test results with biomass addition

4.6.2 Dilation test

Below, Table 10 and Figure 34 present the results of dilation tests conducted on the reference blend with various biomass additions, consistently maintaining a substitution rate of 3%

Identification code	Description	Softening temperature (°C)	Max contraction temperature (°C)	Max dilation temperature (°C)	Max contraction	Max dilation
202348/1	Pallet	401	432	469	-8	85
202348/2	Pine	373	428	473	-21	105
202348/3	Eucalyptus	376	429	467	-20	69
202348/4	Olive branches	391	429	468	-31	81
202348/5	Olive trunks	400	435	469	-11	76
202348/6	Boxes with plywood bottom	389	433	467	-26	74
202348/7	Boxes with chipboard bottom	396	433	468	-24	48
202348/8	Olive pomace	405	433	468	-24	48
202348/9	Vine	397	434	468	-12	83
202348/10	Straw	389	431	474	-27	58
202337/7	Standard mixture	406	441	475	-22	61
202337/10	Technological test mixture	389	423	470	-20	131

Table 11: Dilation test results

As seen from the results, in all cases, biomass led to a reduction in the maximum dilation value, ranging from 131% in the blend to 48% in the case of olive pomace and chipboard boxes. Pine had the least impact, with a maximum dilation of 105%. Regarding maximum contraction, biomasses had varying effects, reducing its magnitude in some cases and increasing it in others. Compared to the blend's contraction of -20%, pallet wood, olive trunks, and vine decreased contraction (less negative value), while all others increased contraction (more negative value).

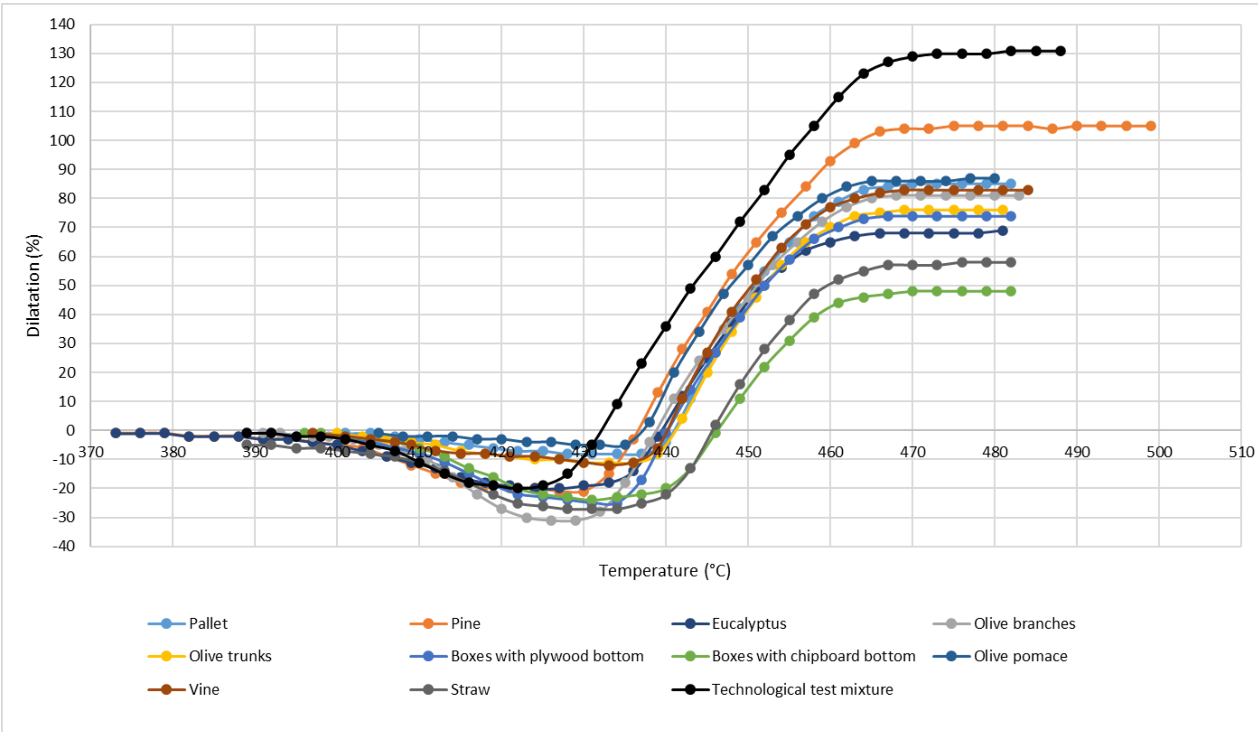

Figure 34: Graphical representation of dilation test results with biomass addition

4.7 Analysis results

The analysis of the characteristics of ten types of biomasses reveals several significant conclusions regarding their potential application in coke production as substitutes for fossil coal. The analysis begins with the selection and pretreatment of biomass, emphasizing their availability, accessibility, and suitability for the cokemaking process. Selected biomasses include industrial residues like pallets and boxes, agro-forestry residues such as pine, eucalyptus, olive branches, and trunks, and others like olive pomace and straw. The analysis detail the moisture content, ash content, and proximate analysis, highlighting the varying thermal decomposition behaviors of each biomass. Moisture content is crucial as it directly affects pyrolysis efficiency, with olive pomace showing the highest moisture content. Ash content, an essential quality metric for coke, varies significantly, with straw showing the highest content among biomasses. Thermogravimetric analysis (TGA) further elucidates the thermal stability and decomposition characteristics, revealing that woody biomasses decompose more gradually than fibrous materials. The characterization also includes ultimate and calorimetric analyses, determining the carbon, hydrogen, oxygen, nitrogen, and sulphur contents, with biomasses generally showing lower sulphur content compared to coal, which is advantageous. XRF analysis of the ash provides insights into the composition of metal oxides, with notable findings on elements like sodium, potassium, calcium, and magnesium which influence the reactivity and strength of the resulting coke. The analysis concludes with technological tests for fluidity and dilation, critical for assessing the rheological properties of the carbons during coke formation, demonstrating the impact of biomass addition on these properties. Among the biomasses analyzed, pine and eucalyptus stand out for their relatively lower ash content and higher fixed carbon content, making them promising candidates for cokemaking. Olive branches and trunks also show potential due to their moderate ash content and favourable thermal decomposition properties. However, olive pomace, despite its high moisture content, exhibits the highest carbon content, indicating a high energy yield, though its high volatile matter could affect coke yeld.

5 Selection and characterization of biochar

Three types of biochar were selected from three different suppliers, all derived from the same biomass, namely virgin wood of forest origin. The selection of the three products was based on their availability in Italy. All the biochar was produced through thermal treatments:

Product	Treatment	Temperature	Time
A	Pyrolysis	480°C	50 minutes
B	1st stage: pyrolysis	380°C	30 minutes
	2nd stage: gasification	1000°C	Few minutes
C	Pyrolysis	600°C	60 minutes

Table 12: Biochar production characteristics

The following tables show the chemical characterization of the three products.

Parameters	Values	Unit of measurement
Density	0.58	g/cm^3 DM
Moisture	40.72	%
Ash	13.66	%
Cl	0.02	% DM
S	0.056	% DM
Higher heating value	13.39	MJ/kg DM
Lower heating value	12.23	MJ/kg DM
H	0.79	%
N	0.36	%
C	45.52	%
Volatile matters	55.9	%
Fixed carbon	20.86	% DM
O	<5	% DM
Cd	<0.06	mg/kg DM
Hg	<0.1	mg/kg DM
Pb	92	mg/kg DM

Table 13: Analysis of product "A"

Parameters	Values	Unit of measurement

Density	0.36	g/cm^3 DM
Moisture	15.05	%
Ash	9.46	%
Cl	0.018	% DM
S	0.051	% DM
Higher heating value	21.66	MJ/kg DM
Lower heating value	21.02	MJ/kg DM
H	1.30	%
N	0.54	%
C	64.29	%
Volatile matters	30.9	%
Fixed carbon	34.77	% DM
O	10.97	% DM
Cd	<0.06	mg/kg DM
Hg	<0.1	mg/kg DM
Pb	1.2	mg/kg DM

Table 14: Analysis of product "B"

Parameters	**Values**	**Unit of measurement**
Density	0.51	g/cm^3 DM
Moisture	35.33	%
Ash	3.34	%
Cl	0.017	% DM
S	0.133	% DM
Higher heating value	19.43	MJ/kg DM
Lower heating value	18.28	MJ/kg DM
H	1.41	%
N	0.32	%
C	52.98	%
Volatile matters	44.6	%
Fixed carbon	33.33	% DM
O	10.10	% DM
Cd	<0.06	mg/kg DM
Hg	<0.1	mg/kg DM
Pb	2.9	mg/kg DM

Table 15: Analysis of product "C"

Below are the graphs related to the thermogravimetric analysis of each biochar.

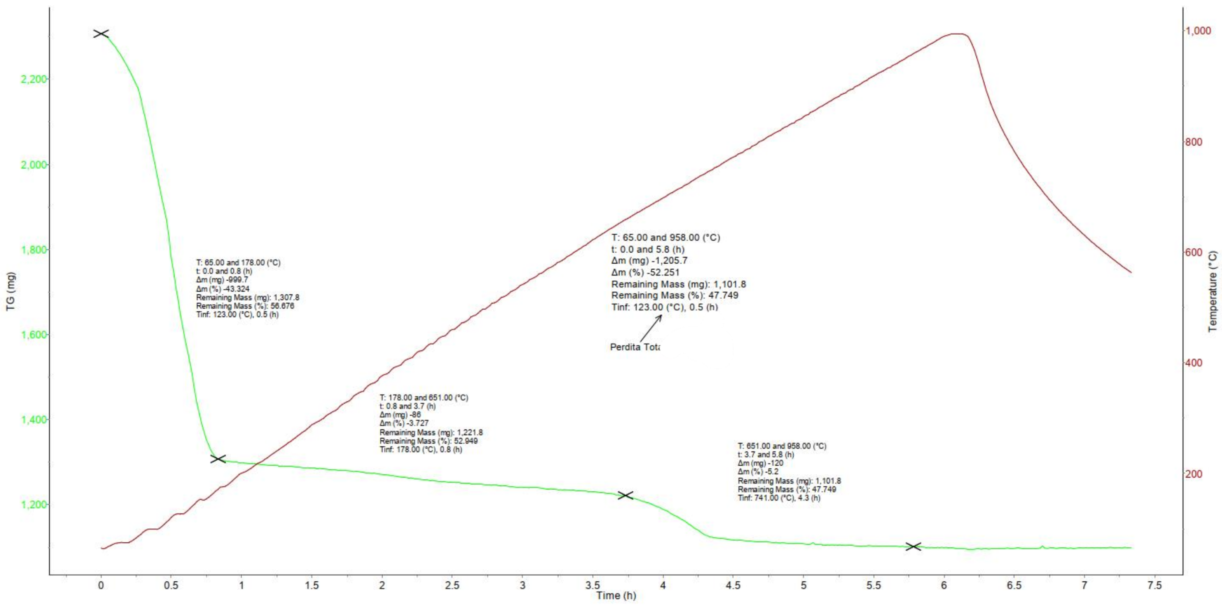

Figure 35: TG biochar "A"

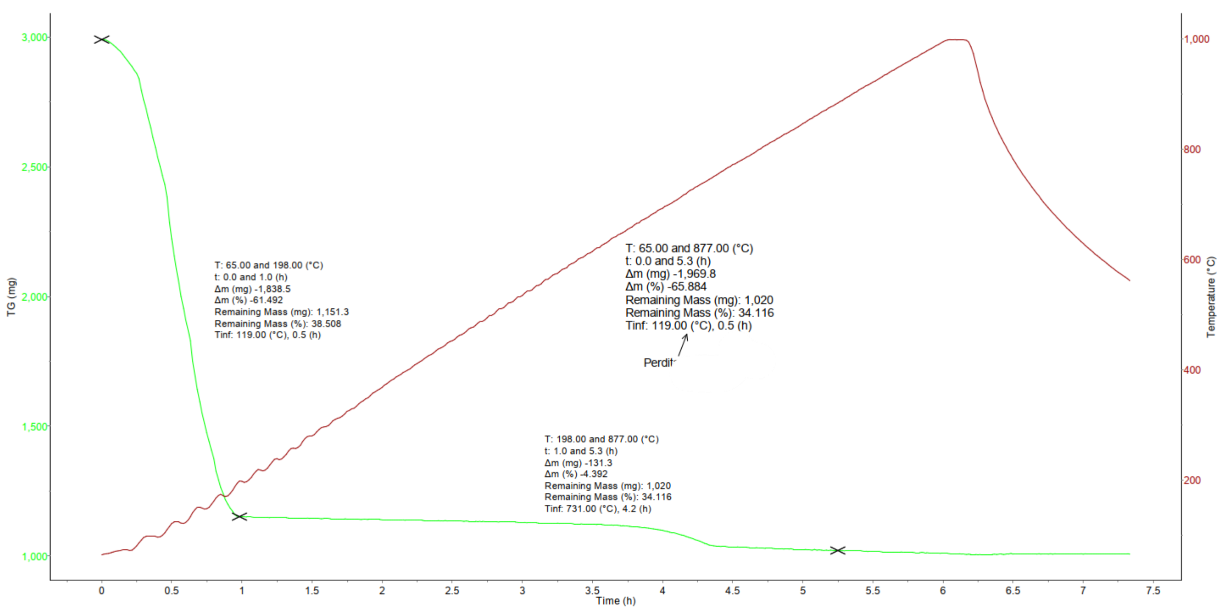

Figure 36: TG biochar "B"

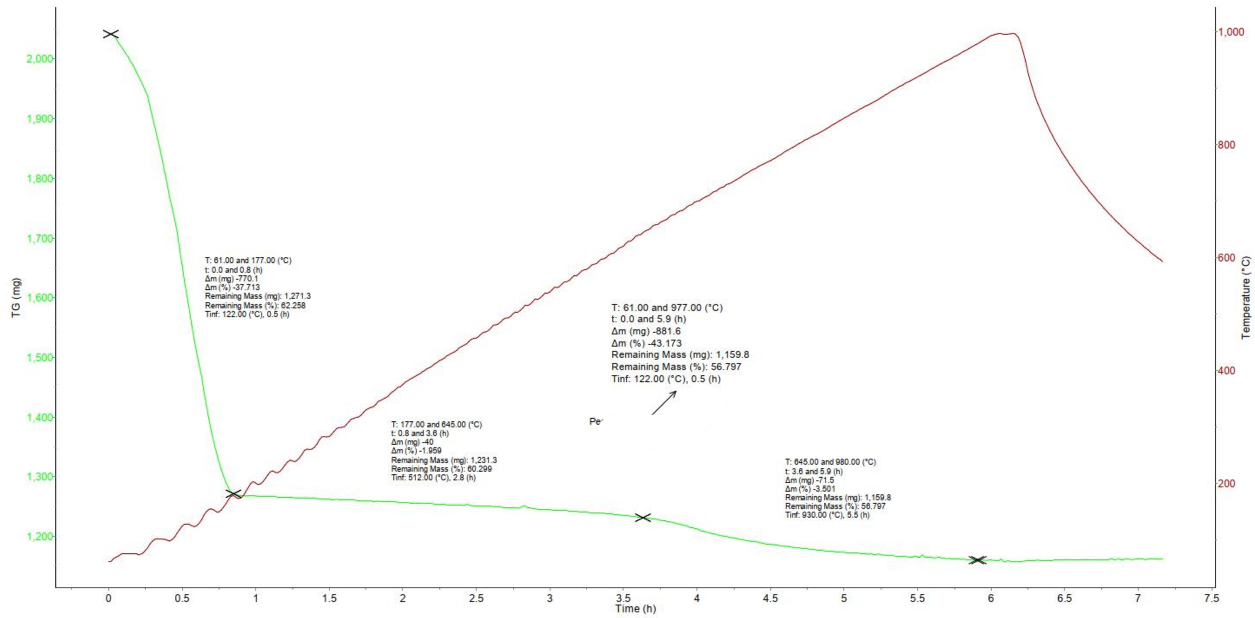

Figure 37: TG biochar "C"

The table below shows an overview of the thermogravimetric analysis performed.

Biochar	$T_{i,loss}$ [°C]	$T_{f,loss}$ [°C]	Initial weight [g]	Final weight [g]	Weight loss [g]	Percentage loss [%]
A	65	958	2.308	1.102	1.206	47.75
B	65	877	2.99	1.020	1.97	34.12
C	61	977	2.042	1.160	0.882	56.8

Table 16: TG analysis results overview

5.1 Analysis results

The analysis of the characteristics of the three types of biochar (A, B, and C), produced through slightly different thermal treatment techniques, reveals several significant conclusions regarding their potential application in coke production as substitutes for fossil coal.

Biochar B stands out due to its high higher heating value (21.66 MJ/kg) and lower heating value (21.02 MJ/kg), making it the most energy-efficient among the three. This indicates a higher combustion efficiency compared to Biochar A (13.39 MJ/kg and 12.23 MJ/kg) and Biochar C (19.43 MJ/kg and 18.28 MJ/kg).

In terms of chemical composition, Biochar B has the highest fixed carbon content (34.77%), followed by Biochar C (33.33%) and Biochar A (20.86%). A high fixed carbon content is desirable in coke production for producing high-quality coke.

Additionally, Biochar C has significantly lower ash content (3.34%) compared to Biochar B (9.46%) and Biochar A (13.66%). Lower ash content indicates cleaner combustion and fewer solid residues, which is advantageous for waste management.

Biochar A has the highest volatile matter content (55.9%), followed by Biochar C (44.6%) and Biochar B (30.9%). Lower volatile matter content is generally preferred in coke production to achieve more stable and predictable combustion.

From an environmental sustainability perspective, Biochar B has the lowest lead levels (1.2 mg/kg), while Biochar A has the highest (92 mg/kg). The presence of heavy metals such as lead is a critical factor for the environmental impact and safety of the final product.

Thermogravimetric analyses indicate the thermal stability and degradation behavior of each biochar. Biochar B, with its dual-stage treatment (pyrolysis followed by gasification), shows greater resistance to thermal decomposition, making it particularly suitable for high-temperature applications typical in coke production.

In conclusion, Biochar B emerges as the most promising candidate for replacing fossil coal in coke production due to its high heating value, high fixed carbon content, and low levels of impurities. However, Biochar C also shows significant potential, especially in terms of low ash content and a good balance between volatiles and fixed carbon. Biochar A, while having some favorable characteristics, is less competitive due to its lower heating value and higher content of ash and volatiles.

6 Conclusions

The BIOCODE project focuses on exploring sustainable alternatives to fossil coal in steel coke production by utilizing biomass and biochar. This initiative aims to reduce greenhouse gas emissions and promote carbon-neutral energy sources. The research involves selecting and characterizing various types of biomasses available in the Mediterranean region, particularly in Apulia, Italy. The selected biomasses, which include industrial and agro-forestry residues like olive branches, pine, and eucalyptus, were chosen based on their availability, accessibility, and proximity to the Taranto steel plant. Biomass samples were pre-treated by chipping to standardize their size for further analysis. Chemical, physical, and technological analyses were conducted to assess their suitability for coke production. Key parameters included carbon content, moisture, and the presence of impurities such as sulphur and phosphorus. The findings indicate that biomasses with high carbon content and low levels of undesirable elements are more suitable for replacing fossil coal without compromising the quality and efficiency of the coke production process.

In addition to biomass, the project evaluated three types of biochar derived from virgin wood through different thermal treatments. These biochar were analyzed for their heating values, fixed carbon content, ash content, and volatile matter. Biochar B emerged as the most promising candidate due to its high energy efficiency, high fixed carbon content, and low levels of impurities. Biochar C also showed potential, particularly for its low ash content and balanced composition, while Biochar A was less competitive due to its lower heating value and higher ash and volatile content.

Thermogravimetric analyses of the biochar revealed differences in thermal stability and degradation behavior, further informing their potential applications in high-temperature processes like coke production. Overall, the BIOCODE project demonstrates the feasibility of using locally available biomass and biochar as sustainable substitutes for fossil coal, contributing to the decarbonization of the steelmaking industry while maintaining the desired metallurgical properties of the final product.