



# BELENUS

## Lowering Costs by Improving Efficiencies in Biomass Fueled Boilers: New Materials and Coatings to Reduce Corrosion

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## BELENUS

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## Executive Summary

Biomass is a renewable, CO<sub>2</sub>-neutral energy resource widely available and increasingly used as an alternative to fossil fuels for energy supply.

For effective utilization of biomass fuel, the knowledge of their characterization is essential. The constituents of biomass fuel vary from region to region. Constituents of biomass depend upon sources from which biomass is collected and its method of preparation [1].

Combustion is a complex phenomenon involving simultaneous heat and mass transfer with chemical reactions and fluid flow. Using an analogy to coal combustion, the biomass combustion can be considered as a three stage process: drying in order to evaporate any water in the fuel at 100-200°C, the volatiles and char release (devolatilisation or pyrolysis) at 200-350°C and the subsequent combustion of the remaining char formed from the previous stage. The water content is significant and important and in some instances may dominate the biomass combustion process.

Combustion characteristics of biomass, as well as sewage sludge, have been studied widely using thermo-analytical techniques. The advantages of thermogravimetric analysis are its rapid assessment of the fuel value, the temperatures at which combustion starts and ends, and other parameters such as maximum reactivity temperature, ash amount and total combustion time [2]. Thermogravimetric analysis is very useful for studying the kinetic of combustion processes. Thermal methods like thermogravimetry (TG), derivative thermogravimetric (DTG) and differential thermal analysis (DTA) have been used for studying an enormous variety of combustion areas. Thermal analysis (TA) determines a set of methods for knowing the selected physical properties of the substance under the temperature influence. Sometimes, simultaneously, the environment (pressure, atmosphere chemical composition, etc.) can be changed. TG is a technique that monitors the sample mass as a function of temperature or time when the sample is subjected to a controlled temperature program. DTG is based on the mass loss rate. DTG profiles make it possible to know, for example, the mass loss that is taking place at a temperature during the combustion process. DTA enables measuring the thermal effects during the studied process. The obtained peaks correspond with exothermal or endothermal reactions.

As part of Work Package 1, agricultural straw (Spain), forestry residue (Scotland) and industrial wood waste (England) have selected to be employed within the framework of BELENUS. These fuel sources have been characterized with regards to the physico-chemical, chemical and thermal properties. The analysis of the three fuels are presented in this report, including the determination of heating value, immediate analysis, elemental analysis, ash analysis, biomass particle size, ash melting point, thermogravimetric and simultaneous differential thermal analysis (SDTA) analysis. The corresponding characterization techniques for these properties are also presented.

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## 1. Introduction

Due to the gradual degradation of the quality of fossil fuels, and consequently, its increasing potential for greenhouse gas emission, acid rain, and climate change problems, renewable energy sources are getting strong interest around the world in place of fossil fuel [3]. Biomass is one of the most attractive renewable and sustainable energy source and an alternative to fossil fuels because it is abundant, clean, and carbon neutral resource [4].

Development of technologies for multiple fuel firing made that biomass a cheap and effective fuel option. However, biomass and wastes have a large amount of impurities (potassium, chlorine and sulphur) that results in the formation of deposits and corrosive gases. They cause problems in the operation in the boiler [5]. Compared with fossil power plants, the content of water vapour, alkali chlorides and hydrogen chloride is higher in biomass- and waste-fired plants (see Table 1) [6]. Such species are highly corrosive towards superheaters, resulting in lower electrical efficiency and higher maintenance costs. On the other hand, the major ash forming elements (Al, Si) and the composition of the gas phase ( $O_2$ ,  $N_2$ ,  $H_2O$ , etc.) have significant influence on the behaviour of chlorine and alkali metals and corrosion formation in heating units [7].

*Table 1. Approximate flue gas composition (volume %) in waste-, biomass and coal-fired boilers.*

Fuel	$O_2$ (%)	$H_2O$ (%)	$SO_2$ (ppm)	HCl (ppm)	KCl+NaCl (ppm)
Coal	~4-5	~4-16	~400-1200	~10-50	-
Biomass	~5-10	~10-20	~0-70	~25-1000	~5-50
Waste	~5-11	~10-20	~0-150	~250-1300	~<120

The corrosion rate in fossil power plants (e.g. coal-fired power plants) is considerably lower than that shown by biomass plants. Thus, the steam temperature can be kept high (e.g. 650 °C) in fossil power plants, while for biomass and waste power plants, the range of temperature is between 350 and 550 °C. However, the electrical efficiency decreases as steam temperature is reduced. For this reason, it is necessary to investigate these corrosion phenomena, in order to find suitable solutions.

In a combustion plant, corrosion attack may occur on almost all metallic structural parts that are in contact with the fuel, combustion air, flue gas or residual products of combustion [8]. Critical parts of a power plant, such as superheaters and water walls, are severely damaged by these corrosion processes that occur at high temperatures in such environments.

Superheater corrosion often occurs due to high material temperatures in combination with alkaline compound phases with low melting points and a reducing atmosphere, which may occur if the fuel is not completely burned when it reaches the superheater. The melting point of the ash depends on its composition, which is principally enrichment with potassium and chloride.

Corrosion phenomenon deteriorates if there is chlorine available in the fuel system. In particular, alkali chlorides cause superheater corrosion both by lowering the first melting temperature (FMT) of superheater ash and by releasing chlorine when they react with sulphur compounds to form sulphates. Alkali salts can form low melting temperature eutectics with other ash materials or can themselves be molten on the tube surface, depending on the superheater temperature. KCl is more corrosive than NaCl and has a lower melting temperature. As in recovery boilers, the presence of molten phases at the tube surface causes accelerated corrosion. Therefore, biomass boiler operators similarly keep tube temperatures well below the FMT of fireside deposits to avoid rapid corrosion. The release of chlorine by the sulphation of ash deposits can produce active corrosion [9].

With the exception of wood and a handful of other fuel crops, biomass fuels contain significantly higher concentrations of chlorine than coal. Field crops, with the exception of nutshells, pits and switchgrass, contain more chlorine than woody materials.

The situation is even worse when the melting point, and thus the threshold for the formation of salt melts on the superheater surfaces, are lowered further. This can take place when transition metals that may form volatile chlorides and sulphates with low melting points, such as Cu, Pb and Zn, are included in the fuel system in significant quantities. These elements are usually present in industrial waste and other industrial recovered fuels, and also in

demolition wood, for instance. Demolition wood is a low-cost biomass fuel, but it sometimes contains Pb and/or Zn impurities that form extremely low melting temperature ashes which cause rapid corrosion on low alloy tube materials [9]. Much of the research on corrosion by Pb and Zn impurities has been done for municipal waste incinerators. Spiegel [10] showed that, if HCl is present in the flue gases, temperatures above about 400 °C can convert  $\text{ZnSO}_4$  and  $\text{PbSO}_4$  to volatile chlorides even if the partial pressure of  $\text{SO}_2$  is relatively high. These volatile chlorides condense on fly ash particles and on superheater tubes, forming molten or sticky deposits or eutectics like KCl-ZnCl<sub>2</sub>.

A corrosion attack can be mitigated in two ways: improving the materials or changing the surrounding environment of the materials. BELENUS aims to expose a number of superheater and reheater materials with protective coatings in some representative biomass environments. For this purpose, representative samples from agricultural waste, industrial waste and wood residues will be employed to evaluate different biomass environments.

Based on previous considerations, for effective utilization of biomass fuel the knowledge of their characterization is essential [11]. The constituents of biomass fuel vary from region to region and depend upon sources from which biomass is collected and method of preparation of biomass. This report provides with a complete characterization of the biomass fuels selected for this project, in terms of its physico-chemical properties which can be useful to anticipate and understand their behaviour in the combustion process.

## 2. Results and Discussion

The combustion properties of a fuel depend on several chemical and physical conditions that are unique or are linked. These properties can also make the fuel more or less appropriate for firing in certain types of equipment. Sufficient information must be available for optimal use of a fuel with regard to efficiency, environmental impact and economy.

For all determinations of both chemical and physical parameters, it is of vital importance that sampling and sample preparation is done correctly before the corresponding analysis is carried out, to ensure that each individual particle has the same opportunity of being included in the analysis samples. The origin and size of the fuel and the sampling place (truck, heap, etc.) determine how sampling, sample reduction and sample preparation should be carried out.

Prior to physical and chemical characterization, received samples were allowed to air-dry at room temperature and then were pelletized. For laboratory analysis, biomass pellets were previously grounded.

### 2.1. Physical and Chemical characterization

A brief description of the methods employed for the determination of the parameters which characterize biomass as an energy source, is shown below, with mention of the technical standards in routine use for solid biofuels characterization at Centre for the Development of Renewable Energy Sources (CEDER)-CIEMAT laboratories (.).

**Sampling Preparation:** It is performed under CIEMAT-CEDER LCB internal procedure, following CEN/TS 14780 (Solid Biofuels - Methods for sample preparation) technical specifications for biomass sample pre-treatment prior to analysis, which is based on different stages such as homogenisation, grinding and drying.

**Moisture content:** This is an important fuel property for assessing wildfire hazard, since it influences fuel flammability and fire behaviour. An internal proceeding is carried out for determining the total moisture in biomass, which is based on simple mass-loss steps until reaching a constant value when sample it is heated at 105°C. This procedure stems from EN 14774-2 European Standard ("Solid Biofuels - Methods for the determination of moisture content – Oven dry method – Part 2: Total moisture – Simplified method").

**Proximate analysis:** It gives ash (550 °C) and volatile matter (950 °C) on percentage weight basis.

- **Ash 550 °C:** It is based on a slow combustion of the biomass sample by different set heating ramps to reach 550 °C, in order to avoid elements release. This procedure derives from European Standard EN 14775 "Solid Biofuels - Method for the determination of ash content". The resulting ash is analysed for major elements determination (Ca, K, P, S, Fe, Al, Mg, Na and Si). Significant differences in combustion properties of biomass is observed on the basis of their ash composition.
- **Volatile matter 900 °C:** Volatile matter is determined as the loss in mass, less that due to moisture, when a sample is heated at 900 °C for a period of 7 minutes. This procedure is undertaken out of contact with air under standardised conditions. Volatile matter is determined according to the procedures outlined in European Standard EN15148-2009 ("Solid biofuels - Method for the determination of the content of volatile matter").

**Ultimate Analysis, C, H, N:** It is performed under internal procedure for carbon, hydrogen and nitrogen determination in biomass, which arises from "Solid biofuels - Determination of total content of carbon, hydrogen and nitrogen - Instrumental methods - SS-EN 15104:2011" European Standard. TruSpec (Leco) elemental analyser is employed for this analysis.

**Chlorine and sulphur:** The concentration of these elements is determined by ion chromatography, after previous Cl-S aqueous extraction from the sample in the calorimetric bomb. The methodology is based on “EN 15289 Solid biofuels — Determination of total content of sulphur and chlorine” standard, which reports on the analysis of chlorine and sulphur in biofuels.

**Oxygen:** It is obtained by subtracting the sum of C, H, N and S contents from 100.

**Higher heating value (HHV) at Constant Volume:** The highest heating value (HHV), at constant volume, is defined as the quantity of heat generated by complete combustion of a mass unit of sample, in an oxygen atmosphere, under standard conditions. It is determined under internal procedure for heating value determination in biomass by means of automatic calorimeters (LECO AC-300 or IKA C-5000), performing the combustion of the biomass with oxygen in excess under controlled conditions. European Standard (EN) 14918 “Solid Biofuels - Determination of calorific value” procedure is undertaken for this measurement. Corrections for side reactions such as producing nitric and sulfuric acids from the nitrogen and sulphur impurities in the biomass are determined.

To determine this parameter on a wet basis, next equation is applied:

$$HHV_{v,x} = HHV_{v,o} (1 - 0.01X)$$

where:

$HHV_{v,x}$  = Higher heating value at constant volume (kJ/kg) with X percent moisture .

$HHV_{v,o}$  = Higher heating value at constant volume, determined by calorimeter (kJ/kg), for zero moisture content.

X = Biomass moisture, % (w.b).

**Lower heating value at constant pressure:**

- On dry basis: is numerically equal to difference between the high heating value and the amount of heat required to the separation of water contained in fuel, and also the water produced in the hydrogen combustion process. In addition, some corrections included in the European Standard (EN) 14918 are made to convert the value from “constant volume” to “constant pressure” conditions. Resulting equation applied is shown below:

$$LHV_{p,o} = HHV_{v,o} - 212.2H_o - 0.8(O_o + N_o)$$

where:

$LHV_{p,o}$  = Lower heating value at constant pressure (kJ/kg) for zero moisture content.

$H_o$  = Hydrogen content in biomass, % (d.b).

$O_o$  = Oxygen content in biomass, % (d.b).

$N_o$  = Nitrogen content in biomass, % (d.b).

Oxygen content in biomass is determined as follow:

$$O_o = 100 - (C_o + H_o + N_o + Ash_o + Cl_o + S_o)$$

where:

$Ash_o$  = ash content in biomass, % (d.b).

$Cl_o$  = chlorine content in biomass, % (d.b).

$S_o$  = sulphur content in biomass, % (d.b).



- On wet basis:

To transform the LHV on dry basis ( $LHV_{p,o}$ ) to a specific humidity ( $LHV_{p,x}$ ), the following dry-to-wet-basis formula is been applied:

$$LHV_{p,x} = LHV_{p,o} (1 - 0.01X) - 24.43X$$

where:

$LHV_{p,x}$  = lower heating value on wet basis (kJ/kg).

$LHV_{p,o}$  = lower heating value on dry basis (kJ/kg).

X = biomass moisture content (% w.b.).

These methods employed for biomass samples have been also applied for ash samples characterization. Unburned carbon in ashes is calculated as a subtraction of the ash content, obtained after sample calcination in furnace at 550 °C for 24 h, from the total percentage (100%).

**Fusibility:** This test is performed on ash calcined at 550 °C and ground within 0.250 mm. A cylindrical tablet of 3 mm in diameter by 3 mm in height is prepared. The sample is introduced into the furnace optical microscope LEICA heating mark where a light beam incident on the tablet reflecting its silhouette. The oven temperature program is:

- From room temperature up to 550 °C, ramp 60 °C per minute.
- From 550 °C up to 1400 °C, ramp 10 °C per minute.

A digital camera records a video with images of the silhouette of the tablet as the oven temperature increases. At the same time, the program automatically records various dimensional parameters (shape factor, angles of corners, etc.), which are used to determine four characteristic temperatures:

- Initial deformation temperature (TDI).
- Temperature sphere (TE).
- Hemispherical temperature (TS).
- Fluid temperature (TF).

This internal procedure derives from the Technical Specification CEN / TS 15370-1 "Solid Biofuels -Methods for the determination of ash melting behaviour".

**Major elements:** The analysis of major elements in biomass and ash samples (Al, Ba, Ca, Fe, K, Mg, Na, P, S, Si, Sr, Ti and Zn) is undertaken under internal procedure, which is based on microwave acid digestion of the biomass sample or ash sample (obtained at 550 °C), following the instrumental method described in CEN/TS 15290 "Solid Biofuels - Determination of major elements". Digested samples are analysed by inductively coupled plasma atomic emission spectrometry making use of IRIS-AP Thermo Jarrell Ash Simultaneous ICP-OES Spectrometer. Next equation is employed to calculate major elements composition in the ash sample with respect to that determined in the original biomass sample or in the reverse order:

$$\% \text{Element- biomass} = \% \text{Element-ash} * 0.01 * \% \text{ash}$$

This equation is not commonly applied to sulphur case, as part of this element is released during calcination.

**Heavy metal analysis in ash samples** (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, V):

- Samples digestion: Samples are crushed, homogenized and pulverized in an agate mortar around to 100 µm. The method consists of two-stage digestion by microwave oven. In the first step, 10 ml of concentrated  $\text{HNO}_3$  is added to 100 mg sample. The mixture is then introduced in microwave oven under conditions detailed in table 2.

*Table 2. First stage microwave heating program.*

STAGE	1	2	3	4
Power / W	100	100	100	100
Pressure / psi	40	80	120	120
Time / min	20	10	10	30
T, P <sub>max</sub> / min	5	5	5	20
Fan / %	100	100	100	100

Once solutions are cooled, 2.5 ml of concentrated HF and 2.5 ml of 30% H<sub>2</sub>O<sub>2</sub> are added in the second stage. After standing for 1 hour, microwave conditions presented in table 3 are applied.

*Table 3. Second stage microwave heating program.*

STAGE	1	2	3	4
Power / W	100	0	0	0
Pressure / psi	120	0	0	0
Time / min	25	0	0	0
T, P <sub>max</sub> / min	20	0	0	0
Fan / %	100	100	100	100

Finally solutions evaporated to dryness under IR lamp and the residue is partly dissolved in 2% HNO<sub>3</sub> and rinse with water to 50 ml. Blackish colour residue remains after this pre-treatment.

- **Sample analysis:** samples digestions are filtered and analysed by inductively coupled plasma atomic emission spectrometry, using VARIAN 735-ES model. Multi-element standard samples prepared in laboratory are employed for instrument calibration, using different concentration ranges and the most suitable conditions for this type of analysis. Successive dilutions are required to determine those elements which are present in high concentrations.

**Direct Hg analysis:** Hg content in samples is determined by direct analysis making use of Milestone DMA-80 Hg analyser. A solid or liquid sample is weighed into a quartz or metal boat, and the sample weight is transferred from the analytical balance to the DMA-80. Sample boats are loaded onto the instrument autosampler. Samples are first dried and then thermally decomposed in an oxygen-rich furnace. Mercury and other combustion products are released from the sample and they are carried to the catalyst section of the furnace, where nitrogen and sulphur oxides, as well as halogens and other interfering compounds, are eliminated. Mercury is selectively trapped, in a separate furnace, through gold amalgamation. Combustion by-products are flushed off. The amalgamation furnace is heated and mercury is rapidly released. Mercury is flown via the carrier gas into a unique block with a dual-cell or tri-cell arrangement, positioned along the optical path of the spectrophotometer, where it is quantitatively measured by atomic absorption at 253,65 nm. The system combines an innovative mercury measuring system with a unique optical path spectrophotometer, achieving a detection limit of 0.0015 ng of mercury.

### 2.1.1. Agricultural Straw

Physicochemical characterization of biomass fuels selected for BELENUS experiments has been conducted. Table 4 shows the proximate analysis, ultimate analysis and heating value of both wheat and barley straw samples. Results exhibit quite similar properties for both straw types. Although barley straw presents a bit higher heating value and

lower moisture content which indicate better burning properties. Ash percentage is also lower in barley straw. The most significant difference between both straw samples is found for chlorine content, with a 0.39 wt% higher in barley straw samples than in wheat straw, which may enhance corrosion processes. Chlorine can form HCl and leave the combustion plant in gaseous form, but it can also be found to ash during salt formation, particularly in alkaline ash. Chlorine is therefore an ash-forming component, although chlorine is not always bound to the ash.

*Table 4. Proximate analysis, ultimate analysis, and HHV of wheat and barley straw samples.*

	Parameter	Units	Wheat straw	Barley straw
As Received Analysis	Moisture	%	8.30	7.20
	Volatiles	%	69.50	73.20
	Fixed Carbon	%	17.30	15.40
	Ash	%	4.90	4.20
	Calorific Value (Higher Heating Value)	kcal / kg	16.40	16.70
	Carbon	%	41.80	42.60
	Hydrogen	%	6.40	6.30
	Nitrogen	%	0.56	0.72
	Sulphur	%	0.11	0.11
	Chlorine	%	0.18	0.57
Net	Calorific Value (Lower Heating Value)	MJ / kg	14.00	14.90
Dry Analysis	Ash	%	5.30	4.50
	Calorific Value	MJ / kg	15.90	16.10
Dry Ash Free Analysis	Volatiles	%	80.10	82.60
	Calorific Value	MJ / kg	16.80	16.80
	Hydrogen	%	7.40	7.10

Table 5 includes ash analyses for both straw samples types evaluated. One of the most remarkable differences found is sodium concentration, which is observed to be significantly higher in barley straw. Sodium generally occurs in much lower contents than calcium and potassium, but has a great influence on ash-related problems in combustion plants. Alkali metals (Na, K) can form volatile forms (e.g. chlorides) that can be vaporized and condense back at a later stage. On contrast, major content of aluminium has been detected in wheat straw.

With respect to trace metals, it is noteworthy mercury content in wheat straw which is twice than that determined in barley straw. Vapour pressure of metallic mercury even at low temperatures is sufficient to permit the mercury vapours to pass through the system and alloy with many commercial metals. This amalgamation of such metals can result in stress cracking or severe corrosion. It has been shown that metallic mercury reacts with many environments to a sufficient extent to produce compounds that are corrosive to commercial metals. It has been demonstrated that concentrations of mercury compounds as low as 0.5 ppm constitute a serious corrosion hazard for a variety of useful metals and alloys [12].

The elevated chlorine and sodium concentration encountered in barley straw represents extreme corrosive conditions in contact to metals alloys. This fact together with barley straw presents a better application as feeding for ruminant animals contrary to wheat straw that is usually burned, justifies the use of wheat straw as cereal straw in BELENUS.

*Table 5. Ash Analyses for wheat straw and barley straw samples in mg/kg or ppm.*

Element	Units	Wheat straw	Barley straw
Al	mg/kg	240	130
Ba	mg/kg	15	16
Co	mg/kg	<6	<6
Cr	mg/kg	28	26
Cu	mg/kg	10	14
K	mg/kg	8200	8000
Mn	mg/kg	29	21
Na	mg/kg	190	2300
Ni	mg/kg	17	15
Pb	mg/kg	<6	<6
Rb	mg/kg	3.5	4.0
Sn	mg/kg	<6	<6
Sr	mg/kg	9.3	28
Tl	mg/kg	8	8
V	mg/kg	<6	<6
Zn	mg/kg	14	23
Zr	mg/kg	16	15
As	mg/kg	-	-
Sb	mg/kg	<6	<6
Cd	mg/kg	<6	<6
Hg	µg /kg	27	13
Br	mg/kg	9.3	15
Ca	mg/kg	4500	4100
Fe	mg/kg	230	170
Mg	mg/kg	1100	1200
P	mg/kg	700	1000
Si	mg/kg	17000	12000
Ti	mg/kg	8	8

### 2.1.2. Forestry Residues

Forestry residues have been characterized with respect to its physicochemical properties. Results are included in Table 6. In comparison to straw samples previously commented, the moisture content is significantly lower, while the volatiles content is higher. Important ash content is determined for this biomass in comparison to straw.

With regards to the ultimate analysis, it is remarkable the low sulphur and chlorine content of this biomass residue in comparison to agricultural residues. Sulphur may form  $H_2S$ ,  $SO_2$  and  $SO_3$ , and also follow-on products. In an oxidizing environment, mainly  $SO_2$  is formed together with minor quantities of  $SO_3$  (usually < 5 %). Both can bind to alkaline ash, although  $SO_2$  is a weaker acid than  $SO_3$  and therefore binds more loosely. However, the main product  $SO_2$  can be arrested during binding to alkaline ash if it is oxidized up to  $SO_3$  simultaneously with the desulphurizing stage. A product is then a sulphate instead of the less stable sulphide. However, sulphur has a low tendency to form toxic organic compounds in or after the combustion environment.

*Table 6. Proximate analysis, ultimate analysis, and HHV of forestry residues samples.*

	Parameter	Units	Forestry Residue
As Received Analysis	Moisture	%	4.30
	Volatiles	%	74.70
	Fixed Carbon	%	12.20
	Ash	%	8.80
	Calorific Value (Higher Heating Value)	kcal / kg	16.30
	Carbon	%	46.10
	Hydrogen	%	6.10
	Nitrogen	%	0.70
	Sulphur	%	0.30
	Chlorine	%	0.08
Net	Calorific Value (Lower Heating Value)	MJ / kg	14.90
Dry Analysis	Ash	%	9.20
	Calorific Value	MJ / kg	15.60
Dry Ash Free Analysis	Volatiles	%	86.00
	Calorific Value	MJ / kg	17.10
	Hydrogen	%	7.00

Table 7 presents ash analyses for forestry residues. Compared with straw samples, significant differences are observed. In relation to ash-forming light metals, attention is drawn to alkali metals (Na and K) with much lower concentration found in forestry residues in comparison to straw, especially for potassium case. This aspect is due to the fact that potassium, together with phosphorus, is employed for soils fertilisation in cereals crops. Phosphorus content in straw samples is thus encountered in much higher concentrations. The lower alkali metals content determined in forestry residues together with the low chlorine concentration would involve a reduction of corrosion processes due to alkali chlorides during combustion.

On contrast, aluminium, iron and calcium are found in important contents, in comparison to straw. Much of the reported aluminium in biofuel ashes is originated from entrained clay earths. Aluminium in combustion processes normally forms no volatile compounds. It is usually found in bottom ash or distributed between bottom ash and fly ash. However finely distributed aluminium forms can be entrained with the flue gas and enriched to fly ash and dust.

Another remarkable difference with regards to straw composition is related with heavy metals content, with major concentrations determined for elements such as chromium, nickel and lead and also for trace metals such as mercury, antimony, titanium, tin, strontium, cobalt and zinc.

*Table 7. Ash Analyses for forestry residues samples.*

Element	Units	Forestry Residue
<b>Al</b>	mg/kg	3400
<b>Ba</b>	mg/kg	120
<b>Co</b>	mg/kg	10
<b>Cr</b>	mg/kg	62
<b>Cu</b>	mg/kg	2600
<b>K</b>	mg/kg	1800
<b>Mn</b>	mg/kg	170
<b>Na</b>	mg/kg	1400
<b>Ni</b>	mg/kg	61
<b>Pb</b>	mg/kg	550
<b>Rb</b>	mg/kg	10
<b>Sn</b>	mg/kg	83
<b>Sr</b>	mg/kg	48
<b>Tl</b>	mg/kg	< 6
<b>V</b>	mg/kg	< 6
<b>Zn</b>	mg/kg	1700
<b>Zr</b>	mg/kg	10
<b>As</b>	mg/kg	< 6
<b>Sb</b>	mg/kg	17
<b>Cd</b>	mg/kg	< 6
<b>Hg</b>	µg /kg	95
<b>F</b>	mg/kg	
<b>Br</b>	mg/kg	< 6
<b>Ca</b>	mg/kg	11000
<b>Fe</b>	mg/kg	4500
<b>Mg</b>	mg/kg	1200
<b>P</b>	mg/kg	300
<b>Si</b>	mg/kg	14000
<b>Ti</b>	mg/kg	900

### 2.1.3. Industrial wood waste

Physicochemical characteristics of industrial wood waste have been determined in terms of proximate analysis, ultimate analysis and heating value. Results are shown in table 8. A comparison among calorific values, proximate and ultimate analyses obtained for the diverse biomasses evaluated is plotted in figures 1, 2 and 3 respectively. The major calorific value (figure 1) has been obtained for industrial wood waste. Proximate analysis (figure 2) is quite similar to that determined for forestry residues, with slightly higher volatiles and fixed carbon content. The most significant difference is found for ash content which is 6% lower in waste wood case.

With respect to ultimate analysis (figure 3), major carbon and nitrogen content has been encountered for this biomass with respect to forestry residues. It is remarkable the low sulphur and chlorine content of this biomass residue in comparison to agricultural residues. Sulphur may form  $H_2S$ ,  $SO_2$  and  $SO_3$ , and also follow-on products. In an oxidizing environment, mainly  $SO_2$  is formed together with minor quantities of  $SO_3$  (usually < 5 %). Both can bind to alkaline ash, although  $SO_2$  is a weaker acid than  $SO_3$  and therefore binds more loosely. However, the main product  $SO_2$  can be arrested during binding to alkaline ash if it is oxidized up to  $SO_3$  simultaneously with the desulphurizing stage. A product is then a sulphate instead of the less stable sulphide. However, sulphur has a low tendency to form toxic organic compounds in or after the combustion environment.

**Table 8. Proximate analysis, ultimate analysis, and HHV of waste Industrial Wood.**

	Parameter	Units	Waste wood
As Received Analysis	Moisture	%	4.40
	Volatiles	%	78.70
	Fixed Carbon	%	14.30
	Ash	%	2.60
	Calorific Value (Higher Heating Value)	kcal / kg	18.10
	Carbon	%	48.50
	Hydrogen	%	6.10
	Nitrogen	%	1.76
	Sulphur	%	0.05
	Chlorine	%	0.08
Net	Calorific Value (Lower Heating Value)	MJ / kg	16.70
Dry Analysis	Ash	%	2.70
	Calorific Value	MJ / kg	17.50
Dry Ash Free Analysis	Volatiles	%	84.60
	Calorific Value	MJ / kg	18.00
	Hydrogen	%	6.60

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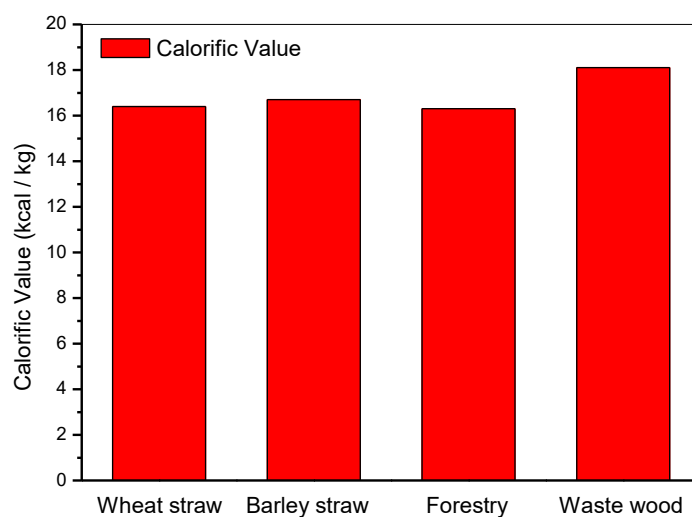


Figure 1. Calorific values obtained for the different biomass fuels studied.

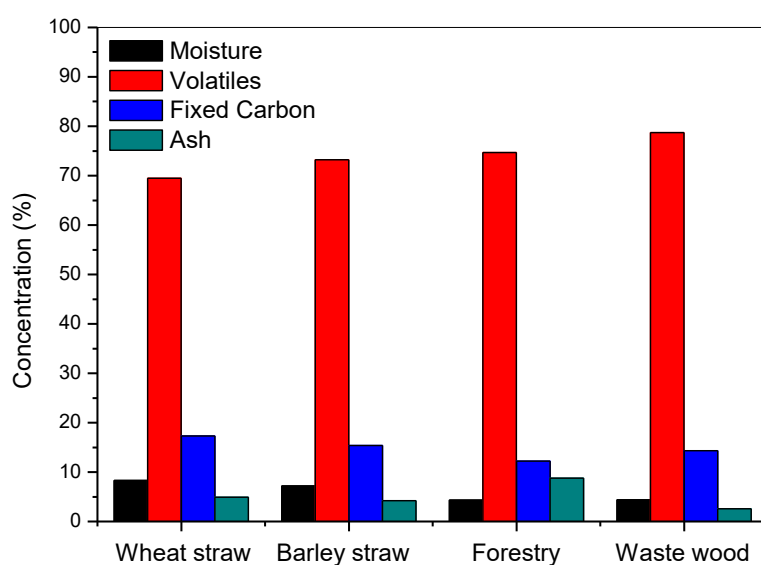


Figure 2. Proximate analysis comparison for the biomass fuels evaluated.

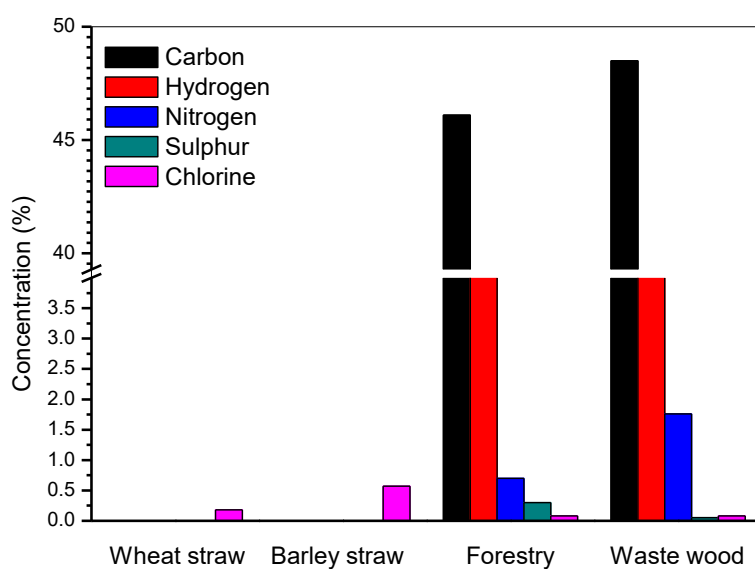


Figure 3. Ultimate analysis comparison for the biomass fuels evaluated.



Table 9 shows ash composition obtained for industrial wood waste. Figure 4 compares ash forming light metals (Al, Ca, K, Mg and Na) content in the different biomass samples studied. In comparison to forestry residues, ash-forming- light metals are found in significantly lower concentrations. The same applies to iron and silicon.

With regards to heavy metals content, previous research [13] has concluded that recovered wood waste contains elevated amounts of heavy metals, causing environmental problems during waste management. Figures 5 and 6 compare heavy metals and trace metals content, respectively, determined in the different biomasses evaluated. In this case, heavy metals content is found in lower quantities than that determined in straw samples. On contrast, when results obtained for waste wood are compared with forestry residues, minor contents are encountered for heavy metals such as copper, nickel and lead. Trace metals concentration is also found in lower concentrations for mercury, zinc, phosphorous and titanium.

*Table 9. Ash Analyses for industrial wood waste samples.*

Element	Units	Waste wood
Al	mg/kg	770
Ba	mg/kg	74
Co	mg/kg	< 6
Cr	mg/kg	34
Cu	mg/kg	60
K	mg/kg	730
Mn	mg/kg	70
Na	mg/kg	670
Ni	mg/kg	19
Pb	mg/kg	84
Rb	mg/kg	4
Sn	mg/kg	< 6
Sr	mg/kg	13
Tl	mg/kg	< 6
V	mg/kg	< 6
Zn	mg/kg	230
Zr	mg/kg	13
As	mg/kg	< 6
Sb	mg/kg	< 6
Cd	mg/kg	< 6
Hg	µg /kg	70
F	mg/kg	-
Br	mg/kg	5
Ca	mg/kg	3300
Fe	mg/kg	570
Mg	mg/kg	490
P	mg/kg	150
Si	mg/kg	2100
Ti	mg/kg	860

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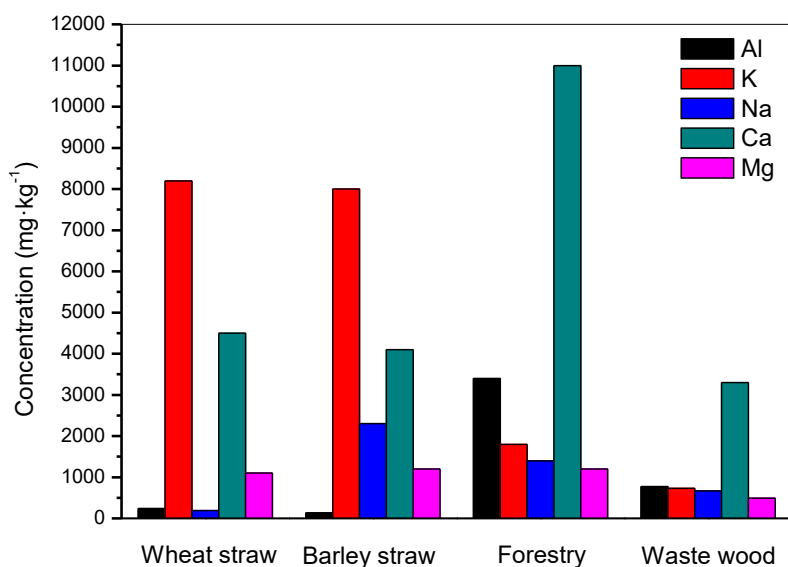


Figure 4. Ash-forming light metals content in the different biomass fuels studied.

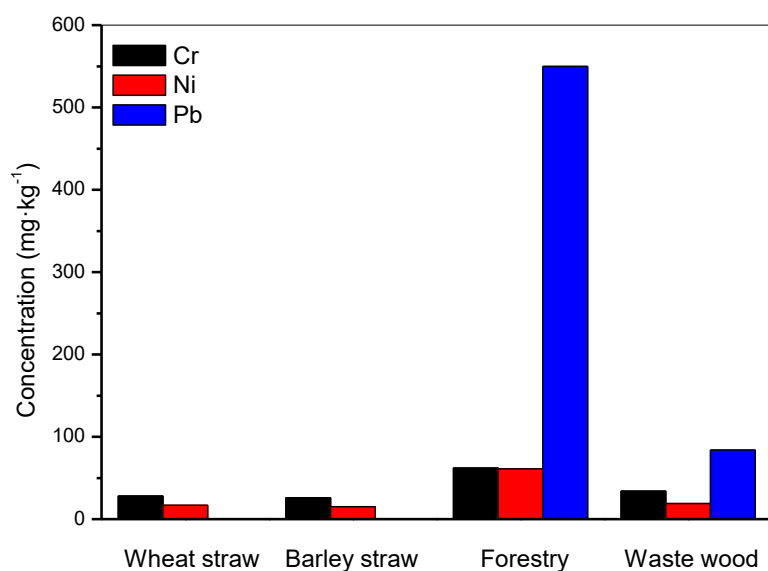


Figure 5. Comparison of most remarkable heavy metals determined in biomass samples evaluated.

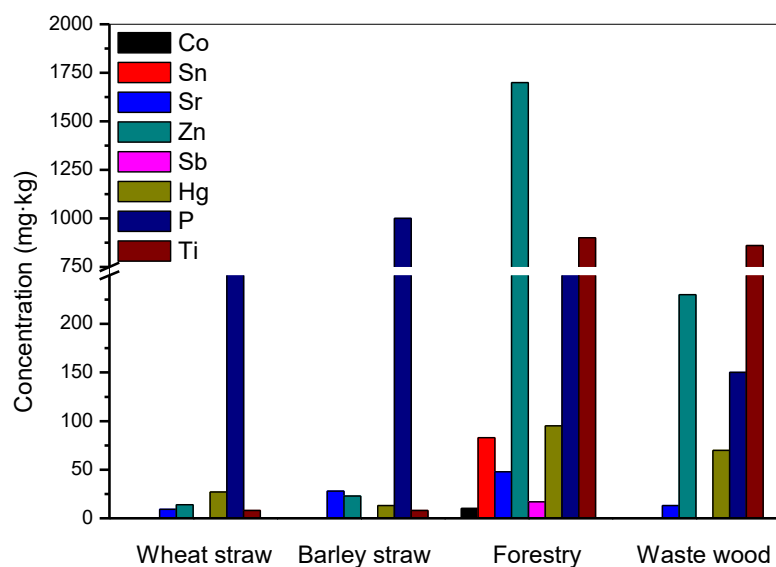


Figure 6. Comparison of most remarkable trace metals determined in biomass samples evaluated.

#### 2.1.4. Slagging propensities of ashes.

The propensity of the biomass ashes towards slagging can be determined through different slagging index, such as Babcock ( $R_s$ ) index, commonly used for coal ashes, which have also shown a good trend with the deformation temperatures of solid recovered fuels (SRF) ashes [14]. This index is determined from the ratio of basic oxides to acidic oxides and the sulphur content.

$$(R_s) = (R_{b/a})S^d$$

where:

$S^d$ : percentage of sulphur in dry fuel.

Basic to acidic constituents in ash ratio ( $R_{b/a}$ ) =  $(Fe_2O_3 + CaO + MgO + K_2O + Na_2O) / (Al_2O_3 + SiO_2 + TiO_2)$

$R_s$  values over 2.6 indicate severe slagging potential. Table 10 exhibits  $R_s$  values determined for biomass fuels selected for evaluation in BELENUS, showing severe slagging potential for all cases studied. Major slagging propensity is observed, to a great extent, for barley straw ashes, followed by wheat straw ashes. Ashes from woody materials exhibit much lower slagging tendency, with no significant differences obtained between both cases.

**Table 10. Slagging index ( $R_s$ ) determined for BELENUS biomass fuels.**

STAGE	$R_s$
<b>Wheat Straw</b>	11
<b>Barley straw</b>	26.5
<b>Forestry wood</b>	8.3
<b>Industrial wood waste</b>	8.5

#### 2.2. Thermogravimetric analysis

*Thermogravimetric analysis (TGA)* has been reported as one of the best techniques to study the Kinetics of thermal decomposition of a high variety of materials. Thermogravimetric analysis (TGA) is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a sample is heated at a constant rate. The Thermogravimetric Analyzer (TGA) measures the change in weight of a sample as tested through a temperature profile. The TGA can provide information about chemical phenomena including chemisorption, desolvation and dehydration, decomposition, and solid-gas reactions such as oxidation or reduction.

A TGA consists of a sample pan that is supported by a precision balance ( $\pm 0.1 \mu g$ ). That pan besides in a furnace and is heated or cooled during the experiment. The mass of the sample is monitored during the experiment. A sample purge gas controls the sample environment. This gas may be inert or a reactive gas that flows over the sample and exits through an exhaust.

One of the most employed methods to study thermal energy changes is *Simultaneous Difference Thermal Analysis (SDTA)*. This technique is particularly advantageous when used in combination with thermogravimetric analysis. The measurement signal represents the temperature difference between the sample and a previously measured and stored blank sample. DTA and SDTA allow to detect endothermic and exothermic effects, and to determine temperatures that characterize thermal effects.

Specifically, Mettler Toledo AG - TGA/SDTA851 is the equipment employed for BELENUS, which main characteristics are detailed in table 10. Continuous monitoring of temperature and sample mass loss is undertaken by METTLER STARe thermal analysis software.

**Table 11. Mettler Toledo AG - TGA/SDTA851 Technical characteristics**

STAGE	1
Temperature range	15- 1000 °C
Sample mass	0.1 µg – 5 g
Maximum sample volume	900 µl
Temperature Accuracy	0.25 °C
Temperature precision	0.15 °C
SDTA resolution	0.005 °C

### 2.2.1. Thermogravimetric analysis comparison of wheat/barley straw samples.

The thermal behaviour of wheat straw and barley straw are shown in figure 7 (air) and figure 8 (nitrogen). These graphs present the mass loss (TGA), derivate mass loss (DTG) and calorimetric (SDTA) profiles as a function of temperature at a constant heating rate of 20 °C/min within the temperature range of 30-900 °C in air and nitrogen respectively. Nitrogen and air atmospheres are compared for both biomass fuels. During the test different heating rates of 10 and 20 °C/min were studied to verify the dependence of the experimental conditions on the thermogravimetric curve, but only profiles obtained at 20°C/min have been used for TG-DTG-SDTA analysis.

From figure 7, different events can be distinguished under air atmosphere, and there is a correlation between mass loss figure 1a, dTG curve (figure 7b), and the evolution of the heat involved in the process, figure 7c . The first one occurs between the initial temperature and around 200°C, depending on the biomass. This zone can be separated in two sections. The first one from the initial temperature up to ~95°C is due to the removal of free moisture ~7%. The second is almost horizontal line from 95 to 200°C, and mass loss in this section is ~2%, probably due to removal of bound moisture and evaporation of small amounts of volatile matter. These phenomena are endothermal, due to the presence of a sharpen decrease in SDTA curve (figure 7c ).

In the second zone, the main devolatilization occurs and maximum mass loss is achieved. This process takes place within 200 up to ~480-490 °C (depending on the biomass). Based on the mass loss rate, this zone could also be divided into three sections. The first section is in between temperature range of 200 up to 350-360°C with mass loss of ~53%. In this section, SDTA (figure 7c) curve shows a peak with maximum rate of mass loss at 304 and 316°C for barley and wheat straw respectively. This section can be ascribed to the degradation of hemicellulose and cellulose. The second section is in the temperature range of 427–472°C with mass loss of 16%; maximum rate of mass loss is obtained at 420 and 435°C for wheat and barley straw samples respectively. This section can be ascribed to the degradation of cellulose.

The third zone presented in TGA curve starts at 470-480 °C and extends up to 800 °C; the mass loss occurs in this zone is very low (≤2%) due to the slow rate of degradation. This zone might be due to the degradation of lignin and is referred as passive pyrolysis zone. At the temperature of about 500 °C; the degradation process is almost completed. The residue of the sample weight is left as char.

Under nitrogen atmosphere conditions, three main stages of mass loss were also described, with no intermediate sections distinguished. Lower mass loss percentage is obtained at the second stage (250-364°C), with major remaining residue, in nitrogen conditions.

When the experiments are performed in nitrogen media (figure 8) pyrolysis phenomena take place instead of combustion and TG, dTG and SDTA profiles change. The most important difference is that peaks in the temperature range 400-500 °C ascribed to a cellulose and lignin transformation, disappear. In this case, a major reactivity on barley sample was observed.

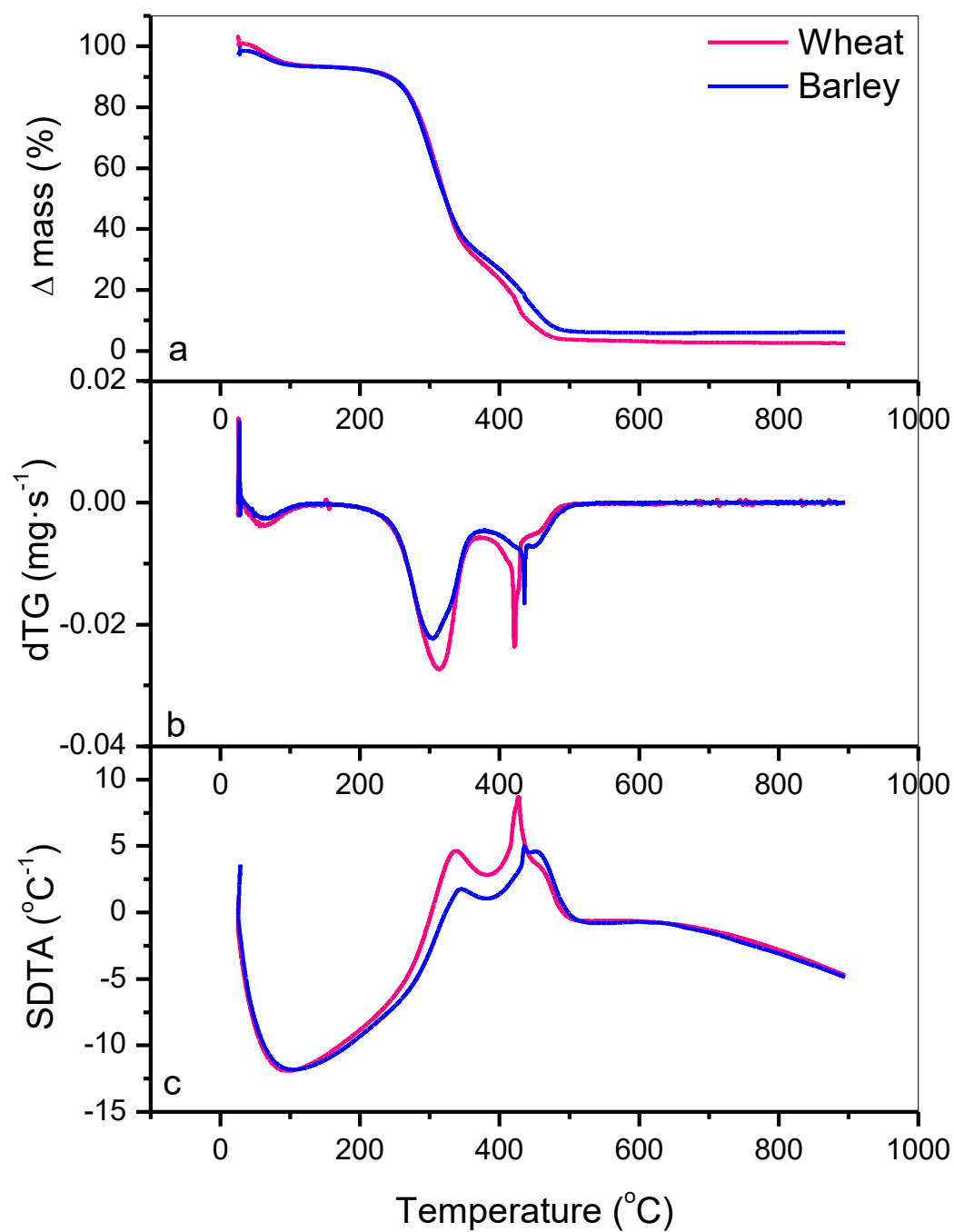


Figure 7. TG/DTG/SDTA curves of straw samples at a heating rate of 20 °C/min in air.

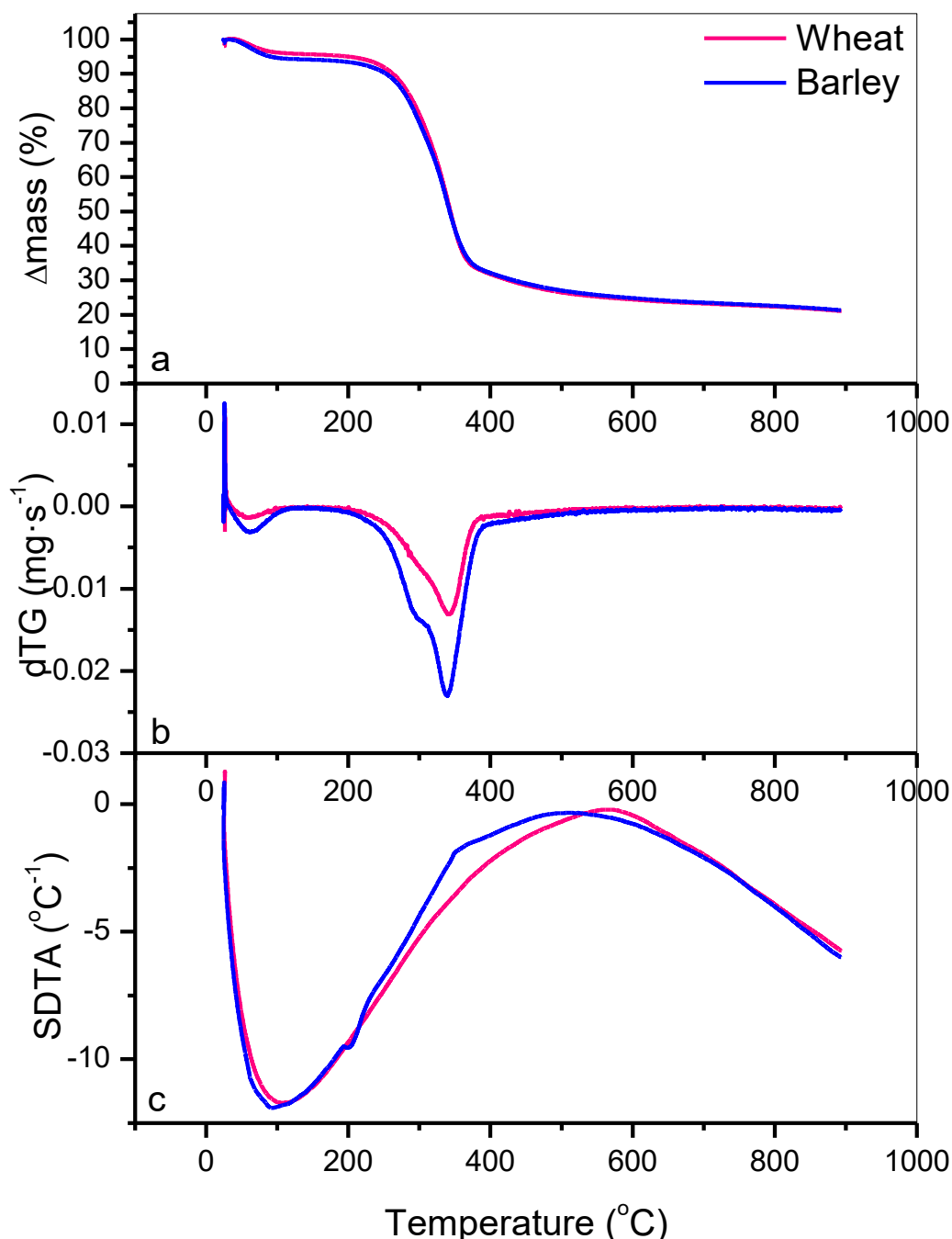


Figure 8. TG/DTG/SDTA curves of straw samples at a heating rate of 20 °C/min in nitrogen.

### 2.2.2. Thermogravimetric analysis comparison of biomass fuels selected.

Thermal behaviour of different biomass fuels selected for BELENUS purpose (wheat straw, forest residue, waste wood) has been determined. Figure 9 present mass loss (TGA) profile as a function of temperature at a constant heating rate of 20 °C/min within the temperature range of 30-900°C, in air atmosphere.

Three main stages of mass loss, previously described for straw samples case, are also observed for forestry residues and waste wood. The first stage, where moisture removal and evaporation of small amounts of volatile matter take place, seems to occur in a lower extent for forest residues and waste wood in comparison to straw samples, as result of the higher moisture content of the last ones, previously observed in the chemical analyses. The profiles obtained for the other two stages of woody biomasses are similar to that obtained for straw case, but each section starts at higher temperature. The major remaining residue is found for forest residue, followed by waste wood.

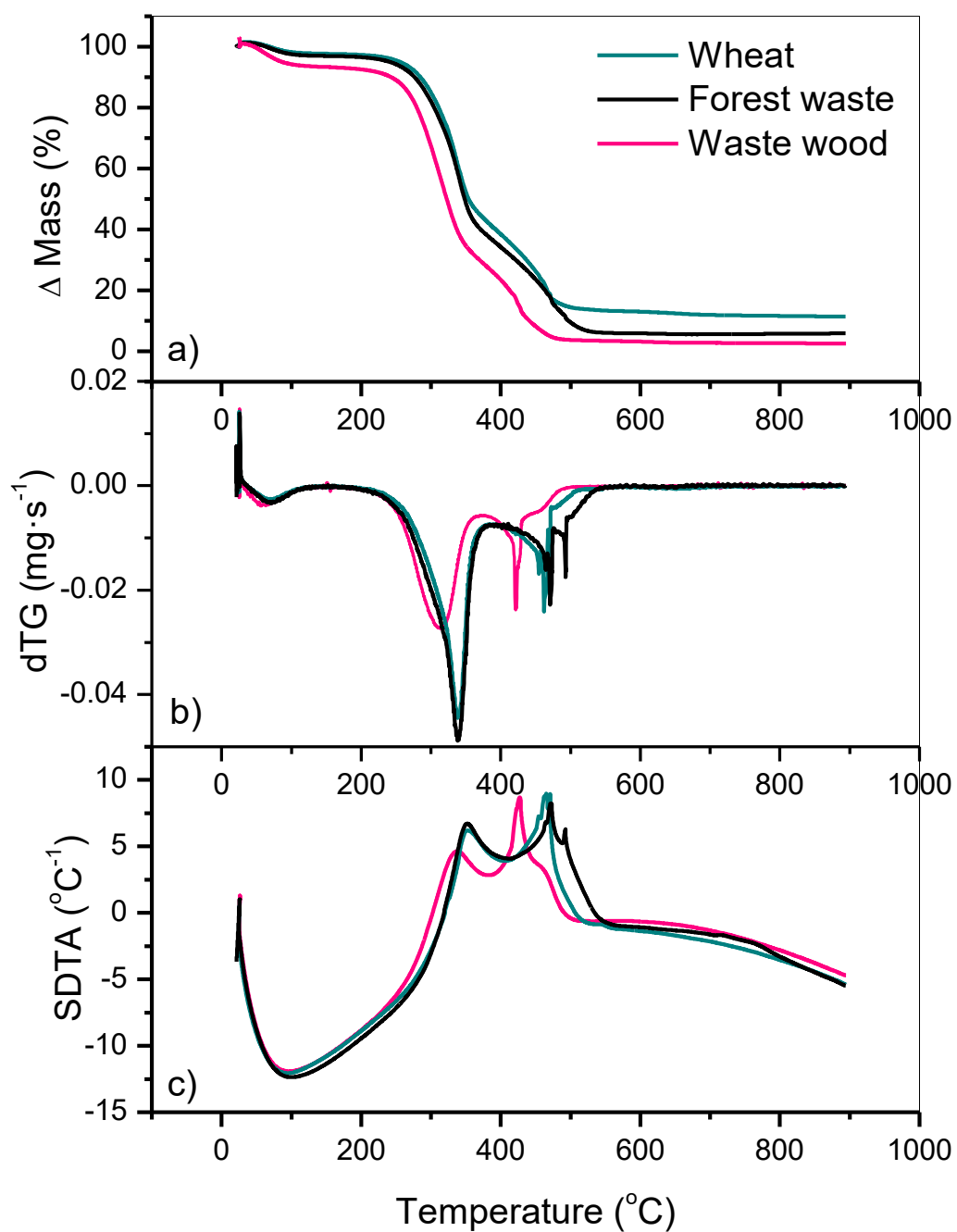


Figure 9. TG/DTG/SDTA curves of different biomass fuels in air, at a heating rate of 20 °C/min

Figure 10 compares the three biomass samples under nitrogen atmosphere conditions, with three clearly defined mass loss sections. Lower mass loss percentage is obtained at the second stage, with major remaining residue, in nitrogen conditions. The highest reactivity is determined for waste wood, followed by forest residues at 360-370°C

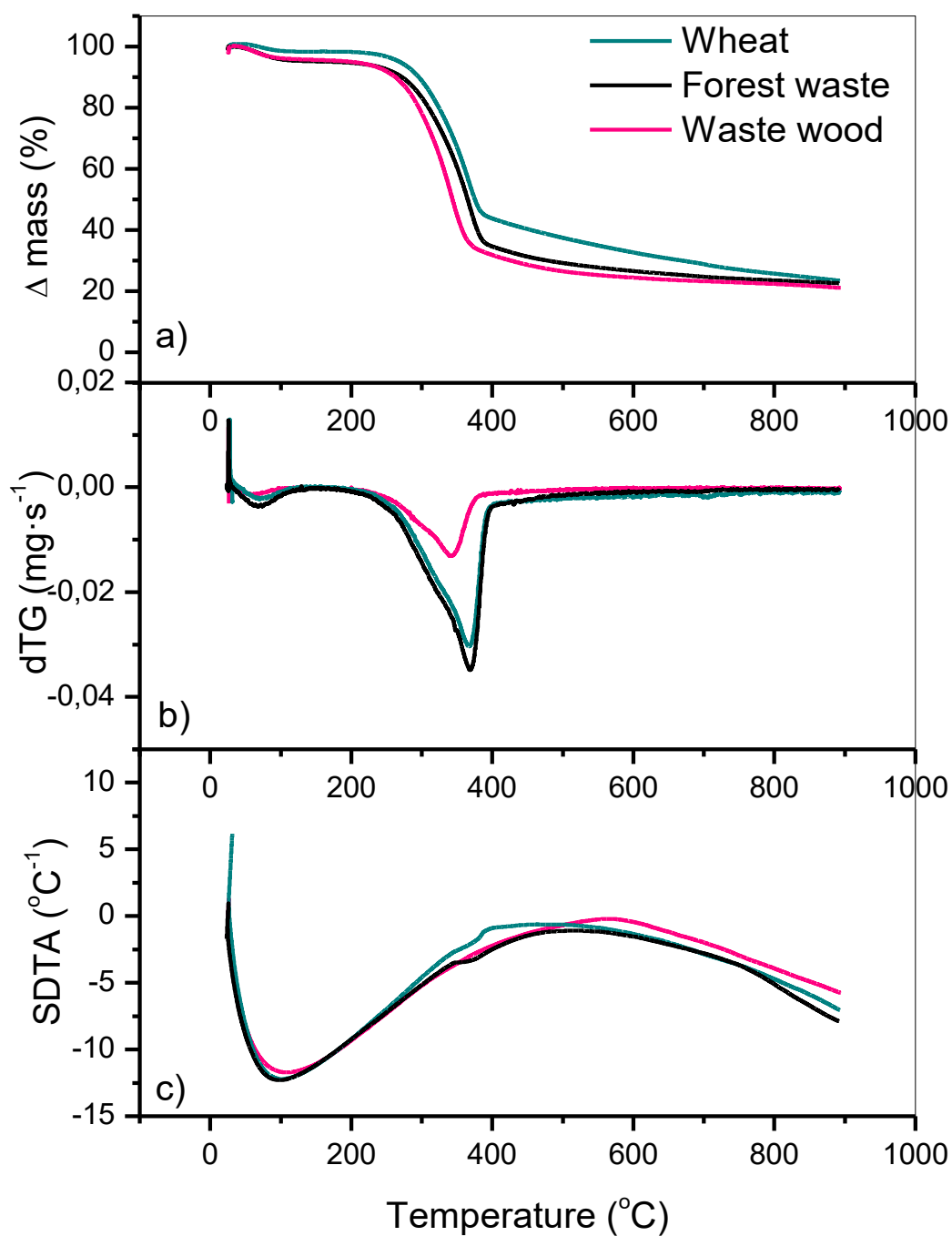


Figure 10. TG/DTG/SDTA curves of different biomass fuels in  $N_2$ , at a heating rate of  $20\text{ }^{\circ}\text{C}/\text{min}$ .



### 3. Conclusions

Physicochemical characterization undertaken has shown great variability among the different biomass fuels selected for BELENUS.

The most significant difference between wheat and barley straw samples is found for chlorine content, with a 0.39 wt.% higher in the first case. Sodium concentration is also determined in significantly higher concentrations in barley straw case. With respect to trace metals, it is noteworthy mercury content in wheat straw which is twice than that determined in barley straw.

Proximate analyses developed for woody biomasses reflect significant differences such as the ash content, with 6 wt.% lower in industrial wood waste case. With respect to ultimate analysis, major carbon and nitrogen content has been encountered for industrial wood waste than for forestry residues, while sulphur and ash-forming light metals are determined in lower concentration.

Comparing woody biomasses with straw samples, the moisture content is substantially lower in the first case, while the volatiles content is higher. Important ash content is determined for forestry residues in comparison to the rest of the biomasses. With regards to the ultimate analysis, it is remarkable the low sulphur and chlorine content of industrial wood waste in comparison to agricultural residues. In relation to ash-forming light metals, attention is drawn to alkali metals (Na and K) with much lower concentration found in forestry residues in comparison to straw, especially for potassium case.

With respect to heavy metals content, major concentration has been encountered in forestry residues in comparison to straw samples, for elements such as chromium, nickel and lead and also for trace metals such as mercury, antimony, titanium, tin, strontium, cobalt and zinc. Nevertheless, in the case of industrial wood waste, heavy metals content was encountered in lower quantities than that found in the rest of the biomasses.

Severe slagging potential has been determined for all biomasses evaluated. Major slagging propensity is observed, to a great extent, for barley straw ashes, followed by wheat straw ashes. Ashes from woody materials exhibit much lower slagging tendency, with no significant differences obtained between both cases.

With regards to the thermal behaviour, thermogravimetric analysis developed for wheat and barley straw samples reflect similar thermal behaviour in both atmospheres with major reactivity detected for wheat straw in air and for barley straw in nitrogen atmosphere. When the different biomass fuels selected are compared under air conditions, profiles obtained for the two later stages of woody biomasses are similar to that obtained for straw case, but each section starts at higher temperature. The major remaining residue is found for forest residue, followed by waste wood. Under nitrogen atmosphere, the highest reactivity is determined for waste wood, followed by forest residues.

#### **4. Degree of Progress**

The D4.1 is 100 % completed.

## 5. Dissemination Level

Public

## 6. References

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