Application of Thermogravimetry for Determination of Carbon Content in Biomass Ash as an Indicator of the Efficiency of the Combustion Process

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Abstract: The determination of the amount of residual carbon in biomass ash is important not only for the assessment of the efficiency of biomass fuel combustion but also as one of the criteria for the estimation of biomass ash potential use. In this paper carbon content in biomass ash was analysed by applying two methods: total organic carbon analysis (TOC) and thermogravimetric analysis (TGA) in an inert (N_2) and oxidizing (O_2) atmosphere. The amount of inorganic (carbonate) carbon can be directly calculated from the TGA curve and the obtained results are in a good agreement with the ones obtained using TOC analyser. On the other hand, the quantitative determination of organic and elemental carbon by TGA is not straight-forward since the temperature range of their oxidation overlaps with dehydration temperature of portlandite that is a constituent of biomass ash. It can be concluded that a basic version of the thermogravimetric analyzer can be used for the determination of inorganic carbon in ash samples, but for total organic carbon determination, it is recommended to use hyphenated techniques, for example, TGA-MS or TGA-FTIR that allows quantitation of evolved gases (CO_2 and H_2O).

Keywords: ash; biomass; carbon content; thermogravimetry; TOC

1 INTRODUCTION

Bioenergy plays an important role in the European Union's energy strategy. According to Asquer and co-workers [1], biomass use is expected to reach 110.5 Mtoe by the end of 2020. This would represent an increase in biomass consumption by 22% compared to the one in 2012. An increase in the use of biomass will inevitably lead to an increase in the amount of ash generated by its combustion, which is estimated to be 15.5×10^7 tonnes by 2020, in EU27 only [2].

Biomass ash is generated as a result of the thermo-chemical transformation, most often the combustion, of biomass-based fuels. The amount and properties of biomass ash depend on the number of factors, including the type of fuel, method of fuel preparation, type of the boiler, parameters of the burning process, etc. [3]. The type of the fuel, particularly the chemical composition of the biomass, determines the quantity of the formed ash that decreases in the following order: animal biomass, aquatic biomass, contaminated biomass, herbaceous and agricultural biomass, wood and woody biomass [4]. One of the most widely used biomass is lignocellulosic biomass, where the amount of ash is in the range of 1% to 20% [5].

Depending on the collection site in the boiler, biomass ash can be bottom and fly (filter) ash. Bottom ash is collected at the bottom of the boiler, while fly ash is accumulated in the filter section or on electrostatic precipitators located downstream from the main combustion section [6]. Fly ash can be additionally differentiated regarding its granularity, into coarse and fine fly ash [7]. The ration between the bottom and fly ash depends on the combustion technology and operating parameters. According to Berra [5], biomass combustion in grate boilers produces equal amounts of the bottom and fly ash, in fluidized bed boilers fly ash is produced in excess, while in the pulverized fuel combustion installations the amount of bottom ash is higher than the one of fly ash.

A number of potential biomass ash applications were reported in the literature. Biomass ash can be used in forest ecosystems and agroecosystems as a fertilizer or fertilizer supplement, as well as for geotechnical constructions and industrial processes, such as the construction of roads and parking areas [6]. Additionally, it can be used as a surface layer in landfills and admixture for concrete, brick or cement production [6]. Moreover, it can be used as an additive in compost production and as a binder for the consolidation of soils [8]. Additionally, if the content of unburned carbon in ash is high, it might be even economically justified to reuse it as fuel.

The potential application of biomass ash is directly linked with its inherent chemical structure. Principal biomass ash components are inorganic minerals, residual carbon, and water. Total (residual) carbon in the ash is comprised of two fractions: combustible (unburned) and carbonate carbon [9]. Combustible carbon corresponds to total organic carbon (TOC) while carbonate carbon corresponds to total inorganic carbon, according to Standard EN 13137 [10]. Total organic carbon can be further divided into organic carbon and elemental carbon [11]. The amount of the combustible carbon content in biomass ash can be used for the determination of the performance and efficiency of biomass boiler furnaces [12], as well as of different thermo-chemical (liquefaction, gasification, and pyrolysis) reactors for carbonaceous fuels [9].

The residual carbon in the ash can be determined by various procedures. One of them is dry combustion of the ash sample in an oxygen atmosphere followed by infrared (IR) spectroscopic determination of evolved CO_2. In this way, the total carbon in the sample is determined, but the fractions of total organic and inorganic carbon remain unknown. For the quantitation of the organic and inorganic carbon, an additional step is needed. The sample is usually treated by an acid to remove carbonated (inorganic) carbon [9, 10]. The dry combustion method is considered as the most accurate one for total organic carbon determination and can be used as a reference for the calibration of other methods [13, 14]. However, this comes with a price - in an instrument and per-test cost.

Loss on ignition (LOI) method has been used for a long time as a conventional method for the determination of the amount of unburned carbon in ash [15]. LOI gained popularity due to its inherent simplicity. The method is

based on the determination of mass loss when a solid combustion residue is subjected to heating at controlled conditions including temperature, time, atmosphere, sample mass, and equipment specifications [16]. The main assumption is that all residual carbon will be converted to carbon dioxide [14]. Brown and Dykstra [17] compared the values for the amount of unburned carbon obtained by the LOI method and the ones obtained by thermogravimetric (TGA) and X-ray diffraction (XRD) analysis of seven fly ash samples, produced by four different coal boilers. They discovered that the results obtained by LOI have a gross systematic error due to minerals, present in fly ash, that are being dehydrated or decomposed during the ignition. Thus, mass loss on ignition occurs due to not only carbon oxidation but also as a result of portlandite dehydration and carbonate calcination [17]. These findings were corroborated by Fan and Brown that subjected around 70 fly ash samples from different boilers operating in the USA, Canada, China, and Australia to similar experimental conditions [18]. Moreover, they found that an additional shortcoming of the LOI method is that volatile organic compounds (VOCs) present in ash contribute to LOI but do not represent accurately unburned carbon content. The authors proposed thermal methods as a better solution for the accurate determination of carbon content in ash samples.

Thermogravimetric analysis (TGA) is a widely used thermal analytical method in which changes in the mass of a sample, subjected to a controlled temperature program under a controlled atmosphere, is recorded over time. The potential of this method for carbon content determination lies in the specific thermal behaviour of carbon species present in ash. TGA and differential thermogravimetric (*DTG*) curves can be used as "fingerprints" for identification, as well as for quantitation, of a specific carbon forms present in ash. However, the determination of carbon content from the TGA curve is not straightforward, as the weight loss that is due to thermal degradation of carbon species is often overlapped with the other thermal events. A number of studies were performed to screen different coal ash samples using TGA. Paya and co-workers [19] analysed unburnt carbon content in coal fly ashes using TGA in an inert and oxidizing atmosphere. Similarly, Mohebbi [15] showed that carbon content in coal ash can be successfully determined if two atmospheres TGA are used. TGA was also successfully applied for screening ashes from incinerators [11, 20] as well as for identifying various carbon forms present in soil [21, 22].

There are scarce data on TGA application for the determination of carbon content and the identification of carbon forms present in biomass ash. Zhao and co-workers [23] performed a nonisothermal TGA analysis in nitrogen and air atmosphere to characterize residual carbon present in biomass fly ash and compared these results to LOI values. Moreover, Straka with his co-workers proposed a TGA method using Boudouard gasification reaction for determination of unburned carbon in biomass ash [24] that enables the simultaneous determination of portlandite and carbonates present in the ash without acid treatment.

The fact that there are some speculations about the TGA procedure that should be used for determining the carbon content and distinguishing between carbon forms present in biomass ash [23, 25] justifies further research in the field. The main aim of the present study is to evaluate the possibility of application of TGA for rapid and accurate determination of carbon content and differentiation between carbon species in biomass bottom ash samples and to compare these results with the results obtained using TOC analyser.

2 MATERIALS AND METHODS
2.1 Materials

Five samples of bottom ash collected from four different residential boilers were used in the present study. Two of them were obtained from ISO 17025 accredited laboratory for testing residential heating boilers for solid fuels and the other three from domestic boilers. Four samples were obtained by biomass combustion, while in one case sub-bituminous coal was used as a fuel (Tab. 1).

Table 1 Bottom ash samples ID, fuel type and ash origin

Sample number	Fuel type	Ash origin
Sample 1	Beech pellets A2	Laboratory
Sample 2	Beech pellets A2	Laboratory
Sample 3	Beech pellets A2	Residential boiler
Sample 4	Austrian oak wood logs	Residential boiler
Sample 5	Subbituminous coal	Residential boiler

Samples 1 and 2 were obtained by combustion of the same fuel (beech pellets, grade A2) in the same (tested) residential boiler, but under different operating conditions (distinct heat outputs: 23.7 kW and 14.8 kW, respectively).

2.2 Experimental Methods
2.2.1 Total Organic Carbon (TOC) and Inorganic Carbon (IC) from TOC Analyser

Total carbon (TC), total organic carbon (TOC) and inorganic carbon (IC) of biomass ash were determined according to a standard accredited procedure [10] using a Shimadzu TOC-VCSH analyser. Each biomass ash sample was divided into two sub-samples. One sub-sample was ignited in the furnace in a stream of oxygen-carrying gas at 900 °C to determine TC. Another sub-sample was pre-treated with 0,5 ml of 2M HCl to remove IC. The evolved carbon dioxide was removed by heating the sample at 200 °C and the resulting carbon dioxide was transmitted by a stream of carrier gas to the detector. The percent of TOC was calculated as the difference between the TC measured in the first and the IC measured in the second sub-sample (TOC = TC − IC). The verification of the method was performed on a certified residue of the pt scheme - lgc sample 3 (Certified Reference Material-LGC PT, Round CN089, sample 3c - Total organic carbon).

2.2.2 Carbon Content Determination by Thermogravimetric Analysis (TGA)

TGA experiments were conducted on Perkin Elmer TGA 4000 thermogravimetric analyzer (Norwalk, CT). The calibration of the instrument: temperature (performed by measuring Curie points of alumel, perkalloy, and iron), furnace, and weight calibration, was carried out according to the manufacturer's recommendation. Although some of the ash samples seemed to be homogenous enough as-

received, all samples were homogenized in a mortar with a pestle for 10 min before the analysis.

Approximately 10 mg of samples were loaded in a TGA ceramic crucible. All samples were subjected to the same temperature program in an inert (N_2) and an oxidizing (O_2) atmosphere [23]. Firstly, the samples were held at 30 °C for 5 min, then heated to 105 °C at 20 °C/min heating rate, held for 30 min at 105 °C to remove moisture, and then heated to 900 °C at 7 °C/min. This heating rate, 7 °C/min, was used as the optimal one considering the resolution of the TGA curve and the TGA run time. During this last step, heating from 105 to 900 °C, the purge gas was switched to oxygen. Purge gas flow rate was set to 20 ml/min. Before each run, a loaded sample pan was placed in the instrument and left to get stabilized for at least 20 min. The residual weight of the sample, the weight loss as a function of time and temperature and the rate of weight loss (DTG curves) were determined using Pyris software.

3 RESULTS AND DISCUSSION

Thermogravimetric (TG) curves of analysed biomass ash samples in an oxidative (O_2) and inert (N_2) atmosphere are shown in Fig. 1.
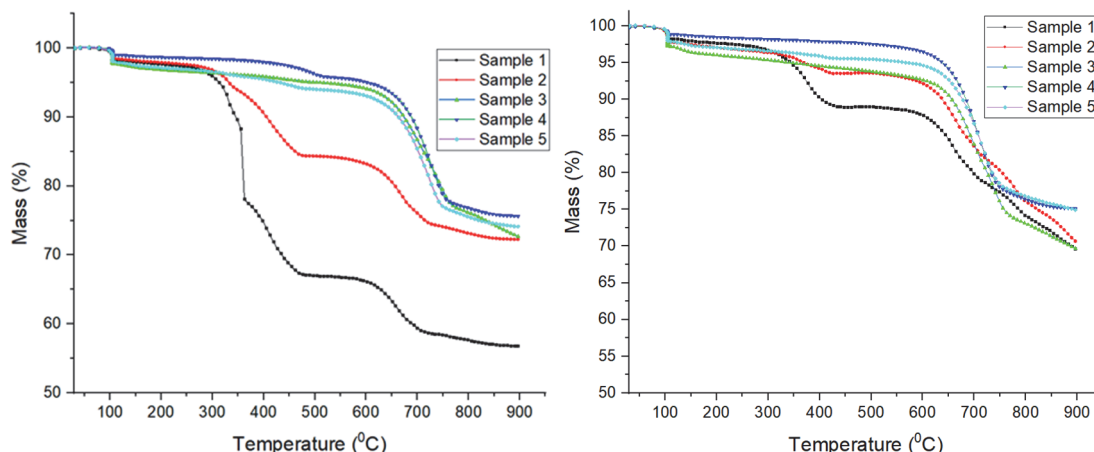

Figure 1 Thermogravimetric (TG) curves for biomass ash samples in oxygen (left) and nitrogen (right) atmosphere

TG curves indicate that there are several areas of weight loss. Upon heating in both, oxidative and inert, atmospheres samples 1, 2 and 5 have three major, while samples 3 and 4 have two major stages of weight loss (Tab. 2).

Table 2 Temperature ranges and weight losses during the TGA analysis of biomass ash

	Sample 1				Sample 2				Sample 3				Sample 4				Sample 5			
	N_2		O_2		N_2		O_2		N_2		O_2		N_2		O_2		N_2		O_2	
	T [°C]	Wt [%]	T [°C]	Wt [%]	T [°C]	Wt [%]	T [°C]	Wt [%]	T [°C]	Wt [%]	T [°C]	Wt [%]	T [°C]	Wt [%]	T [°C]	Wt [%]	T [°C]	Wt [%]	T [°C]	Wt [%]
Stage 1	30	100	30	100	30	100	30	100	30	100	30	100	30	100	30	100	30	100	30	100
	105	98.29	105	98.36	105	97.79	105	98.47	105	97.23	105	97.76	105	98.78	105	99.02	105	97.89	105	97.99
Stage 2	105	98.29	-	-	-	-	-	-	105	97.23	105	97.76	-	-	-	-	105	97.89	105	97.99
	165	97.88	-	-	-	-	-	-	160	96.31	160	97.11	-	-	-	-	165	97.22	170	97.32
Stage 3	320	96.14	310	95.36	315	96.25	300	96.82	-	-	-	-	-	-	-	-	390	96.00	380	95.73
	425	89.19	480	67.13	430	93.52	480	84.39	-	-	-	-	-	-	-	-	440	95.55	490	94.10
Stage 4	590	88.16	600	66.17	600	92.16	595	83.34	620	92.00	620	93.61	630	95.44	635	94.17	620	94.14	625	92.33
	805	73.95	730	58.60	810	75.58	810	75.58	770	74.14	775	76.87	755	77.74	765	77.65	770	77.59	770	76.34
Residue	900	69.62	900	56.80	900	70.59	900	72.25	900	69.34	900	72.63	900	75.09	900	75.62	900	74.93	900	74.10

The start and the end temperature of each step were determined as we had described before by the intersection of tangents from the linear part and the descending parts of the peak of the DTG curve [26]. Stages typical for all samples are the one that starts at 30 °C and ends at 105 °C and the stage occurring at higher temperatures, from ca. 600-800 °C. An additional stage of weight loss, observable only in thermograms of samples 1, 2 and 5, is in the range 300-480 °C and 300-430 °C in an oxidative and inert atmosphere, respectively.

Although the TG curve describes the thermal behaviour of samples upon heating, the characteristic thermal events that occur are more evident from the DTG curve because even small changes in the TG profile are magnified when the corresponding first derivative is used [27, 28].

In O_2 atmosphere (Fig 1. left) the largest overall mass loss corresponds to sample 1 of ca. 43% of the initial mass, while for the other samples it was around 25% of the initial mass. In an inert, nitrogen, atmosphere the overall mass loss of ca. 30% of the initial mass was detected for samples 1, 2 and 3, while for samples 4 and 5 it was around 25%.

The rate of mass loss (differential thermogravimetric - DTG) signal was calculated according to the following formula:

$$DTG = -\frac{1}{2m_0}\left[\frac{m_{i+1} - m_i}{t_{i+1} - t_i} + \frac{m_i - m_{i-1}}{t_i - t_{i-1}}\right] \cdot 100 \text{ , \%/min}$$

where t is time, m_0 is the initial mass of sample and index i pertains to a particular time instance. After differentiation, negative derivative values were removed.
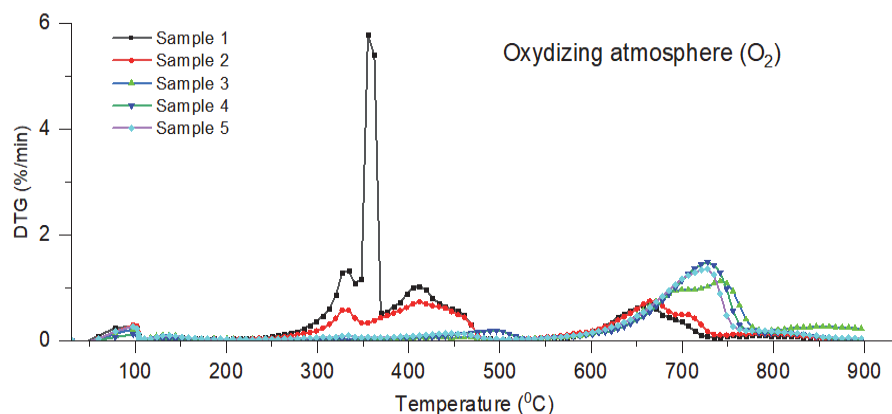
Figure 2 Differential thermogravimetric (*DTG*) curves for ash samples in an oxygen atmosphere

Differential thermogravimetric (*DTG*) curves for all ash samples during the thermal decomposition in oxygen (O_2) and inert (N_2) atmosphere are shown in Fig. 2 and Fig. 3, respectively.
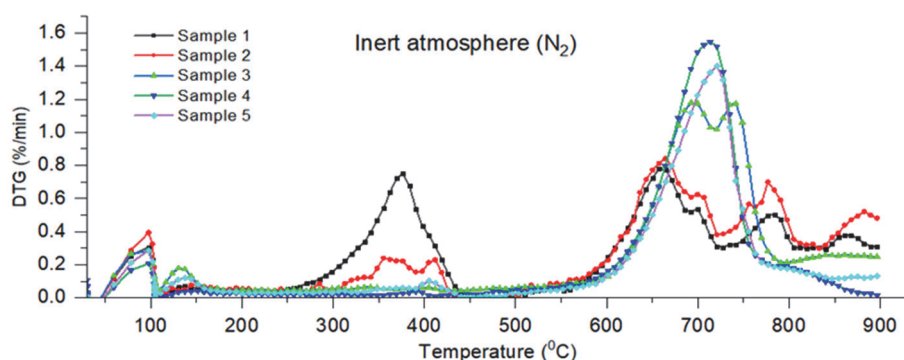

Figure3 Differential thermogravimetric (*DTG*) curves for ash samples in a nitrogen atmosphere

The first stage of mass loss (the first peak on the *DTG* curve) that starts with the beginning of the temperature program and ends at 105 °C corresponds to the evaporation of water present in ash. The moisture content in the analysed samples was 0.5-1.5%. Another stage of weight loss (up to 2.5%) in the range of 105-165 °C occurs, most probably, due to the thermal decomposition of potassium hydrogen carbonate ($KHCO_3$). This compound, frequently present in biomass ash, decomposes in the temperature range between 100 °C and 200 °C [29]. Another area of weight loss, between 300 and 500 °C, observable only in samples 1 and 2, can be ascribed to several thermal processes. Generally, the thermal behaviour of biomass ash is determined by the chemical composition of the ash that depends on the fuel type, boiler type, boiler operating conditions and combustion technology used. The principal constituents of woody biomass ash formed in the biomass boilers, under typical operating temperatures are calcium oxide (CaO), silicon dioxide (SiO_2), calcite ($CaCO_3$), portlandite ($Ca(OH)_2$) and calcium silicate (Ca_2SiO_4) [30]. Calcium oxide is a porous and highly reactive compound that could be easily transformed into portlandite if enough moisture is present in the surrounding atmosphere, or into calcium carbonate in the presence of elemental carbon or CO_2 [31]. The region of the mass loss from 300 °C to 500 °C can be ascribed, at least partially, to the decomposition of portlandite that is the only mineral among the mentioned ones present in the ash, that has the decomposition temperature between 400 °C and 500 °C [17]. Moreover, this temperature region corresponds to the oxidation of organic and elemental carbon [11]. Hence, the mass loss in the temperature range between 250 °C and 400 °C can be solely attributed to the oxidation of organic carbon present in the ash while from 400 °C up to the end of this temperature interval, processes of carbon oxidation and portlandite dehydration are overlapped. The mass loss from 430 °C to 525 °C occurring only in the oxygen atmosphere (Fig. 2) can be ascribed solely to elemental carbon oxidation. This assumption is corroborated by the fact that there is no weight loss in this temperature range in an inert atmosphere.These temperatures are rather low for the oxidation of elemental carbon which usually occurs in the range between 600 and 740 °C [32]. However, Ferrari [11] showed that the temperature of oxidation of elemental carbon can be lowered for even ca. 200 °C in the presence of metals/metal oxides usually present in the ash, that act as catalysts.

The stage of mass loss from 550 °C to 800 °C can be attributed to calcite decomposition that corresponds well to the literature data [22, 33, 34]. The mass loss due to calcite decomposition is manifested as release of carbon dioxide which can be easily recalculated to inorganic carbon. Finally, the mass loss that occurs above 850 °C for woody biomass, could be attributed to K_2CO_3 decomposition [34]. Thus, in the thermal region between 250 and 500 °C the oxidation of organic and elemental carbon occurs, while the mass loss in the region from 550 °C to 800 °C can be attributed to inorganic carbon transformation (calcite decomposition). Comparison of *DTG* curves in an oxygen and nitrogen atmosphere for samples 1 and 2 indicates that these samples contain a significant amount of organic and elemental carbon. Similar *DTG* profiles were reported in

the literature [35]. The possible reason for a higher content of unburned carbon in samples 1 and 2 can be inefficient combustion of samples in boilers in the laboratory conditions due to low combustion temperatures. Additionally, sample 5 contains a small amount of elemental carbon (small peak in *DTG* 425-525 °C, Fig. 3). Finally, flat regions on *DTG* curves from 250 °C to 500 °C

indicate that samples 3 and 4 contain neither organic nor elemental carbon. Inorganic carbon for all samples could be calculated as mass loss from 550 to 800 °C in the O_2 atmosphere. Characteristic temperature regions and corresponding mass losses, for sample 1, are designated in Fig. 4.
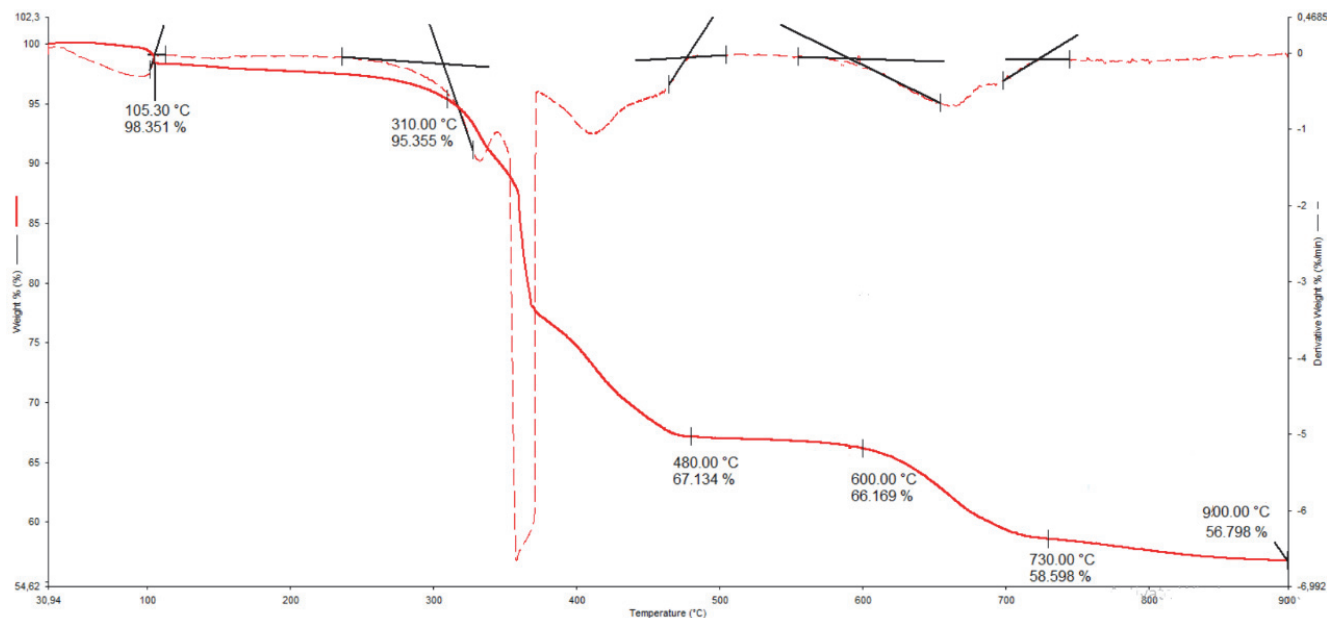

Figure 4 Termogravimetric (TG) (solid line) and Differential thermogravimetric (*DTG*) (dashed line) curves for ash samples 1 in an oxygen atmosphere

Using the same procedure, the content of total organic and inorganic carbon was determined for other ash samples. Findings from TG analysis were compared with TOC results (Tab. 3).

Table 3 Results for TOC and IC from TOC and TGA analysis

Sample number	TOC analysis		TG analysis	
	TOC	IC	TOC	IC
Sample 1	15.15	1.56	28.23	2.06
Sample 2	18.04	1.81	12.43	2.12
Sample 3	< 0.1	6.15	< 0.1	4.56
Sample 4	< 0.1	4.47	< 0.1	4.51
Sample 5	1.63	3.96	1.63	4.36

The values of inorganic carbon content determined by TGA are in good agreement with the results of TOC analysis. Moreover, TGA revealed that samples 3 and 4 contain just minute quantities of total organic carbon that was corroborated by TOC. Additionally, the value for total organic carbon determined by TGA for sample 5 was the same as from TOC analysis. However, as expected, the values for organic carbon content for samples 1 and 2, determined from TG curves considerably differed as compared to TOC results. This indicates that direct calculation of organic and elemental carbon content from TG curves is not straight-forward because the mass loss in the thermal region of 250 °C to 500 °C cannot be ascribed solely to carbon (organic and elemental) oxidation. Mass loss in this region may occur also due to dehydration of portlandite present in the ash. In an oxidative, air and particularly oxygen, atmosphere, during TG runs, complete oxidation of residual carbon in ash sample should be achieved, with CO_2 and H_2O as the only combustion products. The ratio between the amount of evolved CO_2

and H_2O could be used for the precise determination of organic and elemental carbon in the sample. Thus, the solution for TGA determination of organic and elemental carbon content could be a hyphenated TGA technique, allowing continuous monitoring of evolved gases from TGA instrument, and subsequent calculation of the aforementioned ratio. Finally, the organic and elemental carbon content in the ash sample could be calculated by multiplying the overall mass loss in the second thermal region with the aforementioned ratio.

4 CONCLUSION

In this paper different biomass bottom ashes from residential boilers were analysed to experimentally determine their carbon content. Two methods were used: Total organic carbon (TOC) method, according to EN 13137 (dry combustion method) and thermogravimetric analysis (TGA) in two atmospheres (inert (N_2) and oxidizing (O_2)). Obtained results indicate that TGA might be used as a relatively simple, fast and inexpensive method for the determination and differentiation of carbon species present in ash. Organic carbon thermal degradation occurs in the temperature range from 250 °C to 500 °C while for carbonate it occurs in the range between 550 °C and 800 °C. *DTG* curves can be used for precise determination of the onset and offset of temperature interval for carbon oxidation and carbonate decomposition. Inorganic (carbonate) carbon can be directly calculated from the TGA and *DTG* curves and the obtained results for all tested samples are in a good agreement with the ones determined using TOC according to EN 13137. However, the quantitative determination of organic and elemental carbon

is not straight-forward since the temperature range of their oxidation overlaps with dehydration temperature of portlandite that is one of the common constituents of biomass ash. It can be concluded that a basic version of the thermogravimetric analyser can be used for easy, simple, and inexpensive determination of inorganic carbon in ash samples. Nevertheless, for total organic carbon determination, hyphenated techniques, for example, TGA instrument coupled with mass spectrometry (MS) or Fourier transform infrared spectroscopy (FTIR) unit, that allows quantitation of evolved gases (CO_2 and H_2O) during the analysis, should be used. The CO_2 - H_2O ratio during the stage of mass loss in the temperature range 250 °C - 500 °C could be used for correcting the value of mass loss which will lead to the precise determination of organic and elemental carbon in the analysed ash samples.

Acknowledgment

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