



# Analysis of unburned carbon in industrial ashes from biomass combustion by thermogravimetric method using Boudouard reaction



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## ABSTRACT

A novel thermogravimetric method for the determination of unburned carbon in industrial ashes from biomass combustion using the strongly endothermic Boudouard reaction is proposed. The method does not require acid treatment to remove carbonates; it may also be used for samples containing a higher amount of portlandite, calcite and other mineral components typical for biomass-combustion ashes and is utilizable in the wide range of the content of unburned carbon. The correctness of the proposed determination was verified by carbon mass balance in 10 samples of industrial ashes. The interpretation of the course of the TG curves obtained was corroborated by differential scanning calorimetry.

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## 1. Introduction

Biomass is currently an important source for electricity and heat production. In the Czech Republic, ca 6,147,000 tonnes of biomass were used for energy production in 2008: 55% was burned by households, 14% was used in the co-combustion of biomass with fossil fuels in power plants and the remaining 31% was burned in bio boiler plants and bio power stations. A total of 123,000 tonnes of ashes were produced. The energy use of biomass in the Czech Republic grows every year, and this trend may be observed in other European states and the USA as well.

Since the higher amount of the biomass burned increases also the production of ash, the need for its further utilization becomes ever more urgent. Biomass ash may be used as a fertilizer applied to forest and agricultural soils as well as for construction materials. In both cases, it is necessary to assess the amount of unburned (combustible) carbon (UCC), because if the biomass ash is used as a fertilizer, the UCC content determines the amount of harmful polycyclic aromatic hydrocarbons; when it is utilized in the construction industry, the higher content of UCC complicates the preparation of construction materials. In addition, the amount of UCC in the ash is a measure of the efficiency of the incinerator

concerned. It is thus essential to determine correctly the UCC in biomass ashes.

Since UCC is combustible carbon contained in the ash, it may be determined as the total organic carbon (TOC) in the ash mixture. When selecting the assessment procedure, it is possible to proceed from methods prepared for coal-combustion ashes, but not to adopt them, because the starting combustion materials – coal and biomass – are entirely different, and so is the chemical character of the produced UCC. In spite of that, numerous procedures used have adopted the determination methods elaborated for coal-combustion ashes. A traditionally used parameter for the estimation of the UCC content is loss on ignition (LOI), when a dry ash sample is heated in a crucible in a furnace in air atmosphere for a given period (e.g. 2 h) and at a set temperature (e.g. 750, 815, 850, 950 °C). LOI-based methods are listed by e.g. Bengtsson and Enell [1]; they are described by the standardized tests [2–4], but it is possible to mention others as well. The loss on ignition has been studied in terms of exposure time, the position of the crucible in the furnace, the weight of the sample, the comparability of the results in laboratories [5], the influence of volatiles [6] and of calcium hydroxide (portlandite) and carbonates [7]. It arises from these studies that: (a) it is always necessary to evaluate the reproducibility of the method used in the given case, (b) the presence of volatile organic substances causes a significant positive error (e.g. 20%) in the LOI determination, (c) the content of portlandite and carbonates must be very low (e.g. 0.9%) for the method to be utilizable for the determination of UCC. To eliminate these shortcomings, Fan and Brown [6] and Styszko-Grochowiak et al. [7] have proposed that the LOI method be replaced with thermogravimetric analysis.

*Abbreviations:* UCC, unburned (combustible) carbon; LOI, loss on ignition; TOC, total organic carbon; TIC, total inorganic carbon; VOC, volatile organic carbon.

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As it is easy to implement, a method that is frequently used is the measurement of the mass loss on ash ignition at 815 °C [8], but this determination is complicated by a significant systematic error [9], which is caused especially by the thermal transformation of some minerals, mainly calcite and portlandite. Also this procedure is therefore suitable for the determination of UCC in the ashes in which the content of the above-mentioned minerals is very low. The assessment of UCC is dealt with in the Czech standard [10] as well. The method consists in the perfect combustion of the sample in a stream of oxygen at 650–700 °C on a catalyst (products of the thermal decomposition of silver permanganate) and the absorption of the emerging carbon dioxide in soda lime as well as the absorption of water. At the relatively low combustion temperature mentioned above, the thermal decomposition of carbonates is minimized; in the calculation of the UCC content, the amount of carbon dioxide from carbonates is therefore neglected if the content of the carbonates in the measured sample is lower than 0.5%. Under these circumstances, the calculation is very simple and the method provides reliable results. When the content of carbonates is higher, however, it is necessary to measure their content in the sample in a different way and add it to the formula for the calculation of the UCC content.

In general, the presence of calcite and other carbonates causes a positive error in the determination of UCC by LOI-based methods. The reason is their decomposition temperature; in the case of calcite, it is mostly claimed to begin at 800 °C, but a comprehensive study [11] draws attention to measurements proving its decomposition already from 650 °C. Dolomite begins to decompose at 700 °C and FeCO<sub>3</sub> at 500–600 °C; according to [12], it is necessary to count with the decomposition of carbonates already at 500 °C, depending on the presence of other mineral components. Furthermore, the LOI value is distorted by the presence of portlandite, specifically by the water released during its decomposition, because calcium hydroxide decomposes at 330–460 °C [13]. Some authors resolve the mentioned problems by reducing the ignition temperature to 710 °C [14].

If the carbonate content in the sample is unknown or the sample contains a higher amount of carbonates, it is necessary to select a procedure where before the actual ignition, the carbonates and portlandite are removed by dissolving them in HCl of a concentration e.g. 17% or 3 mol l<sup>-1</sup>. In a favorable case, the UCC does not dissolve in HCl, as it is in the case of coal-combustion ashes, but in the case of biomass ash, it should be taken into account that UCC may contain some volatile acid-soluble organic carbon. The LOI of acid-treated dry sample then corresponds to acid-insoluble organic carbon.

The presence of components with structural water – in particular clay materials – which release water when heated, causes a positive error in the assessment. If we determine the UCC of the acid-treated ash sample on a device for elemental organic analysis (e.g. LECO or Flash EA microanalyzer) as the TOC, then the structural water does not cause a positive error, but we determine only the acid-insoluble organic carbon. TOC is however a sum of volatile acid-soluble organic carbon and acid-insoluble organic carbon. If the initial sample contains only acid-insoluble organic carbon, then this instrumental method provides significantly more correct results than the LOI method; if the sample, however, contains also volatile acid-soluble organic carbon, it is necessary to measure this parameter using a different methods and add it to the calculation of the TOC.

As biomass-combustion ashes often contain portlandite and almost always carbonates, mainly calcite, at higher concentrations, LOI-based methods do not provide satisfactory results in UCC determination. Therefore, based on our long-term experience with the measurement of the reactivity of such carbon materials as coke, chars, amorphous and glossy carbon and unburned carbon (since

1987 [15]), we propose a thermogravimetric method for UCC determination using the Boudouard gasification reaction  $\text{CO}_2 + \text{C} = 2\text{CO}$  taking place above 800 °C. In the case of biomass ash, this reaction is specific for unburned (combustible) carbon, is strongly endothermic ( $\Delta H$  172.4 kJ mol<sup>-1</sup>) and is catalyzed by alkali metals [16]. The proposed method does not use acid treatment and thus makes it possible to determine TOC(=UCC) even in the case of the presence of volatile acid-soluble organic carbon. It further records mass losses in the decomposition of calcium hydroxide and carbonates.

One aim of the presented work is to propose a method for the determination of unburned carbon in biomass-combustion ashes using the Boudouard reaction which would also make it possible to determine portlandite and carbonates and not requires acid treatment. The other objective is to present the mass balance of carbon in the ashes considered, proving the correctness of the method proposed.

## 2. Experimental

### 2.1. Materials

For the experiments, 10 samples were used; these came from 7 power plants of the Czech Republic burning biomass-waste wood chips, bark and straw. Each power plant provided 10–15 kg air-dried ash and the samples taken were homogenized by their stirring and grinding to a grain size below 2 mm. From the homogenized ash, approximately 50 g of the sample were randomly selected for analyses, ground to a grain size below 0.2 mm and homogenized again in a plastic container with plastic balls. The samples thus obtained were considered average and were characterized by elemental analysis, by moisture, portlandite content, the carbonate group CO<sub>3</sub> and volatile organic carbon (VOC). The characteristics of the samples are summarized in Tables 1 and 2. The values listed are always the average of three determinations.

### 2.2. Methods

#### 2.2.1. Procedures and methods for characterizing samples

The X-ray diffractometry examination of the crystallographic phases was performed on X'Pert PRO  $\theta$ - $\theta$  powder diffractometer with para-focusing Bragg-Brentano geometry using CuK $\alpha$  radiation. An ultrafast X'Celerator detector was employed over the angular range of 7–70° ( $2\theta$ ) with a step size of 0.017° ( $2\theta$ ) and a counting time of 20.00 s step<sup>-1</sup>. Data evaluation was performed using the software package High Score Plus V 2.2e PANalytical.

Elemental composition was determined by a standard-less X-ray analysis. The powder samples were fixed on a Cu-tape and then analyzed by the EDS Silicon Drift Detector Apollo X, EDAX Inc.

Portlandite was determined by the thermogravimetric method after [17] on the SETARAM Setsys Evolution 18 analyzer. About 23–25 mg of the dry sample were heated at a rate of 10 °C min in an inert atmosphere in the temperature range of 50–550 °C; the mass loss caused by the release of the water formed was recalculated to the portlandite content.

The carbonate CO<sub>2</sub> was determined according to the international standard [18] while using 3 mol l<sup>-1</sup> of HCl. The CO<sub>2</sub> released from the carbonates was captured in Ca(OH)<sub>2</sub> on an inert carrier with a grain size of 1.2–1.7 mm and weighed. Subsequently, it was recalculated using a factor of 1.36 to carbonate CO<sub>3</sub> and utilizing a factor of 0.27 to inorganic carbon; since no other inorganically bound carbon had been found (see below), this was the method used for the calculation of the total inorganic carbon content.

In the samples in which portlandite had not been found, the VOC was determined as the LOI of a dry sample according to the European norm [19]. In the samples with portlandite, the same

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