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# Unburned carbon in combustion residues from solid biofuels

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## HIGHLIGHTS

- Different methods to determine unburned carbon in ash yield slightly different results.
- Unburned carbon is mostly elemental carbon, very little volatile or semi-volatile organic carbon.
- Raman results show that unburned carbon is similar in bottom ash and in fly ash.

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## ABSTRACT

Unburned carbon (UC) in 21 combustion residues from solid biofuels has been examined using several methods of analysis (including LOI and TOC) as well as micro-Raman spectroscopy. The concentration of unburned carbon in the residues varied over an order of magnitude and in several samples accounted for about 10% of the ash mass. It was observed that TOC had a poor correlation to organic carbon, especially for fly ashes. LOI at all tested temperatures showed a better correlation than TOC to the organic carbon content, whereas the TOC is better correlated to elemental carbon. $LOI_{550}$ gave a larger variation and a less complete mobilisation of unburned carbon than LOI at 750 or 975 °C did, but at the highest temperature metal oxidation was notably affecting the mass balance to the extent that some samples gained mass. For this reason, and of the temperatures tested, $LOI_{750}$ seem to be the most stable indicator for organic remains in the incineration residuals. Most of the unburned carbon is elemental, and only slowly degradable, so the potential emissions of organic compounds from ashes should not be assessed by using a TOC test. The structure of the detected elemental carbon in UC is similar to that of activated carbon, which indicates a potentially large specific surface. This should be borne in mind when assessing the environmental impact of using ash for different purposes, including use as a construction material. Field studies are needed to verify the actual impact as it may depend on environmental conditions.



## 1. Introduction

The presence of unburned carbon (UC) in solid combustion residue not only hints at imperfections in the combustion process but also raises fears that the residue might release potentially noxious organic substances. However, examination of unburned carbon in ash from the combustion of different fuels has shown that unburned carbon is largely elemental carbon (EC) rather than organic carbon (OC) (among others [1–4]). Elemental carbon, or charcoal, is chemically stable and degrades very slowly in a natural environment – after several thousand years its structure is mostly unaffected (see e.g. Cohen-Ofri et al. [5] and Spokas [6]). It should therefore be noted that the unburned carbon detected in combustion residue is essentially something other than the presence of organic reactive carbon.

There are several routine methods to determine the content of unburned carbon in combustion residue. These methods are also used for other materials, such as determining the content of organic matter in soil or water. While using the same method of analysis is desirable, some confusion may arise when interpreting the results, as different materials respond in different ways.

Loss on ignition, or LOI, is a convenient method to determine what could have burnt provided the combustion residue has not absorbed water following extraction from the furnace, in which case LOI would consist of unburned carbon, carbonate carbon, hydroxide water or even hydration water [7,8]. LOI is carried out at a variety of temperatures depending on the fuel; 550 °C for biomass and 750 °C for coal [9] or the envisaged area of use, 950 °C for cement, [10]. The lowest temperature is used for biomass to ensure that potassium and chlorine are not counted as oxidisable carbon.

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LOI is not recommended for use with air pollution control (APC) residue from waste-to-energy plants because these materials are very hygroscopic and the adsorbed water will affect the LOI-value [11]. The suitability of the ash material as a silica source in concrete is checked by igniting at 950 °C which is supposed to reveal bound water and carbonates.

On the other hand, TOC yields the carbon content. Although ASTM calls TOC 'Total Oxidisable Carbon' [12], the expression 'Total Organic Carbon' is often used for combustion residues, similar to the use of this method to determine organic content in soil or water [13]. It has been shown [3] that a large proportion of soil carbon may also be elemental. The ASTM definition will be used here.

A factor that complicates the interpretation of thermal or chemical analyses is the complexity of combustion residues as they represent a matrix that may be involved in the processes in which carbon reacts. Although they are products of oxidation, i.e. combustion, their composition hints at reduced conditions when they are extracted. The particle size distribution may be quite broad and not all components in the larger particles may have time to react during the process.

The present paper describes an examination of UC, determined using different analytical methods on solid residues from Swedish combustion plants, complemented by a study of the samples using a spectroscopic method. Three questions are addressed in the paper:

- What is the carbon content of combustion residues and how can it be assessed?
- How much of the unburned carbon is elemental and what is the remainder?
- What are the properties of EC in UC?

As the fuels used in Swedish combustion plants are largely solid biofuels, the focus of this paper is on combustion residues from solid biofuels. Samples were chosen to provide a wide range of unburned carbon content.

## 2. Materials and methods

The 21 samples from 18 combustion plants studied in this investigation represent various types of furnaces (grate, fluidised bed, pulverised fuel with burners). Also represented are different types of residue (bottom ash, various types of fly ash, mixed ash, air pollution control residue), different fuels (wood chips and pellets, bark, waste wood, municipal solid waste), large plants and small plants and different industrial sectors (cogeneration plants, heating plants, pulp and paper mills). These include efficient combustors as well as plants that are not as efficient as they should be, see Table 1 for a summary.

Samples 1, 2, 5, 6, 9, 10 and 12 are bottom ash, which is usually handled separately from fly ash in large plants, whereas mixing fly ash and bottom ash (samples 13–20) is more common in smaller plants. The remaining samples are fly ash or APC residue. In the latter, samples 11 and 21, additives are also found, including activated carbon. With regard to the bottom ash samples, four of the plants were sampled for fresh ash and three were sampled for aged ash.

In the micro-Raman investigation, a sample of activated carbon, DioxSorbBP2, was obtained from Jacobi Carbon Systems and used as reference material.

### 2.1. Sampling and sample treatment

Some of the samples of combustion residues were gathered for this specific investigation and some originate from other studies. Sampling procedures vary widely and the samples should therefore not be considered representative in a regulatory context of the residues produced in these plants. However, collectively they should represent a cross-section of combustion residues that arise in real situations.

All samples were first homogenised at the laboratory and subsamples were ground to <100 μm using a disc stainless steel grinder.

### 2.2. Analytical methods

#### 2.2.1. Total solids

Total solids were determined by weighting after drying at 105 °C for at least six hours.

#### 2.2.2. Loss on ignition

There are numerous procedures for the determination of volatile substances, mainly aimed at quantifying oxidisable substances in a sample. Using different standards, there is considerable variation in the temperature at which ignition takes place.

**Table 1**
A summary of the ash types sampled.

| Sample number | Combustion plant | Type of furnace | Type of combustion residue | Fuel | Nominal power MW fuel |
|---|---|---|---|---|---|
| 1 | Händelö P11 | Grate | Fresh bottom ash | Waste wood and rubber tires | 70 |
| 2 | Händelö P11 | Grate | Aged bottom ash | Waste wood and rubber tires | 70 |
| 3 | Händelö P11 | Grate | Cyclone ash | Waste wood and rubber tires | 70 |
| 4 | Händelö P11 | Grate | Baghouse filter ash | Waste wood and rubber tires | 70 |
| 5 | Dåva | Grate | Aged bottom ash | MSW | 77 |
| 6 | Braviken | Grate | Aged bottom ash | Bark, de-inking sludge | 66 |
| 7 | Skellefteå | CFB | ESP ash | Wood chips | 92 |
| 8 | Iggesund | Grate | ESP ash | Bark | 70 |
| 9 | Wargön | Grate | Bottom ash | Bark | 24 |
| 10 | Avesta | Grate | Bottom ash | MSW | 15–18 |
| 11 | Nynäshamn | BFB | Baghouse filter (APC residue) | Waste wood | 24 |
| 12 | Öresundskraft | PF | Bottom ash | Biomass | 220 |
| 13 | Bureå | Grate | Mixed | Wood pellets | <5 |
| 14 | Burträsk | Grate | Mixed | Wood pellets | <5 |
| 15 | Jörn | Grate | Mixed | Wood pellets | <5 |
| 16 | Kåge | Grate | Mixed | Wood pellets | <5 |
| 17 | Byske | Grate | Mixed | Wood pellets | <5 |
| 18 | PC Vindan | Grate | Mixed | Wood pellets | <5 |
| 19 | Norsjö | Grate | Mixed | Wood pellets | <5 |
| 20 | Boliden | Grate | Mixed | Wood pellets | <5 |
| 21 | Händelö P14 | CFB | Baghouse filter (APC residue) | Sorted waste | 75 |