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Research article

The possibilities to identify combusted fuel based on an analysis of ash from local heating

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ABSTRACT

Combustion of undesirable components with a high calorific value (waste: plastics, rubber, chipboard, plywood etc.) contribute to an increased emissions of PM particles. The possibility of identification of non-desirable fuels was verified by analysis of unburned carbon from bottom ash by means of pyrolysis-GC/MS. Compounds derived from thermal conversion of main wood components in the unburned carbon are formed by aldehydes, ketones, alkanes, alkenes, alkanoates, polycyclic aromatic hydrocarbons, compounds containing benzene, compounds containing phenol and nitrogen. Unburned carbon from plywood/chipboard contains compounds with nitrogen (heterocyclic and aliphatic) in increased concentrations (33–51 ng/mg) compared with unburned carbon from pure wood (7–12 ng/mg). The concentrations increased almost two times were proved for compounds containing phenols in unburned carbon from wood composite. Total amount of determined organic compounds is also almost two times higher than that contained in unburned carbon from wood. The indication of waste wood combustion from unburned carbon is possible using the ratio: phenol/(2-methylphenol + 4-methylphenol).

1. Introduction

Approximately 203 million households in Europe are mostly equipped with a single heating system – boilers (Lasek et al., 2018). Air pollution from households is best characterized as a nonpoint pollution problem (Chávez et al., 2011). The Moravian-Silesian Region, especially Ostrava Region, is among the areas with the highest air pollution formed by PM_{10} within the Czech Republic. Together with the Polish Silesia, it is one of the places with the highest pollution in Europe (EEA, 2016). Emissions of $PM_{2.5}$ from coal and biomass combustion in households and from commercial and institutional buildings are the main contributors to total PM emissions in the EU. Several studies have reported that wood combustion can be a major source of air pollution during the winter months in cold regions where firewood is easily available, including Scandinavian Countries but also North America, New Zealand, and Chile (Mardones and Sanhueza, 2015). The air pollution problem caused by households burning wood in urban areas is also a major regulatory problem. There are several sources of uncertainty related to the problem, including weather conditions, individual households preferences for heating, quality of the fuel used (Gómez et al., 2014).

In the Czech Republic, the local heating of households in the nationwide scale contributes to 34% of PM_{10} air pollution and 51% of $PM_{2.5}$ air pollution. Concerning the new generation domestic boilers, emissions were reduced in mass by 98% approximately for the elemental carbon (EC) and by 40% for the OC compared to the old generation of boilers (Brandelet et al., 2017). The increasing use of biomasses in the production of electricity and heat results in an increased amount of burning residue, fly ash whose disposal is becoming more and more restricted and expensive (Ohenoja et al., 2018).

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By the year 2020, to improve the PM_{10} pollution load, the Ministry of Environment of the Czech Republic will provide, thanks to the European Union, 0.3 billion EUR for the replacement of boilers in houses. This amount will ensure the exchange of up to 100,000 boilers throughout the Czech Republic. In total, however, there are up to 350,000 environmentally unfriendly old boilers in the Czech Republic, which cannot be used after September 2022. Financial investments into boiler replacement are returning because reduction in PM_{10} emissions by almost 8%, improving air quality by about 1% and contributing to a benefit of 8.8 million Euro/year – an example for Grande Porto, Portugal (Silveira et al., 2016).

In the Czech Republic, on the basis of an amendment to the Air Protection Act No. 201/2012 Coll., officials received new authority from 1 January 2017 – in the case when it is justified, they can come to homes and check how the boiler is operated and, above all, what fuel is used. Analysis of the ash or unburned fuel should ensure obtaining information on the type of fuel used. To demonstrate the kind of fuel burnt from unburned carbon contained in the ash from household heating, it is necessary to be able to identify not only waste but also allowed biofuels to ensure a clear distinction between legislatively authorized and unauthorized fuels.

Users have a strong influence on domestic boiler emission behaviour both by selection of the fuel and the burning conditions. An important factor influencing emissions is the use of non-standardised biomass (including treated, painted or insufficiently dried wood, or even agricultural waste), which generates persistent organic pollutant and metal emissions, as well as hinders efficient combustion.

The chemical composition of emissions from combustion of biomass was studied by several authors (Oros and Simoneit, 2000). No marked differences were found for emissions from different wood types (Fachinger et al., 2017). Examination of unburned carbon in ash produced by the combustion of various fuels has shown that unburned carbon is formed mostly by elemental carbon – EC, rather than organic carbon – OC (Bjurström et al., 2014). In the literature, there is very little information on the chemical composition of the unburned carbon from bottom ash, which was also confirmed by Košnář et al. (2016). The aim of this article is to determine the content of organic compounds contained in unburned carbon produced by the combustion of wood and wood waste (composite materials: plywood and chipboard) and to assess the possibility of using the chemical composition of unburned carbon to identify the type of fuel burnt.

The new contribution of this work consists in a demonstration of identification of illegal combustion of wood waste (plywood and wood chipboard) from ash (unburned carbon) formed by combustion in residential boilers. For individual kinds of fuel, specific organic compounds and markers are known to occur in particles PM_{10}. However, it was not known whether chemical compounds indicating particular fuel type are only transferred to emissions, or whether they also remain in char or boiler deposits. It is also not known how long this information is retained in ash and unburned carbon, it means how stable organic compounds, especially volatile organic matter (VOC) are in this matrix. This paper is devoted to these previously not known relationships.

2. Materials and methods

2.1. Materials

Samples for study represent natural wood and for comparison wood waste (composites – plywood, wood chipboard). The total number of the samples in the framework of the experiment was six samples of unburned carbon from the ash of hardwood and six samples of unburned carbon from the ash of wood composite materials (three samples of plywood, and three samples of wood chipboard). Samples of unburned carbon used for analysis were obtained from combustion of wood and wood waste (plywood, wood chipboard). Unburned carbon with particle size ranged from 2 to 5 cm was manually separated from ash. Separated particles of unburned carbon were crushed to the particle size below 2 mm and homogenized. The conditions of combustion were following. The samples were burned in a boiler of emission class 2 (according to the standard EN 303-5 2012) with manual operation. The weight of fuel or waste loaded into the boiler was determined. Combustion was performed daily for 8 h, 6 days in a week. The samples of waste – plywood and wood chipboard were burned two or three days in a week, time of combustion was 8 h. Sampling was performed the next day. The weight of the mixture of unburned carbon and ash was recorded. After separation of unburned carbon and ash, the weight of unburned carbon was recorded. The amount of burned fuel (wood) varied in the range from 44 to 59 kg per 8 h, for plywood and wood chipboard from 40 to 52 kg per 8 h. The amount of separated unburned carbon from wood ranged from 0.8 to 1.3 kg, and from wood waste from 0.05 to 0.9 kg per 8 h. The temperature during combustion reached 600–800 °C. Samples prepared in this way were used for analysis by the method of pyrolysis – gas chromatography with mass spectrometric detection (Py-GC/MS).

2.2. Methods

The purity of separated char particles was determined by scanning electron microscope FEI Quanta 650 FEG (FEI, USA) equipped with EDX (energy-dispersive X-ray spectrometer). Parameters of proximate and ultimate analysis of wood fuel and ash were determined according to: EN 14918 Solid biofuels - Determination of calorific value (calorimeter LECO AC500), EN 14774-2:2009 Solid biofuels - Determination of moisture content - Oven dry method - Part 2: Total moisture - Simplified method (Memmert Oven U), EN 15148:2009 Solid biofuels - Determination of the content of volatile matter (LECO TGA 701), EN 14775:2009 Solid biofuels - Determination of ash content (Digital Oven Carbolite AX 30), EN 15104:2011 Solid biofuels - Determination of total content of carbon, hydrogen and nitrogen - Instrumental methods (Elemental Analyzer EuroEA 300).

Determination of organic compounds present in unburned carbon produced by combustion of wood and wood composites was performed by method of pyrolytic gas chromatography with the mass spectrometry detector (Py-GC/MS). The apparatus consists of pyrolytic unit Pyroprobe 5200 (CDS Analytical Inc.) connected by interface directly with gas chromatograph (HP Agilent 7890 A) with the mass spectrometric detector (type Agilent 5975C). Identification of organic compounds in unburned carbon was performed according to the modified method of Kaal et al. (2009). Identification of chemical compounds in unburned carbon was also developed by Song and Peng (2010). A very fine grinded sample of unburned carbon (100–200 μg) was inserted into a pyrolytic quartz tube sealed at both ends by quartz wool. The internal standard (1 ng/μl of 1,3,5-tri-tert.-butylbenzene) was added to the sample for absolute quantification. The samples were analysed by sequential pyrolysis at the temperatures of 50 °C and 700 °C, for the period of 10 s, the rate of temperature increase was 5 °C/ms. The pyrolysate was then separated by GC/MS at the non-polar column HP 5 ms (60 m × 250 μm x 0.25 μm).

The exploratory data analysis, the statistical analysis for descriptive statistics, and the correlation analysis (at the 0.1 level of significance) were performed using the statistical software OriginPro 8.5 and Statgraphics Plus 5.1. The Dixon's test (at the 0.05 level of significance), and the values of modified MAD Z-Score were used to identify outliers.

3. Results

Purity of separated particles of unburned carbon from the ash was checked by a scanning electron microscope (Fig. 1). Most of the particles were formed by carbon without admixture of inorganic particles. Only a small number of analysed particles contained recrystallized inorganic particles on the surface. Crystals containing K-Ca-Mg-P and zinc sulphate particles (Zn-S-O) were formed from biogenic inorganic