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Zinc nanoparticle formation and physicochemical properties in wood combustion – Experiments with zinc-doped pellets in a small-scale boiler

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HIGHLIGHTS

- Pure pellet fuels were doped with different doses of Zn powder.
- Zn from the fuel efficiently enriched the fine particle fraction of the emissions.
- Structure and state of the zinc particles was highly dependent on fuel Zn content.
- With high Zn content in the fuel, ZnO nanorods were formed.
- Biofuel zinc requires more attention in emissions legislation.

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ABSTRACT

Fine particles are the most important type of pollutant affecting urban air quality. Recent studies have highlighted the relevance for health effects of the zinc component of these particles. Zinc is traditionally associated with industrial and waste combustion plant emissions, although not covered by current regulations (e.g. the EU Waste Incineration Directive). However, pure wood combustion also produces substantial amounts of zinc particles. In this study, pure wood pellet fuels doped with three doses of Zn powder were combusted in a small grate boiler. The emissions were then analysed by a broad array of techniques to shed light on the health-related properties of particles originating from Zn-rich fuel combustion. In addition, reference pellets without Zn doping (during efficient and poor combustion conditions) were studied.

Zinc was found to be efficiently released from the fuel and enriched in the fine particle fraction, a trend supported also by thermodynamic equilibrium calculations. The enrichment was systematically observed as changes in the size, mass, chemical composition, and shape of the particles. The growth of the particles was mainly due to the coagulation and growth of the pure crystalline zinc oxide (ZnO) cores. With high Zn doping ZnO nanorods were clearly formed, whereas with a low Zn content in the fuel other ash-forming species defined the particle morphology better. The ZnO formation process was found to be thermodynamically similar to the production of engineered nanomaterials. This study suggests that more attention should be paid to the zinc content of biomass fuels with regards to emission legislation,

Abbreviations: BC, black carbon; DGI, Dekati Gravimetric Impactor; DLPI, Dekati Low Pressure Impactor. Measure particle mass size distribution; DR, dilution ratio; EC, elemental carbon; ED, ejector diluter; EDS, energy dispersive X-ray spectrometry; ELPI, Electrical Low Pressure Impactor. Measure particle number size distribution; GMD, geometric mean diameter of particles; MMD, Mass median diameter; OC, organic carbon; OM, organic matter; PAH, Polycyclic Aromatic Hydrocarbons; PM, Particulate Mass; PM_1, Particle mass below aerodynamic diameter of 1 µm; PRD, porous tube diluter; REF, experiment case without Zn doping of fuel; RWC, residential wood combustion; SMPS, Scanning Mobility Particle Sizer. Measures particle number size distribution; TEM, transmission electron microscopy; TEOM, Tapered Element Oscillating Microbalance. Real time particle mass monitor; XRD, X-ray diffraction; Zn, zinc as an elemental form; zinc, zinc as a general form; Zn170, experiment case with doping of 170 mg Zn/kg fuel; Zn480, experiment case with doping of 480 mg Zn/kg fuel; Zn2300, experiment case with doping of 2300 mg Zn/kg fuel.

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for example when wood bark is utilised in energy production. This concern, in particular, the small and medium scale (below 1 MW) power plants as efficient particle removal techniques are generally utilised in large scale power plants.

1. Introduction

Current levels of urban air particles are associated with mortality and morbidity, especially for elderly people with cardiovascular disease, asthmatic subjects of all ages, and children. Both the particulate mass and its physico-chemical properties have been suggested to contribute to the health outcomes [1,2]. Important chemical components to be considered include organic matter (OM), PAHs, black carbon (BC), and transition metals, and the important particle physical properties include size, morphology, mass, surface area, and number concentration. In particular, particle emissions from residential wood combustion (RWC) [3], coal and oil combustion [4], traffic [5] and the metal industry [6] are considered as being harmful sources to health.

RWC has become one of the most important sources of fine particles globally. Various combustion technologies (e.g., boilers, burners, stoves, masonry heaters, and open fireplaces) and fuels (e.g., wood logs and pellets from different species) are used, which all generate different specific particulate and gaseous emissions [7–12]. The combustion in small-scale appliances is often partially incomplete and produces significant amounts of OM and BC, whereas the complete biomass combustion, e.g., in pellet boilers, produces mainly fine particles consisting of inorganic alkali and trace metal species [13]. The inorganic elements in fine particles are formed by the volatilisation from the fuel and are dependent, among other aspects, on the chemical composition of the fuel, the reactions of inorganic species and the combustion temperature [14–16]. In wood fuels, potassium, sulphur, chlorine and sodium are very volatile, and in the reducing area of the fuel bed, metals, such as zinc, may also volatilise [14,15]. The formation of zinc particles in wood combustion is believed to occur by the oxidation of elemental Zn vapour, and the subsequent rapid nucleation occurs due to the very low saturation vapour pressure of zinc oxide (ZnO) before other gas-particle conversion reactions occur in the system [16]. Thus, ZnO particles have been observed to act as seeds for the condensation of inorganic vapours and organic material, forming ash particles with a nested structure. Under efficient combustion conditions, the outer layer is mainly composed of alkali salts [16]. In addition, with chlorine-rich fuels (e.g., straw), $ZnCl_2$ vapour can also be formed, which has a considerably higher saturation vapour pressure than ZnO [17].

The importance of zinc containing particles in urban air on human health has recently been identified. Thirteen years ago, Fernandez et al. [18] proposed that the toxic effects of particulate emissions from the co-combustion of coal and biomass, including dried municipal sewage sludge, seem to be associated with the presence of zinc in the particles. In outdoor air, zinc containing particles are particularly associated with industrial emissions from smelters and steel mills, waste combustion plants, and engine emissions due to the Zn emitted from lubrication oils [19–22]. Zn is not currently covered by the EU Waste Incineration Directive, unlike Cd, Tl, Hg, Sb, As, Pb, Cr, Co, Cu, Mn, Ni and V. However, even in pure wood combustion, the concentration of zinc is several orders of magnitude higher than those of the other metals [15] and it releases efficiently from fuel to become fine particles. ZnO has been clearly found to be harmful when produced as engineered nanoparticles (ENPs) [23]. For example, ZnO particles can cause local and systemic inflammation in experimental animals as well as in vitro cellular toxicity [24]. In vivo and in vitro toxicological studies also suggest the possible toxic role of zinc in particle emissions from residential wood combustion [25,26]. Furthermore, in power plants, zinc has been found to have a specific role in the creation of problematic and corrosive deposits in the heat exchangers [27].

Zinc content in biomass fuels vary remarkably: for pure wood fuels, the content is in the range of 7–25 mg/kg fuel [15,28–30] and can be up to 200 mg/kg in wood fuels, including bark [15,30]. In particular, birch bark may contain a high concentration of zinc [15,30]. Even concentrations up to 1000 mg/kg are possible in, for example, waste wood incineration [21]. The volatility of the zinc in combustion seems to be efficient, independent of the fuel type [15]; however, there is a very limited amount of information available on the behaviour of zinc in combustion processes.

In this study, pure pellet fuels doped with different doses of elemental Zn powder were combusted in a small pellet boiler, and the particle emissions were measured and analysed in detail. The aim of this study was to investigate the behaviour of Zn in a fixed bed wood combustion process. The effect of fuel Zn concentration on particulate physico-chemical properties and morphology was studied over a range of Zn concentrations. The main advantage of the study is that the fuel chemical composition is exactly the same for all of the cases considered, excluding the Zn content, which ensures the comparability of the studied cases. In one case, also the poor combustion of doped pellets was applied.

2. Experimental

2.1. Combustion appliance and fuel

Combustion experiments were performed in the emission research laboratory of the University of Eastern Finland at Kuopio using a grate boiler operated with pellets (Biotech GmbH, model PZ-RL 25) and with a nominal output of 25 kW. More details on the boiler can be found in Lamberg et al. [31]. The boiler was turned on approximately three hours before the start of the experiment to ensure the stability during the experiment. Bottom ash samples were collected from the ash box and analysed after each experiment. Temperatures were monitored continuously from the flue gas and particle sample lines using K-type thermocouples. The experimental set-up is shown in Fig. 1.

Pure shavings and sawdust from pine stem wood were used as raw material of the pellets. The material was first ground by using a mill and a 3-mm sieve and then mixed with elemental Zn powder (Sigma Aldrich) in various concentrations or left unaltered. According to thermodynamic considerations in wood fuels, zinc is mainly released as Zn vapour due to reducing conditions in the fuel bed [32] and therefore Zn was added to the pellet as elemental form. However, it should be noted that zinc exists in fuels in different chemical forms, such as elemental Zn, ZnO and organically bound zinc which may affect the release behaviour [21]. After mixing, the materials were pelletized (Hylicpress M 60, Konepaja M. Pappinen Ltd.). The Zn contents of the used fuels were 11 mg Zn/kg of fuel (reference pellets without Zn doping, named “REF”), 170 mg Zn/kg (“Zn170”), 480 mg Zn/kg (“Zn480”) and 2300 mg Zn/kg