Fate of bromine and chlorine in bubbling fluidized bed combustion – Formation of alkali halide aerosols

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HIGHLIGHTS

- Co-firing bark and HBr/HCl in a bench scale bubbling fluidized bed (BFB) unit.
- Cl and Br fate characterization in BFB combustion conditions.
- Addition of HBr/HCl greatly increased alkali release from bark during combustion.
- HBr found more reactive towards alkali metals than HCl.

ARTICLE INFO

ABSTRACT

In solid substances used as fuels, bromine originates mainly from flame retarded plastics and textiles, as well as from wastewater sludge. It has been indicated that bromine behaves in a similar way as chlorine with respect to ash forming matter, aerosol formation and high temperature corrosion in biomass and waste fired boilers. In this work, a measurement campaign was carried out in a 20 kW_{th} bubbling fluidized bed (BFB) bench scale reactor to characterize the fate of Cl and Br in BFB combustion conditions. Spruce bark was used as the base fuel – serving as a source of alkali metals (mainly K, little Na). The gases HCl and HBr were fed with the fluidization air at different proportions into the BFB unit. In total, six experiments were done. The fate of bromine and chlorine was evaluated by means of several measurements including: FTIR (flue gas measurement), a low-pressure impactor (size distribution and chemical composition of aerosol particles) and deposit probe sampling (deposit growth rate and chemical composition of the windward, 90° side and leeward deposits). It was shown that the addition of HBr or HCl greatly increased the release of alkali metals (K, Na) from the original fuel (spruce bark) during combustion. The promoting effect of HBr was more obvious than that of HCl. HBr was found more reactive towards alkali metals than HCl.

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1. Introduction

Combustion of biomass and waste for heat and power production, compared to fossil fuels, represents a technically feasible option to reduce the emission of CO_2, which is the most abundant greenhouse gas. However, replacing conventional fuels with biomass or waste often results in severe ash related problems such as slagging, fouling and high temperature corrosion. Chlorine (Cl) and alkali metals, in particular potassium (K), have been identified as the main contributors enhancing these problems [1–3], whereas data on the effect of bromine (Br) is still scarce. The main reason for this lack of knowledge is the typically low bromine concentration compared to chlorine in municipal solid waste (MSW) and even negligible in biomass. However, if high-level-bromine waste is combusted in a boiler, the potential effects of bromine should be considered. There are indications in the literature that bromine behaves in a similar way as chlorine in high temperature corrosion [4,5]. It was concluded by Vainikka et al. [4] that if there is a source of bromine in the fuel, corrosive high vapor pressure bromides can be formed analogously to chlorides. In addition, it has been indicated from a few studies [6,7] that bromine has a similar promoting effect as Cl upon the volatilization of metals, such as K, Fe, Cu, Zn, Mo, Cd, Sn, Sb and Pb.

Regarding halogens, it is generally known that Cl in waste fuels originates mainly from chlorinated plastics such as PVC (polyvinyl chloride) or sodium chloride (NaCl) from dietary salt in food residues [4,9,10]. The concentration of Cl in MSW is typically ranging

from 0.5 to 1 wt% [7,8]. Bromine is mainly associated with flame-retarded plastics, which are commonly found in specific waste fractions from electrical and electronic equipment (WEEE) (i.e. circuit boards and equipment casings for TV and PC housings) and from plastic heat insulation foams used in the building sector, as well as flame retarded textiles and fabrics used in sofa, upholstery and furniture cushions. The three most widely used brominated flame retardants (BFRs) today and over the past 10–20 years of the plastic era are tetrabromobisphenol A (TBBPA), decabromodiphenyl ether (DecaBDE) and hexabromocyclododecane (HBCD) [4]. It has been shown that WEEE can show bromine levels of up to several wt%, which is much higher than the typical approximate 50–200 mg/kg found in mixed MSW [7,8]. In addition, bromine is also used for water purification and disinfection to substitute chlorine in both commercial and residential water treatment process, which can be a source of Br in both industrial and municipal sewage sludge [11–13].

The release of halogen during waste combustion depends strongly on the chemical form of the halogen. Organic halogen compounds decompose and are released mostly as halogen hydrides (HBr, HCl) or short chain halogen containing organic compounds. While inorganic halogen compounds may evaporate or stay in the ashes. Since organic halogen is the major form in WEEE, textiles and chlorinated plastic waste, halogen hydrides (HCl, HBr) are the major primary halogen products in waste combustion [6].

Data on the formation of alkali bromide in aerosols in fluidized-bed combustion of solid biomass and waste fuels is not yet available. The objective of this work was to establish a basic understanding on the fate of chlorine and bromine, especially the formation of alkali halide aerosols in BFB combustion conditions.

2. Experimental

In this work, a measurement campaign was carried out in an electrically stabilized 20 kW_{th} bubbling fluidized bed (BFB) reactor. Spruce bark was used as the base fuel – serving as a source of alkali metals (mainly K, little Na). The properties and the composition of the main ash forming elements in the bark are shown in Table 1. The gases HCl and HBr were fed with the fluidization air at different proportions into the BFB unit. A total of six experiments with different Br:Cl molar ratios were done, as shown in Table 2. HBr gas was used as the source of bromine. The source of chlorine was mainly from HCl gas and a little from the bark.

The BFB reactor as shown in Fig. 1 has a bed diameter of 0.16 m and height of 0.55 m. The freeboard zone is 3.5 m in height with a

Table 1
Fuel properties.

	Bark
Moisture (wt%, ar)	30
Ash (wt%, db)	3.2
Ultimate analysis of dry solids (wt%, db)	
C	50.7
H	5.7
N	0.4
O	39.9
S	0.02
Main ash forming elements (mg/kg, db)	
Ca	9100
K	2300
Na	140
Cl	140
Br	<10
Heating value (MJ/kg)	
LHV, ar	12.42
LHV, db	18.69

diameter of 0.23 m. The interior walls with flame contact were made of ceramics and quartz. The bed material was natural sand with a mean particle diameter 0.33 mm (0.1–0.6 mm) and a composition (wt%) of Na_2O_3 3.0, K_2O 2.3, MgO 0.59, CaO 2.3, Al_2O_3 11.8, Fe 1.4, SiO_2 77.5. The mean gas velocity in the reactor was about 0.5 m s^{-1}, corresponding to a total residence time of 7–8 s [14]. The air staging was kept constant (primary/secondary/tertiary, 50:30:20). The bed temperature was kept between 850 and 870 °C.

The dried flue gases (O_2, CO_2, CO, NO, SO_2) were analyzed with standard on-line analyzers. The wet and hot (180 °C) flue gases (H_2O, CO_2, CO, NO, SO_2, HCl) were measured by Fourier Transform Infrared Spectroscopy (FTIR). HBr, Br_2, HCl and Cl_2 in the flue gas were sampled by absorption bottles and analyzed by means of ion chromatography, which was based on the EPA Method 26 – Determination of hydrogen halide and halogen emissions from stationary sources (non-isokinetic method) [15]. A schematic picture of the absorption bottles is shown in Fig. 2. Six impingers are placed in an ice water bath. The first empty bottle is called "condensation bottle". When the cooled flue gas passes through, water will be condensed and stay in the first bottle. HBr and HCl will be partially absorbed in the first bottle, since they will dissolve in the condensed water. Br_2 and Cl_2 are not absorbed, since they are only slightly soluble in cold water. The second and the third bottle contains an acidic absorbing solution, 0.1 M sulfuric acid (H_2SO_4), which is used to collect hydrogen halides (HBr and HCl); while the fourth and fifth bottle contains an alkaline absorbing solution, 0.1 M sodium hydroxide (NaOH), which is used to collect the halogens (Br_2 and Cl_2). The sixth bottle filled with silica gel is used to dry the flue gas.

The aerosols in the flue gas were sampled in the upper part of the freeboard, where the flue gas temperature was about 850 °C. In this work, the term "aerosol" is specifically used for the fine particles with an aerodynamic diameter (dp) less than 1 μm, which are mainly formed from particles that are vaporized at fluidized bed combustion temperatures. These vapors nucleate/condense to form fine particles in an aerosol sampling probe [16].

The aerosol sampling was carried out by means of a combination of an air-cooled gas permeable tube probe and two consecutive ejector dilutors. A schematic diagram of the aerosol sampling arrangement is shown in Fig. 3. The sample gas was sucked into the probe and immediately diluted by nitrogen and quenched within a 200 mm long gas permeable tube diluter. The target dilution ratio (DR) of this stage was 4. The sample gas was taken from the probe to a second dilution stage, where it was diluted by an ejector diluter with DR = 8. The sample gas after dilution was then divided between two parallel Dekati® low pressure impactors (DLPI) and an electric low pressure impactor (ELPI). At the location of the division a third gas stream was taken to an FTIR gas analyzer for determining the dilution ratio on the basis of H_2O and CO_2. The reference H_2O and CO_2 concentration for determining the total dilution ratio was taken from the FTIR at the location after cyclone as shown in Fig. 1. Before aerosol sampling lines (DLPI and ELPI), a precutter cyclone was connected to remove particles larger than 10 μm. Furthermore, a third dilution stage was carried out by an ejector diluter with DR = 11 before ELPI. With ELPI, the number-size distribution of particles was observed on-line.

DLPI is a cascade low pressure impactor, which has 13-stages so that airborne particles are size classified into 13 size fractions, from 30 nm up to 10 μm. An additional back-up filter can be used to collect particles smaller than 30 nm. A schematic picture of DLPI is shown in Fig. 4. Each impactor stage has two co-linear plates. One acts as a small nozzle to control the flow velocity; the other one acts as a collection substrate for the particles. When the flue gas passes through the impaction nozzle (following the blue streamlines), it is turned sharply before the collection substrate.