Which chlorine ions are currently being quantified as total chlorine on solid alternative fuels?

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ABSTRACT

Total chlorine content (TCC) is an important quality parameter of refuse derived fuel (RDF) or biomass wastes due to boiler corrosion or ash slagging. These phenomena depend upon the organic or inorganic forms of chlorine (Cl) compounds combustion pathways. Present work investigates the TCC of RDF optimizing the Cl quantification procedure following standard oxygen bomb combustion. Hypochlorite (OCl^-) ion was detected in different absorbing solutions (H_2O; KOH; CO_3^{2-}/HCO_3^-) together with Cl^-. A quantifying titration step was carried out in parallel to chloride quantification by ionic chromatography. TCC (sum of both Cl forms) of wheat straw and four different RDF were found to be 1.5 to 2 times higher than the content (0.6–1.6%) previously obtained, both in KOH 0.2 M. Similar TCC increase ratios were obtained for waste components. OCl^- association with Cl_2 (g) formation during bomb calorimeter combustion is discussed. Further insight on RDF chlorine nature indicates that organic Cl should be the most relevant considering that its Cl is mostly non-soluble and releasable from fuel up to 850 °C. RDF or straw chlorinated emissions or gas phase corrosion are pointed out over ash slagging or fouling. However ash slagging may occur due to recombination of inorganic Cl.

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1. Introduction

Refuse Derived Fuels (RDFs) are solid fuels prepared from nonhazardous waste streams as well as agricultural residues. The use of fuels other than coal brought up new technological constraints like overall energetic efficiency, boiler corrosion and gaseous emission treatment efficacy. Chlorine (Cl) was found to be the RDF main contaminant contributing to such undesirable effects. Cl can reduce fuel burnout [1], increase acidic emissions [2] and alter partitioning of trace element emission [3,4]. Cl may also increase ash deposition rates [5] and potentiate corrosion [6] or slagging (formation of molten or partially fused deposits on furnace walls or convection surfaces exposed to radiant heat). Additionally it may boost corrosion potential as gaseous hydrochloric acid (HCl) or vaporized alkali chlorides react with boiler metal surfaces [7–9]. Chlorine combustion pattern is fuel specific [10] and determined by other elements' abundance. Thus, the way these chlorine-induced phenomena occur is far from being straightforward.

RDF literature suggests that due to the high temperature of flame most Cl can be found in gas phase as gaseous HCl or vaporized alkali chloride species (NaCl, KCl, $MgCl_2$, etc.) [1,11]. Other Cl gaseous species like molecular chlorine (Cl_2) tend to form locally (at high temperature) or in a oxidizing environment by thermal decomposition of HCl [7,8]. Some authors [12,13] suggested that HCl is a combustion product of the organic chlorinated compounds rather than of the inorganic ones despite that it is still not clear of how does the nature of the Cl bond correlate with combustibility [11,14]. Indeed HCl emission from municipal solid wastes (MSW) combustion was found to be related to both organic and inorganic bound chlorides [15–17]. Eighty percent of fuel's Cl was converted into HCl independently of boiler temperature when derived from an organic source like polyvinyl chloride (PVC) [12] but only 42–48% of Cl was released as HCl when derived from an inorganic compound (e.g. NaCl) despite that conversion rate kinetics sharply increases with boiler temperature [12]. While some of gaseous alkali chlorides react to form HCl [8], alkalis will be retained in fly ash silicates (conferring sintering properties to deposits) or aluminosilicate forms [1], depending upon these elements' abundance and chlorine concentration [18]. Remaining vaporized alkali chlorides may either generate nucleates or condense on fly ash surface. Some alkali chlorides may also be found, un-reacted, in bottom ashes. Alkali earth metals (Mg, Ca, etc.) influence the chemical forms, amount and properties of alkali metals released [19]. Often, they are able to decrease the retention of alkali metals on silicates leading to the formation of less adhesive compounds [20,21]. Thus, the identification of chlorine chemical nature and content associated with the combustibility properties of fuel-chlorinated compounds shall allow for a more reliable optimization of combustion systems. RDF chlorine content will be difficult to avoid taking into account that biomass Cl is within vegetation tissues and MSW has an inorganic Cl diffuse loading distribution due to food waste spreading. Cl bond in inorganic salts (NaCl, KCl and as $CaCl_2$)

dominates in kitchen waste while the non-packaging plastics are nearly totally composed of organic Cl [11,22] including PVC. Therefore, RDF total chlorine content (TCC) depends on the source of its components.

Among the existing methods for quantifying chlorine content on alternative fuels are combustion based ones [23] aiming the complete conversion and exhaustive capture of the fuels' Cl. Regarding those taking place at ambient pressure, some authors have successfully addressed the issue of the complex nature of fuels' chlorine and the diversity of its released forms when measuring is undertaken [14,23]. Yet, less is known regarding its influence on the oxygen bomb combustion.

In this work the authors study the chlorine forms and content of four different RDFs obtained from the high calorific fraction (HCF) mechanically separated from unsorted MSW. An initial effort was made towards a more precise quantification of TCC on solid alternative fuels through optimization of the standard oxygen bomb combustion (BC) method [24,25] using water extractable chloride of wheat straw as a reference. The influence of Cl chemistry involved in gaseous species formation and capture in absorption solutions, is discussed. A comparative study of TCC of RDF main components (paper and cardboard, wood, plastics, food and garden) assessed by standard and optimized method aimed to highlight the contribution of the physical composition of RDF to TCC when BC method is used. Besides, efforts were made to identify and quantify the nature of chlorine of straw and RDF (inorganic vs. organic and combustible vs. incombustible) in parallel with other elements' abundance, towards a better understanding of possible effects of alternative solid combustible use on boilers.

2. Material and methods

2.1. Solid fuels and samples preparation

Four types of RDFs (labeled 1 to 4) and wheat straw (15.0 ± 0.1 MJ/kg_{dw}) were analyzed. RDF1 (18.1 ± 0.1 MJ/kg_{dw}) is mostly composed of office waste (a mixture of plastics, paper, cardboard and toilet paper) shredded to a particle size of 30 mm. RDF2 (21.3 ± 1.1 MJ/kg_{dw}) and RDF3 (23.3 ± 0.2 MJ/kg_{dw}) were obtained from the HCF separated from urban unsorted MSW by a double screen trommel (120 mm and 80 mm), followed by magnetic separation. RDF2 corresponds to the fraction above 120 mm and RDF3 to the rejected material above 80 mm (including fraction >120 mm), both after particle size reduction down to 30 mm and supplementary metal removal. RDF4 (21.7 ± 0.2 MJ/kg_{dw}) was also produced from the HCF obtained by MSW mechanical treatment in a different unit. RDF2 to 4 samples look similar and it was possible to detect some putrescible organic waste contamination through odor and "dirty" aspect. Gross calorific value (in brackets) was determined using a bomb calorimeter (LECO AC 600) following the standard procedure for RDF [26].

RDF3 main components, paper and cardboard wastes, wood wastes, plastic wastes (LDPE — low density polyethylene film and PET — polyethylene terephthalate), food and garden wastes were collected in a hand sorting campaign of ca. 250 kg of its own HCF.

All samples were stabilised towards the eventual presence of pathogenic organisms by heating at 70 °C for 2 h spread in thin layers on trays, before any lab processing. A five kilogram sample of each RDF, wheat straw or of each HCF component was milled to a particle size of 10 mm (Retsch SM 2000 cutting mill). Sample mass reduction was then achieved by fractional shoveling [27] using as many increments as possible to avoid material segregation. The new samples were successively milled to 4 mm and 1 mm particle sizes. Wheat straw particles followed a final cryogenic milling step (Spex 6770) to assure subsequent pellet homogeneity for BC tests.

Portion tests for analysis were obtained using a rotary divider (Retsch PT100) with a 6 division head and dried (105 °C until constant weight) before pellet preparation or other analytical procedure.

2.2. Quantification of TCC

TCC was assessed by quantification of chloride ion (Cl⁻) using the standard oxygen BC method followed by ionic chromatography (IC) [24,25] plus quantification of hypochlorite ion (OCl⁻) by titration of BC absorption solution. TCC was calculated as the sum of chlorine as chloride and hypochlorite. Results are the average plus standard deviation of at least three replicates of each sample.

2.2.1. Oxygen bomb combustion of fuel pellets

The calorimeter used (LECO AC 600) comprises a 200 mL combustion bomb (Fig. 1a) where pellets of ca. 1 g of dry sample are held in a stainless steel crucible in contact with a cotton fuse, which promotes pellet ignition after an electrical discharge. At the bottom of the bomb 10 mL of aqueous solution is placed to capture, among others, chlorine ions.

The bomb is closed and filled with pure oxygen up to an oxygen partial pressure of 30 atm and placed in the calorimeter can, enclosed in a thermostatic bath (Fig. 1 b). Combustion takes place at constant volume and under isoperibolic conditions. Temperature is equalized at 25 °C and the rise measured in the calorimeter can (2 °C to 3 °C) is generally used for measuring fuel gross calorific value [26]. Four aqueous solutions: water, KOH (0.2 M and 1.0 M) and a carbonate/bicarbonate solution (Na_2CO_3 23.8 mM, $NaHCO_3$ 30.2 mM, H_2O_2 0.75% v/v, [11]) were added to the bomb to test its capturing efficiency of chlorine ions. After combustion, the aqueous solution was transferred to a 100 mL volumetric flask as well as bomb washings with deionized water and filled up (working solution).

2.2.2. Quantification of chlorine as chloride

Working solutions were analyzed by IC after filtration with a 0.45 μm GF filter and dilution with deionized water. IC operating conditions are resumed in Table 1. The amount of chlorine present as chloride ion, Cl $_{(Cl^-)}$ in g/kg dry fuel, was determined according to Eq. (1).

$$Cl_{(Cl^-)} = [Cl]_{Cl^-} \times Dil \times V_{wsol}/m_s \qquad (1)$$

where, $[Cl]^-_{Cl}$ is the concentration of chloride determined by IC (g/L), V_{wsol} is the volume of the working solution (L), Dil is the required sample dilution and m_s is the pellet dry mass (kg).

2.2.3. Quantification of chlorine as hypochlorite

Determination of aqueous Cl_2 was undertaken in two steps: adjustment of KOH solution molarity prior combustion to assure a final pH higher than 7.54 (HOCl, pka) and preferably above pH 10; quantification of HOCl/OCl⁻. Chlorine free species in solution (Eqs. (2) and (3)) were quantified by titrating 40 mL of working solution with sodium thiosulfate, $Na_2S_2O_3$ 0.1 N (Fluka Analytical 38200) after addition of 2 mL of KI (50% w/w), followed by 5 mL of H_2SO_4 (10% w/w) and some drops of a starch solution (1% w/w) [28].

$$[Cl]_{(HOCl/OCl^-)} = V_{tit} \times 0.1 \times 35.45/V_t \qquad (2)$$

$$Cl_{(HOCl/OCl^-)} = [Cl]_{(HOCl/OCl^-)} \times V_{wsol}/m_s \qquad (3)$$

where $[Cl]^-_{HOCl/OCl}$ is the chlorine concentration in the form of hypochlorite or hypochlorous acid in working solution determined by titration (g/L), V_{tit} is the volume of titrant used (L), 0.1 is the molarity of titrant (mol/L), 35.45 is the molar mass of Cl (g/mol) and V_t is the volume that was titrated (L). Two titrations were carried out for each replicate.

2.2.4. Quantification of Cl in BC residual mass

At the end of each pellet combustion a vitreous residual mass was found left on the stainless steel crucible (Fig. 2). Mass was carefully collected in two of the three burning replicates, weighted and tested for