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Decreased PCDD/F formation when co-firing a waste fuel and biomass in a CFB boiler by addition of sulphates or municipal sewage sludge

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ABSTRACT

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are formed during waste incineration and in waste-to-energy boilers. Incomplete combustion, too short residence times at low combustion temperatures (<700 °C), incineration of electronic waste and plastic waste containing chlorine are all factors influencing the formation of PCDD/Fs in boilers. The impact of chlorine and catalysing metals (such as copper and iron) in the fuel on PCDD/F formation was studied in a 12 MW_{th} circulating fluidised bed (CFB) boiler. The PCDD/F concentrations in the raw gas after the convection pass of the boiler and in the fly ashes were compared. The fuel types were a so-called clean biomass with low content of chlorine, biomass with enhanced content of chlorine from supply of PVC, and solid recovered fuel (SRF) which is a waste fuel containing higher concentrations of both chlorine, and catalysing metals. The PCDD/F formation increased for the biomass with enhanced chlorine content and it was significantly reduced in the raw gas as well as in the fly ashes by injection of ammonium sulphate. A link, the alkali chloride track, is demonstrated between the level of alkali chlorides in the gas phase, the chlorine content in the deposits in the convection pass and finally the PCDD/F formation. The formation of PCDD/Fs was also significantly reduced during co-combustion of SRF with municipal sewage sludge (MSS) compared to when SRF was fired without MSS as additional fuel.

1. Introduction

Replacing coal with biomass in boilers for the production of heat and power is one strategy applied in lowering the emissions of greenhouse gases to the atmosphere. The biomass fuels include forest residues and also fuels from the agricultural sector such as straw and various energy crops. Growing of energy crops (salix, red cannery grass, hemp) is an example where production of food has been replaced by production of bio-energy on agricultural land. Solid recovered fuel (SRF) is also to some extent biomass in terms of the fractions of wood, paper and textile fibres (originating from cotton). Demolition wood is defined as a waste and another waste material is municipal sewage sludge (MSS), which can be regarded as a fuel if dried properly in an energy efficient way. An advantage with MSS and certain other fuels is that the boiler owners can charge for properly and efficiently burning them and also benefit from recovering their energy content. All the biomass fuels mentioned above could be viewed in terms of fuel quality and it could either relate to their boiler performance or their emissions to the environment. Operational problems arise in the presence of certain ash forming elements such as potassium (K) and chlorine (Cl), and are often described as alkali related problems. A low fuel quality can then refer to a fuel causing deposit formation, superheater corrosion, and/or agglomeration of the bed material in a fluidised bed boiler.

High levels of KCl in the flue gas can enhance deposit formation and a high content of KCl in deposits may accelerate superheater corrosion (Nielsen et al., 2000; Theis et al., 2006; van Lith et al., 2009). Low fuel quality can result in deposit formation and superheater corrosion which can be reduced by co-combustion or the use of additives. Coal, peat and municipal sewage sludge (MSS) are among the fuels used for co-combustion with biomass (Aho and Ferrer, 2005; Elled et al., 2010; Kassman et al., 2011). Co-combustion can also have an impact on the bed agglomeration during combustion in fluidised bed boilers (Davidsson et al., 2008). Elemental sulphur or other sulphur/sulphate containing additives can be used to convert KCl to a less corrosive alkali sulphate. In Henderson et al. (2004), Kassman et al. (2010, 2011, 2013), and Kassman (2012)) results are presented from experiments when using elemental sulphur (S) and/or ammonium sulphate (AS, $(NH_4)_2SO_4$), an example of a sulphate containing additive.

Low fuel quality can also relate to the fuel constituents which lead to emissions of nitrogen oxides (NO, NO_2, N_2O), sulphur dioxide (SO_2), hydrogen chloride (HCl), hydrogen fluoride (HF) persistent organic pollutants (POPs) and/or heavy metals such as

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mercury (Hg), cadmium (Cd) and chromium (Cr). The present paper focuses on a particular group of POPs: the polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). These two types of compounds are commonly known as "dioxins", despite the fact that the dioxin molecule itself is not chlorinated. It differs in both build-up from the furan molecule and also in toxicity in relation to its chlorinated fellows. 2,3,7,8-tetra chlorinated dibenzo-p-dioxin (TeCDD) is the most toxic one and toxic equivalent factors for the other 16 with 2,3,7,8-chlorination patterns have also been determined (Van den Berg et al., 1998). Furthermore, in a mixture of the 17 "dioxins", a single value (I-TEQ) can be calculated representing the toxicity of the sample. The PCDD/Fs are present in very low concentrations in the flue gas and a special measurement technique involving a sample train for their collection is required.

The formation mechanisms of PCDD/Fs are complex and not yet fully understood despite intensive research for more than 30 years. Formation of PCDD/Fs can occur both in the gas phase (homogeneous formation) in the 700–500 °C temperature range and by a gas–solid phase reaction for example on fly ash particles in the temperature range of 450–250 °C representing the convection pass of a boiler.

Two major pathways of PCDD/F formations have been described (Aurell et al., 2009).

- De novo synthesis from carbon residuals found in the ash matrix involving chlorination, with subsequent oxidation and release of PCDD/Fs (Stieglitz et al., 1989, 1991; Luijk et al., 1993; Hell et al., 2001; Ryan et al., 2006), and carbon structures such as polycyclic aromatic hydrocarbons (PAHs) (Iino et al., 1999; Weber et al., 2001; Wilhelm et al., 2001).
- Formation from condensation reactions of chlorinated precursors such as polychlorinated phenols (PCPh) and polychlorinated benzenes (PCBz) (Karasek and Dickson, 1987; Altwicker et al., 1992; Luijk et al., 1994; Addink et al., 1995; Sidhu et al., 1995; Ghorishi and Altwicker, 1996; Mulholland and Ryu, 2001; Ryu et al., 2005). The presence of these precursors in the gas phase depends on the degree of burnout of the fuel. They may either be adsorbed on fly ash surfaces (Sidhu et al., 1995) or be formed in reactions catalysed by fly ash/copper chloride ($CuCl_2$) (Dickson et al., 1989; Born et al., 1993; Luijk et al., 1994; Mulholland and Ryu, 2001; Hatanaka et al., 2004).

Several investigations in both full-scale boilers and in laboratory scale facilities have shown that the presence of sulphur during combustion may have an inhibiting effect on the formation of PCDD/Fs. The sulphur required could be obtained by co-firing waste with coal (Manninen et al., 1997; Gullett et al., 1998, 1999; Yan et al., 2006) or by adding sulphur as elemental sulphur or as sulphates (Ogawa et al., 1996; Pandelova et al., 2005, 2007, 2009; Ryan et al., 2006; Aurell et al., 2009; Hajizadeh et al., 2012). Fig. 1 illustrates the possible inhibiting effects of sulphur on the formation of PCDD/Fs. (R1) is the Deacon process forming the chlorinating source. Sulphur in the form of Cu- and Fe-sulphates decreases the formation rate of Cl_2 (Gullett et al., 1990). Alternatively in (R2), sulphur reacts directly with Cl_2 (Griffin, 1986). The third option is a slow-down of the biaryl condensation by sulphates of Cu and Fe (Gullett et al., 1992).

Hunsinger et al. (2004, 2007) claimed that PCDD/F formation occurs almost completely in the deposits in the convection section of the boiler in waste combustion plants with an effective flue gas burnout. The chlorine required is brought to the deposits as alkali chlorides (NaCl + KCl) (Hunsinger et al., 2004). By achieving permanent low molar ratios of Cl/S (HCl/SO_2), the alkali chlorides are converted into alkali sulphates and the PCDD/F formation is lowered at the same time as the corrosion rates of boiler tubes in the convection section.

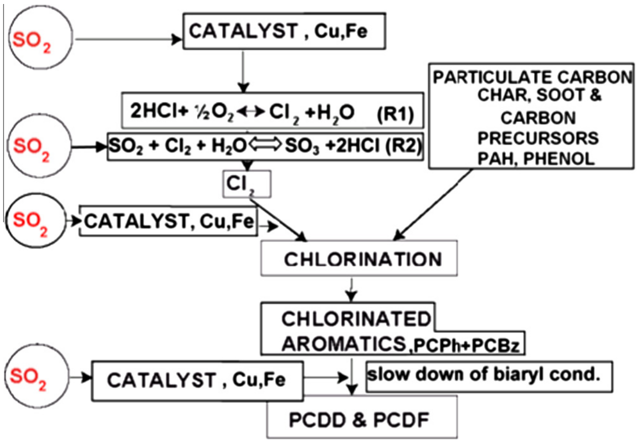

Fig. 1. Illustration of the possible inhibition effects of SO_2 in the formation of PCDD & PCDF. PAH = polycyclic aromatic hydrocarbons; PCBz = polychlorinated benzenes; PCPh = polychlorinated phenols.

Kassman et al. (2010) evaluated ammonium sulphate (i.e. SO_3) and sulphur (i.e. SO_2) for sulphation of gaseous KCl. The sulphate lowered the concentration of gaseous KCl and also reduced the chlorine content in the deposits significantly better than sulphur. Thus, the presence of gaseous SO_3 was proven to be of greater importance than that of SO_2 for sulphation of gaseous KCl. A similar approach is used in the present project where ammonium sulphate is used to lower the concentration of alkali chlorides and thus prevent the formation of PCDD/Fs in flue gases and in fly ashes. Also demonstrated here is the effect of co-firing with municipal sewage sludge (MSS), which is another strategy to decrease the alkali chlorides.

2. Materials and methods

2.1. Experimental strategy

Table 1 shows the experimental matrix for the test cases included in test series I and II. The test case named *100% Wood* represents a clean biomass with a low content of chlorine (Cl) such as wood pellets and wood chips originating from stem wood. PVC was added to a mixture of wood pellets and wood chips to investigate the importance of Cl for the formation of PCDD/F's. This test case corresponded to a biomass with enhanced content of chlorine, without additional metals and still remaining combustion performance of the wood. The addition of PVC corresponded to a 20 time's increase of the Cl content of the fuel from 0.01% to 0.2% calculated on dry and ash free fuel. Ammonium sulphate (AS) was added in test case *Wood + PVC&AmSulf* to investigate the inhibiting effect of sulphur/sulphates on the PCDD/F formation for a biomass with enhanced content of chlorine.

Solid recovered fuel (SRF) is a waste fuel and PVC was replaced by SRF in the matrix in test series II. SRF acted as a chlorine source and it also increased the feed of catalysing metals (also named transition metals) such as copper (Cu), iron (Fe) and chromium (Cr). SRF in test case *21%SRF + 79%Wood* increased the Cl loading 18 times, which corresponded to a Cl content 0.18% in the incoming fuel mix. SRF introduced catalysing metals and thereby reflecting also other common waste fuels such as demolition wood contaminated with residues of paint and coloured plastics.

Municipal sewage sludge (MSS) was used as additional fuel in co-combustion with wood and SRF in test series II. Sewage sludge contains elevated concentrations of both sulphur and nitrogen that can act as inhibitors of PCDD/Fs (Yan et al., 2012) instead of