Decreased PCDD/F formation when co-firing a waste fuel and biomass

Waste Management (ISSN: 0956-053X)

Citation for the published paper:
Åmand, L. ; Kassman, H. (2013) "Decreased PCDD/F formation when co-firing a waste fuel and biomass". Waste Management, vol. 33 pp. 1729-1739.

Volume 33, Issue 8, August 2013 ISSN 0956-053X
ELSEVIER
waste management
International Journal of Integrated Waste Management, Science & Technology
GENERATION
MINIMIZATION
RECYCLING
COLLECTION
TREATMENT
DISPOSAL
ECONOMICS
POLICY
Editor-in-Chief
Raffaello Cossu
iwwg

Waste Management 33 (2013) 1729–1739

Contents lists available at SciVerse ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

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

Lars-Erik Åmand [a], Håkan Kassman [b,*]

[a] Chalmers University of Technology, Department of Energy and Environment, Gothenburg, Sweden
[b] Vattenfall Research & Development AB, Nyköping, Sweden

ARTICLE INFO

Article history:
Received 6 December 2012
Accepted 28 March 2013
Available online 17 May 2013

Keywords:
PCDD/Fs
Dioxins
Alkali chlorides
Co-combustion
Municipal sewage sludge
Ammonium sulphate

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

---

* Corresponding author. Tel.: +46 86998843.
E-mail address: hakan.kassman@vattenfall.com (H. Kassman).

0956-053X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.wasman.2013.03.022

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.

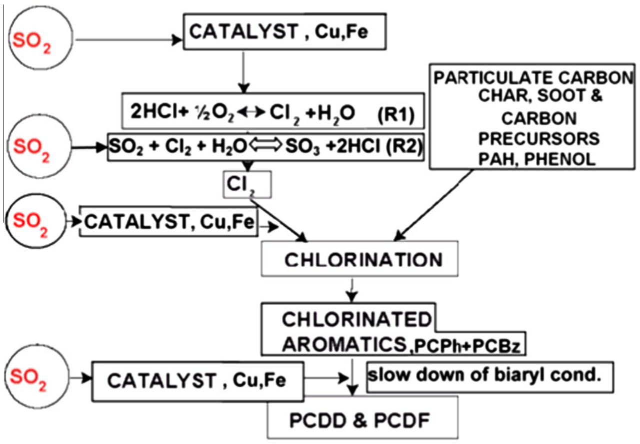

Fig. 1. Illustration of the possible inhibition effects of SO_2 in the formation of PCDD & PCDF. PAH = polycyclic aromatic hydrocarbons; PCBz = polychlorinated benzenes; PCPh = polychlorinated phenols.

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 in-coming 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

Table 1
Experimental matrix.

Test series	Test case	Description of the test cases
I and II	100% Wood	Reference. Combustion of wood chips and wood pellets
I	Wood + PVC	Addition of PVC to the test case "100% Wood".
I	Wood + PVC&AmSulf	Addition of ammonium sulphate (AS) to the test case "Wood + PVC".
II	21% SRF + 79%Wood	Co-firing of solid recovered fuel (SRF) with wood. 21% SRF; 79% wood chips on dry fuel
II	19% SRF + 8%MSS + 73% Wood	Co-firing of municipal sewage sludge (MSS) with SRF and wood. 19% SRF; 8% MSS 73% Wood; on dry fuel

sulphur/sulphates (Pandelova et al., 2005, 2007, 2009; Ryan et al., 2006; Aurell et al., 2009; Hajizadeh et al., 2012; Wu et al., 2012) and urea/ammonia (Ruokojärvi et al., 1998). The ash forming elements in the sludge have an impact on the concentration on gaseous alkali chlorides and chlorine in deposits (Pettersson et al., 2009; Elled et al., 2010) and they could possibly be important in preventing the formation of PCDD/Fs as well.

PCDD/F formation takes place in the boiler deposits of the convection section and long-term combustion tests were carried out to avoid possible influence from so-called memory effects. In test series I, each test period consisted of 96 h with stable operating conditions. The boiler tubes in the convection section were cleaned by soot blowing and the operating parameters were tuned prior to each test. Four flue gas samples were taken altogether for analysis of PCDD/Fs, two after 72 h and two at the end of the test period. Ash samples were taken every 12 h throughout the whole period of 96 h. The test periods were reduced to 48 h for the tests with SRF and MSS based on experiences gained in test series I.

2.2. The boiler and the operating conditions

The experiments were performed in the 12 MW_{th} CFB boiler at Chalmers University of Technology (CTH) shown in Fig. 2. This research boiler offers the possibility to perform measurement campaigns in a near full scale boiler, while maintaining control over important operation parameters such as load, air supply and composition of the fuel mix. The boiler has been described earlier in several publications including Kassman et al. (2006, 2008, 2010, 2013), Pettersson et al. (2009), Elled et al. (2010) and Kassman (2012).

The combustion chamber (1) has a cross section of 2.25 m^2 and a height of 13.6 m. The fuels are fed from various fuel bunkers (2) to the bottom bed through a fuel chute (3). The circulating material is separated in a primary cyclone (4) and returned to the combustion chamber through the cyclone leg (5) and particle seal (6). In test series I, a special feeder (7) was used for adding polyvinyl chloride (PVC) powder to the return leg. Ammonium sulphate (AS) was injected to the upper part of the riser (8) as an aqueous solution (40 wt.%). Mechanically dewatered municipal sewage sludge (MSS) was fed during test series II to the bottom of the bed by a piston pump from a rebuilt cement pump (9). Primary air is introduced through air nozzles located at the bottom of the riser and secondary air 2.2 m above the bottom plate. The combustion gas is leaving the cyclone at the top into the refractory lined exit before being cooled to 150 °C in the convection section of the boiler. Effective soot blowers using steam blown probes (10) are installed along each section of the convection pass. These soot blowers are used regularly to keep the flue gas temperature below 180 °C (once or twice every 24 h). Fly ashes are separated in the secondary cyclone (11) and the textile (bag) filter (12). Silica sand (dp = 0.3 mm) was used as bed material in all tests (13). The operating conditions presented in Table 2 are typical of a commercially operated CFB boiler. This means a fluidising velocity of approx. 5 m/s in the top of the riser that leads to a proper circulation of bed material through the primary cyclone, good heat transfer of moving bed particles and an attrition of fuel ash into small (<100 μm) fly ash particles. This is especially important during co-firing of MSS with its high content of inorganic matter primarily forming coarse ash particles.

Important operating parameters are also proper excess air ratio (20–25% excess air) and combustion temperatures above 850 °C for a residence time exceeding 2 s in order to fulfil the requirements for burning waste within the European Union (Directive, 2010/75/EU). These requirements also include emission limit values of hydrogen chloride (HCl) and sulphur dioxide (SO_2) in the stack. This is achieved by a dry scrubber, e.g. injection of hydrated lime to the inlet duct (14) of the textile filter during the use of the waste fuels (solid recovered fuel and municipal sewage sludge) in test series II.

2.3. Fuel composition

Wood pellets and the wood chips originating from trees used in the forest industry in Sweden were used as the main biomass feedstock. The wood pellets originated from saw dust from a saw mill using pine and spruce trees, whereas the wood chips came from stem wood of spruce not used in the pulp and paper industry. Such a fuel mix is regarded as a so-called clean biomass concerning the content of chlorine, sulphur, nitrogen and alkali metals. Table 3 presents fuel analysis of the biomass fuels (i.e. wood chips) together with the waste fuels (MSS and SRF). The municipal sewage sludge originated from the regional waste water treatment plant of the Gothenburg region, Sweden. Phosphorus is precipitated using iron sulphate and the sludge is digested anaerobically before being mechanically dewatered to a water content of approximately 74%. The dewatered sludge was fed to the boiler by the rebuilt cement pump. The solid recovered fuel (SRF) was produced from mixed waste by IcoPower in the Netherlands in a production unit (in Amsterdam) equipped with mills, sorting units, drier and pelletising machines. The end product is a pellet suitable for storage. It mainly consists of combustible matter of wood, textiles, paper and plastics with a lower heating value ($H_{u,raw}$) that is twice as that using wet wood chips, Table 3. The same type of SRF was used in a previous alkali related project (Pettersson et al., 2008) under the name refused derived fuel (RDF).

2.4. Measurement equipment

PCDD/Fs measurement technique involves a sampling train for collection of the PCDD/Fs on filters and by an adsorbent during a 6 h measurement period. This is followed by a clean-up procedure in the laboratory and analysis on a gas chromatograph equipped with a high resolution mass spectroscopy (GC-HRMS). The collection and analysis of PCDD & PCDF were performed by laboratories accredited by the Swedish accreditation body (SWEDAC). Analysis of PCDD/Fs was also carried out for different ash samples. The locations for sampling of bed ash, primary cyclone (cyclone leg) ash, secondary cyclone ash and bag filter ash are shown in Fig. 2.

The flue gas composition was obtained by conventional instrumentation and an FTIR (Fourier Transform Infra Red spectrometry) instrument (Bomen MB100). Using a gas extraction probe in connection with the FTIR at the same position (15), enabled to control the chlorine in the gas phase in the form of HCl. Also the flue gas burnout of the gas phase can be controlled by the measurement of CO and total hydrocarbons. Measurements of alkali chlorides (NaCl + KCl) were performed upstream of the convection pass

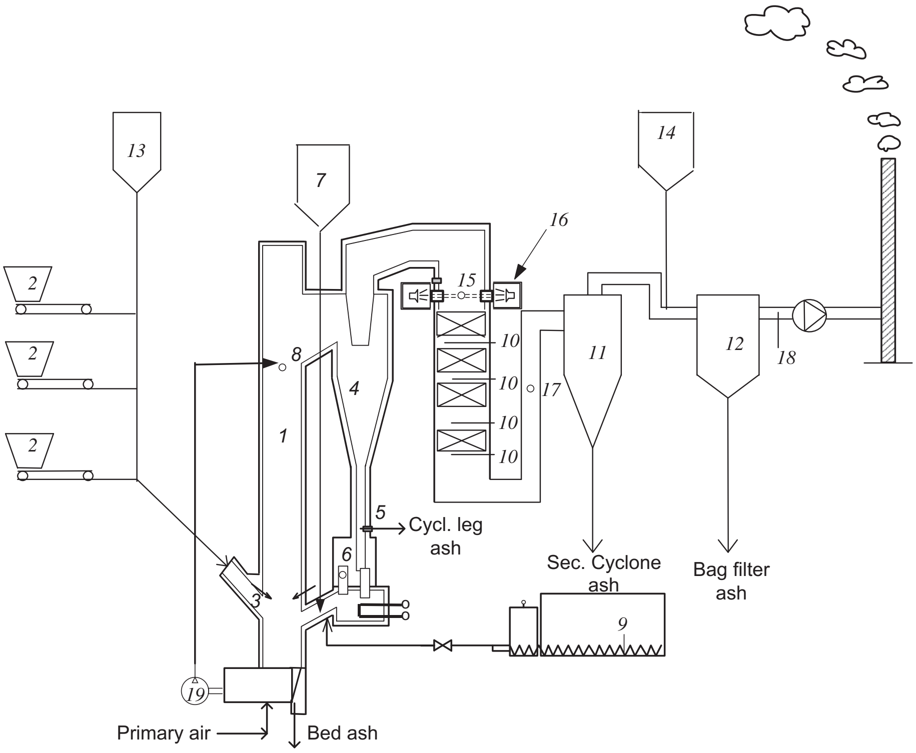

Fig. 2. The 12-MW$_{th}$ CFB boiler at Chalmers University of Technology: (1) combustion chamber; (2) fuel bunkers; (3) fuel chute; (4) primary cyclone; (5) cyclone leg; (6) particle seal; (7) feeder for PVC; (8) probe for injection of ammonium sulphate; (9) sludge pump; (10) steam soot blowers; (11) secondary cyclone; (12) bag house (textile) filter; (13) feeder for silica sand; (14) feeder for hydrated lime; (15) measurement location (before convection pass) IACM instrument, deposit probe and FTIR; (16) in situ alkali monitor (IACM); (17) measurement location (after convection pass) FTIR; (18) measurement location for emissions (stack) FTIR; (19) storage tank for ammonium sulphate.

Table 2
Operating conditions.

Test	Unit	100% Wood	Wood + PVC	Wood + PVC + AmSulf	21%SRF 79%Wood	19%SRF 8%MSS 73%Wood
Load	MW$_{th}$	6.8	6.1	6.7	6.1	6.0
Bed temp. (bottom)	°C	849	849	849	851	848
Comb. temp. (top)	°C	863	861	866	884	884
Comb. temp. after Primary cyclone (15)[a]	°C	827	823	835	808	812
Flue gas temp. After bag filter	°C	163	171	151	157	156
Total riser pressure drop	kPa	4.9	4.8	4.8	5.0	5.0
Excess air ratio	–	1.22	1.25	1.24	1.23	1.22
Air staging: primary air flow Divided by total air flow	%	60	63	62	58	60
Superficial velocity At the top of riser	m/s	5.5	5.4	5.5	5.0	5.2
Cl/S molar ratio	–	0.9	18.4	0.8	1.9	0.9
Cl/(Na + K) molar ratio	–	0.17	4.56	2.75	0.55	0.35
Alkali loading	mol MW^{-1}	3.5	2.9	3.3	15.6	25.0

[a] At position 15 in Fig. 3, SRF = Solid recovered fuel, MSS = municipal sewage sludge.

(15) by an IACM (in situ alkali chloride monitor, 16). IACM is described more in detail by Forsberg et al. (2009), Kassman et al. (2010) and Kassman (2012)). The alkali chlorides are often expressed as KCl during combustion of biomass and as NaCl + KCl during combustion of fuels such as RDF and MSS.

Deposit measurements were carried out before the convective pass (15 in Fig. 2) using an air cooled and temperature controlled deposit probe. The probe was equipped with metal rings maintained at a constant temperature of 500 °C and the flue gas temperature during each test is shown in Table 2. The rings were exposed during a period of 11–23 h in the first test series and the exposure time was 6 h in the second test series. The sample rings were weighed before and after exposure to the flue gas to determine the deposit growth rates. The rings were analysed by means of two independent methods to determine their ash composition: SEM-EDX (scanning electron microscopy electron dispersive X-ray), ICP-OES and IC that is leaching of sample in water followed by analysis of S and Cl with ion chromatography (IC), leaching in strong acid and inductive coupled plasma (ICP) equipped with optical emission spectroscopy (OES) for analysis of other ash elements.

3. Results

3.1. PCDD/Fs in flue gases and fly ashes – Impact of gaseous alkali chlorides

The development of the PCDD/F concentration in the fly ashes was investigated as part of the first test series. The knowledge

Table 3
Fuel properties.

Fuel	Unit	Wood chips	SRF	MSS
Proximate analysis				
Moisture (as received)	wt.%	43.8	4.1	74.3
Ash (dry)	wt.%	0.8	13.3	45.8
Combustibles (dry)	wt.%	99.3	86.7	54.2
Volatiles (daf[a])	wt.%	81.6	89.4	88.8
Ultimate analysis daf[a]				
C	wt.%	50.1	56.4	51.4
H	wt.%	5.9	7.5	7.4
O	wt.%	43.8	34.0	33.4
S	wt.%	0.01	0.3	1.7
N	wt.%	0.16	1.0	6.1
Cl	wt.%	0.01	0.7	0.09
Lower heating value				
LHV	MJ kg^{-1}	9.37	18.93	1.7
LHV (daf[a])	MJ kg^{-1}	18.76	22.87	20.15
Trace elements (mg kg^{-1} dry fuel)				
Hg	mg kg^{-1}	0.02	0.13	0.7
Cd	mg kg^{-1}	0.09	1.2	1.4
Pb	mg kg^{-1}	0.03	9.7	14.2
Cr	mg kg^{-1}	0.2	42	43
Cu	mg kg^{-1}	2	692	473
Ni	mg kg^{-1}	0.2	19	28
Mn	mg kg^{-1}	52	121	520
Zn	mg kg^{-1}	12	294	757
Ash analysis(dry ash)				
K	g kg^{-1}	118	16.8	18.7
Na	g kg^{-1}	7.8	30.0	8.2
Al	g kg^{-1}	9.3	44.5	102
Si	g kg^{-1}	45.3	185	153
Fe	g kg^{-1}	8.5	18.2	115
Ca	g kg^{-1}	221	182	46.1
Mg	g kg^{-1}	32.7	11.5	11.2
P	g kg^{-1}	13.1	4.9	55.3
Ti	g kg^{-1}	0.5	7.7	4.6
Tetra- to octa PCDD/Fs (dry fuel)	ng/g	0.03	4.5	0.87

[a] daf = Dry and ash free.

was limited concerning the required length of operating for each test case for achieving steady state of the concentration of PCDD/Fs in the fly ashes at the time of performing test series I. Therefore fly ash samples from both the secondary cyclone and bag filter were taken after each operating period of 24 h, continuing for 96 h for the two tests *Wood + PVC*, *Wood + PVC&AmSulf*, Fig. 3. The concentrations of PCDD/Fs were building up from a low level during the *Wood + PVC* case and 48 h of operation of the boiler was considered sufficient for an appropriate evaluation. Although a minor decline of the concentrations was observed for the *Wood + PVC&Amsulf* case, a period of 48 h of operation was selected. The same period of time was selected for the second test series. The results in Fig. 3 are presented as I-TEQ PCDD/Fs using toxic equivalent factors on the 17 PCDD/Fs listed in Directive (2010/75/EU). This enabled comparisons with the stricter directive in Japan of 3 ng/g dry fly ash (Kobylecki et al., 2001) and existing and coming limits within the European Union on PCDD/Fs in solid waste and fly ashes. Fig. 3 shows that supply of PVC to the clean wood case resulted in increased concentrations of PCDD/Fs in the fly ashes. It was, however, possible to reduce the concentration of PCDD/Fs in the fly ashes to less than 1 ng/g dry ash by addition of ammonium sulphate (test case *Wood + PVC&AmSulf*).

Fig. 4 presents the concentration of tetra to octa PCDD/Fs in flue gas samples taken after the primary cyclone (15), after the convection pass (17) and in the stack (18) for the three test cases. The corresponding results of the tetra to octa PCDD/F:s in the primary cyclone ash, bed ash, secondary cyclone ash and bag filter ash are shown in Fig. 5. The level of alkali chlorides (KCl + NaCl), SO_2 and HCl after the primary cyclone (15) are shown in Fig. 6.

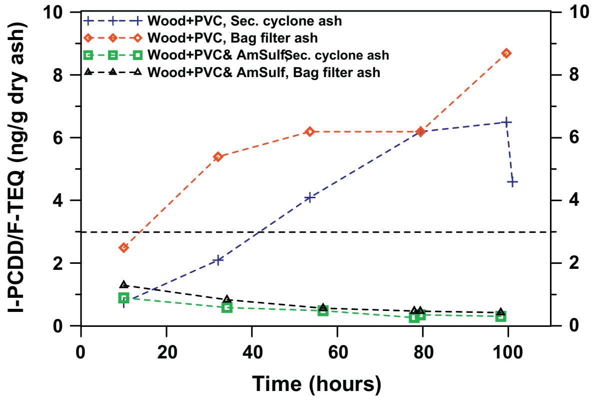

Fig. 3. Development of the concentrations of PCDD/Fs in the fly ashes for the tests: "Wood + PVC" and "Wood + PVC&AmSulf". PCDD/Fs are the sum of tetra to octa PCDD/Fs recalculated to toxic equivalents to be compared to the limits of 3 ng/g dry ash in Japan, the dotted horizontal line in the figure.

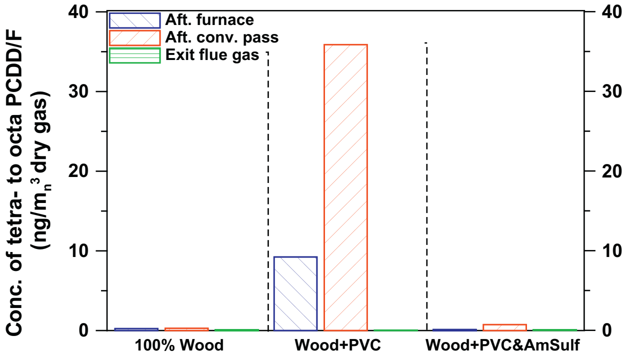

Fig. 4. Sum of tetra- to octa PCDD/Fs in flue gas samples taken at three different positions (15, 17, 18 in Fig. 2) for three tests cases: 100% Wood; Wood + PVC; Wood + PVC&AmSulf.

PCDD/Fs were not detected in the flue gas after the furnace (primary cyclone), nor after the convection pass or in the exit flue gas for "100%Wood". Additionally, the PCDD/Fs in the fly ashes in Fig. 5 were low. The additional chlorine from PVC in the case *Wood + PVC* had a significant effect. PCDD/Fs appeared in the flue gas sample after the primary cyclone and after the convection pass even more was found. The PCDD/Fs in the flue gas were then almost completely captured by fly ash particles and removed together with the fly ash and only very low concentrations were found in the stack. This was achieved even without the addition of activated carbon nor hydrated lime to the bag filter. The major differences compared to *100% Wood* were that substantially higher PCDD/F concentrations were found after the convection pass and in the two fly ashes during *Wood + PVC*. The higher PCDD/F concentrations also connected to increased concentrations of alkali chlorides when PVC was added. The alkali chlorides increased from approximately 5 ppm to 40 ppm during *Wood + PVC*.

Moving onto the test case *Wood + PVC&AmSulf*, addition of ammonium sulphate (AS) prevented the occurrence of PCDD/Fs in the flue gas in Fig. 4 as well as in the two fly ashes in Fig. 5. The concentration of gaseous alkali chlorides was decreased by conversion into alkali sulphates during *Wood + PVC&AmSulf*. The decrease of gaseous KCl was, however, not as great as in Kassman et al. (2010). The lower efficiency is explained by the fact that the injection of AS took place in a location in the upper part of the riser rather than in the cyclone (Kassman, 2012). This resulted in an enhanced SO_2 concentration in the flue gas in Fig. 6. It is possible to

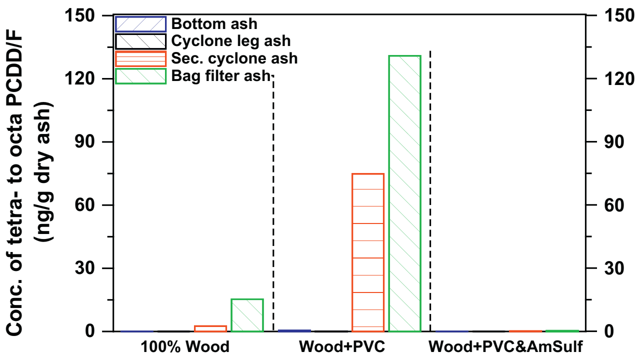

Fig. 5. Sum of tetra- to octa PCDD/Fs in various solid samples taken in the boiler: bed ash, cyclone leg ash, secondary cyclone ash and bag filter ash.

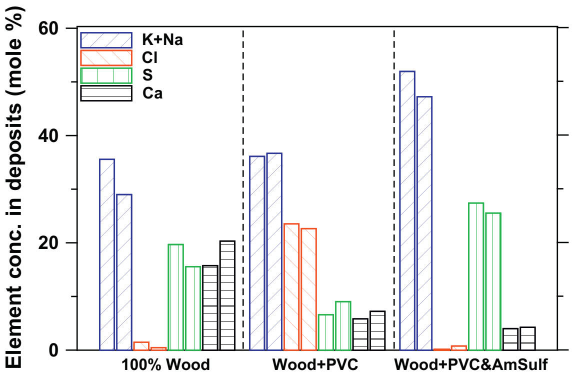

Fig. 7. Mol% of the five major elements (K, Na, Cl, S, Ca) in the deposits for the various test cases. Each test is represented by two individual deposits rings exposed for a period of 12–24 h. ICP-OES used for K, Na, Ca, leaching- and ion chromatography for S and Cl.

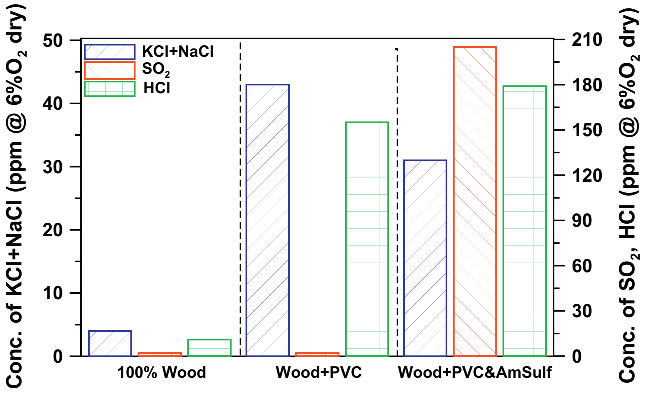

Fig. 6. Concentrations (normalised to 6% O_2 on dry flue gas) of KCl + NaCl, SO_2 and HCl after the primary cyclone (15).

achieve a contribution from heterogeneous sulphation of the alkali chlorides in the deposits at high SO_2 concentrations as well (Kassman, 2012). The concentration of PCDD/Fs was similar or lower for test case *Wood + PVC&AmSulf* than for *100%Wood* although the chlorine loading to the boiler was 20 times higher. These results support previous findings (Hunsinger et al., 2004), i.e. that sulphation of the alkali chlorides in the deposits can prevent formation of PCDD/Fs.

3.2. Alkali chlorides in the deposits and PCDD/Fs in fly ashes

The deposit measurements enabled the collection of deposits from the various test cases before the convection section (15). Analysis was made of the composition of the ash components building up the deposit. The aim was to identify any correlation between the presence of alkali chlorides and PCDD/F formation in the fly ashes. Based on the results presented in Figs. 7 and 8 together with Fig. 5, several interesting observations can be made for the three test cases.

The test case *100% Wood* contains insufficient amounts of chlorine to form alkali chlorides. The lack of chlorine is shown in Table 2 by a molar ratio Cl/(Na + K) of only 0.2. This is too low to form alkali chlorides and the content of chlorine was also low in the deposits analysed in Fig. 7. Instead, the alkali in the deposit is found together with sulphur in Fig. 8. Consequently, almost no PCDD/Fs were formed in the fly ash for this case, Fig. 5. The supply of PVC to the wood case increased the molar ratio Cl/(Na + K) to 4.6 for *Wood + PVC*. The deposits consisted of more than 50 mol% of alkali and chlorine in Fig. 7. There is a clear correlation between K and Cl in the EDX mapping in Fig. 8. High PCDD/F concentrations were found in the two fly ashes in Fig. 5. The secondary cyclone and bag filter ash contained 75 ng/g dry ash and 130 ng/g dry ash PCDD/Fs respectively. The molar ratio of Cl/(Na + K) remained largely unchanged by the addition of ammonium sulphate (AS) whereas the molar ratio of Cl/S decreased to a value similar to *100% Wood* during test case *Wood + PVC&AmSulf*. These changes had a major impact on the PCDD/F formation in the fly ashes. The gaseous alkali chlorides were partly sulphated by addition of AS, Fig. 6, and no alkali chlorides were found in the deposits in Figs. 7 and 8. The PCDD/F formation in the fly ashes, Figs. 3 and 5, was minimised when no alkali chlorides were present in the deposits, Figs. 7 and 8.

3.3. Mass flow rates of PCDD/Fs over the CFB boiler

The fuels used in test series II were biomass, solid recovered fuel (SRF) and municipal sewage sludge (MSS). Their content of PCDD/Fs is shown in Table 3. Mass flow rates of incoming and outgoing flows of PCDD/Fs over the boiler are presented in Figs. 9a and 9b. The flows of PCDD/Fs in the flue gas leaving the furnace, the convection pass and the boiler for the three test cases as well as for the incoming fuels are shown in Fig. 9a. It is noticed that small amounts of PCDD/Fs were present even in clean biomass. These PCDD/Fs are destroyed in the hot furnace of the boiler and the conditions prevailing in the *100% Wood* case were not favourable for forming new ones. The situation is different when using SRF together with biomass in the *21% SRF + 79%Wood* case. The PCDD/F concentration in SRF is 150 times higher than in wood which leads to an input flow of 1300 mg PCDD/Fs/hour to the boiler. The conditions were, nevertheless, sufficient in terms of temperature and residence time in the furnace for thermal destruction of PCDD/Fs according to an estimation performed (Hunsinger et al., 2004). The flow of PCDD/Fs after the furnace was about the same as the fuel feed flow of PCDD/Fs. This is interpreted as a PCDD/F formation boosted by chlorination of particulate carbon and carbon precursors like PAHs and phenol that is favoured by the high chlorine content of the fuel in connection to the presence of catalysts such as Cu and Fe, Al, Ni, Pb, Zn and Cr, Fig. 1. The PCDD/Fs are decreased in the convection section of the boiler. This is partly a capture mechanism explained by increased flows of PCDD/Fs in the secondary cyclone and bag filter ashes, Fig. 9b but also a thermal destruction mechanism not leading to any additional increase of the PCDD/Fs with the fly ashes. This differs from the *Wood + PVC* case shown in Fig. 4 where an increase of the PCDD/F concentration

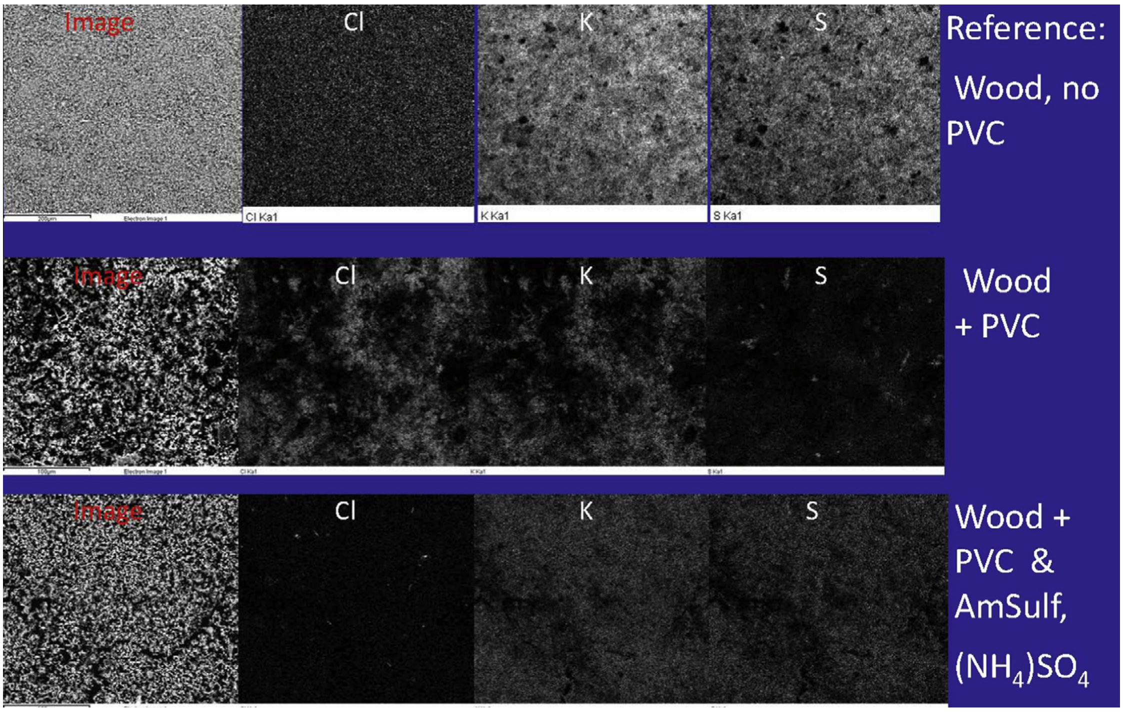

Fig. 8. SEM-EDX of electron images from the deposit rings and the elements chlorine (Cl), potassium (K) and sulphur (S). The tests are presented in the following order: 1st row "100% Wood"; 2nd row "Wood + PVC"; 3rd row "Wood + PVC&Amsulf".

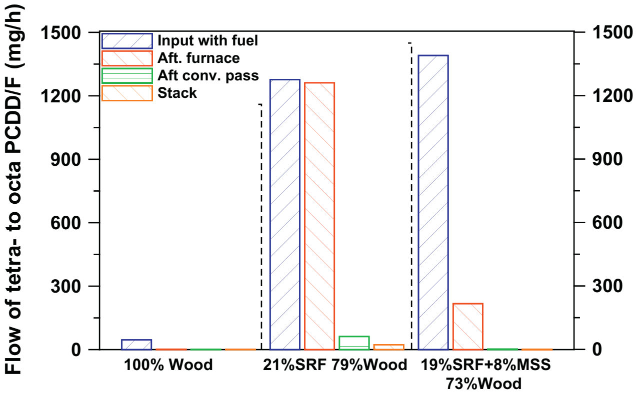

Fig. 9a. Flow of tetra- to octa PCDD/Fs in incomin fuel and in the flue gas samples at three different positions for three tests cases: 100% Wood; 21%SRF 79%Wood; 19%SRF8%MSS 73%Wood.

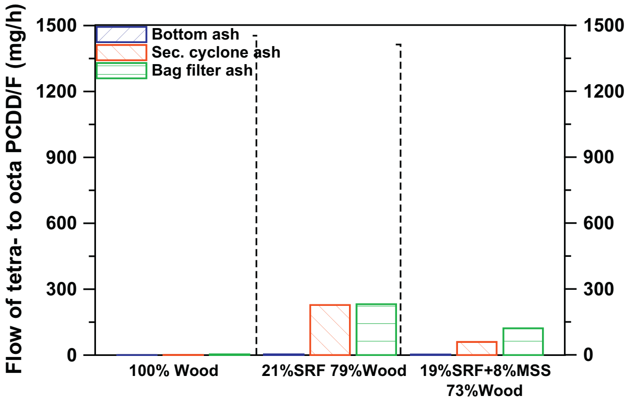

Fig. 9b. Flow of tetra- to octa PCDD/Fs in outgoing ashes for the three tests cases: 100% Wood; 21%SRF 79%Wood; 19%SRF 8%MSS 73%Wood.

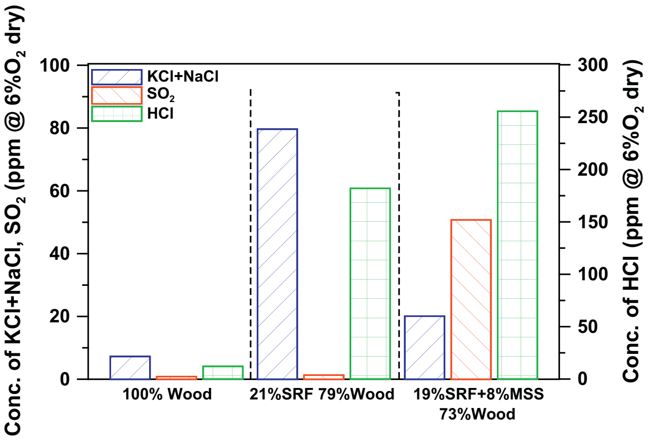

Fig. 10. Concentrations (normalised to 6% O_2 on dry flue gas) of KCl + NaCl, SO_2 and HCl after the primary cyclone (15) for the three tests cases: 100% Wood; 21%SRF 79%Wood; 19%SRF 8%MSS 73%Wood.

was measured after the convection pass. Adding municipal sewage sludge (MSS) to the fuel mixture leads to even higher input flows of PCDD/Fs than in the case *21%SRF + 79% Wood*. Thus significant amounts of PCDD/Fs are also present in MSS and not only in the waste fuel (SRF). If the MSS is co-fired in a boiler operated at the conditions required in the IPPC directive of the European Union (Directive, 2010/75/EU), the PCDD/Fs are not only thermally destroyed, a suppression in formation of PCDD/Fs in the furnace is also achieved, Fig. 9a. This could partly be explained by the higher SO_2 concentrations measured after the furnace, Fig. 10. The flow of PCDD/Fs in the flue gas is decreased to very low levels in the convection section. Again some of these PCDD/Fs appeared in the fly ashes, Fig. 9b and were captured by the fly ash cleaning devices (secondary cyclone and bag filter).

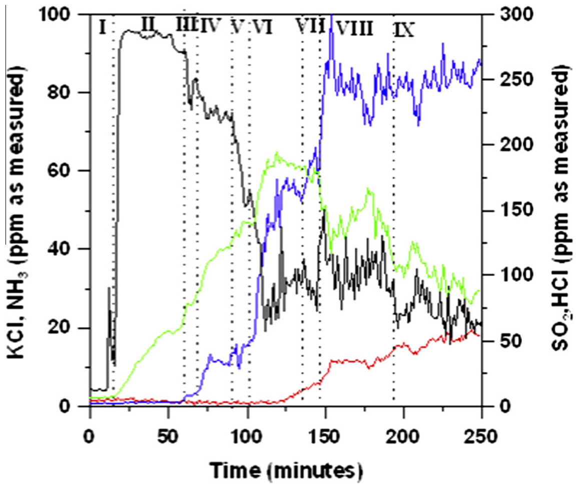

Fig. 11. KCl, NH_3, SO_2, HCl in a transient test when using ammonium sulphate (AS) for sulphation of KCl. –NaCl + KCl, –HCl FTIR, –SO_2 FTIR, –NH_3 FTIR. I. "wood no PVC" case (t = 0 min), II. "wood + PVC" (t = 20 min), III-VIII. Stepwise increasing injection of AS (t = 60 min).

4. Discussion

4.1. The role of chlorine and alkali chlorides in the deposits – PCDD/Fs in fly ashes

There was a build-up of PCDD/Fs both in the flue gases and the fly ashes for the case *Wood + PVC* and, in connection to this, alkali chlorides were present in the deposits in that particular test case. This opens up for an alternative explanation for PCDD/F formation during combustion of a biomass with elevated content of chlorine and how the PCDD/F formation could be prevented. This alternative explanation is hereafter referred to as "the alkali chloride track".

Chlorine from NaCl and KCl in the deposits (shown in Figs. 7 and 8) in the convection section of the boiler became a source of chlorination into PCDD/Fs. The alkali chloride track was first discussed in Hunsinger et al. (2004) as taking place in boiler deposits, when burning municipal solid waste during controlled combustion conditions in grate boilers. Controlled combustion conditions mean proper burn out of the hydrocarbons in the gas phase and are a prerequisite for the alkali chloride track. The PCDD/F formation is thus minimised from condensation reactions of chlorinated precursors such as polychlorinated phenols (PCPh) and polychlorinated benzenes (PCBz). Sulphation of the alkali chlorides to alkali sulphates is demonstrated in test case *Wood + PVC&Amsulf* as one particular strategy to avoid PCDD/F formation in deposits through the alkali chloride track. Sulphur and nitrogen were supplied as ammonium sulphate during the test case *Wood + PVC&AmSulf*. Ammonia was, however, not fully converted before the convection pass which is illustrated by the step response test in Fig. 11. Ammonia/amines in various forms have been shown to have an inhibiting effect on PCDD/F formation (Ruokojärvi et al., 2001a,b,c; Samaras et al., 2001).

The results from test case *Wood + PVC* show that waste fuels are not required in the fuel mix in order to form PCDD/Fs in raw gases and in fly ashes. It could be enough with somewhat enhanced chlorine content than that found in woody biomass. The amount of chlorine available is probably sufficient in annual crops and in residues from the agricultural sector such as straw to produce PCDD/Fs in the raw gas leaving the furnace and in the fly ashes. In a review paper (Lavric et al., 2004) concluded that straw combustion could lead to PCDD/F formation. Wood combustion and PVC addition were also tested at the CANMET Energy Technology Centre (Anthony et al., 2001) with measurement of PCDD/F in the raw gas from the hot cyclone of their pilot-scale CFB combustor. Total concentration of PCDD/Fs was 5 ng/m$_n^3$ which can be compared to 10 ng/m$_n^3$ for the case *Wood + PVC*. Woody biomass grown close to the sea and storage of woody biomass in seawater as in British Columbia (Canada) are other examples. Hog fuel, which is salt-laden wood logs, was used in boilers for producing steam in pulp mills (Preto et al., 2005; Duo and Leclerc, 2007) and this led to high emissions of PCDD/Fs. Co-firing of so-called white demolition wood with hospital waste, built up mainly of PVC-plastics, produced high PCDD/F concentrations (Pandelova et al., 2009; Yan et al., 2012). These are further examples of the importance of understanding the alkali chloride track. The different results concerning PCDD/F formation in test cases *Wood + PVC* and *Wood + PVC&AmSulf* were also explained by the alkali chloride track.

4.2. The role of the transition metals Cu, Fe, Al, Ni, Pb, Zn and Cr

The greatest PCDD/F concentrations in the flue gas from the furnace were achieved in *21%SRF + 79%Wood* in comparison to the other test cases. This could be explained by the high amounts of transition metals such as Cu, Fe, Al, Ni, Pb, Zn and Cr in SRF but also its chlorine content. The release of chlorine from a waste fuel and its importance for the primary formation of PCDD/Fs ahead of the convection pass was discussed in Hunsinger et al. (2002). The metal oxide conversion to metal chlorides and further reactions with SO_2 (if present) to metal sulphates is proven to inhibit the PCDD/F formation via the chlorination and partial oxidation of particulate carbon and the chlorination of carbon precursors such as PAHs and phenol, the so-called de novo synthesis (Ryan et al., 2006). This is illustrated in Fig. 1 as reaction (R2), an equilibrium reaction that determines the availability of Cl_2. The condensation reactions from polychlorinated phenols (PCPh) and polychlorinated benzenes (PCBz) are also illustrated in Fig. 1 as well as the importance of transitions metals like Cu and Fe (Ryan et al., 2006). Cu is generally described as the most important transition metal (Dickson et al., 1989; Born et al., 1993; Luijk et al., 1994; Mulholland and Ryu, 2001), but Fe (Stieglitz et al., 1989, 1991; Gullett et al., 1990; Froese and Hutzinger, 1996) Al, Ni, Pb, Zn and Cr are also mentioned.

4.3. The role of municipal sewage sludge

Municipal sewage sludge also contains transition metals but still the PCDD/F concentration in the flue gas leaving the furnace did not increase in *19%SRF + 8%MSS + 73%Wood*, or when co-firing MSS together with wood only but with simultaneous addition of chlorine (i.e. PVC) in Åmand et al. (2010). The MSS used was representative in terms of the content of PCDD/Fs as shown by the fuel analysis in Table 3. A thorough study of the content of PCDD/Fs in Spanish MSS was carried out by De la Torre et al. (2011), and the average total concentrations for PCDD/s and PCDFs ranged from 0.23 to 8.1 ng/g dry fuel. A recently published study from Sweden (Olofsson et al., 2013) describe the present situation among Swedish waste water treatment plants and the total amount of tetra to octa PCDD/Fs was in the range 0.96–2.2 ng/g dry fuel. The MSS in the present work originated from the regional waste water treatment plant of the Gothenburg region and the content PCDD/F was 0.87 ng/g dry fuel. This value is in the lower range compared to both the Swedish and Spanish investigations. Despite the feed of PCDD/Fs entering the boiler with both SRF and MSS, a sink for the PCDD/Fs is obtained when using MSS as additional fuel during co-combustion.

Deng et al. (2009) reported emissions of PCDD/Fs during mono-combustion of MSS in a laboratory-scale fluidised bed (FB) reactor. This result may be related to the size of the reactor since operation in laboratory-scale could generate unburned hydrocarbons. The

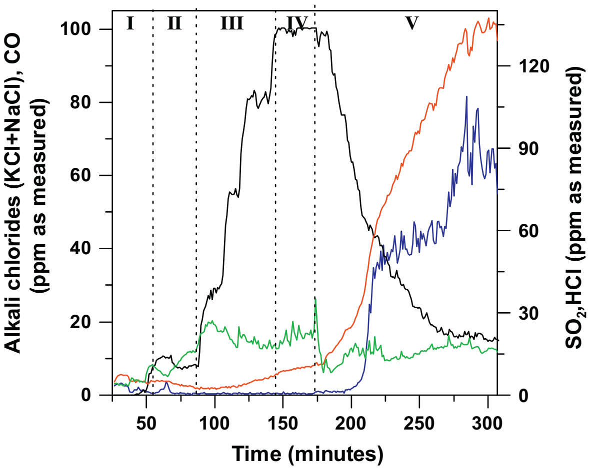

Fig. 12. KCl, SO_2, HCl and CO in a transient test when starting the feed of solid recovered fuel (SRF) and municipal sewage sludge (MSS) for sulphation of KCl. –NaCl+KCl, –HCl FTIR, –SO_2 FTIR, –CO FTIR. I: "100% Wood" case (t = 0 min.); II-III: Stepwise increasing feed of SRF (t = 50-140 min.); IV: Stabilizing the flow of SRF (t = 140-180 min.); V: Stepwise increasing feed of MSS (t = 180-310 min.).

hot cyclone and refractory lined exit in the Chalmers boiler create an after-burning chamber and consequently there are no unburned hydrocarbons present. MSS has a suppressing effect on PCDD/Fs both in the fly ashes and in the raw flue gas at proper burn-out of hydrocarbons as shown for the test *19%SRF + 8%MSS + 73%Wood* in Figs. 9a and 9b. In the work by Yan et al. (2012), the off-gas from drying MSS was used to suppress the formation of PCDD/Fs over fly ash taken from a hospital waste incinerator. The accumulation of nitrogen and sulphur in MSS was believed to be responsible for this suppression especially if the hospital waste was co-fired with MSS. The great potential in lowering emissions of PCDD/Fs in the flue gas and fly ashes for MSS is not only related to its high content of sulphur and nitrogen. The ash chemistry in sludge can be of importance in parallel to the S- and N-tracks. The alkali chloride track could also be relevant since addition of MSS reduced the gaseous alkali chlorides (Fig. 10) as well as the chlorine content in the deposits. The positive effect could then be achieved from sulphation of the alkali chlorides and/or alkali capture reactions involving other elements than sulphur in the sludge ash such as aluminium (Al) and phosphorous (P) (Pettersson et al., 2008, 2009; Elled et al., 2010).

Mininni et al. (2004) used a FBC for mono-combustion of predried MSS with methane as support fuel and even spiked the fuel with chlorinated hydrocarbons. Measurement of PCDD/Fs took place before the bag filter to avoid the influence of the abatement system. The high PCDD/F concentrations were explained as an effect of the transition metals (Cu, Fe, Cr, Zn). However the importance of a proper burnout of hydrocarbons could even be the explanation in the tests reported by Mininni et al. (2004). CO and total hydrocarbons were measured at the same locations as the PCDD/Fs and they were much higher than in the corresponding location in the Chalmers boiler. This is illustrated in a step-response test introducing both SRF and MSS to the *100% Wood* case, Fig. 12. The low SO_2 concentration in the raw gas before introduction of MSS is clearly seen as is the sulphation/capture of alkali chlorides. No CO-peaks are present in Fig. 12, and such peaks indicate the presence of unburned hydrocarbons. The level of CO is also impressively low proving a proper burn-out of combustible matter in the gas phase unlike the situation in the raw gas before the final fly ash removal (Anthony et al., 2001; Mininni et al., 2004).

There are concerns in Spain as to whether combustion of MSS will contribute to increased PCDD/F emissions in the future (Fullana et al., 2004). Pyrolytic gas evolving from sewage sludge at 725 °C passed, after being doped with air and HCl, over sludge ash in a small laboratory reactor at post combustion zone

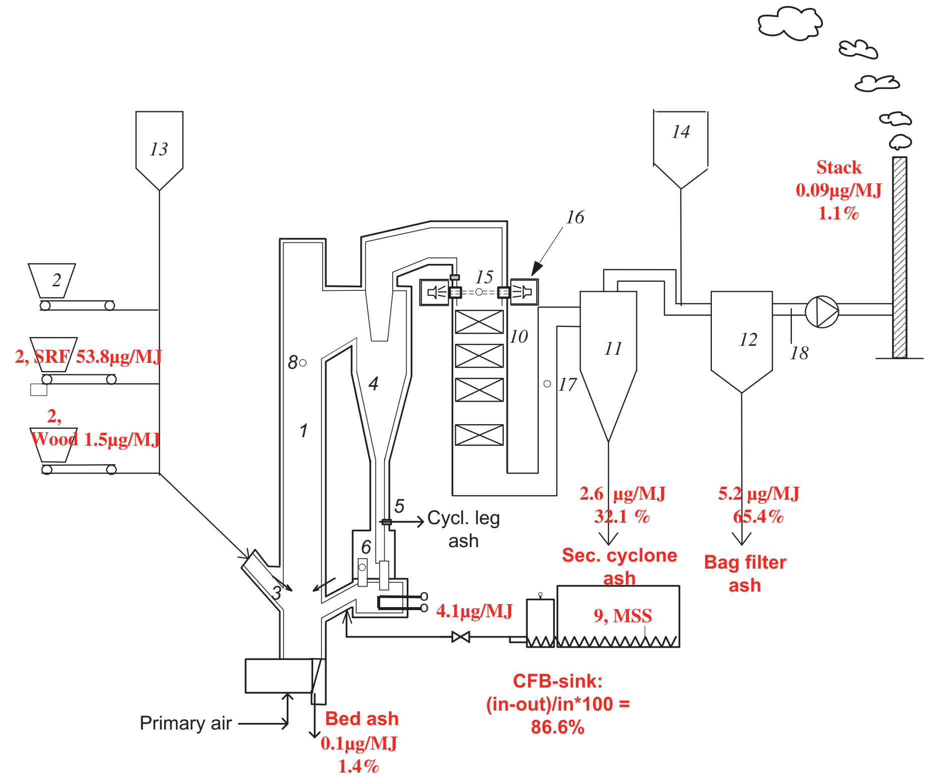

Fig. 13. Tetra- to octa-PCDD/F mass balance for the Chalmers CFB boiler for the test case: "19% SRF + 8%MSS + 73Wood". Flows of PCDD/F expressed as µg/MJ fuel supply base on the lower heating value. Percent (%) is the proportion of individual output to total output. Note that 86.6% of the PCDD/F loading is reduced; the CFB-boiler is a sink for PCDD/F.

conditions (Fullana et al., 2004). This means temperatures in the range 300–500 °C and indeed chlorinated precursors such as PCBz and PCPh were formed. However these precursors do not necessarily form PCDD/Fs if they are oxidised properly before cooling of the flue gas takes place, which was the conditions prevailing in the convection section in the Chalmers boiler.

An interesting feature when performing mass balances on PCDD/Fs is to calculate the individual output to the total output of PCDD/Fs in the various outgoing streams of PCDD/Fs. This feature is illustrated by a mass balance over the CFB-boiler at Chalmers in Fig. 13, and a similar approach is found in Zhang et al. (2012). In Zhang et al. (2012) a large-scale municipal solid waste incinerator of grate-type was used in mass balances of PCDD/F. 84.2% of the total output of PCDD/F was found in the fly ash. The corresponding number for the Chalmers boiler and the test case *19% SRF + 8%MSS + 73%Wood* was 97.5%. The reason for this high number could be related to the use of municipal sewage sludge as additional fuel. As a matter of fact, the CFB-boiler was a sink for PCDD/F and 86.6% of the PCDD/Fs in the fuel feed was reduced during the combustion process.

5. Conclusions

The impact of chlorine and catalysing metals in the fuel on PCDD/F formation was investigated in a measurement campaign in a CFB boiler. The fuel types were a biomass with low content of chlorine, one with enhanced content of chlorine from supply of PVC, and solid recovered fuel (SRF) which contains higher concentrations of both chlorine, and catalysing metals. The focus was on PCDD/F concentrations in raw gas before and after the convection pass of the boiler and in the fly ashes. Additional focus was on the presence of alkali chlorides in the gas phase and in deposits. The approach was to lower the concentration of alkali chlorides and thus prevent the formation of PCDD/Fs in flue gases and in fly ashes. The strategies were addition of ammonium sulphate (AS) and co-firing SRF with municipal sewage sludge (MSS). The following conclusions can be drawn:

- A high quality wood fuel with low content of alkali and chlorine leads to low formation of PCDD/Fs.
- The PCDD/F formation and concentrations of alkali chlorides increased for the biomass with enhanced chlorine content from supply of PVC.
- The PCDD/F formation was significantly reduced in the raw gas as well as in the fly ashes by injection of ammonium sulphate. The gaseous alkali chlorides were also decreased and no alkali chlorides were present in the deposits.
- The alkali chloride track is presented as a link between gaseous alkali chlorides, chlorine in deposits and PCDD/F formation.
- The impact of the alkali track is greater during controlled combustion conditions when proper burn out of the hydrocarbons is achieved minimising the presence of chlorinated precursors such as PCPh and PCBz ahead of the convection section of the boiler.
- The greatest PCDD/F concentrations in the flue gas after the furnace were achieved with SRF in the fuel mix. The explanation is a combination of high amounts of catalysing metals and chlorine which is important for the primary formation of PCDD/Fs ahead of the convection pass.
- Municipal sewage sludge has a suppressing effect on PCDD/F formation both in fly ashes and in the raw flue gas. The ash chemistry in MSS can be of importance in parallel to its content of sulphur and nitrogen. The alkali chloride track could also be relevant since addition of MSS reduced the gaseous alkali chlorides as well as the chlorine content in the deposits.
- Addition of ammonium sulphate and co-combustion with municipal sewage sludge are two established strategies for reduction of deposit formation and superheater corrosion. The measurement campaign shows that both these strategies can be applied to prevent PCDD/F formation.

Acknowledgements

The main financial support for this work was provided by the Swedish Energy Administration. The additional support from Vattenfall's R&D project "Biomass utilization" is also greatly appreciated. Further the authors acknowledge Akademiska Hus AB for maintaining and operating the boiler and the research staff employed by Chalmers University of Technology for carrying out the combustion tests.

References

Addink, R., Cnubben, P.A.J.P., Olie, K., 1995. Formation of polychlorinated dibenzo-p-dioxins/dibenzofurans on fly ash from precursors and carbon model compounds. Carbon 33 (10), 1463–1471.

Aho, M., Ferrer, E., 2005. Importance of coal ash composition in protecting the boiler against chlorine deposition during combustion of chlorine-rich biomass. Fuel 84 (2–3), 201–212.

Altwicker, E.R., Konduri, R.K.N.V., Lin, C., Milligan, M.S., 1992. Rapid formation of polychlorinated dioxins/furans in the post combustion region during heterogeneous combustion. Chemosphere 25 (12), 1935–1944.

Åmand, L.-E., Öhlin, J., Bohwalli, J., Kassman, H., 2010. Primary Formation of PCDD/Fs in a Circulating Fluidized Bed Boiler Burning Biomass – Impacts of Fuel Quality. Impact of Fuel Quality, Saariselkä, Finland.

Anthony, E.J., Jia, L., Granatstein, D.L., 2001. Dioxin and furan formation in FBC boilers. Environmental Science & Technology 35 (14), 3002–3007.

Aurell, J., Fick, J., Haglund, P., Marklund, S., 2009. Effects of sulfur on PCDD/F formation under stable and transient combustion conditions during MSW incineration. Chemosphere 76 (6), 767–773.

Born, J.G.P., Mulder, P., Louw, R., 1993. Fly ash mediated reactions of phenol and monochlorophenols: oxychlorination, deep oxidation, and condensation. Environmental Science & Technology 27 (9), 1849–1863.

Davidsson, K.O., Åmand, L.E., et al., 2008. Countermeasures against alkali-related problems during combustion of biomass in a circulating fluidized bed boiler. Chemical Engineering Science 63 (21), 5314–5329.

De la Torre, A., Alonso, E., et al., 2011. Sources and behaviour of polybrominated diphenyl ethers (PBDEs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in Spanish sewage sludge. Waste Management 31 (6), 1277–1284.

Deng, W., Yan, J., et al., 2009. Emission characteristics of dioxins, furans and polycyclic aromatic hydrocarbons during fluidized-bed combustion of sewage sludge. Journal of Environmental Sciences 21 (12), 1747–1752.

Dickson, L.C., Lenoir, D., et al., 1989. Inhibition of chlorinated dibenzo-p-dioxin formation on municipal incinerator fly ash by using catalyst inhibitors. Chemosphere 19, 1435–1445.

Directive 2010/75/EU of the European Parliament and of the council of 24 November 2010 on industrial Emissions. L334/17, Official Journal of the European Union.

Duo, W., Leclerc, D., 2007. Thermodynamic analysis and kinetic modelling of dioxin formation and emissions from power boilers firing salt-laden hog fuel. Chemosphere 67 (9), S164–S176.

Elled, A.L., Davidsson, K.O., Åmand, L.-E., 2010. Sewage sludge as a deposit inhibitor when co-fired with high potassium fuels. Biomass and Bioenergy 34, 1546–1554.

Forsberg, C., Broström, M., et al., 2009. Principle, calibration, and application of the in situ alkali chloride monitor. Review of Scientific Instruments 80 (2).

Froese, K.L., Hutzinger, O., 1996. Polychlorinated benzene, phenol, dibenzo-p-dioxin, and dibenzofuran in heterogeneous combustion reactions of acetylene. Environmental Science & Technology 30 (3), 998–1008.

Fullana, A., Conesa, J.A., Font, R., Sidhu, S., 2004. Formation and destruction of chlorinated pollutants during sewage sludge incineration. Environmental Science & Technology 38 (10), 2953–2958.

Ghorishi, S.B., Altwicker, E.R., 1996. Rapid formation of polychlorinated dioxins/furans during the heterogeneous combustion of 1,2-dichlorobenzene and 2,4-dichlorophenol. Chemosphere 32 (1), 133–144.

Griffin, R.D., 1986. A new theory of dioxin formation in municipal solid waste combustion. Chemosphere 15, 1987–1990.

Gullett, B.K., Bruce, K.R., Beach, L.O., 1990. The effect of metal catalysts on the formation of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran precursors. Chemosphere 20, 1945–1952.

Gullett, B.K., Bruce, K.R., Beach, L.O., 1992. Effect of sulfur dioxide on the formation mechanism of polychlorinated dibenzodioxin and dibenzofuran in municipal waste combustors. Environmental Science & Technology 26 (10), 1938–1943.

Gullett, B.K., Dunn, J.E., Bae, S.K., Raghunathan, K., 1998. Effects of combustion parameters on polychlorinated dibenzodioxin and dibenzofuran homologue profiles from municipal waste and coal co-combustion. Waste Management 18, 473–483.

Gullett, B.K., Dunn, J.E., Raghunathan, K., 1999. Effect of cofiring coal on formation of polychlorinated dibenzo-p-dioxins and dibenzofurans during waste combustion. Environmental Science & Technology 34 (2), 282–290.

Hajizadeh, Y., Onwudili, J.A., Williams, P.T., 2012. Effects of gaseous NH_3 and SO_2 on the concentration profiles of PCDD/F in flyash under post-combustion zone conditions. Waste Management 32 (7), 1378–1386.

Hatanaka, T., Kitajima, A., Takeuchi, M., 2004. Role of copper chloride in the formation of polychlorinated dibenzo-p-dioxins and dibenzofurans during incineration. Chemosphere 57 (1), 73–79.

Hell, K., Stieglitz, L., Dinjus, E., 2001. Mechanistic aspects of the de-novo synthesis of PCDD/PCDF on model mixtures and MSWI fly ashes using amorphous 12C- and 13C-labeled carbon. Environmental Science & Technology 35 (19), 3892–3898.

Henderson, P., Andersson, C., Kassman, H., 2004. The use of fuel additives in wood and waste wood-fired boilers to reduce corrosion and fouling problems. VGB PowerTech 84 (6), 58–62.

Hunsinger, H., Jay, K., Vehlow, J., 2002. Formation and destruction of PCDD/F inside a grate furnace. Chemosphere 46, 1263–1272.

Hunsinger, H., Song, H.G.J., Seifert, H., Jay, K., 2004. Influence of SO_2 on the Formation of PCDD/F in MSWI. 3rd i-CIPEC, Hangzhou, China.

Hunsinger, H., Seifert, H., Jay, K., 2007. Reduction of PCDD/F formation in MSWI by a process-integrated SO_2 cycle. Environmental Engineering Science 24 (8), 1145–1159.

Iino, F., Imagawa, T., Takeuchi, M., Sadakata, M., 1999. De novo synthesis mechanism of polychlorinated dibenzofurans from polycyclic aromatic hydrocarbons and the characteristic isomers of polychlorinated naphthalenes. Environmental Science & Technology 33 (7), 1038–1043.

Karasek, F.W., Dickson, L.C., 1987. Model studies of polychlorinates dibenzo-p-dioxin formation during municipal refuse incineration. Science 237, 754–756.

Kassman, H., 2012. Strategies to Reduce Gaseous KCl and Chlorine in Deposits during Combustion of Biomass in Fluidised Bed Boilers. Department of Energy and Environment. Göteborg, Chalmers University of Technology. PhD.

Kassman, H., Andersson, C., et al., 2006. Gas phase alkali chlorides and deposits during co-combustion of coal and biomass. In: 19th International Conference on Fluidized Bed Combustion, Vienna, Austria.

Kassman, H., Holmgren, M., et al., 2008. Nitrogen containing additives for simultaneous reduction of KCl and NOx during biomass combustion in a CFB boiler. In: 9th International Conference on Circulating Fluidized Beds, Hamburg, Germany.

Kassman, H., Bäfver, L., Åmand, L.-E., 2010. The importance of SO_2 and SO_3 for sulphation of gaseous KCl – an experimental investigation in a biomass fired CFB boiler. Combustion and Flame 157 (9), 1649–1657.

Kassman, H., Broström, M., Berg, M., Åmand, L.-E., 2011. Measures to reduce chlorine in deposits: application in a large-scale circulating fluidised bed boiler firing biomass. Fuel 90, 1325–1334.

Kassman, H., Pettersson, J., Steenari, B.-M., Åmand, L.-E., 2013. Two strategies to reduce gaseous KCl and chlorine in deposits during biomass combustion – injection of ammonium sulphate and co-combustion with peat. Fuel Processing Technology 105, 170–180.

Kobylecki, R.P., Ohira, K., et al., 2001. Dioxin and fly ash free incineration by ash pelletization and reburning. Environmental Science & Technology 35 (21), 4313–4319.

Lavric, E.D., Konnov, A.A., Ruyck, J.D., 2004. Dioxin levels in wood combustion – a review. Biomass and Bioenergy 26 (2), 115–145.

Luijk, R., Dorland, C., Kapteijn, F., Govers, H.A.J., 1993. The formation of PCDDs and PCDFs in the catalysed combustion of carbon: implications for coal combustion. Fuel 72 (3), 343–347.

Luijk, R., Akkerman, D.M., et al., 1994. Mechanism of formation of polychlorinated dibenzo-p-dioxins and dibenzofurans in the catalyzed combustion of carbon. Environmental Science & Technology 28 (2), 312–321.

Manninen, H., Peltola, K., Ruuskanen, J., 1997. Co-combustion of refuse-derived and packaging-derived fuels (RDF and PDF) with conventional fuels. Waste Management 15 (2), 137–147.

Mininni, G., Sbrilli, A., Guerriero, E., Rotatori, M., 2004. Dioxins and furans formation in pilot incineration tests of sewage sludge spiked with organic chlorine. Chemosphere 54 (9), 1337–1350.

Mulholland, J.A., Ryu, J.-Y., 2001. Formation of polychlorinated dibenzo-p-dioxins by $CuCl_2$-catalyzed condensation of 2,6 chlorinated phenols. Combustion Science and Technology 169, 107–126.

Nielsen, H.P., Frandsen, F.J., Dam-Johansen, K., Baxter, L.L., 2000. The implications of chlorine-associated corrosion on the operation of biomass-fired boilers. Progress in Energy and Combustion Science 26 (3), 283–298.

Ogawa, H., Orita, N., et al., 1996. Dioxin reduction by sulfur component addition. Chemosphere 32 (1), 151–157.

Olofsson, U., Brorström-Lundén, E., Kylin, H., Haglund, P., 2013. Comprehensive mass flow analysis of Swedish sludge contaminants. Chemosphere 90 (1), 28–35.

Pandelova, M.E., Lenoir, D., Kettrup, A., Schramm, K.-W., 2005. Primary measures for reduction of PCDD/F in co-combustion of lignite coal and waste: effect of various inhibitors. Environmental Science & Technology 39 (9), 3345–3350.

Pandelova, M., Lenoir, D., Schramm, K.W., 2007. Inhibition of PCDD/F and PCB formation in co-combustion. Journal of Hazardous materials 149 (3), 615–618.

Pandelova, M., Stanev, I., et al., 2009. Correlation of PCDD/F and PCB at combustion experiments using wood and hospital waste. Influence of $(NH_4)_2SO_4$ as additive on PCDD/F and PCB emissions. Chemosphere 75 (5), 685–691.

Pettersson, A., Zevenhoven, M., Steenari, B.-M., Åmand, L.-E., 2008. Application of chemical fractionation methods for characterisation of biofuels, waste derived fuels and CFB co-combustion fly ashes. Fuel 87, 3183–3193.

Pettersson, A., Elled, A.L., et al., 2009. The impact of zeolites during co-combustion of municipal sewage sludge with alkali and chlorine rich fuels. In: Proceedings of the 20th International Conference on Fluidized Bed Combustion.

Preto, F., McCleave, R., McLaughlin, D., Wang, J., 2005. Dioxins/furans emissions from fluidized bed combustion of salt-laden hog fuel. Chemosphere 58 (7), 935–941.

Ruokojärvi, P.H., Halonen, I.A., et al., 1998. Effect of gaseous inhibitors on PCDD/F formation. Environmental Science & Technology 32 (20), 3099–3103.

Ruokojärvi, P., Aatamila, M., Tuppurainen, K., Ruuskanen, J., 2001a. Effect of urea on fly ash PCDD/F concentrations in different particle sizes. Chemosphere 43, 757–762.

Ruokojärvi, P., Asikainen, A., et al., 2001b. Urea as a PCDD/F inhibitor in municipal waste incineration. Journal of the Air & Waste Management Association 51 (3), 422–431.

Ruokojärvi, P., Tuppurainen, K., et al., 2001c. PCDD/F reduction in incinerator flue gas by adding urea to RDF feedstock. Chemosphere 43 (2), 199–205.

Ryan, S.P., Li, X.-d., et al., 2006. Experimental study on the effect of SO_2 on PCDD/F emissions: determination of the importance of gas-phase versus solid-phase reactions in PCDD/F formation. Environmental Science & Technology 40 (22), 7040–7047.

Ryu, J.-Y., Mulholland, J.A., et al., 2005. $CuCl_2$-catalyzed PCDD/F formation and congener patterns from phenols. Chemosphere 61 (9), 1312–1326.

Samaras, P., Blumenstock, M., et al., 2001. PCDD/F inhibition by prior addition of urea to the solid fuel in laboratory experiments and results statistical evaluation. Chemosphere 42, 737–743.

Sidhu, S.S., Maqsud, L., Dellinger, B., Mascolo, G., 1995. The homogeneous, gas-phase formation of chlorinated and brominated dibenzo-p-dioxin from 2,4,6-trichloro- and 2,4,6-tribromophenols. Combustion and Flame 100, 11–20.

Stieglitz, L., Zwick, G., et al., 1989. On the de-novo synthesis of PCDD/PCDF on fly ash of municipal waste incinerators. Chemosphere 18, 1219–1226.

Stieglitz, L., Vogg, H., et al., 1991. On formation conditions of organohalogen compounds from particulate carbon of fly ash. Chemosphere 23, 1255–1264.

Theis, M., Skrifvars, B.J., et al., 2006. Fouling tendency of ash resulting from burning mixtures of biofuels. Part 2: Deposit chemistry. Fuel 85 (14–15), 1992–2001.

Van den Berg, M., Birnbaum, L., et al., 1998. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. Environmental Health Perspectives 106, 775–792.

van Lith, S.C., Frandsen, F.J., et al., 2009. Lab-scale investigation of deposit-induced chlorine corrosion of superheater materials under simulated biomass-firing conditions. Part 1: Exposure at 560 °C. Energy & Fuels 23 (7), 3457–3468.

Weber, R., Iino, F., et al., 2001. Formation of PCDF, PCDD, PCB, and PCN in de novo synthesis from PAH: mechanistic aspects and correlation to fluidized bed incinerators. Chemosphere 44 (6), 1429–1438.

Wilhelm, J., Stieglitz, L., Dinjus, E., Will, R., 2001. Mechanistic studies on the role of PAHs and related compounds in PCDD/F formation on model fly ashes. Chemosphere 42, 797–802.

Wu, H.-L., Lu, S.-Y., et al., 2012. Inhibition of PCDD/F by adding sulphur compounds to the feed of a hazardous waste incinerator. Chemosphere 86 (4), 361–367.

Yan, J.H., Chen, T., et al., 2006. Evaluation of PCDD/Fs emission from fluidized bed incinerators co-firing MSW with coal in China. Journal of Hazardous materials 135, 47–51.

Yan, M., Li, X., et al., 2012. Sludge as dioxins suppressant in hospital waste incineration. Waste Management 32 (7), 1453–1458.

Zhang, G., Hai, J., Cheng, J., 2012. Characterization and mass balance of dioxin from a large-scale municipal solid waste incinerator in China. Waste Management 32 (6), 1156–1162.