DIOXIN EMISSIONS FROM BIOMASS FIRED ENERGY PLANTS AND OTHER SOURCES IN DENMARK

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Introduction

This paper presents results from a new Danish investigation of emissions of dioxins (PCDD) and furans (PCDF) from various sources[1] carried out for the Danish EPA.

The purpose was to investigate smaller sources (in size or emission), for which the knowledge of the PCDD/F emissions was low or missing. The sources were: Five biomass plants (> 1 MW) using straw, wood and chipboard residue, a farm size boiler (<1 MW) using straw, a wood stove during normal operation and with reduced supply of combustion air, a small stoker boiler (<1 MW) using wood pellets, and three district heating plants (>1 MW) using waste oil. In addition, measurements were made of emissions from barbecuing, and cremation of corpses in two crematories.

Methods and Materials

Emission samplings were performed with a sampling train according to the filter/condenser method described in the CEN standard EN 1948 part 1, Sampling. Most of the measurements did include two parallel 6 hours samplings, both repeated the next day. Other measurements were either one or two parallel or serial samplings lasting from 2 to 6 hours. The measurements of the wood stove and the barbecue were performed in test facilities enabling a constant total flow of flue gas diluted with air in a dilution duct. The obtained samples were analysed according to EN 1948 part 2 and 3. Quantitative determinations of PCDD/PCDF in various samples according to the isotope dilution method were carried out by means of 2,3,7,8-PCDD/PCDF substituted ^{13}C-UL internal standards. Before extraction, internal standards were added to the filter. Condensate and rinse were filtered and this filter was treated together with the sampling filter with hot aqueous acid, afterwards the filters were dried with acetone. Acid, acetone from drying filters, rinsing solution and condensate were combined and extracted with toluene. The filters and the XAD-2 tubes were soxhlet extracted by toluene. Cleanup was done on multicolumn systems involving various kind of treated silica gel, aluminium oxide, carbon-on-fibre or carbon-on-celite. The final extract was reduced to dryness and dissolved in syringe standard. Determination was carried out by using an HRGC/HRMS combination with HP 5890 series II / VG-AutoSpec on DB 5 and SP2331 capillary columns. For each substance 2 isotope masses were measured.

Results and Discussion

The results from the biomass-fired plants are divided in two groups, because plants with similar equipment and type of operation show more comparable results, than same type of fuel in different plants. The two groups are larger plant with good continuous combustion and flue gas cleaning and small plants with semiautomatic or manual combustion and no flue gas cleaning.

Table 1. PCDD/F emission from larger biomass fired energy plants

No	Plant type	Size MW	Fuel	Emission factor ng I-TEQ/ton fuel	Concentration ng I-TEQ/Nm³ (10%O_2)
1	Power and district heating	95	Straw	22	0.003
2	Power and district heating	40	Straw	35	0.005
3	Power and district heating	10	Straw	5	0.001
4	District heating	6.3	Straw	24	0.003
5	Power and process steam	51	Wood chips	95	0.016
6	District heating	6.3	Wood chips	26	0.003
7	District heating	6.3	Chipboard	28	0.003

Larger plants with a good continuous combustion, a high combustion temperature, and efficient flue gas cleaning have very low PCDD/F emissions, when burning either straw, wood chips or chipboard residue. PCDD/F congener pattern calculated in weight percent is presented in Figure 1.

All the larger plant, except one, show very similar congener patterns, with a significant top for OCDD. The 51 MW plant with the different pattern and also the highest emission, had problems with several dust burner stop-downs during the sampling period, which could have both increased the emission and changed the pattern, compared to normal operation. In fact, this pattern is more similar to the pattern from normal operation with birch-wood in wood stove or stoker boiler seen in Figure 2 (No. 10 and 14).

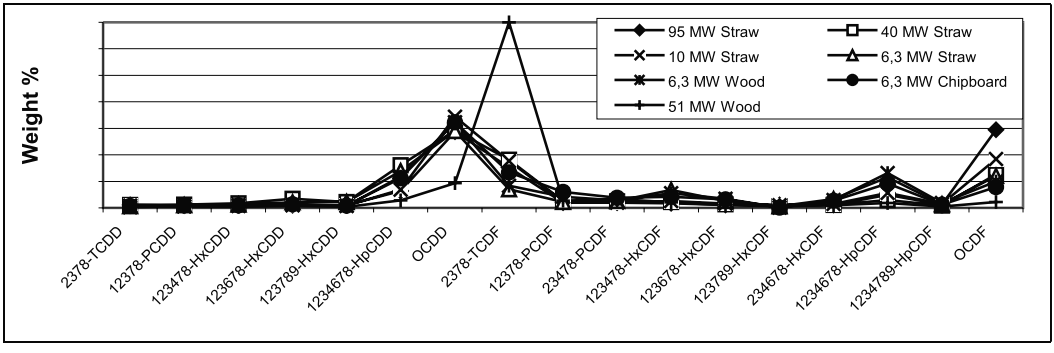

Figure 1. PCDD/F profiles for larger biomass fired plants

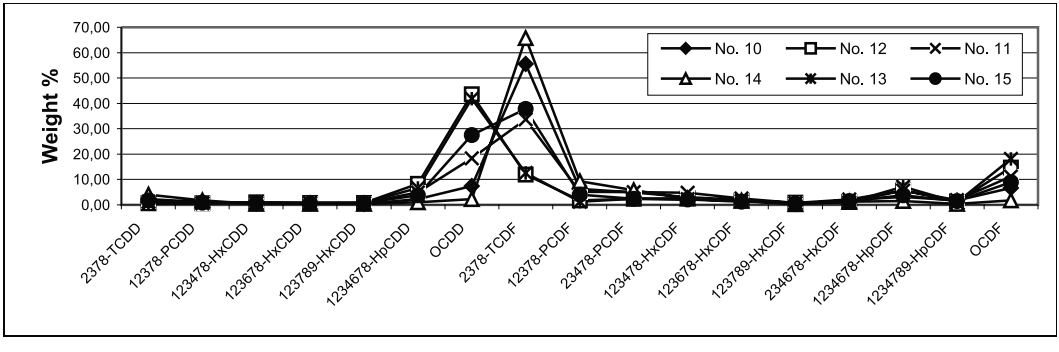

Figure 2. PCDD/F pattern for wood stove and stoker boiler

Table 2. Smaller semiautomatic boiler and wood stove

No	Plant type	Size MW	Fuel	Emission factor ng I-TEQ/ton fuel	Concentration ng I-TEQ/Nm³ (10%O_2)
8	Farm size boiler, 100% load	0.3	Straw	5,300	0.5
9	Farm size boiler, 60% load			9,200	1.2
10	Stove, normal operation	0.005	Birch, air-dried firewood	5,100	0.8
11	Stove, normal operation		Beech, kiln-dried furniture wood	1,900	0.3
12	Stove, reduced comb. Air		Birch, air-dried firewood	610	0.1
13	Stove, reduced comb. Air		Beech, kiln-dried furniture wood	640	0.1
14	Stoker boiler, 100% load	0.019	Wood pellets	530	0.07
15	Stoker boiler, 26% load			210	0.03

The small farm-size boiler with a poor combustion and no flue gas cleaning, has the highest emission, which is more than 400 times higher than the average of the larger plants. Emission from the wood stove and the stoker boiler is somewhat lower, but still much higher than the larger plants. The pattern in Figure 2 shows an interesting difference depending of the operation of the stove and stoker boiler.

The better combustion conditions gives the highest percentage for 2,3,7,8-TCDF, while the poorer combustion with reduced combustion air gives the highest percentage for OCDD. The Stove fired with beech under normal conditions (No. 11) and the stoker boiler with 26 % load (No. 15), seem to be in an intermediate state, between the better and the poorer combustion.

Table 3. PCDD/F emission from barbecuing

No	Grill briquettes type	Emission factor ng I-TEQ/ton briquettes	Emission factor ng I-TEQ/barbecuing with 2 kg briquettes	Concentration ng I-TEQ/Nm³ (10%O_2)
16	A	11,000	22	0.7
17	B	6,000	12	0.6

Four samples were taken each covering a whole cycle of barbecuing which included ignition of 2 kg briquettes with fire-lighters for half an hour as a start, grilling of four steaks, followed by grilling of four turkey sizzles and finally grilling of 8 large sausages. Sampling was continued to achieve a total of two hours sampling time. The energy content of type B briquettes was only 60 to 70 % of type A briquettes. If the PCDD/F emissions are calculated in relationship to the energy content, there is hardly any difference in the emissions from the two types of briquettes. In the dilution channel the temperature was 39 to 56 °C, and the concentrations were between 0.02 and 0.05 ng I-TEQ/Nm³. During normal use of the barbecue, the actual concentrations inhaled by the cook are considered lower, because it is not pleasant to breathe hot air, so anyone will automatically move the head to a position with a lower temperature, where the PCDD/F concentration is lower. The dioxin emission from barbecuing with briquettes is fairly the same, as if the amount of wood needed to produce the briquettes, was burned in the woodstove above.

Table 4. PCDD/F emissions from burning waste oils

No	Plant type	Size MW	Fuel	Emission factor ng I-TEQ/ton fuel	Concentration ng I-TEQ/Nm³ (10%O_2)
18	District heating	23	Refined waste oil	30	0.002
19	District heating				

20	District heating, with very poor combustion.	15	Refined waste oil	36 970	0.002 0.05
21	District heating	3	Unrefined waste oil	950	0.044

Emission of PCDD/F from burning refined waste oil is low, and inside the interval 20 – 90 ng I-TEQ/ton oil from domestic heating with light fuel oil, reported by Erik Hansen *et. al.*[2]. However, the third result is much higher, but it was sampled during a period, where very poor combustion with increased soot emission was observed. There was not found anything indicating any problems or mistakes during sampling or analysis, which could explain the high value. We believe that the high value indicates that there might be a considerable increase in emission of PCDD/F, if a fuel that normally gives low emissions is burned under poor conditions with increased soot emission. The emission from unrefined waste oil is much higher, but still at a low level, which is comparable with the results from a Danish investigation from 1988, reported by Jensen *et.al.*[3], where the emission was found to be 0.005 – 0.13 ng I-TEQ/Nm³.

Table 5. PCDD/F emissions from crematories

No	Plant	Emission factor ng I-TEQ/corpse	Concentration ng I-TEQ/Nm³ (10%O_2)
22	Crematory A	240	0.2
23	Crematory B, furnace 1	930	0.7
24	Crematory B, furnace 2	310	0.3
25	Average, weighted after number of corpses cremated:	350	0.3

Takeda *et. al.*[4] have reported the dioxin emission from 10 crematories in Japan to be between 42 and 62,000 ng-TEQ/cremation, with an average of 9,200 ng-TEQ/cremation. Groschwitzy *et. al.*[5] has reported the emission from crematories in Germany to be between 250 and 28,000 ng I-TEQ/cremation. An explanation for the relatively low emission values in Danish crematories may be that during the 1990s they have all been either replaced or renovated, among other things to observe pre-heating temperatures to at least 850°C before the coffin is inserted, and a flue gas retention time at minimum one second at minimum 850°C.

Acknowledgements

This project was supported by the Danish Environmental Protection Agency. The authors would like to thank Elsamprojekt, the counties of Århus and Fyn, for allowing the use of results from measuring on different plants, and to the Danish Technological Institute for carrying out sampling at some of the plants and the stove.

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