THE EFFECT OF CHEMICAL INHIBITOR ON PCDD/F CONCENTRATIONS IN DIFFERENT PARTICLE SIZE FRACTIONS

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Introduction

The formation of polychlorinated dioxins and furans (PCDD/Fs) during incineration has been proposed to occur via three different pathways: 1) pyrosynthesis, i.e. high temperature gas phase formation 2) formation from macromolecular carbon and organic or inorganic chlorine (*de novo* formation) and 3) through organic precursors such as chlorobenzenes, polychlorinated diphenylethers and chlorophenols. Even though these mechanisms have been studied for years, no detailed reaction mechanisms have yet been established.

Several parameters have been proven to be important in PCDD/F formation during incineration: the fuel itself (especially amounts of chlorine and metal catalysts) and various combustion parameters (e.g. oxygen, hydrogen chloride and water concentrations, temperature profile, residence time). By optimising these parameters dioxin formation can be reduced considerably. Unfortunately, combustion practices and even economic aspects do not always afford optimal conditions for PCDD/F prevention. A convenient and economic way of preventing the formation of dioxins and furans in the incineration process is to block the formation with inhibitors. Some compounds have been proven to reduce PCDD/F concentrations in flue gases. Compounds containing nitrogen and sulphur have given promising results as PCDD/F inhibitors [1-3].

Especially molecules containing amino nitrogen (urea in particular) have proven to have a clear inhibitory effect when sprayed into flue gases [4,5]. Since particles seem to play a remarkable role in PCDD/F formation and inhibition [4-6], we performed a series of tests using urea as an inhibitor and investigated the effect of urea on the PCDD/F concentrations in different particle size fractions in flue gases.

Materials and methods

Light heating oil was incinerated in a 50 kW pilot plant consisting of an oil burner and furnace and the flue gases were directed through the delay chamber and economiser to the stack. Schema of the pilot plant used has been described elsewhere [5]. Chlorine and copper were added into fuel to

increase the PCDD/F formation during the tests. The amounts of these additives were adjusted on the basis of our previous studies [7,8] to correspond to 0.5 % of the total fuel flow.

Urea was selected to be the chemical inhibitor as a result of our previous studies as well [5] and was injected to flue gases as 0.1, 0.5 and 1.0 weight-% of the fuel flow as an aqueous solution at approximately 700 °C. Total (not fractionated) PCDD/PCDF samples from flue gases were collected into XAD-2 resin (gas phase) and glass fibre filter (particle phase).

MS-Select
Comment:

Fractionated particulate samples were taken with a five-stage Cascade Centripeter sampler to study the division of PCDD/Fs into different particles sizes, and the effect of the inhibitor on this division. The modified Bird & Tole Cascade Centripeter fractionates the particles in 5 different size classes [9]. The particle cut sizes are as presented in Table 1.

Table 1: Cut sizes of cascade centripeter

Sampler stage	**Particle diameter (□m)**
1 (upper stage)	> 52
2	14.5 - 52
3	4.4 - 14.5
4	1.6 - 4.4
5 (bottom stage)	< 1.6

The filters of each of the stage were weighed before and after sampling, and they were analysed according to the same methodology as the total PCDD/F flue gas samples.

The analytical procedure has been described in detail elsewhere [10] but briefly it consists of Soxhlet extraction with toluene, purification with multistep columns and analysis with HRGC/HRMS.

Results and Discussion

In total PCDD/F samples, the gas phase PCDD/Fs reductions were modest (reductions of 11-29 % in urea injection tests), whereas in the particle phase the reductions of PCDD/Fs were higher (53-80 %). Consequently, the total PCDD/F reductions were rather high (49 - 74 %) since most of the PCDD/Fs were found in the particulate phase (gas : particle distribution 0.1- 0.4).

The highest PCDD/F reduction was achieved with the 0.5 % concentration of urea. Also in our previous tests [5] no significant further increase in PCDD/F reduction was gained with 1 % urea concentration compared to the 0.5 % concentration.

In size fractionated samples most of the PCDD/Fs (> 68 %) were found in the two smallest particle size classes (i.e. < 1.6 □m and 1.6 - 4.4 □m), both in the test without urea and with 1 % urea. These two smallest particle sizes comprised approximately 97 % of the total particle surface area in our tests. The reduction with 1 % urea injection in each particle size was 56 - 99.6 % (Figure 1), calculated from the PCDD/F concentrations per particle surface area in each particle size fraction. The greatest particle size class (> 52 □m) did not however have as good a reduction, which is probably due to very small amount of particles weighed in the filter (< 0.1 mg) leading to a great uncertainty in mass determination and therefore in reduction, too.

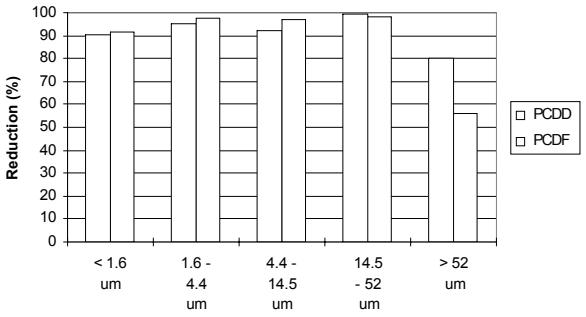

Figure 1: PCDD/F reductions in different particle sizes when 1.0 % urea is used as an inhibitor

To conclude, the smallest particles play the most important role in both the PCDD/F formation and inhibition mechanisms because of their large surface area. When reductions are examined as mass PCDD/F per surface area of the particles (i. e. ng PCDD/F / m^2) in each size fractions, no significant differences can be observed in PCDD/F reductions between different particle size classes.

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