MAJOR AND MINOR PATHWAYS TO DIOXINS IN INCINERATORS

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Introduction

Since the first report on 'dioxin' formation and emission from incinerators, [1] numerous studies have been devoted to this unwanted phenomenon. Based on analyses of concentrations and congener/isomer composition in relation to places of sampling, a major question has concerned *how* PCDD/Fs arise and behave in the various stages of the incineration process. [2,3] At least as important is how to prevent emission, or even better, to suppress or even prevent formation of dioxins. This requires adequate knowledge on *mechanisms*: which 'starting' compounds, reaction intermediates, are involved and how exactly occurs their conversion to the 'end' products, the family of (chlorinated) dibenzofurans and dibenzodioxins?

Most 'mechanistic' papers describe and discuss results on labscale experiments, which are meant to trace, or sometimes prove, the importance of a distinct scenario: either the so-called *de novo* pathway (formation directly from carbonaceous materials in the ashes, after cooling of the raw flue gas well below the temperatures of the primary combustion), or the *precursor* pathway, wherein more volatile organics - especially phenols, but also lower or non-chlorinated 'PICs' (products of incomplete combustion) - are involved; by thermal or catalytic condensation, chlorination and/or partial oxidation. Such types of papers, also of high standard, continue to appear, as is illustrated by references. [4,5] While the chemistry of both scenarios is already quite complex, the mere observation of interesting levels of dioxins in these lab-scale tests still requires translation to proper real-life situations of the time-, technology-, and temperature- dependent incineration practice. The present paper critically discusses salient earlier approaches, while taking recent and new experimental results into account.

Results and Discussion

For the *precursor* scenario the 1983 Shaub and Tsang paper " Dioxin Formation in Incinerators" [6] has long been influential in discarding phenols as possible intermediates to dioxins, to begin with in the primary, thermal combustion. That picture changed after that it was recognized that uncatalyzed condensation of two phenoxy radicals, totally neglected by Shaub and Tsang, can be an efficient route to dioxins. [7,8] Thus, phenol gives Cl-free dibenzofuran as a PIC (in amounts like e.g. naphthalene), and chlorinated phenols lacking Cl at *ortho*-positions behave analogously. With *ortho*-Cl, corresponding chlorinated DDs are also formed, whereas fully *ortho*-chlorinated phenols like 2,4,6-TCP and PCP, give nearly only PCDDs. Realistic mixtures of phenols therefore lead to a mixture of dibenzofuran as well as PCDFs with less (PC)DDs. [5,7]

Admixed with other PICs, including remaining (chloro)phenols, these products can then be subject to catalytic reactions downstream in the boiler, the electrostatic precipitator (ESP), and baghouse sections: condensation, (oxy) chlorination, and (partial) catalytic combustion. Various lab-scale tests have shown that fly-ash-mediated conversion of (chloro)phenols gives rise to especially PCDDs, with yields at the percent level. [8]

With results of these thermal and catalytic model studies combined, the formation and emission of a complex mixture of dioxins can be rationalized at least in a qualitative fashion, the more so if one uses realistic cocktails of model PICs, precursors, rather than single compounds. One big difference with conditions in practice however is that commonly the used concentrations of these (model) phenols etc. have been orders of magnitude higher than those observed in real incinerators. In a recent investigation we have attempted to bridge that gap, by administering relevant PIC/precursor mixtures at very low concentrations as a model combustion offgas to beds of real fly ash at typical temperatures of 325 – 350°C also with varying reaction times, up to hours. [9,10] While the native carbon in the ash produced PCDD/Fs, as expected, during an hour or so, the PIC/precursor cocktail continued to do so steadily,

when followed for 20 hours. Translation of these data to conditions in a real incinerator showed that dioxin outputs (measured at a point before modern, advanced pollution control devices) may for an important part be explained from precursor chemistry. Also new results from tests at ECN – to be presented at the conference – substantiate the conclusions derived on the basis of earlier laboratory model reactions.

When one of the trace components in the PIC/precursor mix, phenol, was replaced by its full $^{13}C_6$-labeled analogue, an important part of the resulting dioxins, esp. the PCDDs, were found to be labeled, but only *one* ring stemmed from the 'heavy' phenol (Figure 1). Clearly, the other 'half' of the dioxin molecule came from another PIC component. 'Fully' labeled compounds were also found, but to a very minor degree only (sec. axis).
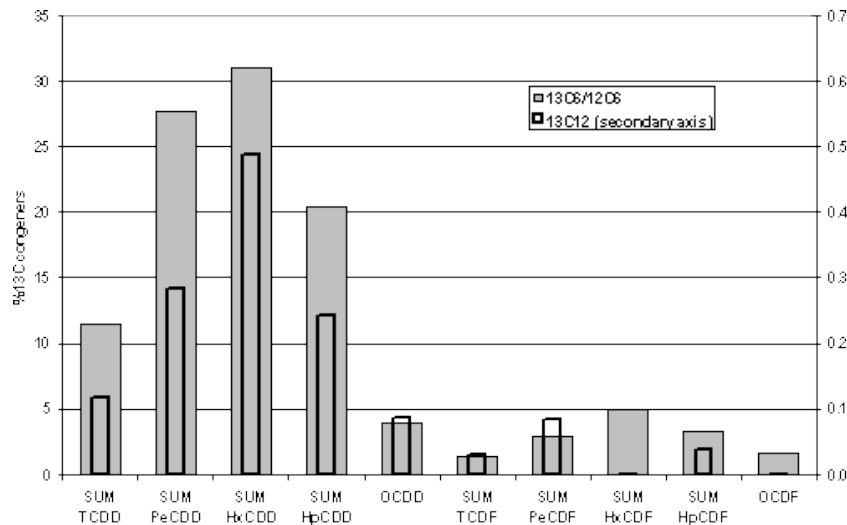

Figure 1 Relative outputs of ^{13}C-labeled PCDD/F in the test with $^{13}C_6$-phenol as the feed

So, with respect to phenol(s) the formation of dioxin appears to be a *first order reaction* rather than second order, as is commonly assumed [11], or possibly true when model catalytic reactions are performed with unrealistic high phenol concentrations.

At this point a critical evaluation of the evidence for the importance of the 'de novo' pathway is worthwhile. Putting numerous studies with model, artificial fly ash surrogates aside here, it is well documented that 'Stieglitz'-type air stripping of fixed beds of fly ash leads to ng/g outputs of PCDD/Fs, decreasing in time, with a composition quite like those in real life. [12] The question here too is how to translate such results to values for real incinerators. A very valuable recent effort to do this is that of Huang and Buekens. [11] They developed a kinetic model with three steps: (1) oxidation of carbon with formation of (sorbed) PCDD/F, (2) desorption, and (3) conversion of sorbed PCDD/F into other products. Based on 4 sets of lab-scale tests the corresponding 3 parameters were assessed, to get optimal coverage of the net PCDD/F formation in the gas and solid phase as a function of temperature and residence time.

While such a mathematical approach does not imply any mechanism in the proper chemical sense ('*how* are the dioxins formed' and 'what is the physical meaning of the parameters'), one can next estimate dioxin outputs for '*de novo*' reaction in a boiler, ESP and a bag filter.

The calculated values of course depend on the allotted time and the temperature. Significant values required 5 minutes 'lifetime' for a boiler, and half an hour for an ESP. Of prime importance also are the accepted fly ash concentration and its carbon content. If one starts with values of 10 g/Nm^3 and 2 wt%, which are on the high end of the scale (as Huang and Buekens did), the calculated result is of course an order of magnitude larger than when taking 2 g/Nm^3 of ash with just 1% of 'native carbon'. With the latter set the dioxin outputs from the (model) boiler are at best 0.06 µg/Nm^3 (gas phase) and 0.06 µg/g (solid phase) respectively. The ESP ash would contain only ~ 0.13 µg/g. Such numbers are at the lower end of, if not below, the values from real incinerators.

When extrapolating data on precursor/phenol model reactions down to real low concentrations by a square-root dependence, as Huang and Buekens did, you get of course formation rates some 6 orders of magnitude below those mentioned above. Then, there is little more left than accepting 'de novo' as the only pathway. However, their statement that "…it is of little practical interest to test precursors in laboratory measurements any more" is too hasty, given the results from our lab. [9,10] Therefore, future research should give proper attention to the importance of both types of reaction, *and* of their possible mechanistic interrelation – by modeling, but more important, by conducting 'smart' experiments, at relevant conditions, also with other labeled starting compounds. Suggestions for this will be presented. Also, further important features will be discussed, including the question how the rather characteristic PCDD/F isomer/congener incineration pattern can be reconciled with the widely varying qualities of incineration and different technologies employed, if two different pathways are yet to be taken into account.

Acknowledgement.

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