Some Problems in Evaluation of PCDD/F Formation from Aromatic Compound Condensation and Solid Carbon Degradation Pathways under Municipal Incinerator Conditions

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1. Introduction
The heterogeneous pathways of PCDD/F formation from aromatic compound condensation and solid carbon degradation were first demonstrated by Karasek and Dickson (1), and Vogg and Stieglitz (2), respectively. The relative importance of these two pathways has been studied in laboratory experiments by a number of groups (3-5). In recent communications (6,7), how to apply the PCDD/F formation rate data measured in laboratory experiments to practical incinerator conditions has been discussed. Since to properly understand these mechanistic pathways and to estimate their relative magnitude under various conditions are useful for development of control techniques, it is of interest to give more attention to this issue.

2. Comparison Using Reaction Rates
On the basis of a comparison of the data reported by different laboratories, the following PCDD/F formation rates have been suggested as typical (6): 0.034 ug-PCDDF/g-FA min for solid carbon degradation pathway, and 1.6 ug-PCDD/g-FA min for aromatic compound condensation pathway, (FA stands for fly ash). The aromatic precursor concentrations in these laboratory experiments were, however, 5 to 6 orders of magnitude higher than incinerator conditions. Milligan and Altwicker (8) have shown that the PCDD formation rates exhibit a first order depedence on precursor concentrations in the range 60 - 700 ng-Pg/mL ($6x10^4$ - $7x10^5$ ug-Pg/m^3), (Pg stands for gaseous precursor). What the reaction order is in the precursor concentration range from $6x10^4$ ug-Pg/m^3 down to incinerator condition 10 ug-Pg/m^3 is not clear. Because when the precursor concentration is lowered, the reaction rate tends to be more sensitive to precursor concentration, as a conservative estimation it is reasonable to assume that PCDD formation rates have a first order depedence on precursor concentrations over the entire range from 10 to 10^5 ug-Pg/m^3. Thus the formation rate 1.6 ug-PCDD/g-FA min measured in laboratory at precursor concentration $3.75x10^5$ ug-Pg/m^3 is extrapolated to incinerator conditions as: $1.6x10/3.75x10^5$ = 0.000043 ug-PCDD/g-FA min. Therefore, PCDD/F formation rate from solid carbon degradation pathway (0.034 ug-PCDDF/g-FA min) is some 3 orders of magnitude faster than from aromatic compound condensation pathway (0.000043 ug-PCDD/g-FA min).

3. Comparison Using Conversion Data

Recently Altwicker [7] has suggested to compute the reactions on a per carbon basis, i.e. how much carbon in the aromatic compound and solid carbon is transformed to PCDD/F. This is appropriately called as conversion or yield (either fractional or percent conversion/yield). Luijk et al. [4] have reported their PCDD/F formation data based on conversion: 4.8% for aromatic compound condensation pathway, and 0.0012% for solid carbon degradation pathway. These conversion data were, however, obtained in laboratory flow reactor packed with a fixed bed of fly ash catalyst: fly ash load 1.0 g, (reactor) volume 0.94 mL, mean residence time 2.8 s. The fly ash loading in this reactor can be estimated as: 1 g-FA/0.94 mL = 1.06×10^6 g-FA/m^3. For heterogeneous catalytic reactions it is reasonable to assume that the conversion at a given reaction temperature and time is proportional to the available catalytic surface area or catalyst loading. In other words, the conversion will decrease as the available catalytic surface area is decreased. When the fly ash loading is zero, the conversion is reported to be 0.014% for residence time 30 s in [4], and can be estimated as 0.0013% for residence time 2.8 s. Under incinerator conditions the fly ash loading is in the order 1 g-FA/m^3; the conversion (X%) at this low fly ash loading is estimated by an interpolation of the above conversion data: (X% - 0.0013%)/(1 g-FA/m^3 - 0 g-FA/m^3) = (4.8% - 0.0013%)/(1.06×10^6 g-FA/m^3 - 0 g-FA/m^3), so that X% = 0.001305%. It is implied that for incinerator conditions the conversion is only 0.001305% because of the lower fly ash loading. Multiplying this conversion with incinerator precursor concentration (10 ug-Pg/m^3), the PCDD formation level is estimated as: 0.001305% x 10 = 0.0001305 ug-PCDD/m^3 for aromatic compound condensation pathway. For solid carbon degradation pathway the PCDD/F formation level is the conversion (0.0012%) multiplied by the incinerator fly ash loading (1 g-FA/m^3) and the fly ash carbon content (0.01 g-C/g-FA): 0.0012% x 1 x 0.01 = 0.12 ug-PCDDF/m^3. Thus, PCDD/F formation level from solid carbon degradation pathway (0.12 ug-PCDDF/m^3) is some 3 orders of magnitude higher than from aromatic compound condensation pathway (0.0001305 ug-PCDD/m^3).

4. Comparison Using Homologue Profile and Congener Pattern

It is known that the PCDD/F distribution from aromatic compound condensation and solid carbon degradation pathways are distinctly different: aromatic compound condensation gives only a few PCDD congeners, whereas solid carbon degradation gives a whole spectrum of PCDD/Fs with more PCDF than PCDD. It is also known that in incinerator measurements some typical PCDD/F distribution is often found: PCDDs are skewed toward higher chlorination degree, but the PCDFs is skewed toward lower chlorination degree; the PCDF/PCDD ratio is larger than 1. And the 2,3,7,8 chlorine-substituted congener patterns have the following features: for H_7CDF, 1,2,3,4,6,7,8-H_7CDF >> 1,2,3,4,7,8,9-H_7CDF; for H_6CDF, 1,2,3,4,7,8-H_6CDF < 1,2,3,6,7,8-H_6CDF >> 1,2,3,7,8,9-H_6CDF << 2,3,4,6,7,8-H_6CDF; for P_5CDF, 1,2,3,7,8-P_5CDF < 2,3,4,7,8-P_5CDF; and for H_6CDD, 1,2,3,4,7,8-H_6CDD < 1,2,3,6,7,8-H_6CDD > 1,2,3,7,8,9-H_6CDD. Furthermore, at different positions of the postfurnace zone of incinerators the PCDF/PCDD ratios are always larger than 1, and the 2,3,7,8 chlorine-substituted congener patterns are quite stable, although the homologue profiles show a greater variation [9]. Comparing the PCDD/F homologue profile and congener pattern from laboratory experiments and incinerator measurements, one

should find out that PCDD/F distributions in incinerator measurements are more similar to those from the solid carbon degradation experiments. In particular, there are always more PCDF than PCDD in incinerator measurements; if the aromatic compound condensation pathway is dominant over the solid carbon degradation pathway, one should find more PCDD than PCDF. Thus, the solid carbon degradation pathway probably makes a greater contribution to PCDD/F formation levels in municipal incinerators than the aromatic compound condensation pathway does.

5. Discussion

There are a number of other possible ways for comparing the relative importance of PCDD/F formation from aromatic compound condensation and solid carbon degradation pathways. For example, the reaction rates may be expressed per unit total area, per weight or volume of catalyst, per volume of packed reactor, or per number of active sites (10,11); and the conversion may be based on weight, mole or number of molecules. Which basis to use and how to extrapolate from laboratory experiments to incinerator conditions are not straightforward. The analysis in Section 2 using reaction rate based on weight of catalyst is most common, and the extrapolation method using a power rate law in terms of reactant concentration is widely practiced in chemical reaction engineering (10,12). The analysis in Section 3 using conversion is also very common. It is worthwhile to note that for a heterogeneous reaction the conversion is determined by the reaction temperature and time, reactant concentration and catalytic surface area. In laboratory experiments of PCDD formation from aromatic compound condensation, flow reactors with a packed bed of fly ash catalyst have been used (fixed bed reactor); but in incinerators the fly ash loading is much sparse (like an entrained flow reactor), so the laboratory conversion data must be reduced when applied to incinerator conditions, as suggested in Section 3.

Our analysis in Sections 2 to 4 corroborates with each other and indicates that the solid carbon degradation pathway is likely to be more important than the aromatic compound condensation pathway in incinerator conditions. Conceptually, PCDD formation from aromatic compound condensation requires only one or two steps, whereas PCDD/F formation from solid carbon degradation requires many steps (13); it is right to think that the aromatic compound condensation pathway is easier than the solid carbon degradation pathway. But one has to keep in mind that in chemical reaction systems the importance of a mechanistic pathway depends not only on how easy this pathway is (fewer steps, lower activation energies, etc.), but also on how much reactant is available for this pathway to proceed. Milligan and Altwicker (8) have found that at low precursor concentrations < 10 ng/mL (10^4 ug/m^3), laboratory experiments have poor reproducibility and product yields are below detection limits. If the precursor concentration is further reduced to incinerator conditions (10 - 100 ug/m^3), one reasonably expects the product yields to diminish. On the other hand, the starting reactants for the solid carbon degradation pathway (O_2 in flue gas and carbon in fly ash) are relatively abundant, which probably explains why the solid carbon degradation pathway could be more important than the aromatic compound condensation pathway (6).

These analyses so far (6,7 and this text) are nonetheless only order of magnitude estimations, since some laboratory data have been chosen and extrapolated in a simple manner to practical situations for comparison. The influences of a variety of factors such as the temperature profile in the postcombustion region of incinerators, the different reactivities of different types of aromatic precursors, the residence time distribution of different sizes of fly ash particles, etc. have all be neglected. More elaborate analyses are needed by mathematical modeling methods ideally; i.e. first kinetic correlations of laboratory experimental data of PCDD/F formation are developed; then the kinetics of PCDD/F formation is combined with other engineering models describing the physical and chemical processes in the postcombustion zone, e.g. flow of flue gases, entrainment and deposition of fly ash particles, mass transport between the gas and solid phases, and material and energy balance; then numerial integration of the model yields information about PCDD/F formation levels from different reaction pathways. Such mathematical modeling is a subject of current research.

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