

OBSERVATIONS ON THE EFFECT OF COMBUSTION PARAMETERS ON DIOXIN/FURAN YIELD

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Abstract

Effects of fly ash loading; ash-borne, extractable organics; sulfur dioxide (SO₂) and hydrogen chloride concentration; and combustion quality on the formation of polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran (PCDD/F) were evaluated in pilot scale tests simulating municipal waste combustion and coal/waste co-combustion testing. Similar PCDD/F yields from reinjection of as-received and extracted fly ash injection along with testing under "poor combustion" conditions show the importance of combustion quality on minimizing precursors. Co-firing coal and municipal solid waste ash leads to increased formation from that of coal alone, indicating that the municipal solid waste ash provides additional reactants and/or catalytic sites for formation. Finally, tests with elevated SO₂ levels found that, at sufficiently high sulfur/chlorine levels, formation of PCDD/F is prevented in both simulated municipal waste combustion and coal/waste co-firing.

Introduction

Formation of PCDD/F from combustion sources has been under study for more than a decade yet significant fundamental questions remain regarding the mechanism of formation. PCDD/F are known to form from heterogeneous gas/solid reactions in the downstream regions (200 to 400 °C) of chlorine-containing waste combustion processes. Recently, work¹⁻³ has started to bridge fixed bed, bench scale studies and field sampling efforts. These studies have altered in a controllable manner the experimental conditions in a pilot scale combustor to determine the effects of measured operating changes on PCDD/F yield. Statistical analyses of these efforts have provided modellable, empirical evidence for the mechanisms of formation, thus providing a link between non-combustive, tube reactor studies and difficult-to-control field sampling tests.

The presence of fly ash in combustion flue gases appears necessary for significant formation. The fly ash provides the necessary catalytic sites for reaction and provides either the surface area for organic precursor sorption and reaction or the organic source itself within the unburnt carbon matrix. The fly ash concentration in the flue gas will be significant if the amount of available catalytic reaction or condensation sites limits the PCDD/F formation reaction.

The absence of condensed organics on fly ash will play a significant role in the formation of PCDD/F if the primary mechanism responsible for observed yields is not related to the unburnt carbon within the fly ash structure. The organic source in this case would be

a result of non-ideal, or "poor" combustion conditions leading to uncombusted organic fragments which could condense on fly ash surfaces.

The apparent absence of PCDD/F from coal combustion processes may be due to a number factors including lack of appropriate catalysts, lack of organic products of incomplete combustion, insufficient chlorine, and the presence of catalyst-poisoning sulfur as SO₂. This raises questions relating to the potential for formation during co-firing of coal with solid waste.

Finally, experiments have shown that facility-specific factors can affect PCDD/F yield. Production of PCDD/F may have a hysteresis or "memory" effect long after waste combustion is terminated indicating that preceding tests can affect production of PCDD/F.

Experimental

The work reported in this paper is based on tests designed to provide initial analysis of some of the above-mentioned potential, fundamental, rate-limiting processes during downstream production of PCDD/F. The tests were predominantly conducted by injection of fly ash from the electrostatic precipitator of a mass-burn municipal waste combustor (MWC) into the Innovative Furnace Reactor (IFR), a pilot scale combustor fired with natural gas. Nominal operating conditions for all tests included excess air of 6 % oxygen (O₂), a fly ash residence time of 1.5 s, and a flue gas quench rate of 30 °C/s. In other tests, the IFR was fired with a Pittsburgh #8 coal (2.6 % S, 0.0 % Cl by weight) during MWC fly ash injection. Operation of the IFR allows for variation of combustion and operating parameters, including doping of process gases, variation of temperature, and regulation of combustion air. Downstream sampling by EPA MM5 trains provided particulate and gas-phase samples for analysis. Samples were analyzed by high resolution gas chromatography / low resolution mass spectrometry. More extensive description of the facility, operating methods, sampling, and analytical methods are available in the literature².

Fly ash from the Quebec City MWC (collected prior to extensive facility modifications) was reinjected into the IFR at about 450 °C. Toluene extraction of the as-received (AR) fly ash showed that it contained about 11-15 ng/g PCDD/F, 89 ng/g chlorobenzene, and 150 ng/g chlorophenol. In some experiments, rigorous pre-test extraction of the surface bound organics was conducted prior to injection. The post-extraction fly ash contained non-detectable levels of PCDD/F. Other tests attempted to vary the concentration of flue gas organics by varying the quality of combustion. These "poor" combustion tests were accomplished with substoichiometric air (85%) at the burner and the balance plus 40 % excess air injected at a downstream, post-flame port. This resulted in an increase in carbon monoxide (CO) from <20 ppm for normal combustion quality to >2000 ppm for poor combustion quality. The effect of various concentrations of HCl and SO₂ on fly ash PCDD/F yield was examined. Tests with coal combustion alone and coal in combination with MWC fly ash explored the potential synergistic or antagonistic effect of co-combustion. Finally, the effect of facility-specific factors was explored by retesting the fly ash injection after facility up-sizing and refractory replacement.

Results and Discussion

MWC Simulation

Figure 1 shows the effects of fly ash feed rate, fly-ash-bound organics, and combustion quality. The AR fly ash generated almost 3,000 ng/m³ of PCDD/F (Test A). The congener distribution had maximum yields at penta-CDD and tetra-CDF, and 86% by weight of the PCDD/F was PCDF. The global PCDD/F reaction rate based on sampled mass and volume is estimated to be 992 ng/g/s and 1858 ng/Nm³/s, respectively. These results show

that AR fly ash, containing about 15 ng/g PCDD/F, is still sufficiently active to result in relatively high PCDD/F formation rates. Reduction of the fly ash injection rate from 110 (Test A) to 61 g/h (Test B) had very little effect on the the yield of PCDD/F. The mass rate of reaction, 1744 ng/g/s, increases significantly from Test A, but the volumetric rate, 1759 ng/Nm³/s, is similar. The congener distribution is similar to Test A. These tests reveal that the formation of PCDD/F in our system is not limited by the quantity of fly ash. That is, sufficient active catalyst sites, particle-bound chlorine, or organic carbon exist for formation, and the reaction is limited by process parameters or reactants unrelated to the fly ash.

Injection of the organic-extracted fly ash (Test C) shows similar PCDD/F yields as the AR, non-extracted fly ash. Since extraction of the fly ash removes substantively all of the non-chemisorbed, condensed chlorobenzenes and chlorophenols, this test shows that the primary organic carbon source for PCDD/F formation is either the fixed and non-extractable carbon within the fly ash matrix or that derived from byproducts of the combustion process. However, since Tests A and B showed no effect of fly ash feed rate, it seems most likely that the primary organic carbon source is derived from combustion byproducts. The mass rate of reaction, 621 ng/g/s, declines with the higher fly ash feed rate but the volumetric rate, 1764 ng/Nm³/s, is similar to Tests A and B. This, again, suggests that the reaction is limited by non-fly-ash-related parameters or reactants, making further rate comparisons on a fly ash mass basis inappropriate. Again, the congener distribution is similar to Tests A and B.

Sampling of injected AR fly ash during conditions simulating poor combustion shows a large increase in PCDD/F yield to over 5,500 ng/m³ and an increase in the rate to 2705 ng/Nm³/s (Test D). The congener distribution displays the same maximums at penta-CDD and tetra-CDF and the same dominance of PCDF over PCDD formation as Tests A-C. These results suggest that increasing the levels of products of incomplete combustion, such as aromatic hydrocarbons (and/or lowering oxygen from 6.1 to 4.7%), increases the yield of PCDD/F, indicating that levels of combustion-derived organic precursors are limiting PCDD/F formation in our system. The similarities in congener class distributions also suggest that the same formation mechanism is underway albeit at different rates.

The next four tests examine the effect of SO₂ addition. Test E establishes the baseline yield of PCDD/F in the absence of doped HCl. Clearly, the Cl source for PCDD/F formation in Test E is derived from Cl within the fly ash matrix. Test F shows that addition of 438 ppm SO₂ reduces the PCDD/F yield.

In the presence of HCl, the effect of adding SO₂ at a S/Cl ratio of 1/1 to the combustion gases was to significantly decrease the PCDD/F yield from about 2,800 ng/m³ (Test A) to less than 1,000 ng/m³ (Tests G and H). This effect appears to be similar regardless of the temperature at which SO₂ is injected. Test G (177 ng/Nm³/s) with SO₂ injected at 850 °C shows more of a decline than that of Test H (463 ng/Nm³/s), with SO₂ injection at 450 °C. This is consistent with the authors' earlier results⁴ which suggest that an effect of SO₂ is to reduce, via gas-phase reaction, the concentration of the available chlorinating agent, either Cl₂ or Cl[•]. Coupled with Tests E and F, one can see that the effect is also applicable to Cl in the fly ash. In this current work, reduction of PCDD/F formation at S/Cl of 1/1 shows that, at HCl concentrations used in Tests G and H (440 ppm), the presence of an available chlorinating species may be reaction-limiting. Because we have also seen an effect of combustion conditions, it is clear that both available Cl and organics are limiting PCDD/F formation.

For all of Runs A to H, the PCDF yield dominated the PCDD yield by about a factor of five. With one exception, the maximum PCDF congener class yield was observed at tetra-CDF. Runs F and H (the only two runs with 450 °C SO₂ injection) both exhibited maximum congener class yields in octa-CDD; all of the other runs had maximums at penta-CDD.

Coal and MWC Tests

Earlier results by the authors⁴ reported on the effect of coal fired operation of the IFR on PCDD/F production. The analyses showed virtually no PCDD/F production despite use of a high Cl Illinois coal (IFR flue gas concentrations: SO₂ = 450 ppm and HCl = 163). However, an increase to 1308 ppm HCl did promote formation of PCDD/F to levels of about 500 ng/m³, primarily PCDF with maximums in the tetra-DD and tetra-DF congener classes. The rate of formation was 126 ng/Nm³/s which is still considerably less than those values reported for Figure 1. The congener class distribution appeared to be similar to that of the MWC fly ash tests discussed above, supporting our earlier inference that the formation in our system is limited by non-fly-ash factors.

PCDD/F formation during coal combustion in the presence of HCl is in contrast to *de novo* synthesis results⁵. This suggests that PCDD/F formation from coal combustion in our facility is governed by a mechanism involving gas-phase precursors and is unrelated to the *de novo* activity of coal fly ash.

When MWC fly ash was added to coal-fired, HCl-doped tests to simulate co-fired fuels, considerably higher yields (> 3,000 ng/m³ versus 446 ng/m³) were observed⁴. The addition of MWC fly ash adds more catalytic activity (and, less likely, organic precursors) into the coal-fired furnace.

These findings were extended in the current work to study the effects of SO₂ addition to a coal/HCl/MWC fly ash condition. Baseline coal tests with HCl and SO₂ addition, but not MWC fly ash, showed very little measurable formation of PCDD/F (Figure 2, Test I). Addition of reinjected MWC fly ash, HCl, and SO₂ resulted in large increases in PCDD/F yield (Tests J to M). Test J shows that addition of MWC fly ash does increase yields to 78 ng/m³. Higher yields (> 200 ng/m³) are observed for tests K and L at S/Cl ~ 0.80/1, which is unexpected in view of the higher S/Cl ratio than in Test J. Test M shows that PCDD/F yields decline at S/Cl values of 1.15/1.

The maximum congener yields for Tests I to M are now observed in the hepta-CDD and hepta-CDF classes, and the PCDD yields are now greater than those of PCDF. The latter is in striking contrast to the Figure 1 results simulating MWC with natural gas and the results obtained earlier⁴.

Effect of Reactor Modification

After the Figure 1 results and prior to the Figure 2 results, the IFR was overhauled extensively. The old refractory and shells were completely replaced. The old IFR had been in operation for over 10 years and had been used extensively for testing coals and sorbent/slurry injection technologies for SO₂ and nitrogen oxides (NO_x) reduction. The new IFR has a firing rate about 75% higher than the old IFR due to expansion of the bore. The duct quench rates in the temperature region from about 500 to 200 °C were increased from about 30 to 60 °C/s, and the residence time was reduced by a factor of two.

While no directly comparable tests have been run, levels of PCDD/F are now an order of magnitude lower. These decreases have occurred despite use of the same fly ash, HCl doping, and system specific (sampling/analytical) factors. The lower PCDD/F yields may be due to better combustion conditions in the burner and higher temperatures resulting in more complete oxidation of fuel carbon and, hence, less combustion byproducts to act as PCDD/F precursors. Shorter residence times (1.5 s) may be significant, although a model derived from earlier results² showed that production was declining from 2 s on. The other possibility is that the refractory replacement eliminated "wall effects" from metal catalysts in refractory bound deposits. The long service of the IFR with alternative fuels and injectants may have rendered the refractory a sink for catalytic materials. At any rate, the large differences in

PCDD/F yields with the overhauled IFR suggest that reactor- and combustion-specific parameters play a significant role in determining yields of PCDD/F, supporting earlier studies² on the effect of operating parameters on yield.

Conclusion

These tests have shown that byproducts of "poor" natural gas combustion are a likely and sufficient source of carbon precursors for formation of PCDD/F. Injection of MWC fly ash during coal combustion increases PCDD/F levels, likely through contribution of additional catalyst activity and/or surface-bound Cl. Addition of SO₂ prevents formation of PCDD/F when S/Cl is greater than about 1/1 for both simulated MWC and coal/MWC combustion. Formation of PCDD/F in these tests was limited by extra-particle factors, likely the concentration of organic and chlorine reactants.

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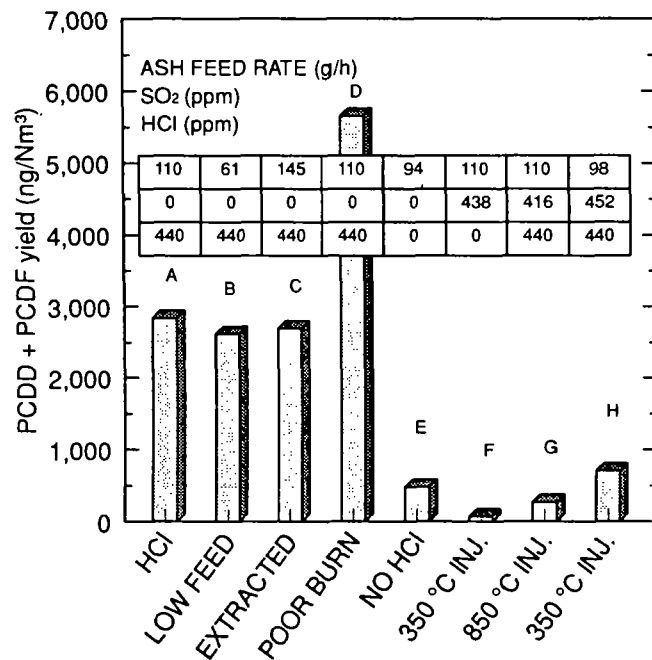


Figure 1. Tests with AR MWC fly ash with natural gas combustion. Effects of feed rate, extracted fly ash, added HCl, poor burn conditions, and added SO₂ on PCDD/F yields. Nominal test conditions: 6 % O₂, 1.5 s residence time, 30 °C/s quench rate.

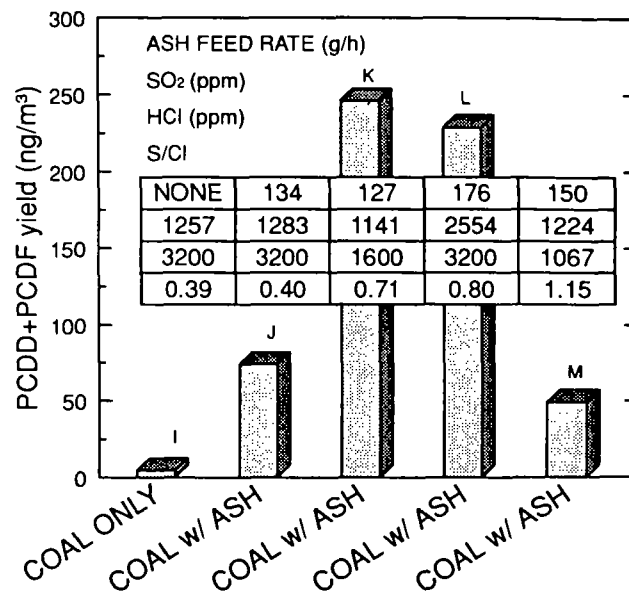


Figure 2. Tests with AR MWC fly ash with coal combustion. Effects of coal sulfur and doped HCl on PCDD/F yields. Nominal test conditions: 5 % O₂, 1.6 s residence time, 60 °C/s quench rate.