Project Title: THE EFFECT OF COAL SULFUR ON DIOXIN FORMATION

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ABSTRACT

Research has been conducted to determine whether the co-firing of coal with municipal solid waste (MSW) will decrease the formation of chlorinated organic compounds, particularly polychlorinated dibenzo-p-dioxins and furans (PCDDs and PCDFs). Previous research has suggested that sulfur present in coal can interfere in PCDD/PCDF formation mechanisms. To test this hypothesis, both bench-scale and pilot-scale experiments simulating MSW incineration were carried out.

Tests were conducted with a MSW fly ash in EPA's pilot-scale Innovative Furnace Reactor (IFR) and a bench-scale Short Time Differential Reactor (STDR). The IFR tests involved MSW injection into both natural gas-fired and coal-fired combustion environments in the furnace. Besides the combustion environment, MSW injection temperature and sulfur-to-chlorine ratio (S/Cl) were varied in these tests. In the STDR, reaction temperature and reaction time were varied, with and without SO₂.

Results showed that coal combustion alone at moderate HCl concentrations resulted in only small levels of PCDD/PCDF. However, at high HCl concentrations (=1145 ppm), a coal combustion environment provides sufficient organic precursors to form significant amounts of PCDD/PCDF. During natural gas firing without coal and added HCl, there were considerable amounts of these toxins formed with MSW fly ash injection. Sulfur (added as SO₂) was found to reduce PCDD/PCDF formation dramatically even at an S/Cl ratio as low as 0.64. This sulfur inhibitory effect was observed in both natural gas and coal tests, suggesting that coal sulfur can be effective in reducing PCDD/PCDF emissions from municipal waste combustors. Bench-scale tests also confirmed the inhibitory effects of sulfur.
EXECUTIVE SUMMARY

The Air and Energy Engineering Research Laboratory (AEERL) of the U.S. Environmental Protection Agency (EPA) has completed a co-funded research program in conjunction with the Illinois Clean Coal Institute (ICCI) to evaluate the potential reduction of pollutant emissions by mixing coal with municipal solid waste (MSW) in incinerators. Positive results will have an important impact on the use of Illinois coals. Co-firing of coal and MSW would provide an economically viable and commercially feasible market for Illinois coal, while providing the operators of MSW incinerators with a low-cost option for controlling emissions of chlorinated organic compounds.

The objectives of the research were to perform tests (both bench-scale and pilot-scale) to determine if the co-firing of coal with MSW will decrease the formation of polychlorinated dibenzo-p-dioxins and furans (PCDDs and PCDFs). Corollary research objectives include determining the mechanism of interference in chlorinated organics formation, measuring the effects of sulfur from the coal on chlorinated organics formation, and investigating the kinetics of interference. The research was be performed over a 12-month period and consisted of three phases: Phase I, MSW testing in a natural gas-fired combustion environment; Phase II, tests in a coal-fired furnace; and Phase III, MSW testing in a bench-scale reactor with SO$_2$ addition.

Tests were conducted with an MSW fly ash in EPA's pilot-scale Innovative Furnace Reactor (IFR) and a bench-scale Short Time Differential Reactor (STDR). The IFR tests involved MSW injection into both natural gas-fired and coal-fired environments in the furnace. Besides the combustion environment, MSW injection temperature and sulfur-to-chlorine ratio (S/Cl) were varied in these tests. In the STDR, reaction temperature and reaction time were varied, with and without SO$_2$.

Results showed that coal combustion alone at moderate HCl concentrations resulted in only small levels of PCDD/PCDF. However, at high HCl concentrations (≈1145 ppm), a coal combustion environment provides sufficient organic precursors to form significant amounts of PCDD/PCDF. During natural gas firing without coal and added HCl, there were considerable amounts of these toxins formed with MSW fly ash injection. Sulfur (added as SO$_2$) was found to reduce PCDD/PCDF formation dramatically even at an S/Cl ratio as low as 0.64. This sulfur inhibitory effect was observed in both natural gas and coal tests, suggesting that coal sulfur can be effective in reducing PCDD/PCDF emissions from municipal waste combustors. Bench-scale tests also confirmed the inhibitory effects of sulfur.
OBJECTIVES

The specific goals of the research are to determine whether products of coal combustion, sulfur species in particular, interfere with formation of chlorinated organics (primarily PCDD/PCDF). One phase of testing involves natural gas firing with additives to closely simulate combined coal/MSW combustion. These tests are intended to examine not only the inhibitory effects of S on formation, but also other potential coal impacts. Phase II tests focus on verifying in a coal-combustion environment the S inhibitory effects. Another phase of tests is in a bench-scale differential reactor, with fly ash and additives injected to simulate municipal solid waste (MSW) combustion. These tests are intended to examine the effects of specific reaction parameters on the inhibitory effects of S on PCDD/PCDF formation. Specifically, the objectives of the research are:

- Perform bench- and pilot-scale laboratory tests to determine whether co-firing coal and MSW decreases formation of chlorinated organics
- Measure the effect of sulfur from the coal on chlorinated organics formation
- Investigate the kinetics of interference

INTRODUCTION AND BACKGROUND

Although significant amounts of polychlorinated dibenzodioxin and polychlorinated dibenzofuran (PCDD/PCDF) have been detected in the emissions of municipal waste combustors (MWCs), the same cannot be unequivocally said of emissions from coal-fired combustors. Despite the presence of chlorine (Cl) and organic ring structures in both systems, tetrachlorodibenzo-p-dioxin (TCDD) was not detected in effluent sampling from a combined coal/municipal waste plant, nor were noteworthy amounts found on coal fly ash. Recently, Lindbauer et al. (1992) reported that co-firing an MSW incinerator with 60% coal drastically reduced the PCDD/PCDF levels. These field results, however, are inconsistent with laboratory studies producing chlorodioxins from experiments with bituminous coal (Mahle and Whiting, 1980). It is possible that conditions within MWCs are sufficient to promote the in situ formation of PCDD and PCDF, although this is not true of coal-fired combustors. Examination of the similarities and differences between conditions in MWCs and coal-fired combustors will thus not only enlighten the mechanism of PCDD and PCDF formation but may suggest potential methods for preventing the formation of PCDD and PCDF.
This research examines the apparently low PCDD and PCDF levels in coal-fired utility boilers through laboratory examination of the effect of S species upon the mechanism of PCDD/PCDF synthesis in MWCs. Experiments were conducted in two reactor systems that simulate the MWC post-furnace gas and temperature characteristics.

EXPERIMENTAL PROCEDURES

REACTOR SYSTEMS

The two experimental systems used are (1) the pilot-scale Innovative Flow Reactor (IFR), and (2) the bench-scale Short Time Differential Reactor (STDR). These two set ups are described briefly below.

(1) Innovative Furnace Reactor (IFR):

The pilot-scale IFR is a down-fired, refractory-lined cylindrical unit with an internal diameter of 15.2 cm and a length of about 3 m. An overall schematic of the IFR set up is shown in Figure 1. The facility is nominally rated at 29.6 kW on either a gaseous fuel or pulverized coal. Ports along the length of the IFR facilitates addition of reactants or sampling. The unique design of the furnace allows for staging of combustion to simulated various applications, including MSW combustion. Continuous emission monitors (CEMs) are provided to measure CO, CO₂, O₂, SO₂, and NOₓ.

IFR tests involved either natural gas or coal, fired at 35,000 Btu/hr. The coal used was pulverized IBC-109. The MSW fly ash sample was from an electrostatic precipitator hopper on a full-scale, mass-burn facility at Quebec City, Canada, prior to facility modifications for improved combustion. The as-received fly ash was fed into the furnace by a K-Tron feeder at a rate of 100 g/hr. For natural gas tests, MSW fly ash was injected through the IFR ports at injection temperatures of 850 and 450°C. For coal tests, only the lower injection temperature port was used. IFR test conditions are shown in Table I.

Furnace emissions were sampled in the downstream duct section of the IFR and passed through heated sample lines to CEMs. Gases analyzed for CO₂, O₂, and CO were first passed through a gas dryer and a desiccant canister of anhydrous CaSO₄. All of the above on-line CEMs are zeroed and spanned with gases of known concentration both before and after each daily trial. HCl concentration in the furnace was determined be using EPA Method 26 protocol.

Organics (PCDD/PCDF) were sampled separately from the duct using isokinetic sampling protocols and EPA MM5 sampling
trains. These trains consist of a quartz sampling probe, followed by a filter, XAD trap, and impingers. The probe rinse, filters, and XAD were analyzed together for PCDD/PCDF congeners. The temperature at the duct sampling port was about 250°C.

(2) Short Time Differential Reactor (STDR):

Initial bench-scale testing in this project utilized a Dioxin Flow Reactor (DFR). However, results from DFR tests were not fully reproducible because of the following:

(a) Non-isothermality in the reactor especially toward the reactor exit. As a result, depending on the reactor temperature, the fly ash particles are subjected to different quench rates as they leave the reactor. The PCDD/PCDF formation is known to be sensitive to the quench rates (Gullett et al., 1993).

(b) A significant amount of the fly ash particles fed into the reactor deposited on the reactor walls; these deposited particles are in the reactive environment much longer and therefore, the fly ash residence times estimated are subject to large errors.

(c) Inconsistent feeding of the fly ash particles to the reactor due to the presence of fines.

To overcome the above problems associated with the DFR, the STDR was designed and built for bench-scale testing. A schematic of the STDR setup is shown in Figure 2. The STDR is a modification of the previously documented design (Gullett et al., 1990) which has been successful in studying kinetics with reaction times as low as 0.2 s (Gullett et al., 1992). It consists of two independent gas streams heated by a Lindberg high-temperature furnace. The fly ash sample is placed on a quartz wool substrate in the slider and can be positioned either under the inert gas flow or the reactive gas flow by means of air cylinders. The movement of the slider is controlled by timers and the duration for which the fly ash sample is exposed to either gas stream can be adjusted with the timers. Initially, the fly ash sample is preheated in the inert stream for a pre-set period. Then, the sample is rapidly introduced in the reactive stream (containing HCl/SO₂). After the pre-set reaction time, the sample is quickly withdrawn back to the inert side and quenched, abruptly arresting the reaction. Thus, with the STDR arrangement, fly ash residence times in actual MWCs can be conveniently simulated. The reactive stream after passing over the sample in the STDR enters impingers to capture any PCDD/PCDF present in the gas phase. However, experience with the DFR has shown that these amounts are negligible.

It was determined that about 2 g of the reacted fly ash sample was required for reliable PCDD/PCDF analysis (described
below). On the other hand, to minimize changes in flow conditions and temperature characteristics in the STDR, a smaller sample amount is desirable. Therefore, about 0.1 g of the fly ash sample was used in each slider operation and the procedure was repeated to make up the sample weight (2 g). STDR tests were carried out at varying reaction times (3, 6, 15 and 45 s) and two temperatures (300 and 350°C). The HCl concentration was set at 1000 ppm in all the STDR tests and for each condition, a pair of tests were performed: one without SO2 and the other with 1000 ppm SO2. Additional tests involved addition of CuO catalyst (1% by weight) to the fly ash sample to examine the effects of SO2 on the catalytic activity.

SAMPLE ANALYSIS

Samples from either reactor system are analyzed in AEERL’s in-house facilities by high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS), using a Hewlett-Packard 5890/5970 Gas Chromatography/Mass Selective Detector (GC/MSD). The methodology is a slight adaptation of EPA Method 23 (1991) and RCRA Method 8280 (1986). Isotopically labelled internal standards for each congener class are incorporated during the extraction and clean-up phases of the analytical procedures to enhance analytical accuracy. An internal standard was used that consisted of a 13C12-labelled congener from each tetra-octa PCDD/PCDF (except for octa-CDF). The recovery standard 6C12-labelled TCDD is added before injection on the GC. The recovery must be within 40-120% to be acceptable. Thus, the results obtained are levels of each tetra-octa PCDD/PCDF congener in the sample.

RESULTS AND DISCUSSION

PILOT-SCALE TESTS

Results of the IFR natural gas tests are shown in Figure 3 as total PCDD+PCDF yield. The gas compositions indicated are furnace concentrations, uncorrected for either H2O or O2. Several observations can be made from these results:

- It is interesting to note that even with no added HCl, PCDD+PCDF yield is significant, especially at the lower MSW injection temperature. This implies that MSW fly ash already has precursors on the surface in sufficient quantities to form these toxins in the natural gas combustion environment. It is to be noted that the analysis of raw fly ash samples showed non-detectable PCDD/PCDF levels.

- It is clear that in general, higher MSW fly ash injection temperature results in lower PCDD+PCDF formation. The
higher temperature may deactivate the CuO catalytic sites where PCDD/PCDF are formed, or destroy the precursors on the fly ash surface.

- The yield increases with HCl concentration.

- When S was added as SO₂, the yield dropped substantially for S/Cl ratio of 0.64 and further increase in S/Cl made little difference to the reduced levels. It is important to note that the S/Cl ratio at which the inhibitory S effect was observed in this work is the lowest reported in literature and much lower than the theoretically derived value of 10 (Griffin, 1986).

The PCDD/PCDF congener distributions on the MSW in these tests are shown in Figures 4 and 5 for MSW fly ash injection temperatures 850 and 450°C, respectively. At both temperatures, the majority of these toxins are present as PCDF congeners. Reduction due to S is not congener-specific, and appears to be distributed among all the congener classes.

Results from the coal-fired IFR sampling are shown in Figure 6, with the following inferences:

- The IBC-109 coal is a low-sulfur, high-chlorine coal, and blank tests (without MSW fly ash) resulted in an HCl concentration of 163 ppm in the furnace. At this concentration, amounts of PCDD/PCDF formed were almost negligible.

- However, when the furnace was doped with HCl to a concentration of about 1145 ppm, some amounts of PCDD/PCDF were formed, even without MSW fly ash injection. This implies that the coal combustion environment contains organic precursors that can form PCDD/PCDF.

- When MSW fly ash is injected into the coal-fired furnace doped with HCl (coal+HCl+MSW), the PCDD/PCDF levels actually increased compared to the natural gas case (MSW+HCl).

- With additional SO₂ (coal+HCl+MSW+SO₂), however, these levels dropped dramatically at an S/Cl ratio of about 0.78.

The congener distribution for the coal tests are shown in Figure 7. As with natural gas tests, the PCDF congeners are in majority and the S inhibitory effect is distributed among the congeners.

Thus, both the natural gas and coal tests show that S can inhibit PCDD/PCDF formation. However, it is important to note
that depending on the coal type, the coal combustion environment can contain organic precursors and Cl that can actually facilitate PCDD/PCDF formation. Therefore, judicious choice of coal type and MSW/coal firing rate is necessary to ensure low PCDD/PCDF emissions. Additional research is needed to develop optimum co-firing conditions and parameters.

**BENCH-SCALE TESTS**

Initially, selected tests on the bench-scale STDR were conducted in duplicate to verify the reproducibility of the data. For two such sets, results are shown as congener distributions in Figure 8. Very good reproducibility is achieved with the STDR for each congener, and hence the total PCDD/PCDF yield.

Effects of added SO₂ on the total yield are shown in Figures 9 and 10 for temperatures 300 and 350°C at various reaction times. The PCDD/PCDF yield appears to increase with reaction time, except for the 350°C, 15 s case. As with IFR tests, the addition of S again results in lower yields, and the inhibitory effect is distributed over all the congeners as shown in Figure 11 (only non-zero congener values are represented). Figure 12 indicates the effect of mixing the formation catalyst CuO to the MSW fly ash, 1% by weight. The catalyst appears to increase the yield, and addition of SO₂ causes a slight decrease in the yield for the CuO-added sample. In summary, the results of STDR tests support the findings derived from the IFR runs.

**CONCLUSIONS AND RECOMMENDATIONS**

- Combustion of IBC-109 alone, at low or moderate HCl concentrations, formed very little dioxin/furans for the coal tested.

- It has been demonstrated through three separate test schemes (IFR natural gas and coal, and STDR) that inorganic sulfur (present as SO₂) can significantly reduce PCDD/PCDF formation. Pilot-scale tests show that such reduction is possible at a sulfur-to-chlorine ratio as low as 0.64.

- At a low S/Cl ratio, however, if the HCl concentration is high, the addition of coal can actually increase the pcdd/PCDF yield.

- The inhibitory effect of S is not congener-specific; reduction in formation is distributed over all the PCDD/PCDF congeners.
Higher MSW fly as injection temperatures lead to lower PCDD/PCDF formation.

In summary, co-firing MWCs with coal can reduce PCDD/PCDF emissions. However, it is critical to choose an appropriate coal type and co-firing conditions to achieve positive results. A better understanding of formation and inhibition mechanisms and parametric studies of reaction variables (e.g., S/Cl ratio) are important next steps in accomplishing the eventual goals.

REFERENCES


Table I. Average gas compositions (dry) in the IFR tests

<table>
<thead>
<tr>
<th>Gas</th>
<th>natural gas tests</th>
<th>coal tests</th>
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<tbody>
<tr>
<td>O₂ (%)</td>
<td>9.5</td>
<td>9.3</td>
</tr>
<tr>
<td>CO₂ (%)</td>
<td>5.4</td>
<td>8.7</td>
</tr>
<tr>
<td>H₂O (%)</td>
<td>(9.9)</td>
<td>(4.5)</td>
</tr>
<tr>
<td>SO₂ (ppm)*</td>
<td>0</td>
<td>510</td>
</tr>
<tr>
<td>HCl (ppm)*</td>
<td>0</td>
<td>171</td>
</tr>
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</table>

* before doping
INNOVATIVE FURNACE REACTOR (IFR)

Figure 1. Schematic of the pilot-scale IFR setup.
Figure 2. Schematic of the bench-scale STDR arrangement.
IFR TESTS

Total yield - Natural gas with MSW

MSW fly ash injection temperature

<table>
<thead>
<tr>
<th></th>
<th>850°C</th>
<th>450°C</th>
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<tbody>
<tr>
<td>SO2 (ppm)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HCl (ppm)</td>
<td>0</td>
<td>1145</td>
</tr>
<tr>
<td>S/Cl</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
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Figure 3. Effect of S in IFR natural gas tests.
Figure 4. Congener distribution in IFR natural gas tests with 850 °C MSW injection.
Figure 5. Congener distribution in IFR natural gas tests with 450 °C MSW injection.
IFR TESTS
Total yield - IBCSP-9 coal with MSW

Figure 6. Effect of S in IFR coal tests.
Figure 7. Congener distribution in IFR coal tests.
STDR TESTS

Congener distribution - 1000 ppm HCl, 6 sec

PCDD concentration, ng/g fly ash

0 2 4 6 8 10 12

\{ 300°C \} \{ 350°C \}

PCDF concentration, ng/g fly ash

0 2 4 6 8 10 12 14

TETRA  PENTA  HEXA  HEPTA  OCTA

Figure 8. Reproducibility of STDR results.
Figure 9. Effect of S in STDR tests at 300 °C.
Figure 10. Effect of S in STDR tests at 350 °C.
STDR TESTS

Congener distribution - 350°C, 1000 ppm HCl, 45

Figure 11. Congener distribution in STDR tests (only non-zero congener values are represented).
STDR TESTS
Total yield - 350°C, 1000 ppm HCl, 45 sec

Figure 12. Effect of S tests with CuO addition.