

Prevention of PCDD/PCDF Formation by Coal Co-Firing

K. Raghunathan

Acurex Environmental Corporation

4915 Prospectus Drive

Durham, NC 27713

Brian K. Gullett, Chun Wai Lee, James D. Kilgroe

Air Pollution Prevention and Control Division

National Risk Management Research Laboratory

U.S. Environmental Protection Agency

Research Triangle Park, NC 27711

James E. Dunn

Department of Mathematical Sciences

University of Arkansas

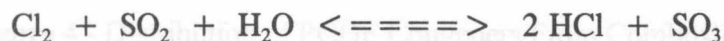
Fayetteville, AR 72701

INTRODUCTION

Formation of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) has been observed in waste combustors. However, PCDD and PCDF yields from coal combustion are relatively insignificant. Previous bench- and pilot-scale research^{1,2} has shown that the presence of sulfur dioxide (SO₂) can inhibit PCDD and PCDF formation, and suggested co-firing high-sulfur coal with refuse-derived fuel (RDF) to reduce the emissions. This work describes research in a large scale combustor which shows that coal/RDF co-firing can significantly lower PCDD and PCDF formation.

PCDD and PCDF formation mechanisms have been reviewed in detail by Addink and Olie.³ Measured yields can be affected by the combustion quality, levels of chlorine and catalyst species, residual carbon on the fly ash, and process parameters such as temperature and residence time. Two candidate mechanisms have been established for the inhibition of PCDD and PCDF formation by sulfur species:

1) Gas-phase reaction where SO₂ converts chlorine (Cl₂) to hydrogen chloride (HCl), a less-likely chlorinating agent^{4,2}:



Our recent work² appears to confirm this mechanism as a possibility.

2) Poisoning of copper catalysts by SO₂¹:



It has been shown that copper sulfate (CuSO₄) is a less active catalyst for the production of Cl₂ through the Deacon process, as well as for the biaryl synthesis step of PCDD and PCDF formation.¹

Lindbauer et al.⁵ have reported that co-firing coal in a municipal solid waste (MSW) incinerator leads to appreciably lower PCDD and PCDF levels. Recently, Ogawa et al.⁶ compared the effect of adding pure SO₂ versus generating SO₂ through coal addition, and found the latter to be more effective. Thus, there may be other benefits with coal co-firing than simply being a source of SO₂.

In this work, experiments were conducted in a large, pilot-scale unit which is a state-of-the-art facility with fuel handling and combustion release rates representative of large field units. The effect of coal co-firing was studied for two types of municipal-waste-based solid fuels. Tests were conducted over a range of process variables (e.g., calcium hydroxide [Ca(OH)₂] injection, HCl concentration, flue gas temperature, quench, and residence time) so that the results could have implications for a wide variety of waste combustors.

EXPERIMENTAL FACILITY AND PROCEDURES

The newly constructed, EPA Multi-Fuel Combustor (MFC) facility was used for conducting tests for this project. The MFC is rated at 0.6 MW (2x10⁶ Btu/hr) thermal output and is capable of burning a wide variety of solid fuels including MSW, RDF, biomass, and coal. The modular design of the

facility provides flexibility for studies on various pollutant emissions and control and for solid fuels with unknown firing and handling characteristics.

A schematic and a layout view of the MFC facility are shown in Figures 1 and 2, respectively. The MFC consists of a waste feeding system, a coal feeder, a lower combustion chamber containing a stoker, a radiant section, a convective flue gas passage, a baghouse, and a scrubber system. In addition, there is a separate fuel preparation system for shredding, screening, and mixing of the fuel. A large loading hopper conveys the processed fuel to the fuel silo.

As indicated in Figure 2, there are several ports for flue gas sampling and temperature measurements along the convective section and the duct. The convective section is equipped with cooling coils with high-pressure water circulation. The cooling coil originally present in location B was removed for this project, to accommodate PCDD/PCDF sampling. A typical temperature drop across the convective section is from 600 to 150°C which includes the PCDD/PCDF formation temperature “window” (200 to 500°C). Residence time/quench across this window is known to be an important parameter, and it can be varied in our tests by changing the temperature set point of the cooling water. From the convective section, flue gas was sampled through continuous emission monitors (CEMs) for recording the oxygen (O₂), carbon dioxide (CO₂), carbon monoxide (CO), HCl, and SO₂ concentrations.

The test program involved two major phases: In Phase I, the waste-derived fuel used was commercial RDF from municipal waste. The as-received RDF did contain some larger pieces and had to be run through the shredder in order to avoid clogging of the feed system. With this shredded fuel (simply referred to as “RDF” in this paper), the feed and burn could not be controlled sufficiently and the temperatures were lower than that observed in typical waste combustor operation. As a result, the flue gas O₂ and CO levels were higher than desired. Therefore, only a few tests were run with the RDF. To alleviate this problem, a commercial, densified refuse-derived fuel (dRDF), again from municipal waste, was acquired for subsequent testing under Phase II. The combustor operation was much improved with more uniform fuel feed and lower CO levels. In both phases, the coal used was an Illinois #6 coal, donated by Monterey Coal Company, Carlinville, IL, for this project. The coal was ground and classified to an average size of about 1 mm. The coal was fed using a screw feeder and entered the burner at the same location as the RDF/dRDF. Analyses of the dRDF and coal are shown in Table 1.

For Phase I, tests included separate RDF and coal baseline tests and a RDF/coal co-fired test. Under Phase II (dRDF), the experiments were structured to provide information on all two-factor interactions among the parameters of coal feed, dRDF feed rate, quench, sorbent injection, and HCl addition. During each test, the fuel feed rate was adjusted, whenever necessary, to maintain a constant flue gas temperature. Nearly the same firing rate was maintained between tests, again, by matching the flue gas temperature reading. For low fuel feed runs, natural gas was co-fired to compensate for the decrease in heat release and maintain similar temperature ranges between runs. Quench was varied by varying the temperature set point of the cooling water used in the convective section of the furnace. For runs with HCl addition, there was about a 100 ppm increase in HCl concentration. The sorbent used was a commercial hydrated lime, fed as a slurry at a Ca/Cl ratio of about 1.5. The sorbent injection temperature was approximately 700°C. Under Phase II, a total of 30 tests, including blanks, were run for various parameter settings.

For most of the runs, flue gas was sampled from two locations (A and B in Figure 2) for PCDD/PCDF according to EPA Method 23.⁷ For selected runs, dioxin samples were drawn from an additional sampling port, just before the convective section (location D). Before and after running Method 23 trains, a velocity traverse of the duct was carried out to measure the flue gas flow rate. The samples were analyzed in EPA's in-house Organics Support Laboratory (OSL), via procedures described elsewhere.² Recently, the OSL has expanded its capability to include quantification of mono-tri PCDD and PCDF congener class mass as well. Thus, the results obtained are levels of each mono-octa PCDD and PCDF congener class in the sample. However, since mono-tri PCDD and PCDF are not subject to regulation, most of the following discussions are based on the tetra-octa PCDD/PCDF yields.

RESULTS AND DISCUSSION

Phase I tests with the RDF

The run conditions and sampling data are provided in Table 2. For the trial RDF burn (run 1), the temperatures were lower, resulting in high CO formation. Runs 2 and 4 involved better combustion conditions, although there were CO excursions exceeding 2000 ppm. Run 3 was a natural gas blank between runs 2 and 4, with no RDF or coal feed. Run 5 was a coal baseline and run 6 the coal/RDF co-fired test. Results from the above tests are shown in Figure 3 as tetra-octa total PCDD+PCDF yield.

Substantial levels of PCDD and PCDF are measured at both sampling locations (A, B) for the RDF combustion. In fact, the difference in yields between the two locations is small. Thus, much of the formation takes place in-flight, within seconds from the burner. It is clear that an effective control technology should discourage this formation, before the flue gas and particles reach the particulate control device. Combustion quality appears to play an important role in PCDD and PCDF formation: run 1 (high CO and lower temperature) yields are much higher than those from run 2 or run 4. Given the variations in the run conditions and the nature of PCDD/PCDF formation, the difference between the two RDF baseline run (runs 2 and 4) yields is small, rendering credibility to the data obtained. Also, as with field units, yields of PCDF are higher than those of PCDD in these tests. However, the CO levels in our RDF baseline tests are higher than in typical municipal waste combustors (MWCs).

Contrary to the RDF, no PCDD or PCDF was detected from coal burning (run 5). Even the natural gas blank test (run 3) yielded PCDD/PCDF, although at much lower levels compared to RDF. Although the system was blown with a high flow of air prior to each test, some particle deposition on the system walls from earlier testing is inevitable, and could cause measurable yields even with natural gas. However, the coal baseline test showed no such residual or hysteresis effect. It appears that flue gas from coal burning, presumably SO₂, strongly inhibits formation.

The addition of coal to RDF in the co-fired test provided better burn conditions -- increased temperatures and lower CO. In this test (run 6), the resulting sulfur-to-chlorine (S/Cl) ratio was about 1.5. Under these conditions, the PCDD and PCDF yields decreased sharply from the RDF baseline levels. Past work at the EPA facilities² had suggested a S/Cl ratio of above 1.2 for effective PCDD/PCDF emission control. Thus, Phase I tests indicate that co-firing RDF with high-sulfur coal is an effective option for MWCs to inhibit PCDD and PCDF formation.

Phase II tests with the dRDF

For each test, temperature and flue gas composition data were stored in the data acquisition system. Run averages of these data were calculated for the duration of PCDD/PCDF sampling so that these values correspond to the measured yields. With the total flue gas flow rate known from the velocity traverse data, the average flue gas temperature profile data were used to determine the flue gas residence times at various locations in the MFC. In the temperature profiles, the residence time variable, t_r , is set to zero at 650°C. The choice of 650°C stems from the fact that most of PCDD/PCDF formation is known to take place below this temperature. In this project, for three runs, PCDD/PCDF levels were measured for the high-temperature ($\sim 600^\circ\text{C}$) dioxin sampling port (Port D), and the yields were relatively small.

Ranges of measured/estimated parameter values for Phase II tests are given in Table 3. The gas composition data show low CO levels from dRDF burning, indicating good combustion quality. In general, yields from dRDF combustion were lower compared to RDF combustion. The possible reasons are that, with the former, the HCl concentration in the flue gas is lower and the combustion quality is better (lower CO).

For one of the dRDF baseline tests (without coal), PCDD/PCDF levels were measured at three different sampling ports and the results are shown in Figure 4. The figure shows the total PCDD and PCDF yields for tetra-octa as well as for mono-octa congener classes. The PCDD/PCDF levels measured at the high-temperature port are relatively low, and the majority of the formation takes place between Ports D and B, in less than 0.5 sec. An examination of the temperature profile, shown in the same figure, indicates that in this region, the temperature decreases sharply. A more gradual temperature decline would result in larger residence times in this temperature window, possibly allowing more PCDD and PCDF formation. After Port B, the change in PCDD and PCDF levels is small. The figure also shows that the yields of mono-tetra PCDD and PCDF are significant, and it is possible that under different process conditions some of them might shift to the toxic, higher chlorinated congeners.

An average analysis of all the experimental data has been performed. The data are divided into three groups, dRDF alone, dRDF with coal co-firing, and dRDF with sorbent injection, although within a group other parameters such as HCl concentration and quench may vary. For each group, average PCDD and PCDF yield is computed for each congener class. Results are plotted for mono-octa PCDD and PCDF congener classes in Figure 5. Both coal co-firing and sorbent injection decrease PCDD and PCDF formation significantly; the congener class pattern is similar to that of the base dRDF case and, therefore, the reduction is not congener-class-specific. The total tetra-octa PCDD and PCDF yields for the three groups are plotted in Figure 6. The results clearly indicate that coal/dRDF co-firing as well as calcium-based sorbent injection reduces PCDD and PCDF formation.

Experimental results have been analyzed statistically for Port A and Port B data separately. The model results for both cases are similar and the model R^2 for the data for each port is 0.76. Among the five exogenous variables (labeled COAL, RDF, QUENCH, SORBENT, and HCL), four 2-factor interactions involving all five variables were found to be significant: COAL-HCL, RDF-QUENCH, QUENCH-SORBENT, and SORBENT-HCL. Thus, model predictions for coal co-firing are available. Model predictions are shown in Figure 7 for Port A data, and similar results are obtained (but not shown) for Port B data. The model predicts that an increase in HCl concentration increases

the PCDD and PCDF yield for dRDF combustion. More importantly, at both low and high HCl levels, the model indicates that coal co-firing reduces PCDD and PCDF formation significantly. More detailed modeling efforts are in progress, and the results will be available later.

CONCLUSIONS AND RECOMMENDATIONS

For commercial dRDF combusted in our 0.6 MW stoker combustor, a majority of the PCDD and PCDF formation took place between 600 and 300°C within about 0.5 sec.

Based on Phase I tests, improving the combustion quality appears to lower PCDD and PCDF yields.

Co-firing Illinois #6 coal with both the RDF and dRDF reduced PCDD and PCDF formation substantially. This reduction appears to be uniform across the entire congener range. Injection of $\text{Ca}(\text{OH})_2$ injection is nearly as effective as coal co-firing.

Co-firing coal with waste-derived fuel is a candidate technology for reducing PCDD and PCDF emissions in commercial waste burning facilities. Further development on a full-scale facility is needed to demonstrate field applicability.

ACKNOWLEDGMENTS

This work was also co-sponsored by Illinois Clean Coal Institute (ICCI) (Project Manager: Ken Ho) and the National Renewable Energy Laboratory (NREL) (Project Monitor: Phil Shepherd). Logistical support from Richard Valentine (U.S. EPA/APPCD) is greatly appreciated. Suh Lee, Joey Valenti, Russell Logan, Scott Moore, John Foley, Dennis Tabor, and Ann Preston (Acurex Environmental Corporation), and Jeff Ryan (U.S. EPA/APPCD) provided extensive technical, sampling, and analytical assistance.

DISCLAIMER STATEMENT

This work was sponsored in part by the Illinois Department of Energy and Natural Resources (IDENR) through its Coal Development Board and Illinois Clean Coal Institute (ICCI). However, any opinions, findings, conclusions, or recommendations expressed herein do not necessarily reflect the view of IDENR and the ICCI.

REFERENCES

1. B.K. Gullett, K.R. Bruce and L.O. Beach, "Effect of Sulfur Dioxide on the Formation Mechanism of Polychlorinated Dibenzodioxin and Dibenzofuran in Municipal Waste Combustors," *Environ. Sci. Technol.*, 26(10): 1938 (1992).
2. K. Raghunathan and B.K. Gullett, "Role of Sulfur in Reducing PCDD and PCDF Formation," *Environ. Sci. Technol.*, 30(6): 1827 (1996).
3. R. Addink and K. Olie, "Mechanisms of Formation and Destruction of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in Heterogeneous Systems," *Environ. Sci. Technol.*, 29(6): 1425 (1995).
4. R.D. Griffin, "A New Theory of Dioxin Formation in Municipal Solid Waste Combustion," *Chemosphere*, 15, 1987 (1986).
5. R.L. Lindbauer, F. Wurst and T. Prey, "Combustion Dioxin Suppression in Municipal Solid Waste Incineration with Sulfur Additives," *Chemosphere*, 25, 1409 (1992).
6. H. Ogawa, N. Orita, M. Horaguchi, T. Suzuki, M. Okada and S. Yasuda, "Dioxin Reduction by Sulfur Component Addition," *Chemosphere*, 32, 151 (1996).
7. Method 23, Title 40 Code of Federal Regulations, Part 60, Appendix A, U.S. Government Printing Office, Washington, DC (1991).

Table 1. Analyses of the densified refuse-derived fuel (dRDF) and Illinois #6 coal

	dRDF	coal
Proximate analysis (%)		
Moisture	7.83	14.96
Ash	8.71	8.32
Volatile matter	70.62	33.51
Fixed Carbon	12.84	43.21
Ultimate analysis (%)		
Moisture	7.83	14.96
Carbon	41.70	60.25
Hydrogen	5.58	4.22
Nitrogen	0.80	1.09
Sulfur	0.09	3.36
Ash	8.71	8.32
Oxygen (by difference)	35.29	7.80
Chlorine	0.14	0.09
Calcium	1.35	n.m.
Copper	0.002	n.m.
kJ/kg (Btu/lb)	16,408 (7,059)	25,257 (10,866)

n.m. not measured

Table 2. Multi-Fuel Combustor test conditions for Phase I tests with the RDF

Run No.	fuel	run type	flue gas conditions					Port B (conv. section)		Port A (pre-baghouse)	
			O ₂ %	CO ₂ %	CO ppm	HCl ppm	SO ₂ ppm	Ts °C	D+F ¹	Ts °C	D+F ¹
1	RDF	trial burn	16.5	3.6	1345	n.m.	n.m.	250	1253	134	1340
2	RDF	baseline	14.8	5.3	201	n.m.	n.m.	302	716	153	798
3	natural gas	blank	13.7	2.7	3	n.m.	n.m.	260	46	117	95
4	RDF	baseline	12.8	6.2	690	n.m.	n.m.	239	497	124	630
5	coal	baseline	17.8	2.3	86	n.m.	n.m.	285	n.d.	151	n.d.
6	RDF & coal	co-fired	17.1	3.9	41	321	492	341	180	180	26

¹tetra-octa PCDD+PCDF (ng/dscm)

All concentrations are dry and not corrected to 7% O₂

Ts sampling temperature

n.m. not measured

n.d. none detected

Table 3. Ranges of test conditions and results for the Phase II MFC tests

Parameter	parameter range	
	dRDF runs	coal/dRDF runs
O ₂ (%)	11.5 - 14.4	9.3 - 16.9
CO ₂ (%)	4.5 - 8.1	4.8 - 10.0
CO (ppm)	0 - 28	2 - 97
HCl (ppm)	11 - 224	21 - 193
SO ₂ (ppm)	3 - 17	136 - 427
Port A		
t _R (sec)	1.90 - 3.06	0.43 - 1.58
T _s (°C)	151 - 192	146 - 196
tetra-octa PCDD + PCDF (ng/dscm)	1 - 1369 ¹	4 - 57
Port B		
t _R (sec)	1.66 - 3.69	0.37 - 1.94
T _s (°C)	296 - 380	299 - 370
tetra-octa PCDD + PCDF (ng/dscm)	9 - 1910 ¹	2 - 104

¹not including sorbent injection runs

All concentrations are dry, not corrected to 7% O₂.

Residence time t_R based on t=0 at 650°C.

T_s=Sampling port temperature.

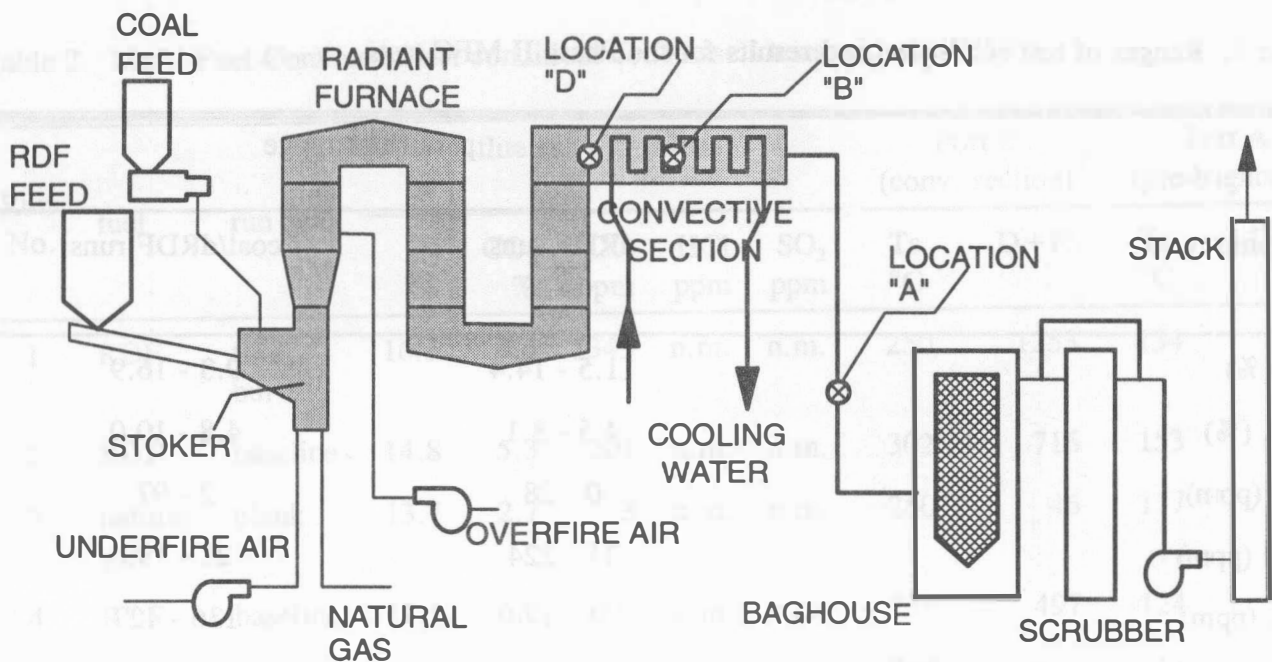


Figure 1. Schematic of the Multi-Fuel Combustor (MFC)

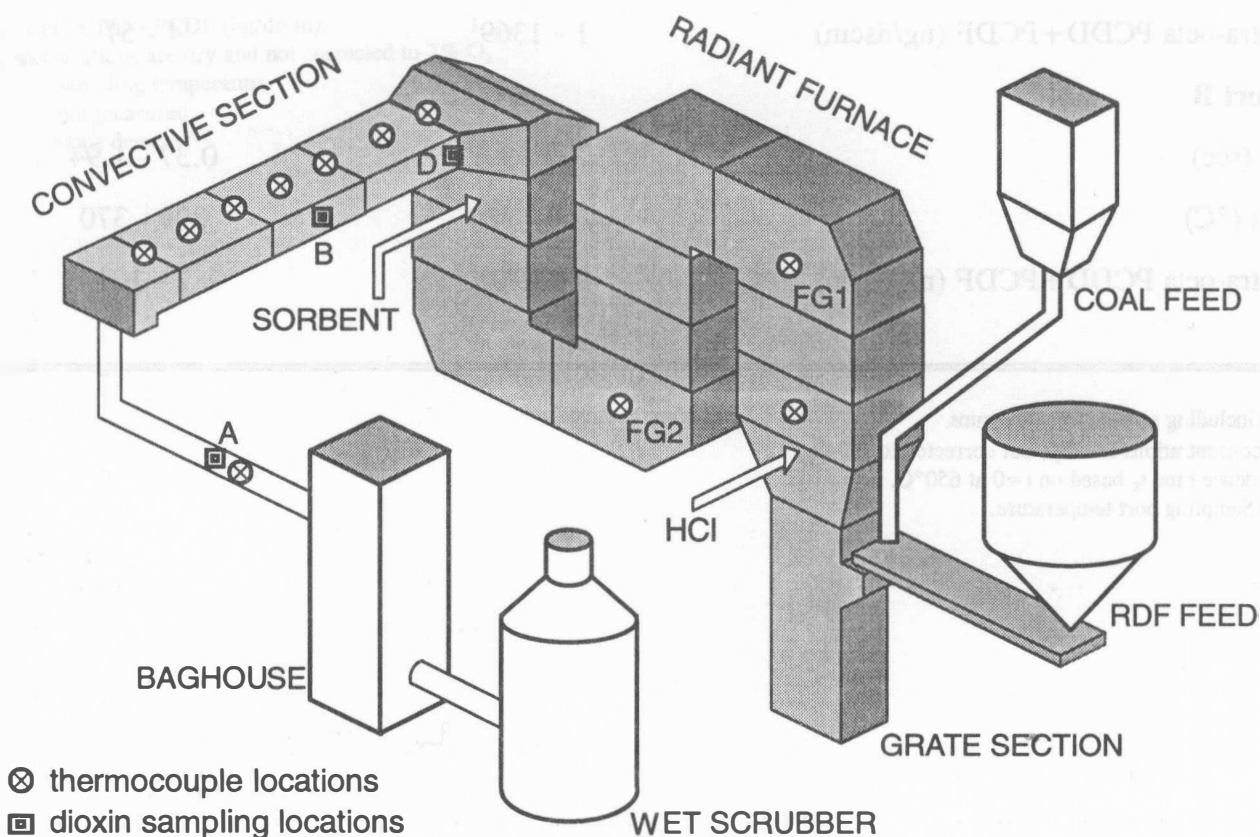


Figure 2. A view of the Multi-Fuel Combustor

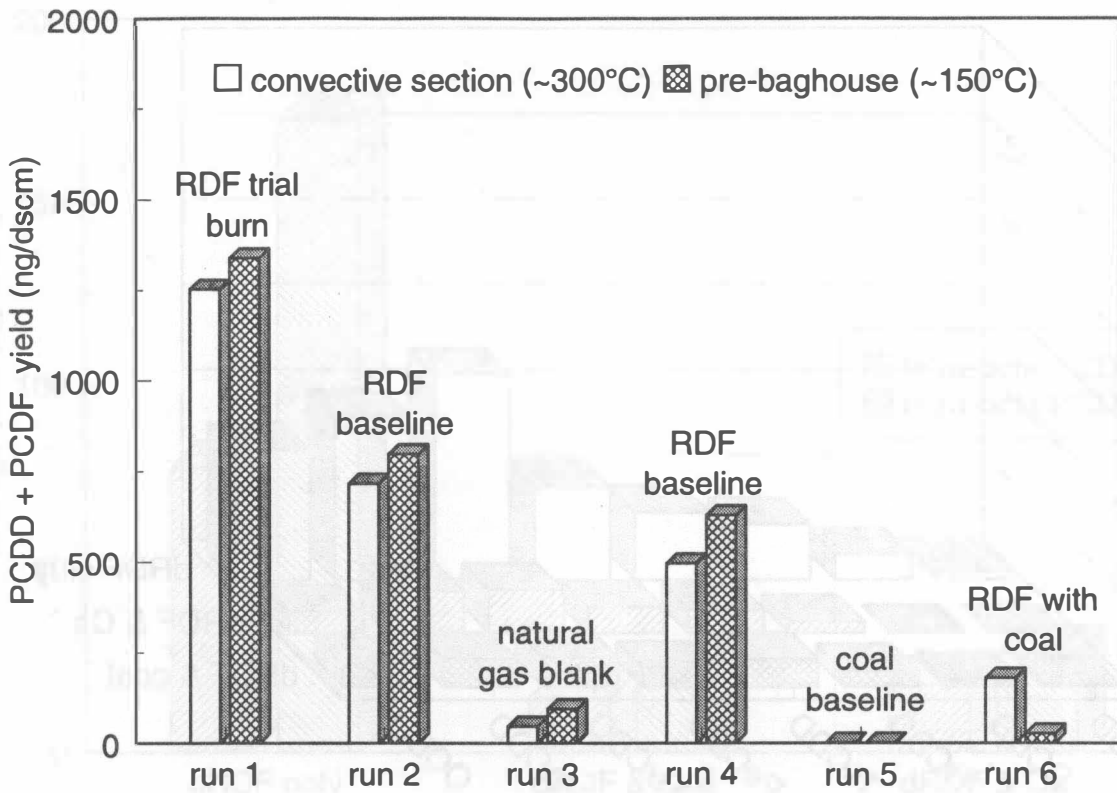
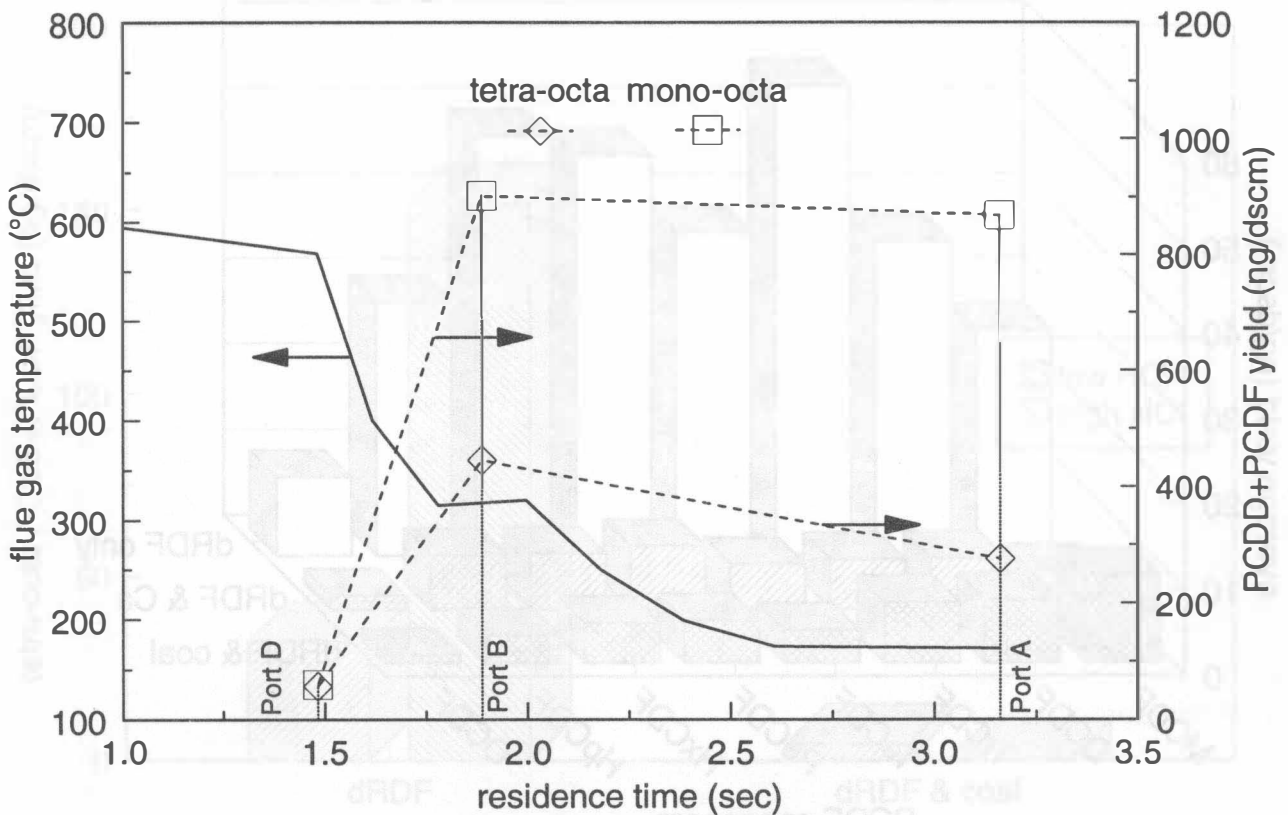


Figure 3. Total PCDD and PCDF (tetra-octa) yields from Phase I RDF tests



t=0 at 650°C

Figure 4. PCDD and PCDF yields from dRDF combustion measured at the three sampling ports

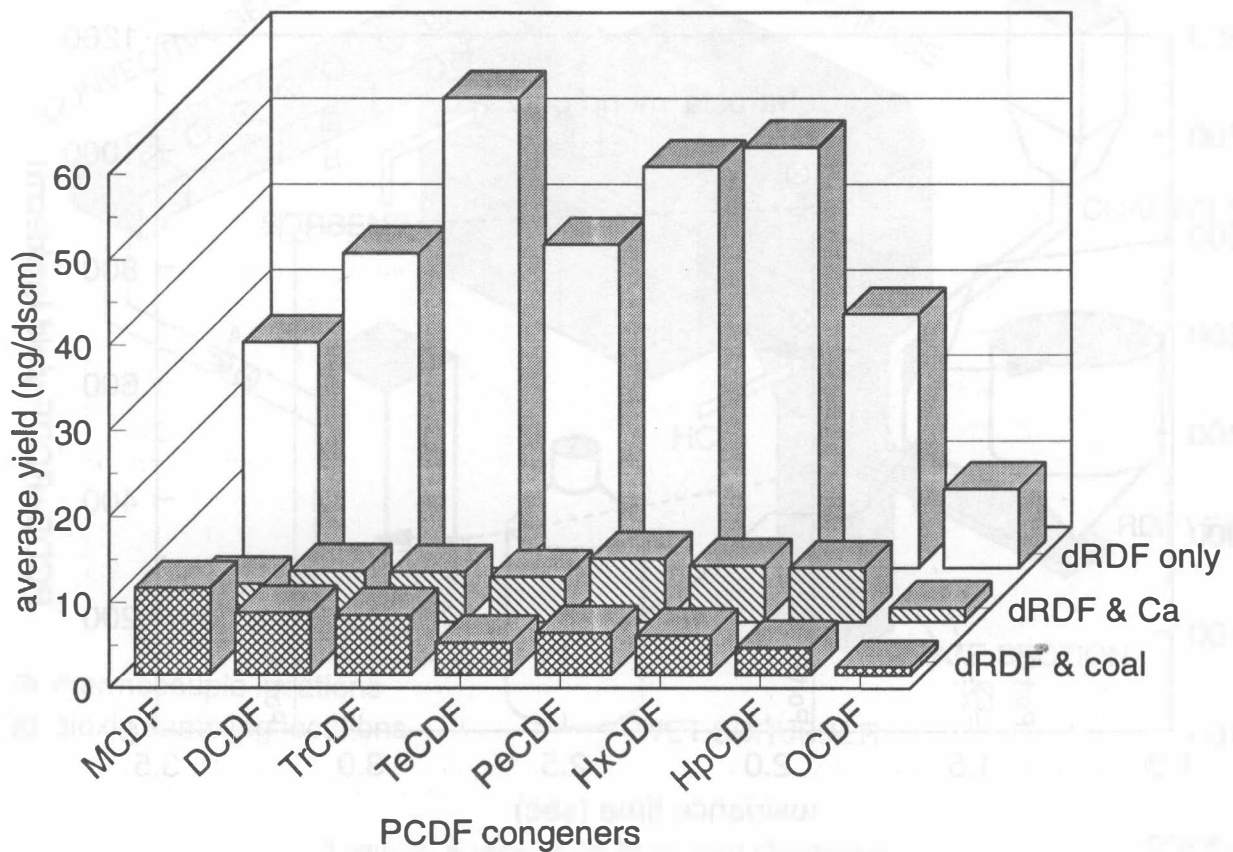
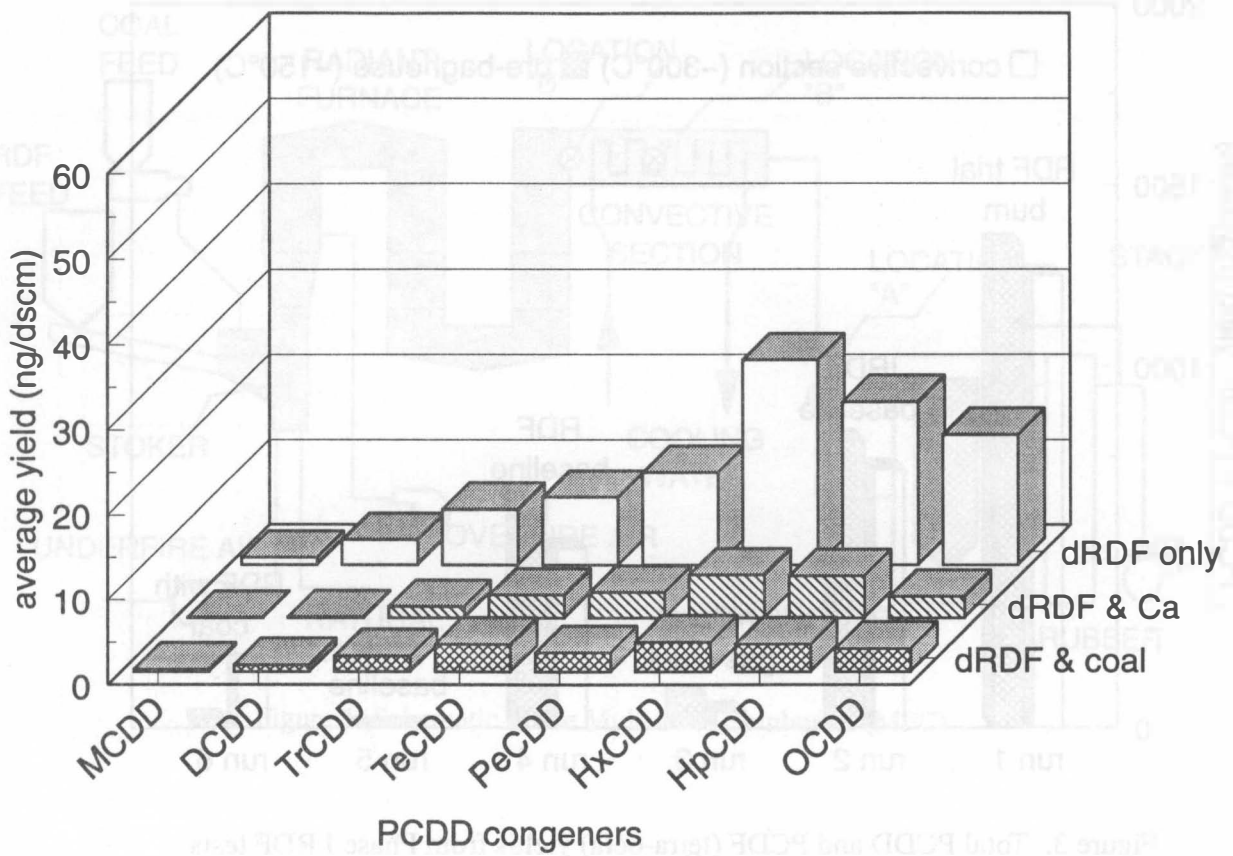


Figure 5. Effects of coal co-firing and sorbent injection on PCDD and PCDF congener yield.

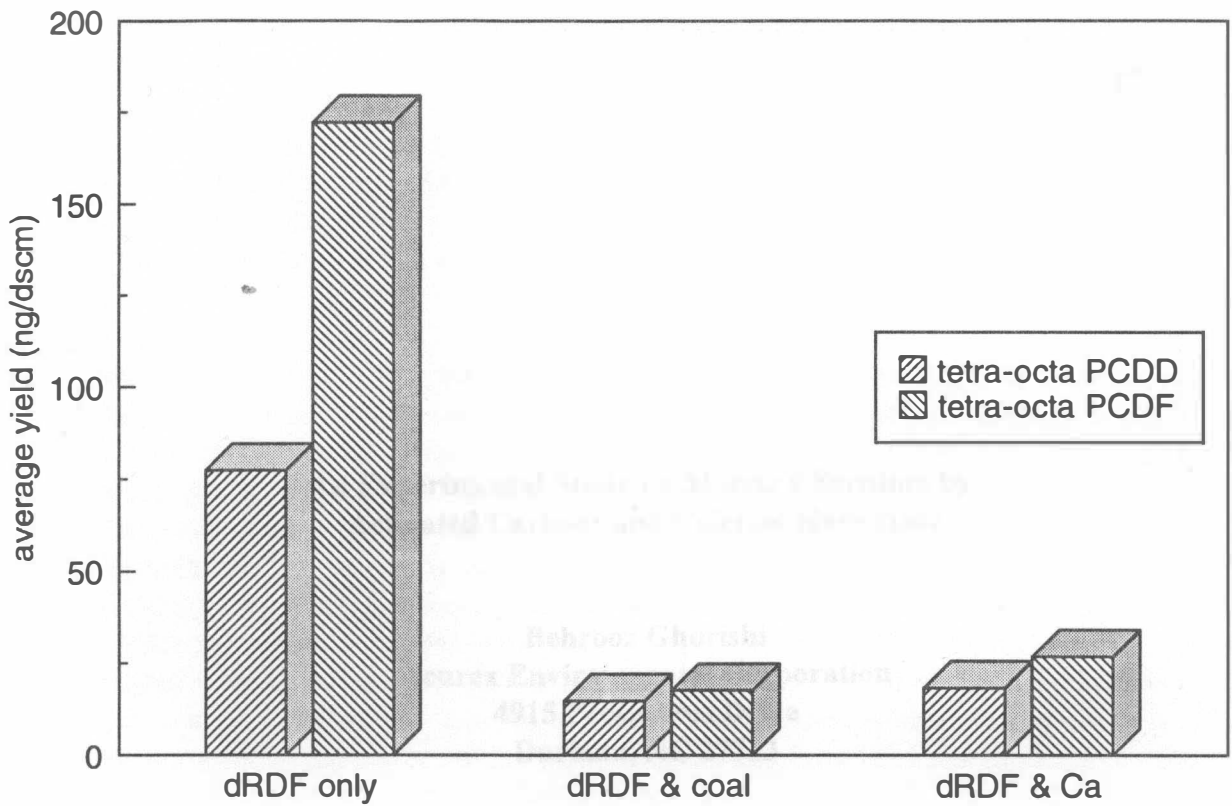


Figure 6. Effects of coal co-firing and sorbent injection on total PCDD and PCDF yield.

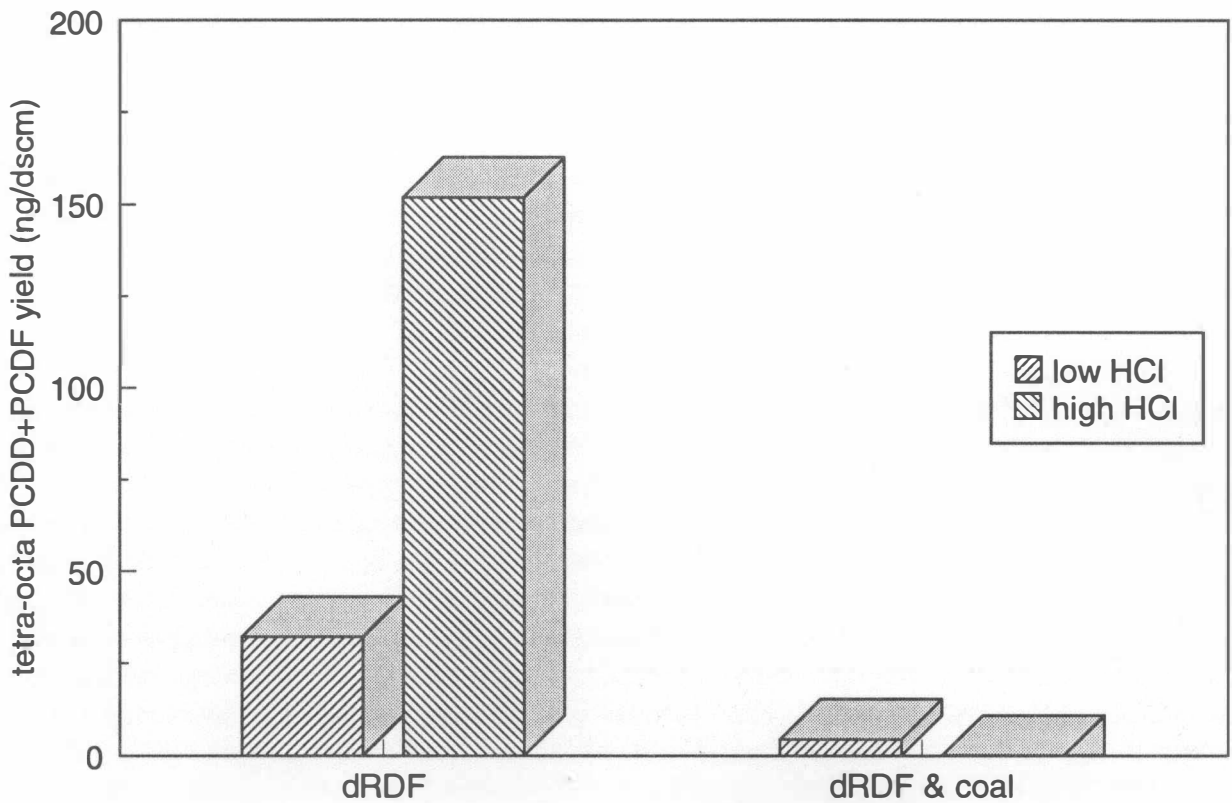


Figure 7. Effect of coal co-firing on PCDD+PCDF yield from the model for Port A