Analysis of PCB's and PCDD's from the Combustion of Quicklime BInder Enhanced Densified Refuse Derived Fuel/Coal Mixtures

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Introduction

Two of the nations current major concerns are energy and municipal solid waste. The combustion of Refuse Derived Fuels (RDF) is increasingly being viewed as an attractive solution to both problems. Densification of RDF producing dRDF is typically performed to minimize the problems of handling, transporting and storing the low bulk volume material. When densification is performed with the use of a binding agent additional performance and environmental benefits can be gained.

In 1985 the University of North Texas (UNT) under contract with Argonne National Laboratory investigated over 150 potential binding agents. Evaluations were made based upon economics, toxicity, availability and performance. The top 13 binder candidates were tested in a large scale demonstration. End results found calcium hydroxide or quicklime ($Ca(OH)_2$) to be the best performing binder. UNT also hoped that this binder's basic nature might help reduce the emission of acid gases. Further conjecture was made that the binder might physically absorb halogens, such as chlorine and thus reduce the production of polychlorinated biphenyls and dioxins. (1,2)

These hypotheses were tested at a pilot plant operation at Argonne National Laboratory in 1987. The six week program combusted over five hundred tons of binder enhanced dRDF (bdRDF) blended with Kentucky coal at heat contents of 10, 20, 30 and 50 percent. The $Ca(OH)_2$ binder content ranged from 0 to 8 percent by weight of dRDF. Emission samples were taken both before and after pollution control equipment (multicyclone and spray dryer absorber). All samples were taken to UNT for analysis.

Experimental

Isokinetic samples were taken for the analysis of polychlorinated biphenyls (PCB's), polyaromatics (PAH's), polychlorinated dioxins (PCDD's) and polychlorinated furans (PCDF's). The following sampling sites were investigated.

Site 1	combustion zone (2000°F), sample site (1200°F)
Site 2	prior to pollution control equipment (300°F)
Site 3	after pollution control equipment (170°F)

Sample collection was completed using an EPA Method 5 modified sampling train, and a XAD-2 resin for trapping the majority of organics. After extractions, sample clean-up was accomplished using various acid/base modified silica and alumina gels to remove interferents. Response factors, recovery and detection limits were established through internal standards. The gas chromatography mass spectrometer analysis was performed with a Hewlett-Packard Model 5992B. (3)

Results and Discussion

The EPA's sixteen most hazardous PAH's (Table 5) and all congener groups of PCB's were tested. The results of site 2 and site 3 sampling areas are found in Tables 1 and 2. Figures 1 and 2 clearly depict a reduction in PAH and PCB emission as the binder concentration is increased. Data is not available on all compositions due to the mixing and sampling methods used. Tables 3 and 4 show the calcium and chloride contents of fly ash from the multicyclone for a series of specific compositions. The calcium is used as an indicator of the binder present in the boiler system during a particular sampling period. The increase in calcium occurring between the first coal "blank" run and the second blank occurring 3 weeks later, suggest a build-up of residual binder throughout the boiler configuration. It is noteworthy that the increase in water soluble chloride in the fly ash for the 10% RDF samples is on the same order as the reduction of PCB's seen in Figure 2. This is presumably due to the lime's ability to bind the chloride in the combustion area. The much higher chloride content of the second coal blank ash relative to the first blank can be explained by assuming a longer contact time for chloride absorption on the residual binder as the binder became saturated throughout the boiler system. (4)

The dioxin and furan analysis initially concentrated on the tetra chlorinated species present after the pollution control equipment at sample site 3. Table 6 shows that no dioxins or furans were found at the listed detection limits. Composited fly ash samples were also analysed for absorbed PCDD's and PCDF's, and again results were below detection limits. Additional analysis was performed for penta, hexa, hepta, and octa congeners at sample site

3. In all cases, no dioxins or furans were detected. These results were confirmed by collaborating with Triangle Laboratories at Research Triangle Park, NC, using their high resolution mass spectrometer. Detection limits were generally improved only on the order of one magnitude, and as before, no detectable quantities of dioxins or furans were found. (5)

Conclusion

Results of the pilot plant program indicates that the binder enhanced densified refuse derived fuel can be cofired with coal, at the levels tested, without producing detectable amounts of dioxins or furans. PCB's and PAH's are apparently reduced as a function of the quicklime binder content.

References

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4. Matthew Poslusny Ph.D. Dissertation, "Analysis of PAH and PCB Emissions From the Combustion of dRDF and the Nondestructive Analysis of Stamp Adhesives", University of North Texas, May 1989.

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Table 1

Polyaromatic Hydrocarbons (PAH's);

Polychlorinated Biphenyls (PCB's) at Site 2

Run#/Sample#	Site	mg PAH's cubic meter of gas sampled	mg PCB's cubic meter of gas sampled
Run 1 Sample 1	2	1.7×10^{-2}	6.2×10^{-3}
Run 2 Sample 2*	2	1.0×10^{-3}	1.3×10^{-2}
Run 2 Sample 2	2	7.6×10^{-2}	2.7×10^{-1}
Run 3 Sample 1	2	1.6×10^{-2}	1.4×10^{-2}
Run 4 Sample 1	2	4.0×10^{-3}	7.6×10^{-3}
Run 4 Sample 2	2	8.1×10^{-3}	7.7 xx 10^{-3}
Run 5 Sample 1	2	3.5×10^{-2}	9.7×10^{-3}
Run 5 Sample 2	2	4.6×10^{-2}	7.7×10^{-3}
Run 7 Sample 1	2	2.2×10^{-1}	2.0×10^{-3}
Run 7 Sample 2	2	3.5×10^{-1}	2.9×10^{-1}
Run 8 Sample 2	2	2.4×10^{-1}	1.3×10^{-2}
Run 8 Sample 4	2	3.0×10^{-1}	3.4×10^{-3}
Run 12 Sample 1	1	3.4×10^{-1}	5.4×10^{-3}
Run 12 Sample 2	2	1.3×10^{-1}	3.9×10^{-4}

* This sample was lighter in color than all the rest

Table 2

Polyaromatic Hydrocarbons (PAH's); Polychlorinated Biphenyls (PCB's) at Site 3

Run#/Sample#	Site	mg PAH's cubic meter of gas sampled	mg PCB's cubic meter of gas sampled
Run 1 Sample 1	3	4.6 x 10^{-3}	5.3 x 10^{-4}
Run 2 Sample 1	3	6.3 x 10^{-3}	1.2 x 10^{-3}
Run 2 Sample 2	3	1.5 x 10^{-2}	*
Run 2 Sample 3	3	8.1 x 10^{-3}	1.6 x 10^{-3}
Run 3 Sample 1	3	7.3 x 10^{-3}	9.1 x 10^{-3}n
Run 4 Sample 1	3	7.3 x 10^{-3}	1.1 xx 10^{-4}
Run 4 Sample 2	3	3.1 x 10^{-3}	3.1 x 10^{-3}
Run 5 Sample 1	3	3.6 x 10^{-4}	2.8 x 10^{-4}
Run 5 Sample 2	3	4.0 x 10^{-3}	1.2 x 10^{-3}
Run 7 Sample 1	2	7.9 x 10^{-2}	4.2 xx 10^{-2}
Run 7 Sample 2	3	4.9 x 10^{-2}	6.5 x 10^{-3}
Run 8 Sample 1	3	1.0 x 10^{-3}	2.4 x 10^{-3}
Run 8 Sample 2	3	8.1 x 10^{-3}	8.5 x 10^{-4}
Run 12 Sample 1	3	7.0 x 10^{-2}	4.0 x 10^{-3}
Run 12 Sample 2	3	1.4 x 10^{-3}	4.3 x 10^{-4}

* Interference made it impossible to determine the quantity of PCB's in this run

Table 3

Calcium Levels in Fly Ash

Fuel	ppm of Calcium
First coal blank	3,000
Coal - 10% dRDF (0% binder)	6,700
Coal - 10% dRDF (4% binder)	10,600
Coal - 10% dRDF (8% binder)	15,000
Second coal blank	4,200

Table 4

Inorganic Chloride Levels in Fly Ash

Fuel	ppm of Chloride
First coal blank	100
Coal - 10% dRDF (0% binder)	190
Coal - 10% dRDF (4% binder)	280
Coal - 10% dRDF (8% binder)	320
Second coal blank	280

Table 5

EPA Priority PAH's

Napthalene	Benzo-a-anthracene
Acenapthylene	Chrysene
Acenapthene	Benzo-b-fluoranthene
Flourene	Benzo-k-fluoranthene
Phenanthrene	Benzo-a-pyrene
Anthracene	Dibenzo-a,h-anthracene
Fluoranthene	Benzo-g,h,i-perylene
Pyrene	Idendo-1,2,3,-g,d-pyrene

Table 6

Tetra-Chlorinated Dioxins and Tetra-Chlorinated Furans at Site 3

Run#/Sample#	Site	Tetra-Chlorinated Dioxin Level	Tetra-Chlorinated Furan Level	Detection Limit
Run 1 Sample 1	3	BDL	BDL	0.72 ng/m^3
Run 2 Sample 1	3	BDL	BDL	1.99 ng/m^3
Run 2 Sample 2	3	BDL	BDL	4.07 ng/m^3
Run 2 Sample 3	3	BDL	BDL	5.24 ng/m^3
Run 3 Sample 1	3	BDL	BDL	4.80 ng/m^3
Run 4 Sample 1	3	BDL	BDL	4.27 ng/m^3
Run 4 Sample 2	3	BDL	BDL	4.27 ng/m^3
Run 5 Sample 1	3	BDL	BDL	0.49 ng/m^3
Run 5 Sample 2	3	BDL	BDL	0.47 ng/m^3
Run 7 Sample 1	3	BDL	BDL	4.16 ng/m^3
Run 7 Sample 2	3	BDL	BDL	4.10 ng/m^3
Run 8 Sample 1	3	BDL	BDL	4.78 ng/m^3
Run 8 Sample 2	3	BDL	BDL	4.78 ng/m^3
Run 12 Sample 1	3	BDL	BDL	3.85 ng/m^3
Run 12 Sample 2	3	BDL	BDL	4.85 ng/m^3

ng/m^3 = nanograms per cubic meter

BDL = Below Detection Limits

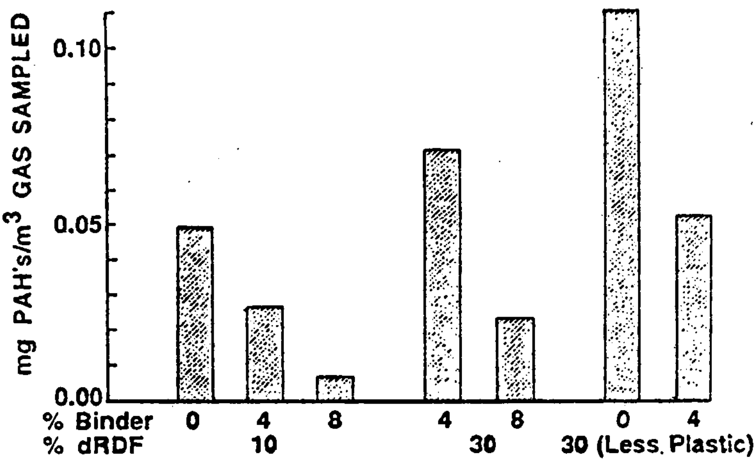

Figure 1

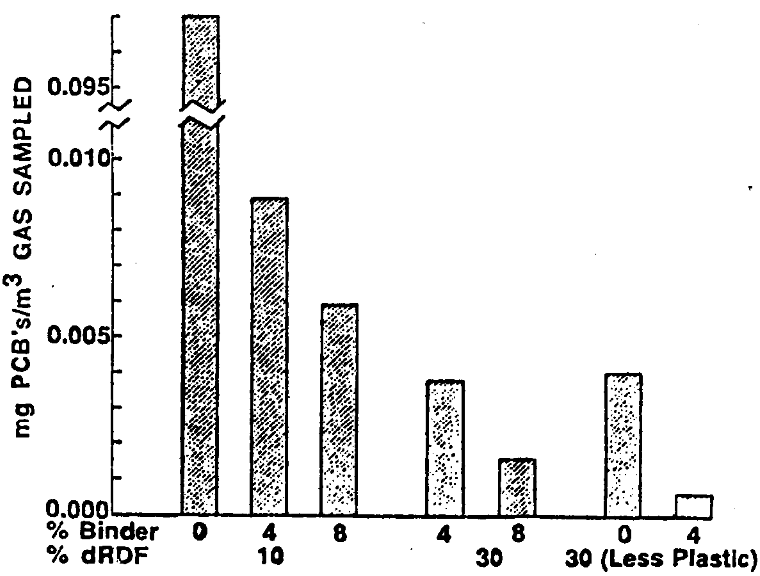

Figure 2