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Project Summary

Environmental Assessment of a Wood-Waste-Fired Industrial Watertube Boiler

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This report describes emission results from field tests of a wood-waste-fired industrial watertube boiler. Two series of tests were performed: one firing dry wood waste (11% moisture), and the other firing green wood waste (34% moisture). Emission measurements included: continuous monitoring of flue gas emissions; source assessment sampling system (SASS) sampling of the flue gas with subsequent laboratory analysis of samples to give total flue gas organics in two boiling point ranges, compound category information within these ranges, specific quantitation of the semivolatile organic priority pollutants, and flue gas concentrations of 73 trace elements; Method 5 sampling for particulate; controlled condensation system sampling for SO_2 and SO_3; and grab sampling of boiler mechanical collector hopper ash for inorganic and organic composition determinations.

Flue gas CO emissions from the boiler were quite high, averaging about 10,000 ppm (dry at 3% O_2) firing dry wood and about 2,000 ppm firing green wood. These high emissions were attributed to the high excess air levels at which the unit operated: approaching 400% while firing dry wood and about 200% while firing green wood. NO_x emissions were comparable, with both fuels in the 175 - 200 ppm (3% O_2) range. SO_2 and SO_3 emissions levels were less than 10 ppm, in keeping with the low sulfur content of both fuels. Total organic emissions from the boiler decreased from 60 - 135 mg/dscm firing dry wood to 2 - 65 mg/dscm firing green wood, in parallel with corresponding boiler CO emissions. The more volatile organics (boiling point less than 100°C) accounted for most of the total organic emissions measured. Emissions of 11 polycyclic organic matter (POM) species and phenol were quantitated for one or both tests. Again, emission levels were higher for the dry wood test.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in two separate volumes of the same title (see Project Report ordering information at back).

Introduction

In recent years, wood has experienced a revival as a primary or alternate source of energy for steam raising in industrial boilers as well as for space heating in the commercial and residential sector. As an indirect consequence, emissions from wood combustion and associated air quality impacts have received attention since recent studies have suggested that wood combustion can produce significant emissions of potentially hazardous organic pollutants. The report describes the results of comprehensive emissions testing of an industrial watertube boiler converted to burn wood waste from a furniture manufacturing plant. The unit was tested firing both a dry wood waste and a green wood waste. The flue gas was analyzed for criteria pollutants as well as total organic and several organic and inorganic species.

The tests were conducted in conjunction with an independent test program by the North Carolina Department of Natural Resources and Community Development

(DNR) to measure POM species emissions from this boiler and other wood-fired boilers located in North Carolina.

The tests were performed on a balanced draft Wickes stoker-fired industrial boiler modified to burn wood waste (a mixture of chips, shavings, and saw dust from oak and pine woods). The boiler was originally rated at 6.3 kg/s (50,000 lb/hr) of 1.7 MPa (250 psig), 338°C (640°F) superheated steam when burning bituminous coal. However, modifications to allow 100% wood burning resulted in a decrease in steam capacity to about 3.2 kg/s (25,000 lb/hr), with lower superheater steam pressure and temperature. The unit was equipped with a mechanical collector (cyclone) for particulate control.

Summary and Conclusions

Boiler Operation

The test program for this unit called for emissions evaluation while firing dry wood (Test 1) and green wood (Test 2). Table 1 summarizes boiler operating characteristics and ultimate analyses of wood fuel for both tests. As indicated, boiler operation was not held constant during either test. Changing steam requirements by the plant caused fluctuations in boiler steam load and wood feed rate. Because of the extremely high excess air levels (almost 400% for Test 1 and over 200% for Test 2), boiler efficiencies were a modest 55 and 61% for Tests 1 and 2, respectively, based on the standard ASME heat loss calculation method.

Wood feed rates listed in Table 1 are not measured values: they were calculated based on the stack conditions (volumetric gas flowrate and O_2 level) and the fuel analysis. These wood feed rates should thus be considered approximate. In addition, the steam flowrates shown in Table 1, which were taken from the control room steam meter (deemed unreliable by plant personnel), should also be viewed with caution. If the boiler steam flowrate is calculated based on the heat input (wood flowrate x heating value), boiler efficiency (ASME heat loss), and steam conditions, the resulting steam flows would be 1.1 and 1.6 kg/s (8,400 and 13,000 lb/hr) for Tests 1 and 2, respectively. This is quite different from what the control room steam meter indicated.

Emission Measurements and Results

The sampling and analysis procedures used in this test program conformed to a modified EPA Level 1 protocol. The flue gas measurements included:

- Continuous monitoring for O_2, CO and NO_x
- SASS train sampling
- Controlled condensation system (CCS) for SO_2 and SO_3
- EPA Method 5 for particulate
- Grab sample for onsite analysis of C_1 to C_6 hydrocarbons by GC

In addition, samples of the mechanical collector hopper ash and the fuel fired for each test were collected for analysis.

The analysis protocol included:

- Analyzing the fuels, SASS train samples, and the mechanical collector hopper ash for 73 trace elements using spark source mass spectrometry (SSMS), supplemented

Table 1. *Summary of Boiler Operation and Fuel*

Test parameter	Test 1 (dry wood)		Test 2 (green wood)	
Boiler operation:				
Steam load, kg/s (10^3 lb/hr)	1.8-2.2	(14-17)	0.88-1.4	(7-11)
Superheater steam temp., °C (°F)	227-274	(440-525)	271-296	(520-565)
Superheater steam press., MPa (psig)	1.00-1.17	(145-170)	1.13-1.30	(165-190)
Economizer inlet water temp., °C (°F)	63-69	(145-155)	66-69	(150-155)
Economizer outlet water temp., °C (°F)	121-133	(250-270)	113-121	(235-250)
Stack temperature after collect., °C (°F)	216-238	(420-460)	216-233	(420-450)
Bridgewall temperature, °C (°F)	354-483	(740-900)	538-594	(1,000-1,100)
Silo A (dry wood) feed, rpm	390-700		—	
Silo B (wet wood) feed, rpm	—		500-620	
Furnace draft, Pa (in. H_2O)	0 to-100	(0 to-0.4)	-25 to-50	(-0.1 to-0.2)
Underfire air, Pa (in. H_2O)	75-200	(0.3-0.8)	125-175	(0.5-0.7)
Overfire air, kPa (in. H_2O)	5.5-5.6	(22.0-22.5)	5.5-5.6	(22.0-22.5)
Pressure before collector, Pa (in. H_2O)	450-600	(1.8-2.4)	320-500	(1.3-2.0)
Pressure after collector, kPa (in. H_2O)	0.5-1.0	(2.0-4.0)	0.55-0.75	(2.2-3.0)
Wood feed rate[a], kg/s (lb/hr)	0.29	(2,270)	0.54	(4,310)
Excess air, percent	387		213	
Boiler efficiency[b], percent	55.3		61.3	
Wood fuel ultimate analysis (percent by weight as fired):				
Carbon	45.27		35.07	
Hydrogen	5.44		3.60	
Sulfur	0.04		0.02	
Nitrogen	0.12		0.10	
Oxygen	37.78		26.06	
Ash	0.33		1.29	
Moisture	11.02		33.85	
Higher heating value kJ/kg (Btu/lb)	17,900	(7,719)	13,300	(5,738)
Bulk density kg/m^3 (lb/ft^3)	233	(14.52)	192	(11.95)

[a] As-fired (wet) basis (a calculated value)
[b] Based on heat loss method

by atomic absorption spectrometry (AAS)

- Analyzing SASS train samples and the mechanical collector hopper ash for total organic content in two boiling point ranges: 100° to 300°C by total chromatographable organics (TCO) analysis, and greater than 300°C by gravimetry (GRAV)
- Analyzing the SASS train sorbent module extract for 58 semivolatile organic species including many of the POM compounds
- Infrared (IR) spectrometry analysis of organic sample extracts
- Liquid chromatrography (LC) separation of selected sample extracts with subsequent TCO, GRAV, and IR analysis of LC functions
- Direct inspection probe and batch inlet low-resolution mass spectrometry (LRMS) of selected sample extracts
- Obtaining aqueous leachates of the mechanical collector hopper ash and analyzing the leachate for 73 trace elements and 9 leachable anions
- Determining the alpha and beta radiometric activity of particulate and mechanical collector hopper ash samples
- Performing several mutagenicity and toxicity health effects bioassays and several toxicity ecological effects bioassays of SASS samples and the mechanical collector hopper ash

Table 2 summarizes emissions measured in the stack gas from the boiler. Emissions are presented as both nanograms per Joule (ng/J) heating input and micrograms per dry standard cubic meter (μg/dscm) of flue gas. As a measure of the relative potential significance of the emissions, an occupational exposure guideline concentration for each species is also noted in the table. The guideline noted is the time-weighted-average Threshold Limit Value (TLV). These are noted only to aid in ranking the potential significance of pollutant species emissions. Conclusions regarding the absolute risk associated with emission levels compared to occupational exposure guidelines are not, and should not be, drawn. With respect to ranking, however, species emitted at levels several orders of magnitude higher than their occupational exposure guidelines might warrant further consideration. Species emitted at levels significantly lower than their occupational exposure guidelines could be considered of little potential concern. Only species emitted at levels exceeding 10% of their occupational exposure guidelines are noted in Table 2.

CO was emitted during both tests in concentrations well over an order of magnitude higher than its occupational exposure guidelines. During the dry wood test, CO was measured in concentrations ranging from about 1,000 - 3,400 ppm at stack conditions averaging 9,800 ppm corrected to 3% O_2 (3.0 g/dscm). During the green wood test, CO emissions were measured in the range of about 280 - 2,300 ppm at stack conditions averaging 2,810 ppm corrected to 3% O_2 (1.3 g/dscm). CO emissions varied with the amount of O_2 in the flue gas, increasing substantially with increasing O_2.

NO_x was emitted at levels over an order of magnitude higher than its occupational exposure guidelines. NO_x emissions averaged 175 and 194 ppm for Tests 1 and 2, respectively, both corrected to 3% O_2. In contrast to CO emissions, NO_x levels were found to be relatively

Table 2. *Summary of Flue Gas Emissions*

Species	Test 1 (dry wood) emissions[a]			Test 2 (green wood) emissions[a]			Occupational exposure guideline[b] (μg/m³)
	ng/J	μg/dscm	g/kg fuel	ng/J	μg/dscm	g/kg fuel	
Criteria pollutant and total organic emissions							
CO	3,690	2.77×10^6	66.0	1,080	1.31×10^6	14.4	5.5×10^4
NO_x (as NO_2)	108	0.87×10^5	1.93	123	1.49×10^5	1.63	6,000
Solid particulate	204	1.64×10^5	3.64	267	3.24×10^5	3.55	1.0×10^4
Condensible particulate	16	0.13×10^5	0.29	4	0.05×10^5	0.05	—
Total volatile organics (C_1 to C_6)	58 to 150	$(4.7 \text{ to } 12) \times 10^4$	1.0 to 2.7	2.8 to 63	$(0.34 \text{ to } 7.6) \times 10^4$	0.037 to 0.84	—
Total chromatographable organics (C_7 to C_{16})	7.7	6,200	0.14	0.60	730	0.008	—
Total GRAV oragnics (C_{16+})	12	9,500	0.21	1.2	1,400	0.015	—
Trace elements							
Silver, Ag	0.98	790	0.017	0.012	14	1.6×10^{-4}	10
Nickel, Ni	0.15	120	0.0026	0.24	290	0.0032	100
Phosphorous, P	>0.20	>160	>0.0035	>0.23	>280	>0.0031	100
Barium, Ba	>0.20	>160	>0.0035	>0.27	>330	>0.0037	500
Potassium, K	>0.37	>300	>0.0066	>1.1	>1,300	>0.014	2,000
Iron, Fe	>0.24	>190	>0.0042	>0.39	>470	>0.0052	1,000
Sodium, Na	>0.87	>720	>0.016	>0.31	>370	>0.0041	2,000
Chromium, Cr	0.010	8.2	1.8×10^{-4}	0.014	17	1.9×10^{-4}	50
Copper, Cu	0.014	11	2.4×10^{-4}	0.049	59	6.5×10^{-4}	200
Lead, Pb	0.007	5.2	1.1×10^{-4}	0.015	18	2.0×10^{-4}	150
Cobalt, Co	0.007	5.6	1.2×10^{-4}	0.0007	0.79	8.8×10^{-6}	50

[a] *Average flue gas O_2 at the stack was 16.4 and 13.9% for Tests 1 and 2, respectively*
[b] *Threshold Limit Value*

insensitive to O_2 levels. Higher wood moisture during Test 2 did not result in a net decrease in NO_x emissions as might have been anticipated. Any combustion temperature reducing effect of the higher water content in the fuel was most likely insignificant compared to the expected low combustion temperature associated with the high excess air levels fired. The nitrogen content of both fuels were comparable and low (see Table 1). Sulfur oxides (SO_2 and SO_3) emissions were measured, but not detected in the flue gas above a detection limit of 10 ppm for either test. This is not entirely surprising since total conversion of sulfur in the wood to SO_2 would have resulted in, at most, about 12 ppm at stack conditions for both tests.

Other pollutants emitted at levels exceeding their occupational exposure guidelines were Ag, Ni, and P for both tests.

Tables 3 and 4 summarize organic emission results for the dry wood and green wood tests, respectively. The top portion of each table summarizes the semivolatile TCO organic content and the nonvolatile GRAV organic content of the XAD-2 sorbent extract, as eluted (by polar character) into the seven LC fractions, and the TCO and GRAV of the OMC. The bottom portion of the tables summarizes organic compound categories identified by LRMS of the LC fractions and the OMC, supplemented by IR spectra.

Total organic emissions during Test 1 (dry wood) were significantly greater than those from Test 2 (green wood). This result is consistent with the higher CO emissions measured. Organics trapped in the XAD-2 sorbent accounted for over 95% of the nominal $\geq C_7$ organics with boiling points $\geq$100°C (212°F). The inferences from IR and LRMS data are that the XAD-2 extracts contained primarily aliphatic hydrocarbons, aldehydes, and carboxylic acids for both tests. Phenols, aromatic hydrocarbons, and heterocyclic oxygen compounds were additional significant components in the dry wood test extracts. The POM compounds detected at highest levels in the XAD-2 organic extracts were naphthalene, phenanthrene, and acenaphthylene in concentrations corresponding to emissions in the 5 - 7 μg/dscm range, as shown in Table 5.

The TCO results shown in Tables 3 and 4 are compromised somewhat because the XAD-2 sorbent resin used in these tests had been inadvertently contaminated with acetone prior to field use. This resulted in high TCO values in both the sample extracts and the field blank. Gas chromatography/mass spectrometry (GC/MS) analyses were performed to identify and quantitate specific contaminant species, thereby allowing corrected sample and blank TCO values to be obtained. The resulting data are defensible, though still compromised to some degree.

Trace element analyses were performed on the two fuels fired, the emitted particulate, and the mechanical particulate collector hopper ash. The trace element compositions of the two fuels (dry and green wood) were very similar. In addition, the trace element compositions of the coarse particulate emitted in the flue gas (10 μm + 3 μm cyclone catches) and the

Table 3. *Organic Extract Summary — Test 1 (Dry Wood) XAD-2 and OMC Extracts*

	XAD-2 extract liquid chromatography fraction[a]					
	LC1	LC2 + 3	LC4 + 5	LC6 + 7	OMC	Total
Total organics, mg	4.5	17	32	132	13	200
TCO, mg	1.2	12	16	16	4.9	50
GRAV, mg	3.3	5	16	116	8.0	150
	Assigned intensity — mg/dscm					Total, mg/dscm (mg/kg fuel)
Category	LC1	LC2 + 3	LC4 + 5	LC6 + 7	OMC	
Aliphatic hydrocarbons	100—0.21					0.21 (4.6)
Carboxylic acids		10—0.70			100—0.091	0.79 (17)
Polynuclear aromatic hydrocarbons, MW>216		1—0.07			1—0.001	0.0071 (0.16)
Aldehydes			100—1.2	10—0.5	10—0.009	1.8 (40)
Ethers					100—0.091	0.091 (2.0)
Nitriles					100—0.091	0.091 (2.0)
Amines					100—0.091	0.091 (2.0)
Heterocyclic sulfur compounds					100—0.091	0.091 (2.0)
Halogenated aliphatics					10—0.009	0.009 (0.2)
Aromatic hydrocarbons			10—0.1	10—0.5	10—0.009	0.61 (13)
Phenols			10—0.1	100—4.7	100—0.091	4.8 (110)
Heterocyclic oxygen compounds			10—0.1	10—0.5	100—0.009	0.61 (13)
Ketones					10—0.009	0.009 (0.2)
Heterocyclic nitrogen compounds					10—0.009	0.009 (0.2)

[a] *Fractionation by polarity: LC1 is nonpolar, LC7 is higher polar*

mechanical collector hopper ash for the dry wood test were similar to respective discharges for the green wood test. Furthermore, for both tests, the coarse particulate trace element composition was similar to that of the mechanical collector hopper ash, but somewhat different from that of the fine particulate (1 μm + filter catches) in th flue gas. This is consistent with the mechanical collector being more efficient in collecting coarse particulate.

The organic content of the mechanical collector hopper ash was similar for both tests (about 0.70 mg/kg). These high levels are consistent with the relatively inefficient boiler operation during both tests.

An aqueous leachate of the mechanical collector hopper ash from the dry wood test contained levels of Ba, Cr, Pb, and Ni which exceeded respective water quality criteria by factors of 1.5 - 10. However, these were the only elements with leachate concentrations exceeding water quality criteria.

Radionuclide emissions were indirectly measured by analysis of the alpha and beta activities of the particulate and mechanical collector hopper ash samples. The alpha plus beta activities of the particulate samples, converted to emission rates, correspond to 770 and 760 pCi/kg wood for Tests 1 and 2, respectively. These are similar to emission rates from controlled model coal-fired powerplants.

Table 4. *Organic Extract Summary — Test 2 (Green Wood) XAD-2 and OMC Extracts*

	XAD-2 extract liquid chromatography fraction[a]					
	LC1	LC2 + 3	LC4 + 5	LC6 + 7	OMC	Total
Total organics, mg	5.4	1.8	2.5	13	0.2	23
TCO, mg	0.53	<0.04	<0.04	1.7	0.2	2.3
GRAV, mg	4.9	1.8	2.5	11.2	<3.0	20.4

	Assigned intensity — mg/dscm			Total, mg/dscm (mg/kg fuel)
Category[b]	LC1	LC2 + 3 + 4 + 5 + 6 + 7	OMC	
Aliphatic hydrocarbons	100—0.20			0.20 (2.2)
Aldehydes		100—0.32	100—0.003	0.32 (3.5)
Carboxylic acids		100—0.32	100—0.003	0.32 (3.5)

[a] Fractionation by polarity: LC1 is nonpolar, LC7 is highly polar

[b] Summary of organic emissions are based on IR results primarily since LRMS did not show any organic groups

Table 5. *POM and Other Organic Species Emission Summary — Total Flue Gas*

	Test 1 (dry wood)		Test 2 (green wood)	
Compound	μg/dscm	μg/kg fuel[a]	μg/dscm	μg/kg fuel[a]
Acenaphthene	—[b]	—	0.1	1.1
Acenaphthylene	0.5	11	5.2	57
Anthracene	—	—	0.2	2.2
Benzo/j+k/fluoranthenes	0.10	2.2	—	—
Chrysene	—	—	0.04	0.4
Fluoranthene	—	—	0.3	3.3
Fluorene	0.65	14	—	—
Naphthalene	4.5	100	—	—
Phenanthrene	7.0	160	2.0	22
Phenol	4.7	100	0.96	11
Pyrene	0.30	6.7	0.2	2.2
Other polynuclears	<0.05	<1.1	<0.04	<0.44

[a] kg fuel on wet basis

[b] Dashes indicate compound was not found to have concentration above the detection limits of 0.05 μg/dscm for Test 1 results and 0.04 μg/dscm for Test 2 results (more flue gas was sampled in the Test 2 SASS run resulting in a lower detection limit)

Bioassay tests were performed on the organic sorbent (XAD-2) extracts, flue gas particulate, and the mechanical collector hopper ash. Both health and ecological effects tests were performed. The bioassay tests performed on the XAD-2 extracts were health effects tests only. These were the Ames mutagenicity assay and the CHO cytotoxicity assay. In addition to the Ames test, health effects bioassay tests performed on mechanical collector hopper ash and the particulate catch were the rabbit alveolar macrophage (RAM) cytotoxicity assay and the whole animal acute toxicity (WAT) test in live rodents.

Table 6 summarizes the results of the Ames, CHO, RAM, and WAT assays. Overall, the results suggest that all samples except the XAD-2 extracts were of nondetectable to low toxicity and mutagenicity. The XAD-2 extracts showed high toxicity and mutagenicity. Flyash samples from the mechanical collector hopper were also tested for acute toxicity to freshwater invertebrates (Daphnia magna), freshwater fish (fathead minnow, Pimephales promelas), and freshwater algae (Selenastrum capricornutum). Table 7 summarizes the results of these assays, which suggest that samples are of nondetectable to low toxicity.

Conclusions

Emission tests of a wood-waste-fired industrial boiler suggest that emissions of potential concern can arise from inefficient (very high excess air) operation of the unit. In the tests, CO emissions were very high and varied with the excess air level fired, decreasing as excess air was decreased. Total organic emission levels (the volatile, boiling point less than 100°C, organics predominated) and POM emission levels paralleled CO emission levels; they were higher in the test with the higher average CO emissions. Differences in relative emission rates of the pollutants analyzed between firing a dry wood fuel and a wet wood fuel were not discernable. Major differences noted between the tests were best ascribed to the different excess air levels fired for each fuel.

Table 6. Health Effects Bioassay Results

Test	Sample	Bioassay Ames[a]	CHO[b]	RAM[b]	WAT[b]
1 (Dry wood)	Combined particulate (cyclones and filter catches)	ND	—	—	—
	XAD-2 sorbent extract	H/M	H	—	—
	Flyash	ND	—	L/ND	ND
2 (Green wood)	10 μm + 3 μm cyclone catches	ND	—	L/ND	
	1 μm cyclone and filter catches	ND	—	M	—
	XAD-2 sorbent extract	H	H	—	—
	Flyash	ND	—	ND	ND

[a] Mutagenicity test
[b] Toxicity test

ND — Nondetectable
L — Low
M — Moderate
H — High
— Assay not performed

Table 7. Ecological Effects Bioassay Results

Test	Sample	Aquatic organisms Invertebrate[a]	Freshwater fish[b]	Freshwater algae[c]
1 (Dry wood)	Flyash	ND/L	ND	L
2 (Green wood)	Flyash	ND/L	—	L

[a] Daphnia magna
[b] Pimephales promelas
[c] Selenastrum capricornutum

ND — Nondetectable toxicity
L — Low toxicity
— Assay not performed

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The complete report consists of two volumes, entitled "Environmental Assessment of a Wood-Waste-Fired Industrial Watertube Boiler:"
"Volume I. Technical Results," (Order No. PB 87-177 523/AS; Cost: $18.95)
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