Product of Incomplete Combustion from Direct Burning of Pentachlorophenol treated Wood Wastes: Result of a Study Performed for U.S. EPA[1]

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INTRODUCTION

The use of waste wood as fuel for producing energy is a promising supplement to fossil fuels for many regions of the country. In addition to recovering energy and conserving landfill space, burning waste wood fuels also mitigates global warming created by fossil fuel combustion. However, the environmental consequences resulting from emissions generated by combustion of waste wood which contains paints, resins, or preservatives are not well understood. The combustion of waste wood treated with chemicals may produce potentially hazardous products of incomplete combustion (PIC) emissions such as dioxins.[1,2]

Characterization of PIC emissions from the combustion of waste wood previously treated with pentachlorophenol is reported in this study. Utility poles and crossbars are typically treated with a preservative such as pentachlorophenol in order to prolong their service life. They are disposed of by landfilling after being taken out of service. Burning such wood waste in boilers for steam generation becomes an increasingly attractive waste management alternative as it contains substantial energy values and reduces landfilling costs. Pilot-scale combustion tests were conducted under well controlled conditions in a 0.58 MW (2 million Btu/hr) combustor to compare PIC emissions from burning untreated wood and pentrachlorophenol-treated wood. Sampling and analyses for a wide variety of PICs, including volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), and dioxins and furans, were performed to assess the effect of pentachlorophenol preservative present in wood on PIC emissions.

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EXPERIMENTAL

Test Facility

The combustion testing was conducted using a multifuel combustor (MFC) installed in the Environmental Protection Agency's research facility located at Research Triangle Park, North Carolina. The MFC, shown in Figure 1, is a pilot-scale stoker combustor with 0.58 MW (2 million Btu/hr) maximum thermal output which is sufficient for simulating the full range of conditions that might be encountered in practical systems. The MFC is capable of burning a wide variety of solid fuels including municipal solid waste, refuse derived fuel, biomass fuel, and coal singly or in combination. The combustor is constructed with modular sections, which provides maximum flexibility for modifying the combustor for research purposes. Access ports are installed throughout the entire combustor for sampling and visual observation.

The combustor was operated in a spreader stoker firing mode. Wood fuel was stored in a large roll-off container located near the building which houses the MFC. A tote bin filled with the wood fuel was transported to the MFC facility and the fuel was sequentially dumped into a loading hopper installed outside the facility building, using a forklift. An electric drive conveyor belt, installed under the loading hopper and penetrating through the facility building wall, moved the fuel to a vibrating active storage silo installed inside the building. The silo is designed for a 2 hour turnover time using an average fuel density of 80 kg/m^3 (5 lb/ft^3) and a feed rate of 163 kg/hr (360 lb/hr). The silo is large enough to dampen out effects of spurious loading yet small enough to fit inside the facility building. A vibratory silo is designed to improve mixing and reduce wall sticking. The fuel was distributed from the silo onto an airtight horizontal vibratory feeder conveyor connecting the silo to the transition section of the spreader stoker. The mass flow of the conveyor was calibrated for control of the fuel feed rate. The fuel traveled horizontally along the conveyor and dropped through the transition section into the feed injection port of the spreader stoker. The vibratory transition section is designed with an inlet air plenum area and adjustable inlet angle plate to facilitate spreading fuel onto the 61 by 30 cm (2 by 1ft) stoker grate where a burning fuel bed is formed.

Wood Fuel

Two different wood fuels, untreated wood and treated wood, were obtained from a plant where wood poles are treated with pentachlorophenol. The untreated wood was pine poles that are typically treated in the plant. The treated wood was a mixture of recently treated poles, mostly small pieces cut from the end to meet customers' length specifications and aged treated poles taken out of service. Both treated and untreated poles were ground into chips less than 7.6 cm (3 in.) in diameter. The two fuels were characterized by proximate, ultimate, and chlorine analyses: results are shown in Table 1. It can be seen that the treated wood fuel is drier with higher heating value as compared to the untreated wood. The chlorine content of the treated wood fuel is 10 times higher than that of the untreated wood.

Combustion Test Parameters

The only parameter investigated was the difference in emissions when burning treated vs. untreated wood fuels under similar combustion conditions; no attempt was made to conduct parametric tests for this study. In general, the operating conditions of the test were considered optimal when the fuel was burning at the designed heat release rate with nominally 160 % excess air and a low level (< 100 ppm) of carbon monoxide (CO) emissions in the flue gas.

The amount of fuel burned was not measured continuously during a test. It was estimated by weighing the fuel before it was dumped into the loading hopper of the MFC and measuring the time required for its complete consumption to calculate an average feed rate. The average feed rate was used to estimate the amount of fuel burned during a timed emissions sampling period. The MFC is equipped with continuous emission monitors (CEMs) -- for measuring oxygen (O_2), CO, carbon dioxide (CO_2), nitrogen oxide (NO), sulfur dioxide (SO_2), total hydrocarbon (THC), and hydrogen chloride (HCl) -- and equipment for continuously monitoring process temperatures and pressures.

Sampling and Analytical Procedures

The emissions sampling point for the present study was selected at the duct which connects the convective section of the furnace to the baghouse. The selection of a sampling point prior to any gas cleaning device was made to ensure that any difference in flue gas pollutant concentrations generated by combustion of treated and untreated wood fuels would be observed. Emission measurements made after the flue gas cleaning device would be expected to mask this difference and would be reflective of the effectiveness of the devices (i.e., baghouse and caustic scrubber) used.

The sampling program of the present study focused primarily on organic emissions, particularly those which are considered potentially hazardous, from the combustion of wood fuels. Sampling and analytical protocols used were based on existing EPA methods for measuring organic constituents in flue gases. Samples for measuring volatile organic PIC emissions were taken using EPA SW Method 0030, Volatile Organic Sampling Train (VOST), and the volatile PICs in the VOST samples were identified and quantified using SW Methods 5040 and 8240.[3-5] Samples for measuring SVOC emissions were obtained using SW Method 0010, and SVOCs in the samples were analyzed using SW Method 8270B.[6-7] Method 23 was used for measuring dioxin and furan emissions.[8]

RESULTS AND DISCUSSION

Test Conditions

Six combustion tests, three tests each for both the untreated and the treated wood fuels, were performed under similar combustor operating conditions. The untreated wood tests were performed first followed by the treated wood tests to avoid cross contamination. Triplicate runs were made to determine experimental repeatability. Since it was not practical to measure fuel feed rate continuously, the tests were performed under constant excess air level (nominally 160% excess air) and a constant combustion gas temperature (850° C) measured by a thermocouple located 152 cm (60 in) above the grate. The estimated heat release rates for all the tests are shown in Table 2 and the average CEMs-measured emission rates are shown in Table 3. The heat release rates are calculated based on the average fuel feed rate estimated by the amount of fuel consumed during the test period and the heating value of the fuel measured experimentally. It can be seen from Table 2 that the calculated heat release rates and the measured flue gas flow rates for Untreated Tests 2 and 3 are lower than those of the other tests. The lower flue gas flows for Untreated Tests 2 and 3 are consistent with their low fuel feed rates. The heat release rate was set at 80% of the maximum designed output of the MFC for the present study. The fuel feed rate was adjusted manually throughout all tests in order to maintain a constant temperature of 850° C above the stoker grate and keep CO emissions below 100 ppm, which were considered optimum conditions for the tests. The combustion gas temperature measured may not have been always truly representative. The tremendous turbulence generated above a burning hot fuel bed when the cold underfire air passing through the grate and the cold overfire air injected into the furnace above the grate may create a non-uniform gas temperature profile. Observations through installed viewing ports indicated that turbulent flow passed along the entire furnace during the tests. The heating values measured from the two fuel samples may not be truly representative due to the nonhomogeneous nature of the wood fuels. These two uncertainties may have contributed to the lower estimated heat release rates for the two tests.

It was difficult to produce exactly identical combustion conditions for all the tests, mainly due to the fact that the two wood fuels are not homogeneous. The treated wood fuel contains aged wood, which is drier, and has 30% higher heating value than the untreated wood fuel. Uneven fuel feed rates resulting from the fairly frequent manual adjustment of the fuel feeder could have caused fluctuations in air-to-fuel ratio and momentary excursions of CO emissions. CEM data for CO and CO_2 and visual observations of fuel flow into the stoker suggest that small excursions occurred during the tests. The nonhomogeneous nature of the fuels coupled with the practical difficulties to burn such fuels under well defined conditions make the accurate estimation of heat release rates during tests impossible. The high CO emissions, shown in Table 3, calculated after the untreated wood tests, are another indication that combustion conditions were difficult to control when burning the untreated wood, which has low heating value and high moisture content.

Pentachlorophenol Destruction Efficiency

The concentration of pentachlorophenol in the treated wood fuel was analyzed to be 4,100 mg/kg (ppmw). For the six tests, pentachlorophenol was not detected in any of the semivolatile organic samples. The estimated pentachlorophenol destruction efficiency (DRE) for each test has been conservatively calculated based on the pentachlorophenol analysis practical quantitation limit (PQL). DRE results are presented in Table 4. The PQL is based on the lowest calibration concentration and does not include factors such as percent recovery or matrix effects. It is evident from these results that burning of the pentachlorophenol-treated waste wood in a stoker combustor destroys the pentachlorophenol efficiently with a DRE higher than that required for hazardous waste destruction (99.99%).

Volatile Organic Compound (VOC) Emissions

Analyses were performed for 50 VOCs in each of the test samples. The VOC emission results presented in Table 5 are the compounds found in concentrations higher than the analytical detection limit in at least one test. Higher levels of benzene were found in the untreated wood test samples, while bromomethane was found at higher levels in the treated wood test samples. Chloromethane, 1,3-butadiene, iodomethane, acetone, chloroform, and 1,2-dichloroethane were found in both untreated and treated wood test samples. The trace levels of chlorinated VOC emissions found in the untreated wood tests may possibly be caused by small amounts of naturally occurring chlorine in untreated woods. More chlorinated VOCs were found in the treated wood tests, probably as a result of higher chlorine content in the pentachlorophenol-treated wood.

SVOC Emissions

Of the 87 semivolatile organic compounds for which analyses were performed in the SVOC samples, only the following five targeted compounds were found to be above the analytical detection limits: phenol, acetophenone, naphthalene, 2-nitrophenol, and phenanthrene. The total SVOC emission rate for all six tests is calculated by adding all the quantifiable SVOC emissions in the test, and results are summarized in Table 6. The typically low SVOC emissions for both the untreated and treated wood tests are an indication that good combustion conditions were achieved during the tests. The slightly lower SVOC emissions for the treated wood tests compared to those for the untreated wood tests also suggest that the combustion of the drier treated wood fuel produced lower PICs. More moisture released during the combustion of the "green" untreated wood fuel may lower the localized combustion zone temperature and cause more PIC formation.

Dioxin/Furan (PCDD/PCDF) Emissions

The dioxin/furan samples measured by Method 23 were taken at the exit of the convective heat exchanger and before the baghouse. The temperature of the flue gas at the sampling point was between 150 and 160° C. It has been shown that the dioxin and furan formation "temperature window" in flue gases is between 200 and 450° C.[9] It is reasonable to expect that the formation of dioxins and furans has already been completed before the sampling location.

As shown in Table 7, total PCDD/PCDF emissions from the untreated wood tests [using the International Toxic Equivalency (I-TEQ) method of accounting for different toxicities of PCDD/PCDF congeners] averaged 0.274 ng I-TEQ/dscm and from treated wood tests 1.190 ng I-TEQ/dscm. These emission rates are prior to any control devices. Particulate control devices could potentially remove part of this material from the gas stream, depending on the fly ash collection efficiency, PCDD/PCDF formation, and solid-to-vapor-phase partition with the device. Since the temperature at the sampling point is below 160° C, it is likely that the rates of formation and desorption of fly-ash-associated PCDD/PCDF in a subsequent particulate collection device would be low.[10] The PCDF emissions are significantly greater than PCDD emissions for both the untreated and treated wood tests, indicating de novo synthesis formation reactions rather than condensation reactions.[11] The PCDD/PCDF congener distributions for the treated and untreated tests also differ. In the untreated wood tests, the distribution is peaked at the the lower-chlorinated tetra-PCDD and di-PCDF congeners; in the treated wood tests, the distribution is shifted to the higher-chlorinated hexa-PCDD and penta-PCDF congeners. The PCDD/PCDF emission rates measured from both the untreated and treated wood tests are considered low when compared to the stack emissions from commercial municipal waste combustors, which range from 0.01 to 400 ng I-TEQ/dscm.[12] The low PCDD/PCDF emissions measured from the untreated wood tests are similar to those from burning natural wood, which range from 0.066 to 0.214 ng I-TEQ/dscm.[1] The PCDD/PCDF emissions from the treated wood tests are higher than those (0.0359 ng I-TEQ/dscm) from a waste-to-energy plant burning a mixture of clean wood and pentachlorophenol-treated waste wood.[13]

The higher PCDD/PCDF emissions from the treated wood tests compared to those from the untreated wood tests are consistent with their higher chlorinated VOC emissions. Approximately 200 ppm of HCl was measured in emissions from the treated wood tests, while HCl was not detected in the untreated wood tests. The PCDD/PCDF samples were collected into front half and back half of the sampling train and analyzed separately, which gives an indication of the PCDD/PCDF associated with the particulate material and as gaseous emissions. Table 8 shows that the percentage of PCDD/PCDF in the front half catch is greater in the treated wood tests than in the untreated wood tests. The treated wood tests had a higher flue gas flow rate (see Table 2) as a result of the higher heating value of the treated wood burned, which would enhance particulate load at the sampling point. This information suggests that particulate carryover may affect the total amount of PCDD/PCDF, especially in the treated wood samples where a larger percentage is in the front half catch. Combustor operating conditions in addition to the wood treatment may also contribute to higher measured PCDD/PCDF emissions for the treated wood tests.

CONCLUSIONS

This study was conducted to identify potential air emissions problems associated with the combustion of waste wood, primarily utility poles treated with pentachlorophenol preservative, as a fuel for energy production in a boiler. The emphasis of the study was placed on the characterization of the PIC emissions from combustion of pentachlorophenol-treated waste wood. The methodology used was a comparative test of emissions prior to the air pollution control device of a pilot-scale combustor burning untreated wood and wood treated with pentachlorophenol preservative as a fuel. The tests showed that combustion of pentachlorophenol-treated wood is an effective method of destroying the pentachlorophenol contained in the wood, with destruction efficiencies higher than 99.99 %.

Differences in VOC, SVOC, and PCDD/PCDF emissions from the combustion of untreated and treated wood fuels have been noted. The data do not enable identification of the exact cause of these differences in emissions. These differences are possibly caused by the significantly different moisture content, heating value, and chlorine content of the two fuels. The difference in flue gas flow rate required for the combustion of these two fuels with different combustion characteristics (moisture content and heating value) may also cause the differences in PCDD/PCDF emissions. These emissions are representative only of this facility and configuration and may not be quantitatively comparable to other combustors.

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Table 1. Fuel analysis.

Component (as-received basis)	Untreated Wood	Treated Wood
Moisture, %	33.44	21.46
Ash, %	0.25	0.57
Volatile Matter, %	57.92	66.28
Carbon, %	33.83	43.24
Fixed Carbon, %	8.39	11.69
Hydrogen, %	4.20	4.92
Nitrogen, %	0.28	0.28
Sulfur, %	0.01	0.05
Oxygen, %	27.99	29.48
Heating Value, Btu/lb	5569	7237
pentachlorophenol, ppm	6.7	4100
2,4 -dimethylphenol, ppm	2.4	3.6
Chlorine, %	0.02	0.20

Table 2. Combustor operating conditions.

Test	Average Fuel Feed Rate kg/hr (lb/hr)	Combustor Thermal Output MW (Million Btu/hr)	Flue Gas Flow dscm
Untreated 1	134.4(296.4)	0.48(1.65)	19.4
Untreated 2	117.1(258.1)	0.42(1.44)	16.6
Untreated 3	114.1(251.6)	0.41(1.40)	17.9
Treated 1	100.6(221.8)	0.47(1.61)	25.0
Treated 2	102.3(225.6)	0.48(1.63)	21.0
Treated 3	102.5(225.9)	0.48(1.63)	25.8

Table 3. Summary of flue gas temperature and CEM data.

Location	Temperature, deg C					
	Untreated Test 1	Untreated Test 2	Untreated Test 3	Treated Test 1	Treated Test 2	Treated Test 3
Stoker Exit	849	801	827	869	921	870
Sampling Port	152	153	153	155	160	160
Constituent	Concentration, %					
O_2	12.5	13.2	12.9	13.1	13.3	13.3
CO_2	7.5	7.2	7.1	6.7	6.5	6.5
H_2O	11.0	9.8	9.8	8.7	8.7	9.0
CO^a	203	249	456	66	21	20
NO^a	103	133	83	295	178	210
THC^a	77	56	2	4	3	3
HCl^a	<1	<1	<1	195	194	183
SO_2	10	11	13	<1	<1	<1

[a] in ppm @ 7% oxygen

Table 4. Destruction efficiency for pentachlorophenol.

Test	DRE, %
Treated Test 1	>99.9974
Treated Test 2	>99.9976
Treated Test 3	>99.9975

Table 5. VOC emission rates.

VOCs	Flue Gas Concentrations, g/dscm @ 7% O_2					
	Untreated Test 1	Untreated Test 2	Untreated Test 3	Treated Test 1	Treated Test 2	Treated Test 3
Chloromethane	53.3	28.5	16.9	55.8	96.7	51.5
1,3-Butadiene	0.6	0.2	1.2	0.1	0.1	0.1
Bromomethane	1.7	1.4	2.1	15.4	33.9	70.5
Iodomethane	0.8	2.4	5.7	1.7	5.1	24.1
Acetone	11.6	7.2	7.5	4.5	11.7	14.3
Chloroform	0.9	0.3	0.3	2.6	1.8	3.9
1,2-Dichloroethane	1.3	5.2	0.1	1.6	0.7	2.9
Benzene	25.4	16.2	27.9	2.1	2.6	3.0

Table 6. SVOC emission rates.

Test	Concentration, g/dscm @ 7% O_2
Untreated Test 1	10.1
Untreated Test 2	11.4
Untreated Test 3	11.7
Treated Test 1	7.0
Treated Test 2	7.7
Treated Test 3	5.9

Table 7. Total PCDD/PCDF emission rates.

Test	Emission Rate @ 7% O_2			
	Total PCDD ng/dscm	Total PCDF ng/dscm	Total PCDD/PCDF ng/dscm	Total PCDD/PCDF ng I-TEQ/dscm
Untreated Test 1	8.4	22.3	30.7	0.5
Untreated Test 2	2.6	17.2	19.8	0.2
Untreated Test 3	1.0	11.1	12.1	0.1
Treated Test 1	15.0	42.2	57.2	1.3
Treated Test 2	20.9	56.5	77.4	1.2
Treated Test 3	18.7	45.0	63.8	1.1

Table 8. Distribution of PCDD/PCDF in sampling train.

Test	% of PCDD I-TEQ in Front Half	% of PCDF I-TEQ in Front Half
Untreated Test 1	31.6	24.1
Untreated Test 2	53.0	40.1
Untreated Test 3	49.0	33.3
Treated Test 1	75.8	63.4
Treated Test 2	70.4	59.4
Treated Test 3	68.0	59.7

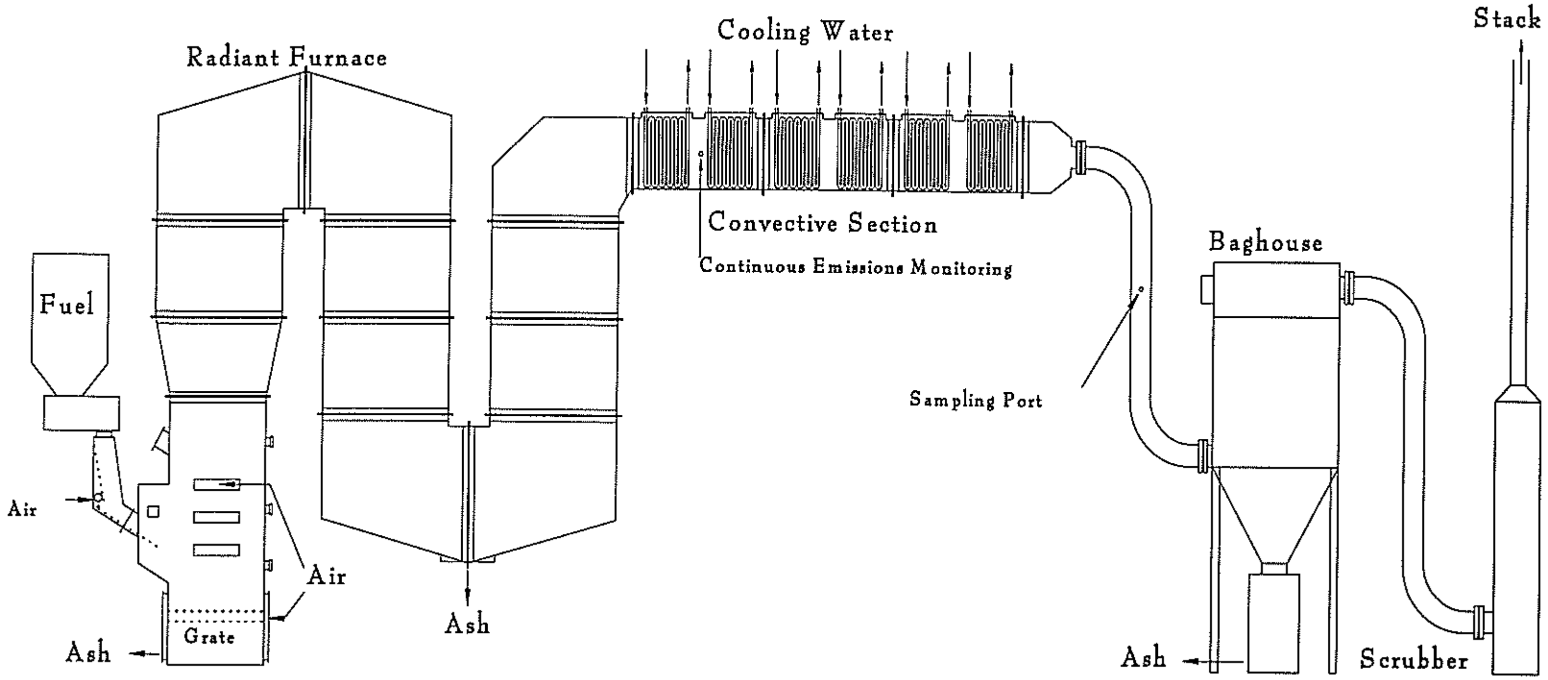

Figure 1. Schematic of the multifuel combustor.