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Used Agricultural Plastic Mulch as a Supplemental Boiler Fuel
- A Report on Combustion Test Results -
Part 2: Full Scientific Report

for the

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August 2002

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Used Agricultural Plastic Mulch as a Supplemental Boiler Fuel

Note: This report, Part 2, describes technical test methods and procedures in full detail, written for those interested in combustion principles or emissions testing and analysis. The abbreviated version, Part 1, is written for readers who may not have training or interest in science and engineering, yet want an overview of the combustion testing. Refer to Part 1: Streamlined Report.

EXECUTIVE SUMMARY OF COMBUSTION TEST RESULTS

A series of batch-scale stoker combustion tests were performed to evaluate the emissions of: 1) criteria pollutants, namely carbon monoxide, sulfur dioxide, and nitrogen oxides; 2) polycyclic aromatic hydrocarbons (PAHs); and 3) dioxin toxic equivalents (TEQ). For emissions reference purposes, baseline combustion tests were run burning coal alone. Additional testing entailed burning the baseline coal blended with plastic fuel nuggets made from discarded agricultural (watermelon) mulch films. Samples were obtained from growers in California, Pennsylvania, and Florida. The plastic nuggets comprised 5% and 10% of the thermal input of the fuel blend.

Regarding criteria pollutants, tests revealed that SO₂ and NO_x emissions using the nugget/coal blends were similar to those when coal alone was burned. CO emissions were very variable, which is a deficiency of batch-type tests.

Regarding PAH and dioxin TEQs, the addition of plastic nuggets to the fuel blend did result in elevated emissions for two of the three plastics used. The emissions from the California plastic tests were similar to those observed when firing only the baseline coal. Complex PAHs and dioxin TEQ emissions were elevated when firing the Pennsylvania and Florida plastics, with the Florida plastic tests exhibiting the highest level of PAHs/dioxin TEQ emissions. The emissions from the Florida plastic tests contained the greatest quantity of the more toxic compounds. Although opinions vary, agreement on two points is generally accepted as 'rules-of-thumb' within the combustion industry: PAH toxicity increases with molecular complexity, and PAH benzo(a)pyrene is considered to be only 20 times less toxic than 1 dioxin TEQ. The PAH concentrations in the Florida emissions should therefore be considered significant.

For future testing, steady-state operation in a large test unit or full-scale system would address the O₂/CO variability and would provide emissions data more comparable to an actual boiler. Pesticide residues on the mulches were not analyzed. The variability in dirt and pesticide contamination prevalent on most waste plastics could be better addressed through utilizing a fluidized bed combustion system rather than a stoker system. A fluidized bed combustion system can handle fuels that exhibit more variability and contain higher ash contents. It is recommended that future testing using plastic nuggets be performed using pilot-scale fluidized bed combustors, or if stoker boilers are to be considered further, a full-scale stoker boiler test should be performed to eliminate the deficiencies of batch-scale testing.

INTRODUCTION

Plasticulture has been an economic salvation for many fruit and vegetable growers worldwide. However, the disposal of these plastics has been difficult for the farmers to manage. Traditional on-farm disposal options such as open burning and on-farm dumping are becoming environmental liabilities. To compound the problem, recycling currently is not an economic disposal option for dirty plastics, while landfilling the plastic costs more than farmers are willing to pay.

The Pennsylvania State University has developed a process to densify all types of dirty plastics into fuel nuggets. The nugget process will redirect used agricultural plastics from on-farm burning and dumping sites into a new raw material stream for energy recovery when co-fired with coal in community and agricultural boilers. Although the fuel nugget production process works well, the combustion of the nuggets has remained untried until this series of laboratory-scale tests was conducted.

Samples of plastic mulch film (low density polyethylene, or LDPE) used in the production of watermelons were received from growers in three states: California, Pennsylvania, and Florida. Growers were asked to follow a specified sampling procedure after the 2001 harvest was complete, which included documentation of all pesticides applied to the watermelon crops and packaging the samples in self-mailer packages. Due to circumstances beyond our control, only one grower supplied the plastic in a timely fashion and listed the pesticides applied during the growing season. Due to insufficient history of usage data, pesticide residues were not analyzed in this investigation.

Research was conducted at Penn State's The Energy Institute using a traveling-grate stoker simulator. The simulator was selected because similar types of combustion units are prevalent in coal-fired community boilers and agricultural operations. Tests were performed firing 100% coal as well as blends of nuggets and coal, with plastics added to provide 5% and 10% of the energy content of the fuel. Three different plastics were tested. The flue gas from the stoker simulator was sampled and analyzed, per EPA test protocol, for CO₂, CO, SO₂, NO_x, O₂, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDD/Fs) emissions.

A total of 39 combustion tests were performed. The fuels used and the dates the tests were conducted are given in Table 1. The original test matrix consisted of 21 combustion tests – triplicate tests of the baseline coal, Florida 5%, Florida 10%, California 5%, California 10%, Pennsylvania 5%, and Pennsylvania 10%. However, additional tests were conducted for the following reasons:

- The fuel charge did not ignite properly during one test (see discussion on stoker simulator operation for description of test procedures)
- A leak was found in the line leading to the continuous emissions monitoring system (after several tests were already conducted)
- A malfunctioning CO₂ analyzer was identified
- Additional data was needed to determine repeatability
- The team wanted to ensure that there was no bias occurring during the testing.

These additional tests will be discussed in detail in the results section.

Table 1. List of fuels and dates tested.

Date	Fuel	Date	Fuel
Nov. 6, 2001	Baseline Coal Test #1	May 14, 2002	PA 5% Test #2
Nov. 8, 2001	Baseline Coal Test #2	May 15, 2002	PA 5% Test #3
Nov. 11, 2001	Baseline Coal Test #3	May 16, 2002	PA 10% Test #1
Nov. 28, 2001	Baseline Coal Test #4	May 17, 2002	PA 10% Test #2
Feb. 26, 2002	FL 5% Test #1	May 20, 2002	PA 10% Test #3
Feb. 28, 2002	FL 5% Test #2	June 3, 2002	Baseline Test #8
March 4, 2002	FL 5% Test #3	June 4, 2002	Baseline Test #9
March 5, 2002	FL 10% Test #1	June 4, 2002	Baseline Test #10
March 11, 2002	FL 10% Test #2	June 5, 2002	CA 5% Test #4
April 17, 2002	FL 10% Test #3	June 5, 2002	CA 5% Test #5
April 18, 2002	CA 5% Test #1	June 6, 2002	CA 5% Test #6
April 19, 2002	CA 5% Test #2	June 6, 2002	CA 10% Test #4
April 22, 2002	CA 5% Test #3	June 7, 2002	CA 10% Test #5
April 23, 2002	CA 10% Test #2	June 7, 2002	FL 5% Test #4
April 24, 2002	CA 10% Test #2	June 10, 2002	FL 5% Test #5
May 1, 2002	Baseline Test #5	June 10, 2002	FL 5% Test #6
May 3, 2002	Baseline Test #6	June 11, 2002	FL 10% Test #4
May 8, 2002	Baseline Test #7	June 11, 2002	FL 10% Test #5
May 9, 2002	CA 10% Test #3	June 12, 2002	FL 10% Test #6
May 13, 2002	PA 5% Test #1		

EXPERIMENTAL PROCEDURES AND METHODS USED

Plastic Nugget Maker

The process of making plastic fuel nuggets was developed for waste agricultural plastics, but will also work with plastics found in all sectors of society. Both film and rigid thermoplastics can be accommodated. The process uses a hydraulic cylinder to force plastic items through a heated extrusion die, thereby melting a thin layer of plastic which forms a jacket to seal in plastic pieces and any contaminants. As the extrudate exits the die, a heated cutoff knife melts the end portions to ensure that all pieces of plastic and debris remain encapsulated. The densified plastic cools and becomes a rigid nugget which can be safely stored and easily shipped.

All samples from the growers arrived wet, but were allowed to air dry for three hours prior to being made into fuel nuggets. The California lot included LDPE drip irrigation tubing which had become completely filled with mud, thus the mud became part of the nuggets. The Florida samples were covered with sand, thus the sand became part of the nuggets. Likewise, the Pennsylvania film was contaminated with clay and plant material, which became part of the nuggets. All nuggets were cut into approximately one gram-sized pieces to be of similar size to the coal particles used in the stoker simulator.

Stoker Simulator Test Unit

General Discussion of Coal Combustion on a Traveling Grate

Combustion of coal involves bringing air into contact with the fuel to completely convert all the carbon to CO_2 and hydrogen to H_2O within the residence time available in the combustion chamber. Although this appears to be a simple process, the practical aspects of achieving this objective are far from being simple. In stokers, a variety of physical, chemical and petrographic characteristics govern the combustion behavior. A schematic diagram of a section of a fuel bed on a traveling-grate stoker is shown in Figure 1. The raw fuel, which is usually graded in size, is fed onto the grate and exposed to the ignition source. The bed height usually varies from 4 and 4.5 inches. The primary source of ignition energy in a large stoker boiler is radiation from the arch and hot combustion chamber walls. Once the top layer of fuel has ignited, heat is transferred to lower layers by radiation and convection, which initiates further combustion. In Penn State's stoker simulator, the ignition source is electrically-heated silicon carbide rods as will be described in the next section.

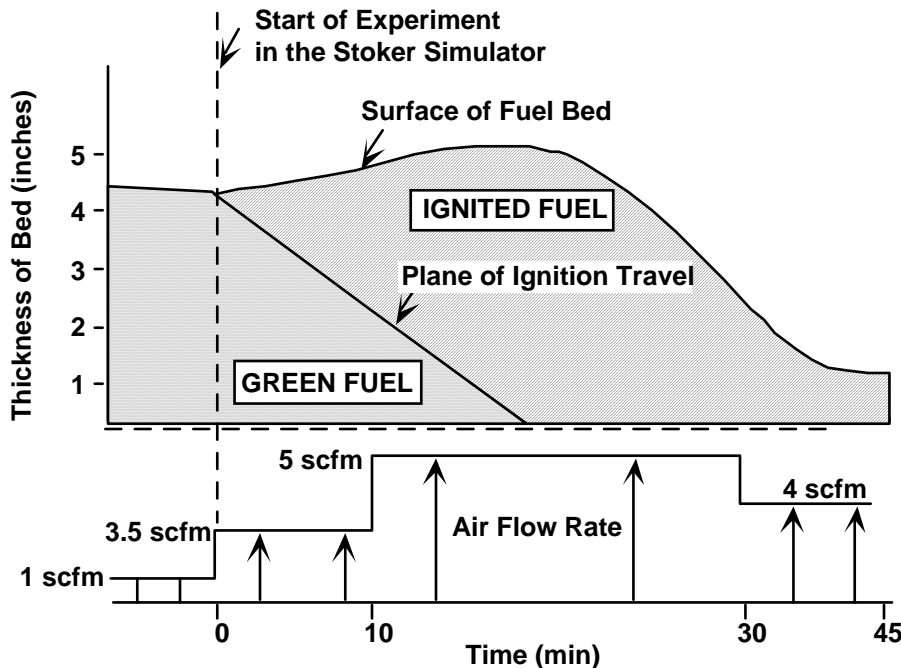


Figure 1. Combustion of fuel in a traveling grate stoker -- section of a fuel bed with time.

Combustion of coal on a traveling grate can be divided into three zones:

- 1) Ignition zone -- where ignition occurs initially at the top of the bed and the bed height remains constant. In this zone, the fuel devolatilizes and the volatiles burn above the ignition plane. The plane of ignition travels slowly downwards to the grate;
- 2) Combustion zone -- where the semi-coke formed after ignition and devolatilization is burned. The semi-coke may swell and resist the flow of air, resulting in an increase in the pressure drop across the fuel bed. The development of plasticity increases the pressure drop, which measures the resistance to the flow of air. Various properties such as the rank of coal, particle size, operating pressure and petrographic characteristics determine thermoplastic behavior. As the ignition proceeds to the grate (with most of the bed being in the burning stage) the air requirement for combustion increases; and
- 3) Burn-off zone -- where the surface of the semi-coke or coke bed recedes as burning continues, leaving residual ash and clinkers containing some combustibles. The combustion air requirement in this zone is minimal.

Design and Operating Procedure of the Bench-Scale Stoker Simulator

A stoker simulator, which simulates a section of a traveling grate was used for the testing in this project. Test time is used to replace the distance the grate has traveled with respect to changes in air requirement, bed density, bed height, and residence time.

A schematic diagram of the apparatus is given in Figure 2. The chamber is constructed from a 14 inch steel pipe with 1.25 inches of concentric, castable HYDRECON 3000 refractory material to withstand 3,000°F, and 3.5 inches of concentric

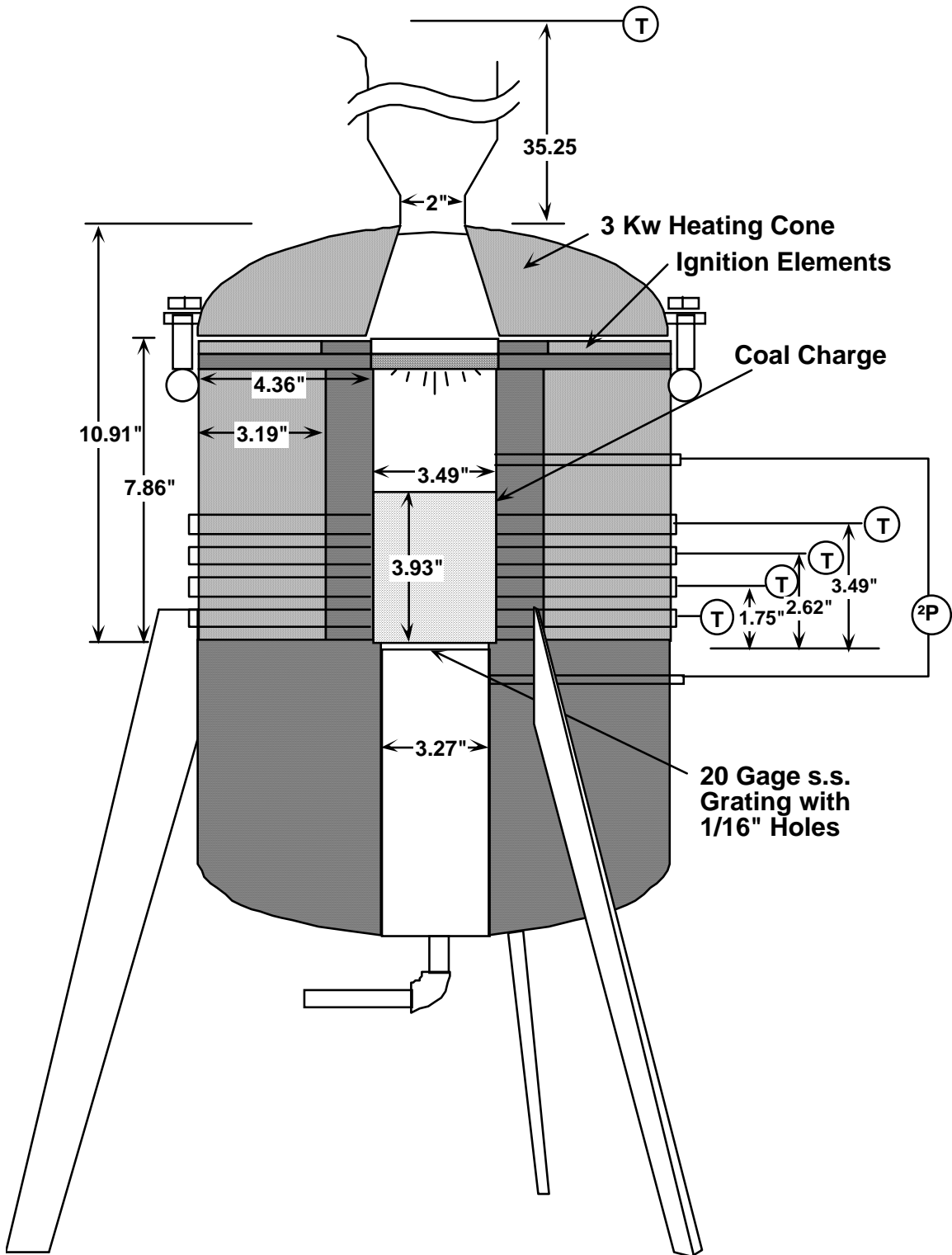


Figure 2. Schematic diagram of the modified stoker simulator.

annular insulation (light weight, high alumina) to minimize heat loss. The coal charge is typically around 800g (1.76 lbs), which corresponds to a bed depth of about 4.5 inches. The weight of the coal charge corresponds to the mid range area firing density of large-scale utility stokers (8-50 lbs/ft²). The area firing density ($J_{f,A}$) was calculated as follows:

$$J_{f,A} = \frac{m_f}{A_c}$$

where, m_f is the fuel charge (lb) and A_c is the grate area (ft²). The area firing density in the stoker simulator typically varies from 16.7 to 23.4 lb/ft². The area combustion density, I_A , is a more common means of specifying grate heat release rate. Depending on coal type, grate design, and method of operation, the area combustion density ranges from 1×10^5 to 6×10^5 Btu/ft² h, when calculated as follows:

$$I_A = \frac{M_f h_f}{A_c t}$$

where I_A is the area firing intensity (Btu/ft² h), m_f is the fuel charge (lb), h_f is the higher heating value of the fuel (Btu/lb), A_c is the grate area (ft²), and t is the residence time or duration of the test (h). A test duration of 45 minutes is used, simulating the bed residence time in a utility traveling-grate stoker. The calculated coal firing density in the stoker simulation typically varies from 200,000 to 260,000 (Btu/ft² h). This is clearly in the mid range of typical stoker area combustion densities.

Combustion air to the stoker simulator is supplied at the bottom of the chamber through a distributor plate and is controlled with a rotameter. The air flow rate is varied during a test to simulate the variable air flow rate in an operating stoker boiler. During each of the 45 minute tests, the air flow rate for the first 10 minutes is set at 3.5 standard cubic feet per minute (scfm), then changed to 5 (scfm) for the next 20 minutes and then lowered to 4 (scfm) for the last 15 minutes. The variation of air flow rate with time is shown in Figure 3. During the peak combustion period at an air flow rate of 5 (scfm), the cold air velocity through the grate is approximately 1 ft/s. Although this velocity is lower than the conventional velocity of 1.2 to 1.5 ft/s, it is consistent with the trend of reducing the combustion air flow rate through the grate and increasing the overfire air flow rate to minimize pollutant emissions.

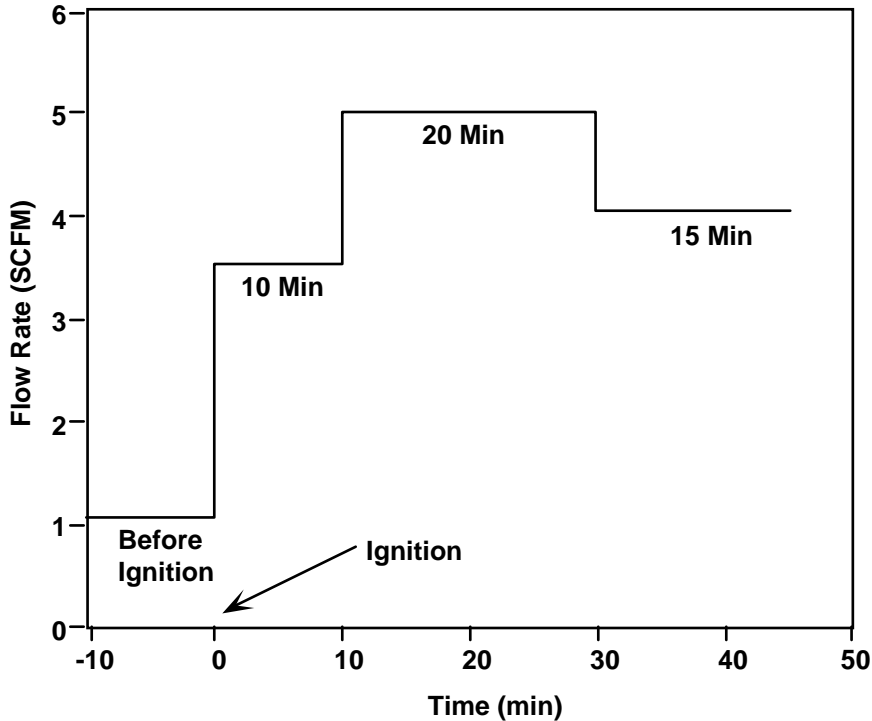


Figure 3. Variation in air flow rate with time in the stoker simulator.

Four sampling ports (3/8" diameter) are installed radially at 90° angles to each other at one-inch intervals (axially) above the grate. The ports protrude into the coal bed to allow for the measurement of either gas concentration or radial temperature profile. Type S thermocouples are installed in the reactor, four in the coal bed and one at 14 inches above the top of the coal bed to measure the axial temperature profile and the exhaust flue gas temperature, respectively. The pressure drop across the bed is measured using a differential pressure transducer to monitor the physical state of the fuel bed during combustion.

A gas sampling port is installed at the simulator outlet to extract flue gas for collection and measurement. A tee was installed for this project and a portion of the flue gas was extracted through an EPA sampling train (described in the next section) while a portion was extracted to a continuous emissions monitoring system (CEM).

A computer was used to collect the temperatures, the gas concentrations, and the pressure drop across the bed. The thermocouple signals were sent to a EXP-16A multiplexer with a gain setting of 200. The gas analyzers, with the exception of the Teledyne Max 5, had output signals of zero to five volts dc, which were collected in a separate EXP-16A multiplexer, with a gain of 1. The signals (except that from the Max 5) were then relayed to a DAS8 board in an IBM compatible Gateway computer and processed through a Viewdac software package. The Viewdac display was updated every second and data were recorded from each signal every ten seconds.

Continuous Emissions Monitoring Sampling Procedures

The flue gas analyzers used during the testing included: Beckman Oxygen Analyzer, model 755; Beckman Carbon Dioxide Analyzer, model 864 infrared; Thermo Electron Pulsed Fluorescent SO₂ Analyzer, series 40; and Thermo Electron Chemiluminescent NO-NO₂-NO_x Analyzer. The analyzers were used per the following EPA Methods:

Method 3A	Determination of Oxygen and Carbon Dioxide Concentration in Emissions from Stationary Sources (Instrumental Analyzer Procedure);
Method 6C	Determination of Sulfur Dioxide Emissions from Stationary Sources (Instrumental Analyzer Procedure);
Method 7E	Determination of Nitrogen Oxide Emissions from Stationary Sources (Instrumental Analyzer Procedure);
Method 10	Determination of Carbon Monoxide Emissions from Stationary Sources.

Polycyclic Aromatic Hydrocarbons (PAHs) and Polychlorinated dibenzodioxin and Polychlorinated dibenzofuran (PCDD/Fs) Emissions Testing

The Clean Air Act Amendment (CAAA) of 1990 contains provisions that will set standards for the allowable emissions of 190 species designated as hazardous air pollutants (HAPS). Many of these HAPS could be emitted from coal-fired electric generating facilities. The Energy Institute has developed expertise in the collection and analysis of some of these HAPS. Of these HAPs, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDD/Fs) were collected and measured in this project. The techniques used in sample collection and analysis are discussed in the following sections.

Determination of PAH and PCDD/F Concentrations in a Flue Gas Stream

A majority of the 190 species listed in the CAAA including PAHs and PCDD/Fs can be collected by what is generically termed a Modified Method 5 (MM5) sampling train. The train is used to isokinetically collect samples at desired locations in flue gas streams. The collected flue gas stream sample can be separated into solid, condensed liquid and gaseous phases. The analytes of interest are extracted from the collected sample, concentrated, then separated and quantified by Gas Chromatography/Mass Spectrometry (GC/MS) and enzyme immunoassay (EIA) techniques.

Analysis and Toxicity of Dioxins and Furans

There are 75 polychlorinated dibenzodioxin (PCDD) and 135 polychlorinated dibenzofuran (PCDF) congeners. Of these, 17 are considered to be toxic. Based on a variety of toxicity tests, the EPA has assigned Toxic Equivalency Factors (TEFs) of 1.0 to 0.0001 (relative to 2,3,7,8-tetrachlorodibenzo-p-dioxin) to these 17 compounds. In any given sample, the concentrations of each of these compounds can be determined, and,

when their individual TEFs are factored in, the total Toxic Equivalency (TEQ) of a sample can be determined. This TEQ is generally considered the data most revealing about a sample's dioxin-like toxicity.

Method 23 requires use of a High-Resolution GC/MS (HRGCMS) for determination of dioxin and furan concentrations. This equipment is quite expensive and not available at The Energy Institute, and analyses performed at commercial laboratories are also quite expensive. TEQ determinations can be made using other methods. The method selected by The Energy Institute is High Performance Enzyme Immunoassay (EIA) colorimetric analysis.

Using EIA, a cleaned, extracted sample containing PCDDs and/or PCDFs is added to test tubes coated with a known amount of anti-dioxin antibody EIA. PCDD/Fs are specifically bound to the antibody in proportion to their TEF. A competitor Horseradish Peroxidase (HRP) conjugate is added, binding to the remaining active sites on the antibody. The amount of conjugate bound by the antibody is inversely proportional to the amount PCDD/Fs present. Color development is inversely proportional to the amount of PCDD/Fs present. Color development is accomplished by adding a solution of chromogenic HRP substrate in hydrogen peroxide. Optical density of the developed color is determined with a spectrophotometer. A series of standards with known TEQ values and optical densities are analyzed, a calibration curve developed, and the TEQ of a sample is calculated.

Methodologies for PAH and Dioxin TEQs

A single 25,500 Btu (British thermal unit) charge of either coal or a coal/plastic nugget blend was placed into the stoker simulator. The fuel was ignited and gas samples containing entrained particulate matter were collected from the stack. Temperature, pressure, and flue gas concentrations were recorded. Samples removed from the stack were analyzed for PAHs and PCDD/Fs. The following EPA test methods were used in collecting and analyzing the samples generated from the stoker simulator for PAHs and dioxin TEQs:

- EPA Method 1A - Sample and Velocity Traverses for Stationary Sources with Small Stacks or Ducts;
- EPA Method 4 – Determination of Moisture Content in Stack Gases;
- EPA Method 23 – Determination of Polychlorinated Dibenzo(p)dioxins and Polychlorinated Dibenzofurans From Stationary Sources;
- EPA Method 3510C – Separatory Funnel Liquid/Liquid Extraction;
- EPA Method 3540C – Soxhlet Extraction;
- EPA Method 3630C – Silica Gel Cleanup;
- EPA Method 8270C – Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); and
- Cape Technologies Method IN-DF1 - High Performance Dioxin/Furan Immunoassay Analysis of PCDD/Fs in Prepared Sample Extracts.

Presampling Considerations

Prior to sampling, the stack of the stoker simulator was modified to accept the MM5 sampling train. A modular sampling train meeting all of the requirements of EPA Methods 5 and 0010 was used. EPA Methods 1, 3 and 4 were utilized to determine various parameters needed for sampling. EPA Method 5 was used to collect the samples. Extraction of PAHs from the collected particulate matter and the XAD-4 polymeric resin fractions was accomplished by using EPA Method 3540-C. Extraction of PAHs from liquid samples was accomplished using EPA Method 3510-C. Sample cleanup was accomplished by using EPA Method 3630-C. EPA Method 8270-C was selected as the analytical method for determining the concentrations of PAHs in the collected samples. Determination of dioxin TEQs in collected particulate matter and condensed vapor fractions was accomplished using portions of the above methods and Pace Technologies Method IN-DF1. All ancillary materials necessary to perform these methods were purchased prior to sampling.

The EPA Method 5 Sampling Train

The EPA Method 5 sampling train is designed to isokinetically sample a flue gas stream. A portion of the gas stream is withdrawn from the duct through a heated probe where the particulate matter is filtered out of the stream. The remaining portion of the gas stream is passed through a condenser, a module containing the polymeric resin, and a series of glass impingers immersed in ice water where the remaining condensable species are collected.

Specifically, the sampling train contains the following components, listed from the most upstream component to the most downstream component.

A buttonhook borosilicate glass nozzle is located at the end of a sampling probe. The nozzle opening is placed into the flue gas stream facing upstream with pitch and yaw angles of 0°. The inside diameter of the nozzle is precisely known, as its size affects the sampling rate.

The nozzle is connected to a probe of borosilicate glass. The probe is long enough to completely traverse the duct or stack of interest. The probe is encased in a stainless steel heated jacket. While sampling, the probe is maintained at 250°F by a temperature controller. The nozzle is connected to the probe by a Teflon® union.

The probe is connected to a glass filter assembly located within a heated oven. The filter assembly is also maintained at 250°F. A filtering media was selected to retain particles larger than 0.2 µm.

Gases exiting the filter assembly are passed through a water-cooled glass condenser to condense PAHs and PCDD/Fs that may be in the vapor phase to the liquid phase. This condensate and remaining gas phase components are passed over the water-cooled porous polymeric resin contained in a glass module.

Gases and condensed liquids exit the glass resin module into a chilled condensate knockout trap. This trap is similar in design to an empty impinger. Many PAH species not retained on the resin are collected in this knockout impinger.

Next, three downstream chilled impingers are used to collect additional water condensate. The final impinger contains indicating-type silica gel to protect the pump

from unwanted moisture. The temperature of the gas stream exiting this final impinger is maintained at or below 68°F. All glass ball-and-socket connections are clamped and made airtight with Teflon® O-rings.

The gases are passed through an airtight pump, dry gas meter, across a manometer, (gas samples may be collected at this point if desired,) and released through a vent. These devices, along with thermocouple readouts, temperature controllers, manometers, valves, timer and other equipment are contained in a metering console.

Operation of the MM5 Sampling Train

Prior to sampling, data sheets were prepared, stack access ports were cleaned, and leak checks were performed on the sampling system. The train was operated for a twenty minute segment of the combustion test. Leak checks were also performed at the conclusion of the sampling runs. Appropriate EPA sampling methodologies were followed to the extent possible.

Sample Recovery and Preparation for Analysis

The collected sample can be separated into six (or more) fractions. The sub-samples contain materials collected from these particular sections of the sampling train. Typically, the first sub-sample contains recovered materials from the nozzle to the filter assembly. The second sub-sample contains the filtering media, filtered solids, and other solids removed from the filter assembly. The third sub-sample contains recovered materials from the back half of the filter paper assembly and the condenser. The fourth sub-sample contains recovered materials from the resin module. The fifth sub-sample contains recovered materials from the condensate knockout trap. The sixth and final sub-sample contains recovered materials from silica gel-filled impinger. These six sub-samples can be processed and analyzed separately or combined in any manner and analyzed. Ultimately, the analyst combined five of the six sub-samples into two lab samples in the following manner.

The first of the two lab samples was generated using the following procedure. The recovered particulate matter from the front half rinse, recovered particulate matter from the filter and the filter itself were spiked with a known amount of a PAH surrogate (but not a PCDD/F surrogate) spiking solution and transferred into a glass Soxhlet extraction thimble. (The surrogate compounds are compounds chemically similar to the analytes of interest, but not expected to be contained in the extract. The surrogate compounds were utilized to monitor unusual matrix effects or sample processing errors during the extraction and recovery process.) The glass thimble was placed into a Soxhlet extractor and connected to a round bottom flask containing a clean Teflon® boiling chip. The remaining front half rinse was quantitatively transferred to a separatory funnel, and serially extracted three times with toluene, cleaned up, and transferred to the extractor. Additional toluene was added to maintain an appropriate fluid level for continuous extraction cycling. A bulb type condenser was connected atop the extractor. A heating mantle was placed under the flask and adjusted to cycle the extractor about once every thirty minutes or less for a total of approximately 18 hours. After digestion, the sample was divided for separate PAH and dioxin TEQ determinations.

For the PAH split, a Kuderna-Danish (K-D) concentrator was assembled by attaching a 10 ml concentrator tube with Teflon[®] boiling chips to a 500 ml evaporation flask. The extract was passed through a sodium sulfate filter to remove any residual water and transferred into the concentrator. A pre-wetted three-ball macro Snyder column was placed atop the concentrator. The concentrator assembly was placed into a hot water/antifreeze bath and concentrated to 6-8 ml within 30 minutes. The apparatus was allowed to cool. The three-ball macro column and evaporation flask were removed and replaced with a two-ball micro Snyder column and the extraction was further concentrated to approximately 4ml. The extract was then quantitatively transferred to a vial, and blown down to dryness under a dry nitrogen stream. The sample was reconstituted to 1ml and stored at or below 4°C until analyzed by GC/MS.

For the dioxin TEQ split, a Kuderna-Danish (K-D) concentrator was assembled by attaching a 10 ml concentrator tube with Teflon[®] boiling chips to a 500 ml evaporation flask. A pre-wetted three-ball macro Snyder column was placed atop the concentrator. The concentrator assembly was placed into a hot water/antifreeze bath and concentrated to 6-8 ml within 30 minutes. The apparatus was allowed to cool. The three-ball macro column and evaporation flask were removed and replaced with a two-ball micro Snyder column and the extraction was further concentrated to approximately 4ml. The sample was blown down to dryness under nitrogen. A 20 x 230 mm glass column was obtained and a cleanup column was prepared by sequentially adding 1g of silica gel, 2 g of sodium hydroxide impregnated silica gel, 1g of silica gel, 4 g of acid-washed silica gel, and 1 g of silica gel. The column was pretreated with 30ml of hexane. The sample was reconstituted in 5ml of hexane. The sample was quantitatively transferred to the column and eluted with 100ml of hexane. The eluate was blown down with nitrogen to 1ml. The cleaned-up extract was then quantitatively transferred to a vial, and blown down to dryness under a dry nitrogen stream. This extract was transferred to another column packed with 12 g of alumina. 120 ml of a 0.5% dichloromethane in hexane solution was passed through the column and discarded. 120 ml of a 35% dichloromethane in hexane solution was added to the column. This eluate was blown down to 0.5 ml using nitrogen. A 2 x 2.5cm AX-21 Carbon/Celite 545 column was prepared. It was sequentially pre-washed with 2 ml 50% benzene in ethyl acetate solution, 1 ml 50% dichloromethane in cyclohexane solution, and 2ml of hexane. The extract was quantitatively transferred to the column. To the column was sequentially added 1ml of hexane, 2 ml of a 50% dichloromethane in hexane solution, and 2 ml of a 50% benzene in ethyl acetate solution. The eluates were discarded and the column was inverted. Thirteen (13) ml of toluene was added to the column. The sample was blown down to approximately 200 µl under nitrogen. The extract was solvent exchanged by adding 150 µl of an 80% methanol and 20% TEG Triton X-100 solution (MeOH/TEG or keeper). The extract was blown down again under nitrogen. 2 ml of dichloromethane was added to the extract then evaporated. The sample was reconstituted to 15 µl with methanol and stored at or below 4°C in darkness until analyzed.

The second lab sample was generated using the following procedure:

- 1) The condensate and condensate rinse samples were combined and transferred to a separatory funnel, PAH spiked, and serially extracted with toluene exactly as was done with the front half rinse.

- 2) The porous polymeric resin was transferred to a glass extraction thimble, PAH spiked and processed identically as the particulate matter sample. The condensate and resin extracts were combined, residual water removed, and then concentrated, cleaned and analyzed as described above.
- 3) Blank samples were extracted concurrently with the collected samples.
- 4) All lab PAH samples were spiked with internal standards just prior to analysis.

Gas Chromatography/Mass Spectrometry System Evaluation

A Gas Chromatograph/Mass Spectrometer (GC/MS) system was used for extract analysis. The system was temperature programmable and had a splitless injection option. A fused-silica capillary column capable of PAH separation was used. Other GC/MS equipment met specifications for the GC/MS system including GC/MS interface, data acquisition system and other ancillary equipment as described in EPA Method 8270.

The GC/MS system was properly hardware-tuned. Background subtraction techniques designed to eliminate column bleed or instrument background ions were available but not utilized as they were not necessary. GC column performance was evaluated and injection port inertness was confirmed. Calibration standards were analyzed and their response factors were calculated and evaluated. A system check using approved system performance check compounds was performed and the results evaluated. The percent relative standard deviations of the compounds were calculated. The linearity of the calibration curve was determined. When system tuning, calibration check, performance check, and internal standard response data met minimum method requirements, analysis of the lab samples began. An external calibration curve was generated as a check against the internal calibration.

GC Screening Analysis

Prior to GC/MS analysis, 1 μ l aliquots of the samples were analyzed on a Perkin Elmer 8500 GC system. The system was equipped with a J&W Scientific DB-5 capillary column. This screening procedure checked the concentrations of the analytes of interest and determined if dilution or further concentration of the samples was necessary.

GC/MS Analysis

A Hewlett Packard (HP) Model 5890 Series II Gas Chromatograph was used for specie separation. The system was equipped with a 30 m x 0.25 mm ID 1 μ m film thickness silicone-coated fused-silica capillary column; a J&W Scientific DB-5 capillary column. The GC temperature program held the initial temperature at 40°C for 5 minutes to remove the solvent. The temperature was ramped to 280°C at a rate of 6°C per minute and held there for 18 minutes. The helium carrier gas flow rate was 30 ml/min. This flow rate is lower than that recommended by Method 8270C, causing the analytes of interest to elute at a later time than published, but this did not present a problem for either identification or quantification. After the system parameters were set, a spiked 1 μ l aliquot of concentrated extract was injected (splitless) into the GC/MS system. An HP

5971A mass selective detector was interfaced with the GC scanning up to 500 amu per second at 70 volts. The qualitative identifications of compounds determined by this method are based on retention time in the GC and on comparison of the sample's mass spectrum with characteristic ions in a reference mass spectrum. The reference library used was the NBS49K library. Compound identification was not hampered by component coelution, that is, all species of interest were sufficiently separated chromatographically. When a compound had been identified, the determination of specie concentration was based on the integrated abundance from the Extracted Ion Current Profile (EICP) of the specie's primary characteristic ion.

Calibration of the Spectrophotometer for Dioxin TEQ Determinations

A Milton Roy Spectronic® 401 spectrophotometer was used in the dioxin TEQ determinations. Instrument setup was performed according to the manufacturer's recommendations. Dioxin TEQ calibration standards, purchased from Wellington Laboratories, were obtained in five different appropriate concentrations. A dioxin TEQ concentration vs. absorption calibration curve was generated according to Beer's Law. Dioxin TEQ values for the unknown samples were determined. (HRP Substrate colorimetric optical densities are measured at 450 nm.)

Test tubes lined with known amounts of the anti-dioxin antibody were pre-rinsed and 500 µl of reagent grade water was added to each tube. A 50 µl aliquot of each sample or standard was added to individual EIA tubes. The samples were allowed to incubate for 20-24 hours. The contents of the tubes were discarded. Each tube was rinsed four times with a 100 ppm Triton X-100 solution (in water). A 500 µl aliquot of a Competitor-HRP conjugate was added to each tube. After 15 minutes the conjugate was removed and the tubes were rinsed 4 times with reagent grade water. A 500 µl aliquot of HRP substrate was delivered to each tube. After 30 minutes, a 500 µl aliquot of 1N hydrochloric acid was added to each tube. The optical density of the standards and samples was determined with the spectrophotometer adjusted to 450 nm.

Notable Departures From EPA Standard Methods

Dioxin TEQ was determined for all samples instead of individual congener concentrations. Individual concentrations of dioxin and furan congeners cannot be determined by the EIA method.

EPA methods for the isokinetic sampling of stationary sources require steady state conditions in the stack. The stoker simulator used is a single-charge unit. Steady state conditions do not exist in the stack during the test. Since the requirements of EPA Method 2 cannot be achieved during combustion, representative (isokinetic) flue gas samples within EPA limits of 90-110% cannot be collected from this unit. Data generated from the collected entrained particulate matter may therefore exhibit either a positive or negative bias.

Method 23, Section 4.2.5, directs the analyst to discard the water in the first impinger. However, this sub-sample may contain PAHs. This sample was collected, analytes of interest for PAH analysis were liquid/liquid solvent exchanged into toluene, and Soxhlet extracted with the XAD-4 resin and condensed vapor samples.

Method 23, Section 5.3, describes High Resolution Gas Chromatography/Mass Spectrometry (HRGCMS) analysis but was not followed. Dioxin TEQ analysis by the EIA method was substituted for the HRGCMS method.

Neither Method 23 nor Method 8270C recommend dividing a collected sample into multiple fractions, as the repeatability of these techniques at the 95% confidence interval are quite large.

Fuel Composition and Combustion Efficiency

Proximate and ultimate analyses and heating value were determined for the coal and plastic samples. The carbon, hydrogen and nitrogen contents of the coal and plastic samples were determined using a Leco CHN-600 elemental analyzer. Total sulfur was determined using a Leco SC-132 sulfur determinator. Heating value of the coals and plastics was determined in a Parr 1241 adiabatic oxygen bomb calorimeter.

The ash tracer technique was used to calculate the combustion efficiencies (carbon burnouts) reported in this study. The percentage burnout was calculated using the following formula:

$$\text{Burnout (\%)} = \left[1 - \frac{A_c(100 - A_r)}{A_r(100 - A_c)} \right] \times 100$$

where:

A_c = wt percent ash of the coal

A_r = wt percent ash of the residue

COMBUSTION AND EMISSIONS TEST RESULTS

Fuel Composition

The composition of the fuels is given in Table 2. The coal used for the testing was a high volatile A coal from the Middle Kittanning seam in Pennsylvania.

Compositionally, there was much variation among the plastics. This appears to be due to the level of inorganic contaminants (i.e., ash level) in the plastic samples, which ranges from ≈ 14 to 48 wt.%.

The chlorine content of the plastics was greater than that measured in the coal. The chlorine content of the coal was 1,538 ppm as compared to $\approx 2,500$ to 2,800 ppm in the plastics.

Table 2. Fuel composition.

Sample	Parent Coal	California Plastic	Pennsylvania Plastic	Florida Plastic
Proximate Analysis, wt.% (dry basis)				
Moisture	2.0	1.1	0.6	8.0
Volatile Matter	30.6	67.6	85.9	51.6
Fixed Carbon	64.3	2.1	0.5	0.1
Ash	5.1	30.3	13.6	48.3
Ultimate Analysis, wt.% (dry basis)				
Carbon	80.4	55.1	67.2	43.6
Hydrogen	4.8	9.4	11.2	6.6
Nitrogen	1.4	0.3	0.1	0.4
Sulfur	0.7	0.1	0.0	0.2
Oxygen	7.6	4.8	7.9	0.90
Ash	5.1	30.3	13.6	48.3
Chlorine (ppm)	1,538	2,513	2,523	2,775
Higher Heating Value, Btu/lb	13,904	13,011	15,813	11,641

Final Test Matrix

The final test matrix contained several more tests than originally proposed, i.e., 39 versus 21. Additional tests were performed because:

- One baseline test did not ignite properly;
- A leak was found in the sampling line leading to the continuous emissions monitoring system after several tests were already performed;
- The CO₂ analyzer malfunctioned during a test;
- To obtain additional data to determine repeatability; and
- To obtain additional data to ensure that there was no bias occurring during the testing.

It must be noted that the leak in the sampling line and the malfunctioning CO₂ analyzer affected only the readings from the CEM (i.e., O₂, CO₂, CO, NO_x, and SO₂) and did not affect the HAPs and PCDD/Fs (Dioxin TEQ) emissions results as the flue gases were collected separately for the CEM and HAPs/dioxin TEQ sampling system. Therefore, earlier tests contained accurate HAPs/dioxin TEQ emissions data and inaccurate CEM data. Consequently, additional tests were performed to obtain accurate CEM data. During these latter tests, only CEM data was collected. This is important to note when reviewing the results in the following sections as some of the CEM and HAPs/dioxin TEQ emissions comparisons use different tests for the same fuel types. In summary (and referencing Table 1):

- Baseline tests #1 through #4, the HAPs/dioxin TEQ results are accurate but the CEM data is not. However, baseline test #2 was not used as the bed did not ignite properly.
- Florida 5% tests #1 through #3, Florida 10% tests #1 through #3, California 5% tests #1 through #3, and California 10% tests #1 and 2 – the HAPs/dioxin TEQ results are accurate but the CEM data is not;
- The sampling line leak was identified and repaired after the California 10% test #2;
- Additional baseline tests were then conducted, baseline tests #5 through #7. The CO₂ analyzer malfunctioned during baseline test #5 and was repaired prior to conducting tests #6 and 7. Both CEM and HAPs/dioxin TEQ results are good for tests #6 and 7.
- California 10% test #3, Pennsylvania 5% tests #1 through #3, and Pennsylvania 10% tests #1 through #3 – both CEM and HAPs/dioxin TEQ results are good but Pennsylvania 10% #3 is not used in the comparisons because the combustion efficiency was very poor compared to the other tests;
- Additional baseline tests were then conducted, baseline tests #8 through #10, to obtain additional CEM data; and
- The following tests were performed to obtain CEM data – California 5% tests #4 through #6, California 10% tests #4 and 5, Florida 5% tests #4 through #6, and Florida 10% tests #4 through #6.

Examples of Data Collected During Each Test Using the Data Acquisition System

Data that was collected during each test using the on-line data acquisition system included flue gas composition (i.e., O₂, CO₂, CO, NO_x, and SO₂), four bed temperatures (see Figure 2), and pressure drop across the bed. Upon completion of each test, these data were plotted, averaged, and tabulated. Examples of the graphs produced are contained in this section while the tabulated data is presented in the following sections as part of the discussion of the results. All of the graphs are not presented in the final report due to the large number of them and the desire to keep the final report brief; however, all data and graphs are in Excel spreadsheets and graphs and can be made available upon request.

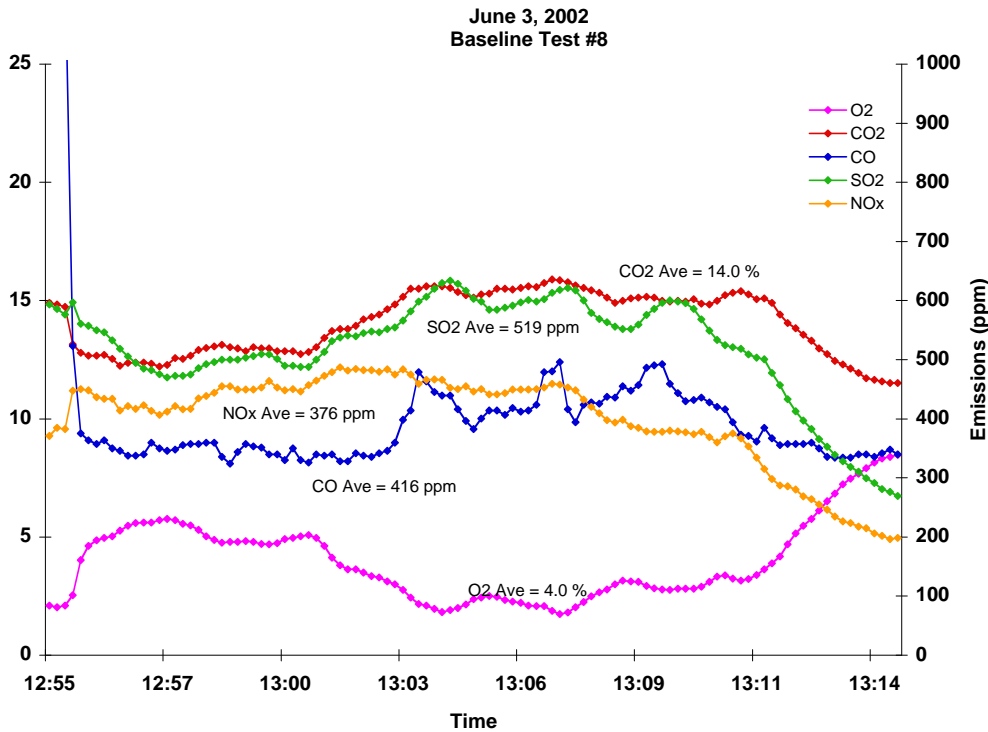


Figure 4. Emissions data from baseline test #8.

Figure 4 is an example of the emissions data from baseline test #8. The data are plotted over the 20-minute period where the maximum air flow was introduced (see Figure 3) as this was the period when sampling was also conducted for the HAPs/dioxin TEQ. Figures 5 and 6 are the corresponding bed temperature and pressure drop curves, respectively, for the same test. These graphs are plotted over a 30-minute period starting from the point of ignition (defined as thermocouple 1 reaching 500°F). The first 10 minutes of these graphs correspond to the first ten minutes of the test which were conducted with an air flow rate of 3.5 scfm while the last 20 minutes are correspond to the test period performed using 5 scfm of air. This explains the sharp increase in the bed pressure drop at 10 minutes (Figure 6). The temperature curves shown in Figure 5 are typical of most tests.

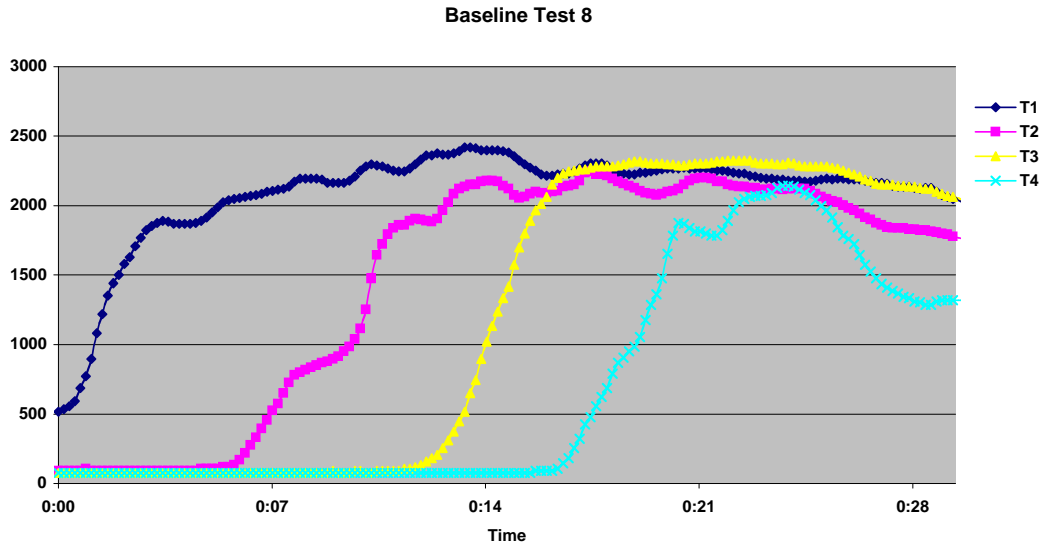


Figure 5. Bed temperature profile during baseline test #8.

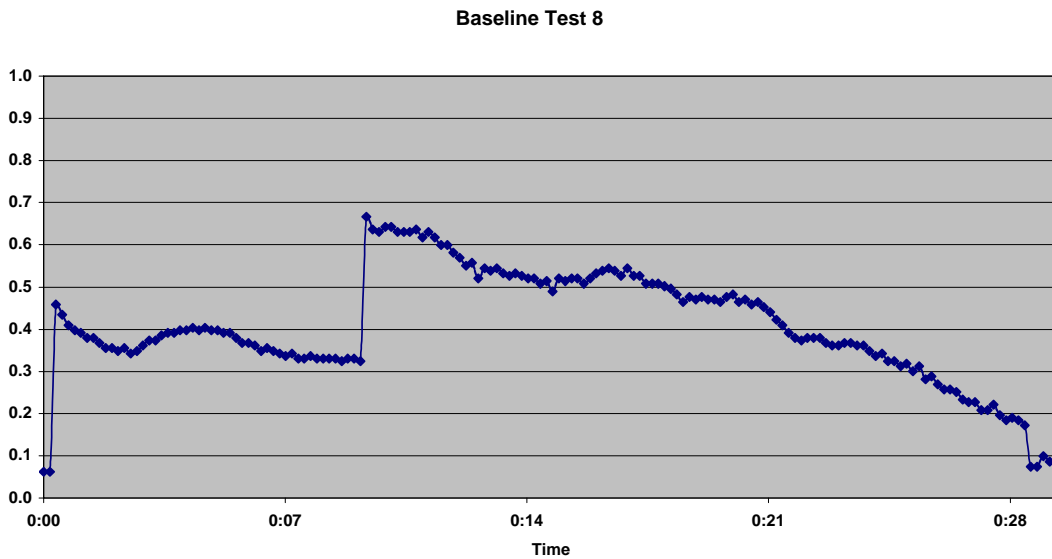


Figure 6. Pressure drop during baseline test #8.

There is much variability experienced when performing tests in a batch mode. This is illustrated in Figure 7, which is an emissions plot for baseline test #9. Note that there are periods where the O₂ level was very low and, consequently, the CO levels became very high. This type of behavior was experienced during some of the tests and involved both the baseline coals and the coal/nugget blends. This is one shortcoming of the batch-type tests. In a normal boiler operation, the oxygen content is monitored and the air flow rate is adjusted to maintain approximately 4% O₂ in the flue gas. This O₂ level was observed in Figure 4 but a lower level is observed in Figure 7 even though the air flow rate to the simulator was introduced at identical rates. The procedure to vary the air flow rate was strictly maintained to ensure uniformity between tests, especially

because of the PAH/dioxin TEQ sampling. There are several reason for the non-uniform O₂ concentrations observed between tests, which can be caused by varying combustion efficiencies, clinkering in the bed, and, in the case of coal/nugget blends, possibly different combustion profiles.

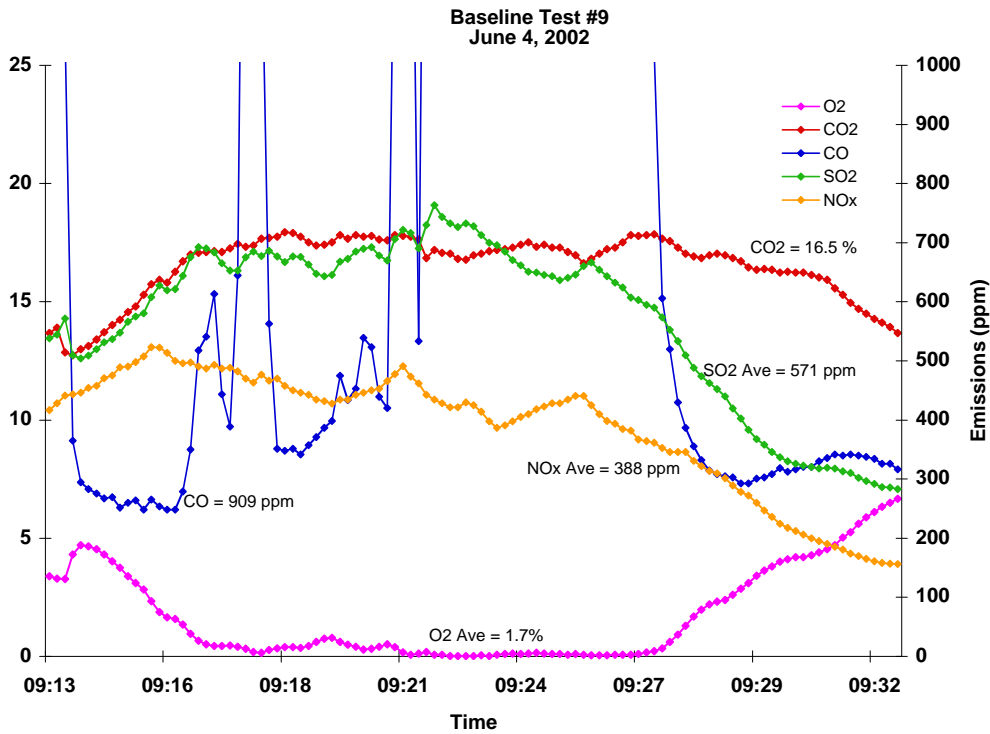


Figure 7. Emissions data from baseline test #9.

In order to compare data from emissions profiles such as that observed in Figure 7, CO averages reported in the tables in the following sections were reported by two methods: 1) using all the data points collected (such as the 909 ppm shown on Figure 7); and 2) averaging only the periods where CO spikes were not observed (which results in an average of 259 ppm for baseline test #9). This was done for two reasons. First, when CO spikes, the reading is off the instrument's scale; therefore, the value recorded is less than the actual value. This in turn leads to an average that is less than the actual value. Second, if the system were operated continuously while monitoring the O₂ concentration, as in a boiler, versus in a batch mode, the CO spikes would be minimized if not eliminated. Therefore, the non-spiking segments were averaged and listed in the following tables for comparison.

Baseline Tests

The emissions results from the baseline coal tests are given in Table 3. The CEM data for baseline tests #6 through #10 are given in Table 4 while the PAH and dioxin TEQ emissions for California plastics are also provided in Table 4.

Table 3. PAH and PCDD/F concentrations from the baseline coal tests.

Test No.	Percent Plastic	Fraction	Percent Carbon Burnout	Naphthalene (ng/dscf)	Fluorine (ng/dscf)	Phenanthrene (ng/dscf)	Anthracene (ng/dscf)	Fluoranthene (ng/dscf)	Pyrene (ng/dscf)	Benz(a)anthracene (ng/dscf)	Benzo(a)pyrene (ng/dscf)	Benzo (g,h,i) perylene (ng/dscf)	Dioxin TEQ (pg/dscf)
1	0	Vapor	95.2	18	--	<1	--	<1	<1	--	--	--	49
1	0	Solids	--	<1	--	<1	--	<1	--	--	--	--	39
3	0	Vapor	95.2	34	--	<1	--	<1	<1	--	--	--	50
3	0	Solids	--	<1	--	<1	--	<1	--	--	--	--	22
4	0	Vapor	92.9	<1	--	1	--	1	<1	--	--	--	26
4	0	Solids	--	2	--	<1	--	<1	<1	--	--	--	24
5	0	Vapor	82.2	137	--	9	<1	3	1	--	--	--	58
5	0	Solids	--	--	--	<1	--	<1	<1	--	--	--	8
6	0	Vapor	94.8	161	--	<1	--	<1	<1	--	--	--	34
6	0	Solids	--	<1	--	<1	--	<1	<1	--	--	--	13
7	0	Vapor	91.5	117	--	<1	--	<1	<1	--	--	--	23
7	0	Solids	--	--	--	<1	--	<1	<1	--	--	--	6

-- = not detected

Table 4. Flue gas emissions when firing the baseline coal and blends of California plastic and coal.

Test	%O ₂	ppm CO (@ 4%O ₂)	ppm CO ^a (@ 4% O ₂)	%CO ₂ (@ 4% O ₂)	ppm SO ₂ (@4% O ₂)	ppm NO _x (@4% O ₂)
Baseline 6	6.8	1,069	227	13.2	539	461
Baseline 7	6.1	280	248	13.8	525	429
Baseline 8	4.0	416	384	14.0	519	376
Baseline 9	1.7	801	228	14.5	503	342
Baseline 10	4.0	681	355	14.4	557	369
California 5% 4	7.2	402	402	14.0	605	416
California 5% 5	1.9	838	461	14.3	N/D ^b	321
California 5% 6	3.2	758	554	14.1	468	320
California 10% 3	5.8	281	237	14.8	460	320
California 10% 4	6.5	505	333	14.3	422	354
California 10% 5	4.3	N/D	N/D	14.3	428	371

^a Average CO emissions without spikes

^b Not determined

The CEM data have been normalized to a 4% O₂ basis in order to compare results between tests. This is a standard industry practice as emissions results are normally compared on either a 3 or 4% O₂ basis. The results from this study have been normalized to 4% O₂ as this was the O₂ concentration expected with the given air flow rates used. The CEM results are typical of those observed when burning Middle Kittanning seam coal in other test units.

The results from the PAH and dioxin TEQ emissions measurements are given in Table 3. It should be noted that the PAH emissions are given in units of nanograms (ng) per dry standard cubic foot (dscf) while the dioxin TEQ emissions are given in picograms (pg) per dscf. Although sixteen PAHs were analyzed for, only nine were detected during all the testing. All nine compounds are listed in each of the PAH/dioxin TEQ tables to make it easier to compare the results between the different plastics and plastic quantity used; however, not all nine HAPs were detected during each test. For example, during the baseline testing, only naphthalene, phenanthrene, fluoranthene, and pyrene were detected. Values listed as <1 ng/dscf indicate that a spike in the GC results was observed but that the concentration was below <1 ng/dscf. The PAH compounds are listed in the order in which they elute from the GC.

The primary PAH compound observed during the baseline testing is naphthalene, which is consistent with other work at Penn State when firing coal in a boiler [1]. The naphthalene concentration varied an order of magnitude from 18 to 161 ng/dscf, which is also consistent with previous work [1]. Naphthalene forms at lower temperatures and its rate of conversion to other compounds is greater than its rate of formation as the temperatures increases (e.g., >1,300°C) [1]. As naphthalene conversion increases, more complex PAHs form. Table 3 shows that for the baseline coal testing, mainly naphthalene formed.

There is one anomaly in the PAH data in Table 3. The naphthalene concentration measured during baseline test #4 was <1 ng/dscf, which appears to be low. This low value suggests that the sampling system may have experienced a leak; however, neither the mandatory (per EPA procedures) leak check at the conclusion of the test nor the dioxin TEQ values (i.e., vapor values > than solid values) support this observation. The reason for the low naphthalene value is unclear.

To date, legislation limiting concentrations of PAH emissions from stationary sources has not been enacted. However, under USDOE Contract DE-AC22-93PC93251, [2], flue gas samples were collected prior to an electrostatic precipitator in a 108 MW pulverized bituminous coal burning power plant in Niles, OH. The naphthalene concentrations in the flue gas stream were found to be 6 ng/dscf. This concentration is approximately 15 times lower than the average concentration found in the baseline stoker tests.

The dioxin TEQ emissions during the baseline tests ranged from 29 to 88 pg/dscf (total of vapor and solid concentrations) and averaged 58 pg/dscf. Although no EPA limits for allowable dioxin TEQ concentrations exist for coal-fired units, the allowable dioxin TEQ limit for medium to large hospital/medical/infectious waste incinerators is 700 pg/dscf [3]. Dioxin TEQ at the Niles power plant was found to be approximately 275 fg/dscf. The dioxin TEQ concentrations for the stoker baseline tests fall between these values.

Tests Using California Plastic

Tables 4 and 5 contain the CEM and PAH/dioxin TEQ emissions, respectively. The CEM values are comparable with the baseline coal emissions. Likewise the range of the PAH/dioxin TEQ emissions, 26 to 86 pg/dscf (total solid and vapor), is similar to the baseline tests. However, the tests conducted with 10% plastics tended to have slightly lower PAH and dioxin TEQ emissions. Again, these concentrations fall between the concentrations allowed for incinerators and what was found at the Niles Station utility boiler data.

Tests Using Pennsylvania Plastic

The CEM and PAH/dioxin TEQ emissions for the Pennsylvania Plastic tests are given in Tables 6 and 7, respectively. The CEM values are comparable to the baseline coal emissions; however, the complex PAH and dioxin TEQ emissions are elevated. The tests with more plastic (i.e., 10% by thermal input) tended to have higher levels of complex PAHs and dioxin TEQ emissions. From the Niles plant, concentrations of phenanthrene were found to be 10 ng/dscf, fluoranthene was 3 ng/dscf, and pyrene was 1 ng/dscf.

Tests Using Florida Plastic

Tables 8 and 9 contain the CEM and PAH/dioxin TEQ emissions, respectively, when testing the Florida plastic. As with the Pennsylvania and California plastic tests, the CEM data is comparable to the baseline tests. The PAH and dioxin TEQ emissions however, were significantly elevated and contained many complex PAHs. These results were the worst of all of the testing and are sufficiently high to cause concern. The Florida plastic contained the highest level of chlorine and was the most contaminated (i.e., \approx 48 wt.% ash) of the three plastics. Testing from the Niles Station showed the following concentrations of PAHs: fluorine at 4 ng/dscf, anthracene at 1 ng/dscf, benz(a)anthracene at 1 ng/dscf, benzo(a)pyrene at 600 pg/dscf, and benzo(g,h,i)perylene at 50 pg/dscf.

Table 5. PAH and PCDD/F concentrations from the California plastic coal tests.

Test No.	Percent Plastic	Fraction	Percent Carbon Burnout	Naphthalene (ng/dscf)	Fluorine (ng/dscf)	Phenanthrene (ng/dscf)	Anthracene (ng/dscf)	Fluoranthene (ng/dscf)	Pyrene (ng/dscf)	Benz(a) anthracene (ng/dscf)	Benzo(a) pyrene (ng/dscf)	Benzo (g,h,i) perylene (ng/dscf)	Dioxin TEQ (pg/dscf)
1	5	Vapor	89.3	175	--	2	--	2	2	--	--	--	62
1	5	Solids	--	--	--	<1	--	<1	<1	--	--	--	18
2	5	Vapor	89.6	40	--	2	--	1	<1	--	--	--	42
2	5	Solids	--	<1	--	<1	--	--	<1	--	--	--	18
3	5	Vapor	95.3	135	--	1	--	<1	<1	--	--	--	55
3	5	Solids	--	<1	--	<1	--	<1	--	--	--	--	31
1	10	Vapor	92.5	46	--	4	--	2	1	--	--	--	13
1	10	Solids	--	<1	--	<1	--	<1	<1	--	--	--	10
2	10	Vapor	92.9	40	--	1	--	1	1	--	--	--	24
2	10	Solids	--	<1	--	<1	--	<1	--	--	--	--	9
3	10	Vapor	89.1	87	--	1	--	1	1	--	--	--	26
3	10	Solids	--	<1	--	<1	--	<1	<1	--	--	--	24

-- = not detected

Table 6. Flue gas emissions when firing the baseline coal and blends of Pennsylvania plastic and coal.

Test	%O ₂	ppm CO (@ 4%O ₂)	ppm CO ^a (@ 4% O ₂)	%CO ₂ (@ 4% O ₂)	ppm SO ₂ (@ 4% O ₂)	ppm NO _x (@4% O ₂)
Baseline 6	6.8	1,069	227	13.2	539	461
Base line 7	6.1	280	248	13.8	525	429
Baseline 8	4.0	416	384	14.0	519	376
Baseline 9	1.7	801	228	14.5	503	342
Baseline 10	4.0	681	355	14.4	557	369
Pennsylvania 5% 4	6.4	649	265	14.6	518	299
Pennsylvania 5% 5	3.0	470	282	14.4	454	275
Pennsylvania 5% 6	6.7	1,494	350	13.4	497	243
Pennsylvania 10% 3	3.5	345	290	13.4	486	373
Pennsylvania 10% 4	3.5	559	223	14.1	507	328
Pennsylvania 10% 5	6.1	311	285	14.0	548	382

^a Average CO emissions without spikes

Table 7. PAH and PCDD/F concentrations from the Pennsylvania plastic/coal tests.

Test No.	Percent Plastic	Fraction	Percent Carbon Burnout	Naphthalene (ng/dscf)	Fluorine (ng/dscf)	Phenanthrene (ng/dscf)	Anthracene (ng/dscf)	Fluoranthene (ng/dscf)	Pyrene (ng/dscf)	Benz(a)anthracene (ng/dscf)	Benzo(a)pyrene (ng/dscf)	Benzo (g,h,i) perylene (ng/dscf)	Dioxin TEQ (pg/dscf)
1	5	Vapor	79.7	56	--	3	--	1	2	--	--	--	18
1	5	Solids	--	<1	--	1	--	<1	<1	--	--	--	25
2	5	Vapor	94.3	140	--	2	--	1	3	--	--	--	29
2	5	Solids	--	<1	--	1	--	<1	<1	--	--	--	28
1	10	Vapor	88.1	84	--	3	--	2	2	--	--	--	33
1	10	Solids	--	<1	--	<1	--	1	1	--	--	--	20
2	10	Vapor	94.8	70	--	22	1	20	17	--	--	--	50
2	10	Solids	--	<1	--	1	--	2	2	--	--	--	35
3	10	Vapor	93.7	49	--	14	1	13	13	1	2	--	49
3	10	Solids	--	<1	--	<1	--	1	1	--	--	--	31

-- = not detected

Table 8. Flue gas emissions when firing the baseline coal and blends of Florida plastic and coal.

Test	%O ₂	ppm CO (@ 4%O ₂)	ppm CO ^a (@ 4% O ₂)	%CO ₂ (@ 4%O ₂)	ppm SO ₂ (@ 4% O ₂)	ppm NO _x (@4% O ₂)
Baseline 6	6.8	1,069	227	13.2	539	461
Base line 7	6.1	280	248	13.8	525	429
Baseline 8	4.0	416	384	14.0	519	376
Baseline 9	1.7	801	228	14.5	503	342
Baseline 10	4.0	681	355	14.4	557	369
Florida 5% 4	6.5	278	276	14.1	468	430
Florida 5% 5	3.3	671	331	14.3	491	367
Florida 5% 6	2.7	1,088	474	14.9	546	280
Florida 10% 4	8.5	823	370	15.0	461	246
Florida 10% 5	6.0	381	351	13.9	486	374
Florida 10% 6	7.3	412	341	14.4	426	350

^a Average CO emissions without spikes

Table 9. PAH and PCDD/F concentrations from the Florida plastic/coal tests.

Test No.	Percent Plastic	Fraction	Percent Carbon Burnout	Naphthalene (ng/dscf)	Fluorine (ng/dscf)	Phenanthrene (ng/dscf)	Anthracene (ng/dscf)	Fluoranthene (ng/dscf)	Pyrene (ng/dscf)	Benz(a)anthracene (ng/dscf)	Benzo(a)pyrene (ng/dscf)	Benzo (g,h,i) perylene (ng/dscf)	Dioxin TEQ (pg/dscf)
1	5	Vapor	91.5	382	19	83	6	88	161	10	8	11	58
1	5	Solids	--	<1	--	<1	--	1	1	--	--	--	31
2	5	Vapor	90.8	111	9	31	2	28	44	6	-5	3	55
2	5	Solids	--	1	--	--	--	--	--	--	--	--	28
3	5	Vapor	89.5	19	--	6	--	4	4	1	<1	<1	39
3	5	Solids	--	<1	--	<1	--	<1	<1	--	--	--	24
1	10	Vapor	92.3	72	2	31	2	23	23	7	8	2	44
1	10	Solids	--	<1	--	<1	--	<1	<1	--	--	--	27
2	10	Vapor	95.0	317	9	47	3	57	98	10	7	6	63
2	10	Solids	--	--	--	<1	--	<1	<1	--	--	--	31
3	10	Vapor	92.5	140	--	6	--	14	11	<1	4	2	57
3	10	Solids	--	<1	--	<1	--	<1	<1	--	--	--	33

-- = not detected

Concluding Statements

A series of batch-scale stoker combustion tests were performed to evaluate the emissions of criteria pollutants (carbon monoxide, sulfur dioxide, and nitrogen oxides), polycyclic aromatic hydrocarbons (PAHs), and dioxin toxic equivalents (TEQ). Tests were conducted using a baseline coal, which was a Middle Kittanning seam Pennsylvania high volatile bituminous coal, and blends of the baseline coal with three plastics (obtained from California, Pennsylvania, and Florida) with the plastic nuggets comprising 5 and 10% of the thermal input of the fuel blend.

The SO₂ and NO_x emissions from the tests using the nugget/coal blends were similar to those firing only coal. CO emissions were very variable which is a deficiency of batch-type tests. In normal boiler operation, the oxygen content is monitored and the quantity of air used for combustion is adjusted to maintain a constant O₂ level, e.g., 4%, in the flue gas. However, in the batch scale tests, the air flow rate was maintained constant for all tests to ensure uniformity between tests, especially because of the PAH/dioxin TEQ sampling. Hence, variations in O₂, which adversely affects CO as the O₂ level drops very low, are experienced due to varying combustion efficiencies, clinkering in the bed, and, in the case of coal/nugget blends, possibly different combustion profiles.

The addition of plastic nuggets to the fuel blend did result in elevated PAH/dioxin TEQ emissions using two of the three plastics. The emissions from the California plastic tests were similar to those observed when firing only the baseline coal. Complex PAHs and dioxin TEQ emissions were elevated when firing the Pennsylvania and Florida plastics with the Florida plastic tests exhibiting the highest level of PAHs/dioxin TEQ emissions. The emissions from the Florida plastic tests contained the greatest quantity of the more toxic compounds. Although opinions vary widely, agreement on two points is generally accepted as 'rules-of-thumb': PAH toxicity increases with molecular complexity and benzo(a)pyrene is considered to be only 20 times less toxic than 1 dioxin TEQ. The PAH concentrations in the Florida emissions should therefore be considered significant.

Steady-state operation in a larger test unit or full-scale system would address the O₂/CO variability and would provide emissions data more comparable to an actual boiler. The variability in plastic contamination could be better addressed through utilizing the plastics in a fluidized bed combustion (FBC) system rather than a stoker system since an FBC can handle fuels that exhibit more variability and contain high ash contents. It is recommended that future testing using plastic nuggets be performed using pilot-scale FBCs or, if stoker boilers are to be considered further, a full-scale stoker boiler test should be performed to eliminate the deficiencies of batch-scale testing.

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ACKNOWLEDGMENTS

The research team would like to thank the National Watermelon Promotion Board for their financial support of this project. Ms. Diana Musto, Research Associate with the NWPB, was especially helpful throughout the nearly two-year program. Diana's patience was truly appreciated, since delays seemed to spring up routinely during the contract period.