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Co-firing High Sulfur Coal with Refuse Derived Fuels

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I. ABSTRACT

This project was designed to evaluate the combustion performance of and emissions from a fluidized bed combustor during the combustion of mixtures of high sulfur and/or high chlorine coals and municipal solid waste (MSW).

The project included four major tasks, which were as follows:

1. Selection, acquisition, and characterization of raw materials for fuels and the determination of combustion profiles of combination fuels using thermal analytical techniques.
2. Studies of the mechanisms for the formation of chlorinated organics during the combustion of MSW using a tube furnace.
3. Investigation of the effect of sulfur species on the formation of chlorinated organics.
4. Examination of the combustion performance of combination fuels in a laboratory scale fluidized bed combustor

Several kinds of coals and the major combustible components of the MSW, including PVC, newspaper, and cellulose were tested in this project. Coals with a wide range of sulfur and chlorine contents were used. TGA/MS/FTIR analyses were performed on the raw materials and their blends. The combustion profiles of the various fuels and fuel blends indicated their various thermal behaviors. Furthermore, the fuels selected for study showed various decomposition rates and products under different heating rates. The results indicated that there are greater possibilities that more organic compounds are formed during co-firing coals with RDF at high heating rates than with low heating rates.

The possible mechanism for the formation of chlorinated organics during combustion was investigated by conducting a series of experiments in a tube furnace. The results showed that molecular chlorine is a key intermediate for the formation of chlorine-containing organic

compounds during the combustion of MSW. The formation of chlorinated organics during combustion is illustrated by a four-step process, as follows:

From a series of experiments using pure organic compounds this mechanism has been demonstrated to be a possible chemical pathway in certain temperature ranges for the formation of chlorinated organics during combustion.

The effect of sulfur dioxide on the formation of molecular chlorine during combustion processes was examined in this study. The results illustrated that once sulfur dioxide is introduced into the Deacon Reaction system, the production of molecular chlorine is decreased. Sulfur dioxide was shown to be an effective inhibitor for the formation of molecular chlorine through the Deacon Reaction and, subsequently, the production of chlorinated organics. The co-firing of MSW and high sulfur coal seems to be a promising method for reducing the possibility of forming PCDD/Fs during combustion.

The preliminary laboratory-scale fluidized bed combustion tests were conducted on a low sulfur KY # 9 coal. The results showed a good compatibility of coal and pelletized wood in the fuel blends. Combustion efficiency greater than 97% was easy to obtain by co-firing the high-sulfur coal with the MSW. Two 1000-hour test runs were completed to test for the emissions of chlorine, sulfur and organic compounds for two coals. These results serve as a baseline study for the AFBC system, and are used for comparison to test runs when various types of RDF are added during combustion. A mixture of coal and PVC pellets was burned and no detectable amounts of chlorinated organics were detected. This is likely due to the efficient combustion conditions. Also, the limestone used absorbed most of the sulfur dioxide in the co-firing process. The above results indicated the practical effects of using coal as a combustion support fuel when burning MSW.

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VI. EXECUTIVE SUMMARY

This project was coordinated with a project at Western Kentucky University (WKU) that was supported by the Southeastern Regional Biomass Energy Program (SERBEP) through the Tennessee Valley Authority (TVA). Fluidized bed combustion tests were performed on municipal solid waste (MSW) blended with high sulfur and high chlorine coals in a laboratory scale combustor. The purpose of the tests was to evaluate combustion performance, the extent of inorganic acid gases (HCl and SO_x) and chlorinated organic compound formation, the effect of chlorine species on SO_2 removal with a sorbent, and the effect of sulfur species on the formation of chlorinated organic compounds from MSW for a range of bed temperatures, excess air levels, MSW/coal ratios, and S/Cl ratios. Flue gas samples were collected and analyzed at three locations in the AFBC freeboard area. Analytical methods used included ion chromatography (IC), gas chromatography (GC), and mass spectrometry (MS). Waste stream ash samples were collected from the cyclone catch and analyzed for unburned carbon, chlorine, sulfur, polycyclic aromatic hydrocarbons (PAH) and metal content. Major, minor, and trace elements in the ash were determined by x-ray fluorescence and inductively coupled plasma-atomic emission spectroscopy.

In this study, we examined the quality of fuels used, performing fundamental laboratory tests on a variety of raw fuels and fuel mixtures. Each fuel used in this study was also characterized by thermal analytical techniques. TG/FTIR/MS studies of the organic compounds evolved during combustion of blends of coal and refuse derived fuels (RDF) showed the production of phenols, furans, and various other organic materials during the combustion of paper and other cellulosic materials blended with coals. The production of molecular chlorine during the combustion of polyvinyl chloride was also confirmed. Phenol, furan, and molecular chlorine could provide the important precursors for the formation of PCDDs and PCDFs during the combustion process. Meanwhile, we found that under high heating rates, the TG/FTIR/MS analysis indicated that more hydrocarbons were released, owing to incomplete combustion of the fuels. Consequently, the concurrent evolution of HCl (which may be converted to molecular chlorine through the

Deacon Reaction) and the large amount of hydrocarbons, especially the aromatics, may facilitate the formation of the undesirable organics. In summary, chlorinated organic compounds may be formed at high heating rates, whereas products such as organic acids and alcohols are generally observed at slower heating rates.

The proposed four-step mechanism for the formation of PCDD/Fs was investigated in this study in a series of tube furnace experiments with pure organic compounds. A PCDD/Fs source of chlorine has been confirmed as Cl_2 and the latter's derivation from the Deacon Reaction has been determined. The following conclusions were made from the experimental results:

1. The Deacon Reaction for the production of molecular chlorine is generally favored at temperatures over 600°C .
2. The gas phase chlorination of phenol is generally favored at temperatures over 600°C .
3. Tetrachlorodibenzofuran, dichlorodibenzodioxin, and other chlorinated organic compounds are formed during the combustion of 2,4-dichlorophenol.

In summary, the proposed four-step mechanism appears to be a possible chemical pathway for the production of PCDDs and PCDFs in co-combustion processes.

To examine the inhibitory effect of sulfur species on the formation of PCDD/Fs during co-combustion, experiments were conducted in a preheated furnace to simulate the conditions in an AFBC system. Sulfur is considered to be an interferant in the formation of molecular chlorine. Based on the mechanism proposed above, the study focussed on the effect of sulfur dioxide gas on the formation of molecular chlorine through the Deacon Reaction. As expected, sulfur species suppress the formation of chlorine and, consequently, diminish the formation of PCDD/Fs during the co-firing process.

The objective of the AFBC study is to evaluate combustion performance of and emissions from a fluidized bed combustor during the co-firing of mixtures of high sulfur and high chlorine coal with MSW. Laboratory scale fluidized bed combustion tests were first conducted on a low sulfur coal (95011) in the fluidized bed combustor. The six-hour run started with coal, gradually

switching to sawdust pellets. No difficulties were encountered in using a mixture of 95% sawdust and 5% coal to maintain the bed temperature around 1500°F and keep the high combustion efficiency and thermal efficiency. The results indicated that co-firing wood and coal is a potential pathway to deal with the wood waste. Two 1000-hour runs were completed to burn two kinds of coal with different chlorine and sulfur contents. No PAHs and PCDD/Fs were detected in the evolved gas and fly ash samples. A test to burn high sulfur coal with PVC pellets was then conducted. As expected, no chlorinated organics and PAHs were detected under our experimental conditions during these combustion runs. In addition, the limestone used proved to be an efficient sorbent to remove the undesirable SO₂ emissions during the co-firing. Therefore, co-firing high sulfur coal with MSW appears to be a promising way to deal with solid waste.

VII. INTRODUCTION

The amount of municipal solid waste produced in the United States each year has risen to more than 180 million tons. According to the prediction of the Environmental Protection Agency (EPA) this amount will raise to 216 million tons in the year 2000.¹ Land filling, which is the traditional way to deal with this waste is becoming more and more impractical owing to the rapidly declining availability of landfill space and stricter environmental regulations.

Incineration of the MSW is one of the alternative waste management technologies that has some advantages over the conventional methods. There are several MSW incinerators in U.S. and Europe constructed for burning municipal wastes alone or combined with wood waste.² However, due to the concern over emissions of hazardous chlorinated organics, especially the harmful PCDD/Fs, the development of technology for the incineration of MSW has slowed significantly.

While significant amounts of dibenzodioxins (PCDDs) or dibenzofurans (PCDFs) have been detected in the emissions of municipal waste combustors, the same cannot be unequivocally said of emissions from coal-fired combustors. From a combustion chemistry standpoint, the presence of molecular chlorine and the basic organic structures of both systems would provide the initial aromatic compounds necessary for the basic formation of triple ring structures of dioxins and furans, which in turn are the basic structures for the highly toxic polychlorinated species.³ In fact, despite PCDDs and PCDFs in the parts-per-billion to parts-per-trillion range that have been found in the precipitator fly ash and the flue gases of a number of incinerator facilities, they were not detected in the effluents from a combined coal/municipal waste plant, nor were noteworthy amounts found in the fly ash.⁴ Coal appears to be a desirable co-firing fuel for MSW.

Several mechanisms have been proposed to explain the formation of PCDD or PCDFs during the combustion of MSW. Although some of them are contradictory and confusing, molecular chlorine has been recognized as a key intermediate. One of the possible pathways for the

formation of PCDDs and PCDFs is associated with *de novo* synthesis from compounds within the flue gas and fly ash. This synthesis involves the Deacon Reaction and is represented by the following steps:

From the Deacon reaction, molecular chlorine is produced and subsequently chlorinates aromatic compounds through substitution reactions.

In our study, the source of HCl has been confirmed as the thermal decomposition of chlorine-containing plastic. Chlorine gas may be generated in-situ from HCl and oxygen in the combustion gases of MSW incinerators via the Deacon Reaction. It is known that plastic wastes make up a large fraction of U.S. domestic refuse. Some plastics are chlorine-containing polymers, such as polyvinyl chloride (PVC) and polyvinylidene chloride (PVDC) and are widely used in our daily life. During incineration such materials may release chlorine gas upon heating which is a precursor for the formation of carcinogenic and highly toxic chlorinated organic compounds.

However, the use of coal as a co-firing energy source for municipal wastes may inhibit the formation of chlorine-containing organic compounds. Some conclusions have suggested an inhibitory effect of increased SO_2 concentration with regard to PCDD/PCDFs formation. Scheidle and co-workers demonstrated that adding lignite coal as an auxiliary fuel to paper recycling residues decreased the levels of dioxins in fluidized-bed incinerator emissions.⁵ Based on thermodynamic evaluations and published test data, Griffin proposed that as long as the Cl/S ratio is high, chlorine formation for the elevated production of chlorinated aromatics and PCDD/Fs is prevalent, but in the presence of substantial amounts of sulfur, chlorine production and consequently, PCDD/Fs formation is suppressed.⁶ Gullett and co-workers reported that high concentrations of a sulfur species (sulfur dioxide) are responsible for the apparent lack of PCDD

and PCDF in the emissions from coal-fired combustors.⁷ Lindbauer showed that co-firing MSW with 60% coal drastically reduced the formation of PCDD/PCDF.⁸ All the above studies indicate that the addition of coal, especially high-sulfur coal, to municipal solid wastes would help diminish the level of dioxin emissions during combustion. Therefore, co-combustion has the dual advantage of being a source of energy and having the potential of reducing the formation of chlorinated species in combustor emissions.

There are several different mechanisms proposed for the limiting of PCDD production involving the sulfur species, one of which suggested that in coal combustion, the role of sulfur interference with the chlorination step (and hence the formation of PCDDs) is critical. When sulfur is present in excess over chlorine, in any system, the forward reaction predominates:

Thus the chlorinating agent, chlorine, is converted into HCl, which is very unlikely to undergo aromatic substitution reactions to form PCDD and PCDF precursors. In this project, this reaction was examined in a tube furnace. The results indicated the apparently inhibiting effect of sulfur on the Deacon reaction.

Another proposed role of sulfur in the formation of chlorinated organics is to react with the copper-based Deacon reaction catalyst. In the presence of oxygen, sulfur dioxide may react with CuO to produce CuSO₄ through the following reaction:

In fact, some previous studies showed that the reaction of Cu²⁺ with SO₂ forms CuSO₄, which makes the catalyst less active, thus decreasing PCDD formation. However, this inactivity is not a result of decreased Cl₂ formation, but rather of reduced ability of Cu²⁺ to promote a second catalytic step of biaryl synthesis. The role of Cu compounds, both in ring condensation and chlorination, appears well established. Therefore, conversion of CuO to CuSO₄ not only affects the production of molecular chlorine, but also decreases the rate of further condensation of chlorinated phenols.⁹

The adsorption capacity of coal surfaces may also play an important role in reducing the formation of toxic chlorinated organics. Chlorine gas produced during co-combustion of coal and MSW could be adsorbed by the coal, which results in a decrease in the emission of toxic organics. The negative effect of coal on the formation of toxic chlorinated organics during co-combustion may be attributed to a combination of sulfur effects and chemisorption by coal.¹⁰ Although it is not the only criterion, sulfur is a crucial factor in suppressing the toxic emission in co-incineration.

Municipal solid waste (MSW) varies considerably in composition. The ranges of composition for several MSW samples are shown in Table 1. The noncombustibles of MSW, such as metals and glasses, are excluded from this study. Refused-derived fuels (RDF) are made from the combustible components of MSW.

Compatibility is one of the problems encountered when co-firing the different materials. Coal is an energy rich fuel, containing about 12,500 Btu/lb (bituminous coal) compared to refuse-derived fuels and wood waste with energy contents of about 4,000-8,000 Btu/lb. The parameter used to measure the rate of burning for a fuel is the volatile matter. For bituminous coals, the volatile matter is about 36%, whereas the volatile matter for RDF or MSW is 60-80% and wood waste is about 55-85%. This means that coal burns much slower and has about 50-150% more energy than MSW, RDF or wood waste. The burning profiles of coal, RDF, MSW and wood waste are quite different, but blends of these fuels, when co-fired under the right conditions, can perform satisfactorily as boiler fuels. In this project, thermal analysis was employed to obtain the combustion profiles of different raw materials and their blends.

Thermal analytical techniques are versatile and very powerful for predicting the performance of fuels in various industrial boilers. The efficient operation of each type of boiler requires the use of fuels with the proper mix of volatile matter and char. Some components of volatile matter ignite and burn at a much more rapid rate than others. As mentioned above, the lignin from paper or wood ignites much faster than the volatile components in coal. Unfortunately, the

Table 1. Composition Ranges for MSW Components.

<u>Components</u>	<u>Composition Range (%)</u>
Paper	30 to 50
Glass	8 to 10
Metals	7 to 10
Plastics	1 to 5
Rubber-leather	1 to 3
Wood	1 to 4
Textiles	1 to 5
Food wastes	10 to 20
Yard wastes	5 to 20
Other	1 to 4

Agrawal, R.K., "Compositional Analysis of Solid Waste and Refuse Derived Fuels by Thermogravimetry," in *Compositional Analysis by Thermogravimetry*, (C.M. Earnest, Ed.) ASTM, STP 997, American Society for Testing and Materials, Philadelphia, PA, 1988, p.259

volatile matter and char contents of a fuel mixture can not be predicted from a weighted average of these properties in the raw materials. However, one can use the combustion profiles from thermogravimetric analysis/differential thermal analysis (TG/DTA) to measure the relative amounts of volatile matter and char in a fuel mixture. Additionally, TG/DTA experiments can be used to determine the correct amount of limestone to add to a mixture to effectively trap all sulfur oxides as CaSO_4 . Information such as mass loss as a function of temperature, rate of combustion as a function of temperature, and total heat produced, or absorbed, per given mass of material can readily be evaluated from these thermograms.

TG/FTIR/MS analysis provided additional information for the combustion behavior of the materials. It was employed to understand the nature of the gas decomposition products flowing out from the TG, and obtain a comprehensive picture of the combustion process. The combination of TG/FTIR and TG/MS offers complementary techniques for detection and identification of the evolved gases. This kind of on-line analysis has advantages in providing the relationship between the combustion products and time/temperature.

To determine if any chlorinated organic compounds were formed during the combustion reactions, the combustion gases were collected in Tenax adsorption tubes. The collected samples were extracted separately with hexane (99.9%) for 24 hours using a soxhlet extraction apparatus. The samples were then analyzed using a GC/MS system. The principle objective of the GC/MS analysis of the TGA and AFBC combustion gases and leachates of residues and fly ash was to determine the extent of production of organic compounds and the classes of organic compounds formed, with particular emphasis on chlorinated organic compounds.

VIII. EXPERIMENTAL

A. TGA/FTIR/MS System

The spectra and profiles of gas species flowing out of the TGA are recorded and analyzed by the TGA/FTIR/MS analytical system. The three key components of this system are as follows:

- Model 951 Thermogravimetric Analyzer (Dupont Instruments)
- Model 1650 Fourier Transform Infrared Spectrophotometer (Perkin Elmer)
- VG Thermalab Gas Analysis System (Fisons Instruments)

The TGA is interfaced to the FTIR using an insulated teflon tube heated to a temperature of 150°C by a Powerstat variable autotransformer. The 25 mm x 10 cm gas cell with KBr windows used with the FTIR is heated using a Barnant thermocouple controller. The tube and gas cell are heated to prevent possible condensation of the gaseous products. The time lag between the sample chamber and gas cell is 1 min with an air flow rate of 50 mL/min during combustion.

The TGA is also interfaced to the mass spectrometer using a fused silica capillary sampling inlet that is heated to approximately 170°C. The MS system can automatically sample the gases, analyze them with its quadrupole analyzer, and save the mass spectra. The system uses an electron impact ionizing system operated at 70 eV.

B. Studies with the Tube Furnace

To simulate the conditions used in the AFBC system, tests were performed in a concentric tube, quartz reactor inserted into the horizontally mounted electric Lindberg furnace. Process gases were preheated by flowing through the outer quartz tube and into the inner tube reaction zone. The composition of the process gases can be adjusted by the calibrated teflon flow meters before being introduced into the reaction system.

The reaction products were swept into cooled trap containing a chosen absorbent. After the reaction was completed, the solvent was concentrated, and the sample analyzed using the GC/MS system. A Shimadzu QP 5000 system with a NIST/EPA/NIH 62,000 compound database was used for GC/MS analysis. The identification of compounds was accomplished by using a computerized library search and by comparison with literature mass spectra. Moreover, comparing to the GC retention time of the pure compounds may confirm the identification of the unknowns. The area of the detectable ion current peak was integrated and compared to the area of the standard, and normalized to the mass of the solid to provide a semi-quantitative indication of the amount of material collected in the trap. Standard materials were tested to establish the detection limits of the experimental set-up.

C. Laboratory Fluidized Bed Combustion Tests

The laboratory scale atmospheric fluidized bed combustor at Western Kentucky University was built by the University with support from the U.S. Department of Energy. The active bed area is 125 in². The freeboard zone of the combustor is 10 feet high, providing adequate residence time for the combustion of fine fuel particles which may be entrained in the gases leaving the bed. This also allows time for the entrained fine particles of bed material and ash to lose their upward velocity and fall back into the bed, thus minimizing dust loading in the cyclone and providing a stable bed height. The fuel is injected into the fluidized bed by using pneumatic injectors. The injectors used for these tests are located about 9 inches above the air distributor of the combustor. The bed temperature is controlled by fuel feed rate adjustment.

The principal components of the fluidized bed combustor are the fuel bunkers, combustor housing, heat exchangers, wet cyclone, and stack and cooling fans. A detailed schematic diagram of the AFBC system can be found in Figure 1.

Combination fuels are selected on the basis of the thermal analysis tests run. The bed medium in the FBC system is limestone, and the various materials are injected into the bed with screw

Figure 1. Schematic drawing of the AFBC combustor.

feeders. The operating conditions for the WKU AFBC system are similar to those used at the TVA 160-MW AFBC Pilot Plant located near Paducah, Kentucky.

D. Reagents and Materials Used in the Study

The fuels used in the study are as follows:

- Newspaper
- Cellulose (Whatman No. 1)
- PVC homopolymer resin (Oxy225, Occidental Chemical Corporation)
- Commercial RDF (from the Robertson County Recycling Center in Springfield, TN)
- Coals 90003, 92073, 95010, 95011, and 95031 (Analytical data are given in Table 2)

Chemical reagents used in the project are as follows:

- MC&B reagent grade phenol
- EM Scientific HPLC grade dichloromethane
- Aldrich 99% grade 2,4-dichlorophenol, 4-chlorophenol, 2-chlorophenol, dibenzofuran, and hexane

Specialty gases used included:

- HCl (1% and 10% in nitrogen)
- SO₂ (4.86% in nitrogen)
- Cl₂ (0.5% in nitrogen)
- Compressed air

Table 2. Proximate and Ultimate Analysis Data for Raw Materials

Parameter	90003	92073	95010	95011	95031	PVC**	Newspaper	Cellulose
Coal Seam	IL #6	KY #9	Blend	KY #9	IL # 6			
Rank of coals	B	C	A	B	B			
% Moisture*	8.76	9.88	2.32	7.32	8.32	0.00	4.21	3.12
% Ash	8.12	26.34	7.22	9.37	10.78	0.36	4.12	0.00
% Vol. Matter	34.25	32.56	39.97	43.34	37.21	99.64	81.21	96.88
% Fixed Carbon	57.63	41.10	52.82	47.29	52.02	0.00	0.00	0.00
% Carbon	75.07	59.53	79.38	74.08	72.61	38.71	45.67	43.44
% Hydrogen	5.21	3.50	5.31	5.08	4.82	4.20	6.67	6.80
% Nitrogen	1.64	1.17	1.63	1.54	1.54	0.07	0.00	0.00
% Sulfur	1.26	4.44	0.67	3.20	2.38	0.22	0.05	0.02
% Oxygen	8.32	4.99	5.69	6.72	7.57	0.00	43.12	49.76
Chlorine, ppm	3,800	289	1,039	118	3,065	56.45	260	0.00
Cal. Value (Btu/lb)	13,428	10,334	14,077	13,203	12,842	8,556	7,741	6,723

* Moisture is as-determined. All other analyses are reported on a dry basis. The rank of each coal is high volatile A, B or C bituminous.

** The unit for chlorine in PVC is percent.

IX. RESULTS AND DISCUSSION

A. Characterization of Raw Materials and Their Blends

Analytical data for the coals used in this study (90003, 92073, 95010, 95011, 95031) and other raw materials used in this study are summarized in Table 2. In order to identify the individual gases from the volatile species produced during the combustion, the pure gases HCl, H₂S, SO₂, CH₄, CO, CO₂ and H₂O were analyzed by the FTIR system in our laboratory. The IR spectrum of other possible combustion gas products were obtained from the literature.

1. Studies of the Different Materials Heated at a Slow (10°C/min) Heating Rate

1.1. Studies of Individual Materials. The purpose of this set of experiments was to understand the processes and mechanisms of thermal decomposition of different raw materials. To help accomplish this task, profiles for the evolution of different gaseous products were obtained and were used to assess the relative thermal stability and temperature relationships of the materials. The results are important to the analysis and control of the performance of an AFBC.

Thermal stabilities for the five coals and the three components of the standard synthetic RDF were evaluated, by heating them in air at 10°C/min from room temperature to 700°C in the TGA system. Concurrent FTIR and MS analyses of the off gases during each run provided considerable additional and confirmatory information about the thermal decomposition processes of each material.

When interpreting the three-dimensional FTIR spectra, the relative axes are absorbance (vertical), wavenumber (horizontal) and time-temperature (perspective). The time scale corresponds to the decomposition temperature based on the heating rate.

The MS instrument, in common with most other gas analyzers, is a low-range quadrupole mass spectrometer. As it analyzes unchromatographed mixtures of gaseous molecules, its output

requires great care in interpretation. Nevertheless, some useful information can be obtained, especially in conjunction with other sources of structural information, such as FTIR spectroscopy. To understand the MS spectrum, one of the more useful methods is to construct an evolved gas profile which shows the relationship between the signal of a given m/z and the temperature.

The TG/FTIR/MS analyses of the five coals indicated the similarities and the differences of various samples. Figure 2 compares the TG curves of five different coals. As can be seen, these thermal curves are quite similar. The first weight loss step is usually due to the loss of moisture absorbed by the sample. The second weight loss step corresponds to the major decomposition of coal, accompanied by the release of H_2O , O_2 , CO_2 , COS , SO_2 and a small amount of HCN . Figure 3 is the 3D FTIR spectrum of coal 92073 and Figure 4 shows some major MS peaks of the gaseous products evolving from the same sample. In FTIR/MS spectra, a similar trend of decomposition is shown for CO_2 , CO , and CH_4 peaks. There are two methane peaks for all coals. The first peak is shown at 230-380°C, owing to the methane already present in the micropores of coal. The second peak appears at around 500°C, resulting from the pyrolytic decomposition of the coal matrix.

However, there are considerable differences among the various coals because of their elemental contents. As illustrated in the FTIR spectra: (a) there are more water peaks in coal 90003 than in 92073. This can be attributed to more volatile matter and different hydrogen contents in 90003. (b) The COS and SO_2 peaks are stronger in coal 92073, which could reflect their different sulfur contents. In both IR and MS spectra, the SO_2 peaks of 92073 provide some information about the sulfur forms in this coal. The aliphatic sulfur decomposes first at 300-400°C, then pyrite and thiophene rings decompose at 400-600°C, then finally sulfate salt decompositions are predominant at 700-800°C. In addition, from the CO_2 profile, coal 90003 appears to be a lower rank coal with a lower initial decomposition temperature and lower final decomposition temperature. From the data for HCl and SO_2 , 95031 is a high chlorine and high sulfur bituminous coal, which is in good agreement with the elemental analysis results.

Figure 2. Comparison of TG curves for five different coals heated at a slow heating rate.

Figure 3. 3D FTIR spectra of combustion products from coal 92073 heated at a slow heating rate

Figure 4. Some MS peak profiles of gases evolved from coal 92073 heated at a slow heating rate

In the case of PVC, the TG curve (Figure 5) shows obvious a three-step weight loss. Combined with its IR spectrum (Figure 6) and MS spectra (Figure 7 and 8), it is shown that the first step loss at 230-400°C results from the loss of HCl, along with some CO₂ from low molecular weight PVC. The second and third peaks are due to the combustion of carbon skeleton chains. The loss of major volatile aromatic components such as: benzene, toluene, styrene, indene and their derivatives, evidently form the second step weight loss at 420-460°C. Combustion of the residue takes place at about 570°C, as shown by the profiles of CO and CO₂. This corresponds to the third weight-loss region of its TG/DTG curve. The unusually high combustion temperature reflects the flammability resistance of PVC, apparently arising from the capacity of chlorine to remove a stoichiometric equivalent of hydrogen at a relatively low temperature. The methane peak is apparent in the FTIR spectrum of PVC combustion, which may be from the reaction of the carbon chain in the polymer.

Upon interpretation of the MS spectrum obtained from the combustion of PVC one finds a very notable result. As shown in Figure 8, it appears that the production of molecular chlorine accompanies the release of a large amount of HCl during the combustion of PVC. As shown in this figure, masses 36 and 38 are formed at the same time, and strongly suggest the presence of isotopes of H³⁵Cl and H³⁷Cl. The integrated ratio is close to the chlorine isotope ratio. Furthermore, three additional m/z peaks appear at exactly the same point, with apparent masses of 70, 72, and 74 corresponding to ³⁵Cl₂, ³⁵Cl³⁷Cl, and ³⁷Cl₂. This is strong evidence suggesting that some fraction of the abundant HCl may be undergoing a thermal Deacon Reaction to produce molecular chlorine. It is a plausible starting point for the formation of chlorinated organics from the combustion of chlorine-rich fuel mixtures. When changing the atmosphere from air to nitrogen, chlorine is not identified in the products from the thermal decomposition of PVC. This can be ascribed to the absence of oxygen, a necessary reactant in the Deacon Reaction. However, instead of Cl₂, HCl is still the major product from the combustion of PVC, even in the air.

Figure 5. TG curves for blend 735122 and its components; coal 92073, PVC, cellulose, and newspaper heated at a slow heating rate.

Figure 7. Some MS peak profiles of gas from heating PVC at a slow heating rate.

Figure 8. Profiles of HCl and Cl₂ evolved during the combustion of PVC.

As illustrated in Figure 5, the first weight loss step in the decomposition of newspaper and cellulose is caused by the loss of moisture. Combustion of newspaper and cellulose yield strong water peaks between 250-450°C with the release of CO₂ and CO. This reflects the large oxygen content and numerous OH functional groups in their molecular framework. Another result of this high oxygen content is the absence of methane formation during combustion. Also, more organic acids (formic and acetic acid) are produced during the combustion of newspaper and cellulose, which can be attributed to the polyhydroxy structures in these systems. This can be inferred from their FTIR spectrum by groups of peaks at 2500-3400 cm⁻¹ (OH), 1700-1800 cm⁻¹ (C=O), 1033 cm⁻¹ for methanol, 1106 cm⁻¹ for formic acid and 1175 cm⁻¹ for acetic acid.

Cellulose is a polysaccharide, therefore it is expected that its major pyrolysis products include a series of furan derivatives which are common products from the thermal decomposition of saccharides such as 3-methyl-2-duranone and furfuryl alcohol ($m/z = 98$), furfural (96), methylfuran (82) and furan (68). Since cellulose is the major component in newspaper, the two materials should have similar decomposition products, although the mineral fillers will cause the incomplete decomposition of newspaper. As expected, the common decomposition products from both are furfural, which can be identified from their MS spectra.

The possible products from the combustion of the raw materials, as identified from their FTIR spectra are summarized in Table 3. In summary, the combustion of the different raw materials is quite efficient under these experimental conditions. From the IR and MS spectra, CO₂ is the most abundant combustion product for all the tested materials. Most of the carbon in the materials is oxidized to carbon dioxide and carbon monoxide

1.2. Studies of the Blends. After testing the individual raw fuels, we began to study the thermal behavior of mixtures of the selected materials. The blends were prepared and labeled as follows:

- 73PVC50 is a mixture of coal 92073 and PVC (50% each)
- 73NEW50 is a mixture of coal 92073 and newspaper (50% each)
- 73CEL50 is a mixture of coal 92073 and cellulose (50% each)
- 73P2N25 is a mixture of coal 92073 (50%), PVC (25%) and newspaper (25%)

**Table 3. Tentative Identification of FTIR Peaks from Blends of
Coal 92073 Heated at a Slow Heating Rate**

<u>Compound</u>	<u>73PVC50</u>	<u>73CEL50</u>	<u>73NEW50</u>	<u>73P2N2</u>	<u>735122</u>
CH ₄	3018	3018	3018	3018	3018
HCl	2798	2798	2798	2798	2798
CO ₂	2360	2360	2360	2360	2360
CO	2175	2175	2175	2175	2175
COS	2074	2074	2074	2074	2074
C=O	1700	1700	1700	1700	1700
	1800	1800	1800	1800	1800
SO ₂	1374	1374	1374	1374	1374
Ethyl acetate (?)					1245
Acetic acid	1176	1176	1176	1176	1176
Formic acid	1107	1107	1107	1107	1107
Methanol			1036		
Ethylene	950	950			
1,3-Butadiene	910	906		906	906
p-Xylene	793				
CH ₂ Cl ₂ (?)	756	756	756	756	756
Furan		745	745	745	745
Chlorobenzene (?)	741	741	741	741	741
HCN	712	712	712	712	712

- 075122 is a mixture of coal 92073 (50%), PVC (10%), newspaper (20%) and cellulose (20%)

The TG curve and the FTIR/MS spectra of the blends are almost a combination of those of the individual components. Figure 5 shows the TG curves for blend 735122 and its components. Comparing the results of individual newspaper and its blends, the notable weight loss for newspaper at $T_{\max}$ of 690°C was not observed in the blends. This may be attributed to some reactions between coal and the residues of newspaper to form volatile products at a lower temperature.

The presence of several components in the mixture adds to the difficulties in deciphering the IR and MS spectra obtained from the combustion of the blends. There are several noteworthy findings obtained from the TG/FTIR/MS analysis of the blends. Figure 9 shows the 3D FTIR spectra of blend 735122. Figure 10 is the profile of some major peaks for combustion products of blend 735122.

Through the analysis of MS spectra, it was found that chlorine species such as chlorobenzene appears in all the blends that include PVC. As displayed in the MS spectra, the profiles of peak 112 has the same trend as that of the peak at m/z 36. This suggests a relationship with the chlorine species. In the FTIR spectra, the observed peak at 741 cm^{-1} matches that of chlorobenzene. Thus, the presence of chlorobenzene may be a product from molecular chlorine. All of the different PVC-containing blends show similar trends as those observed in the combustion of pure PVC, that is, mass spectrometric evidence that Cl_2 is produced concurrently with the strong HCl release. This indicated the production of chlorine through the Deacon Reaction during the thermal decomposition of PVC. Following the in-situ generation of Cl_2 , aromatic compounds are readily attacked to form the chlorinated organics.

Figure 9. 3D FTIR spectra of combustion products from blend 735122 heated at a slow heating rate.

Figure 10. Profiles of some major peaks for combustion products of blend 735122 heated at the slow heating rate.

2. Study of the Combustion Behavior Using a High Heating Rate (100°C/min)

In order to study combustion performances under conditions similar to those for AFBC systems, a series of experiments were carried out at a heating rate of 100°C/min. By comparing the results obtained from the different heating rates, an improved picture for the combustion performance of an AFBC during co-firing coal with RDF is obtained.

Figure 11 is an example showing the effect of heating rate on the DTG curves of PVC. On comparing the data with those at the heating rate of 10°C/min, we find two obvious changes. The maximum rates of major weight loss increase 2-8 times. Also the major decomposition temperatures at $R_{\max}$ increase about 50°C. This indicated that the decomposition reaction of fuels occur at a faster reaction rate and higher temperature as the heating rate increases. In fact, the heating rate in an AFBC system is much higher than 100°C/min, whereby one can expect decomposition reactions in it to occur at higher $T_{\max}$ and greater $R_{\max}$ values.

Figure 12 is the comparison of TG curves for blend 735122 and its components at the high heating rate. It was found that under the high heating rate, the major decomposition stages of blends are in between those of the components. In contrast, under the slow heating rate, the blends decompose before the majority of their components.

From the combustion profiles of the blends, the different decomposition stages can be separated only at a slow heating rate. Unlike those at the slow heating rate, the profiles of decomposition reactions for blends display only one continuous weight loss at the higher heating rate.

Figure 13 is the IR spectrum of PVC heated at the higher heating rate. A notable result is the appearance of peaks near 1000, 1750, and 3000 cm^{-1} which occur after the rapid decomposition of fuels and always appear at almost the same wavenumbers. It is possible that these peaks come from some kind of high molecular weight aliphatic acids formed by the rapid decomposition of carbon skeletons. Similar trends can be found in the FTIR spectra from newspaper and cellulose at the higher heating rate.

Figure 11. DTG curves for PVC heated at a slow ($10^{\circ}\text{C}/\text{min}$) and fast ($100^{\circ}\text{C}/\text{min}$) heating rates .

Figure 12. TG curves for blend 735122 and its components; coal 92073, PVC, cellulose, and newspaper heated at a fast heating rate.

Figure 13. 3D FTIR spectra of combustion products of PVC heated at a fast heating rate.

Figure 14 shows 3D FTIR spectra of decomposition products of coals 92073 at the higher heating rate. Unlike the three peaks resulting from the different sulfur forms in the profile of sulfur dioxide at the slow heating rate, only one overlapping peak of sulfur dioxide is observed, along with other gases at the higher heating rate. This change indicates that the oxidative decomposition of different sulfur forms occurs in a narrow temperature range, except for sulfate sulfur, which decomposes continuously over a longer time.

Figure 15 shows the 3D FTIR spectra for decomposition products of blend mixture 735122 at the higher heating rate. A trend similar to the slow heating rate is observed. At the slow heating rate carbon monoxide always evolves along with carbon dioxide. There is only a small amount of methane released at the higher temperature after HCl evolves. On the other hand, at the higher heating rate carbon dioxide appears only at the very beginning. Also, enhanced methane evolution is released at the same time as the evolution of HCl. The greater amount of methane produced at the higher heating rate may be a result of the incomplete combustion of fuels.

Table 4 summarizes the tentative identification of FTIR absorption bands of products resulting from the combustion of the raw materials at the slow and fast heating rates. More than 15 kinds of gaseous species can be identified. The data indicates that at the higher heating rate, it is easier to find methane and xylenes in the evolved gases. However, at the slow heating rate, more oxidation products such as acids and alcohols are found. Table 5 is a summary of tentative identification of FTIR peaks for combustion products of 92073 blends at both heating rates.

From all the FTIR data, the chlorine and hydrocarbon species formed during the combustion of blends are released at the same time for the higher heating rate, whereas they evolved at different times for the slow heating rate. Also, more hydrocarbons are produced at the higher heating rate. These results indicated that there are greater possibilities for yielding harmful chlorinated organic compounds during co-firing coals with RDF in an AFBC system.

Figure 14. 3D FTIR spectra of combustion products of coal 92073 heated at a fast heating rate.

Figure 15. 3D FTIR spectra of combustion products of blend 735122 heated at a fast heating rate.

Table 4. Tentative Identification of FTIR Peaks from Thermal Decomposition of Raw Materials (Wavenumbers, cm^{-1})

Name	PVC	HPVC*	News*	HNews	Cell*	HCell	90003	H90003	92073	H92073
methane	3018	3016		3016		3016	3016	3016	3016	3016
formaldehyde			2800	2800	2800	2800				
HCl	2798	2798					2798	2798	2798	2798
CO ₂	2358	2358	2358	2358	2358	2358	2358	2358	2358	2358
CO	2178	2178	2178	2178	2178	2178	2178	2178	2178	2178
COS							2074	2074	2074	2074
C=O (multiplet)	~1750	~1750	~1750	~1750	~1750	~1750		?	?	?
SO ₂							1374		1374	1374
acetic acid	1175		1175		1175	1175	1175	1175	1175	1175
formic acid	1106		1107		1107	1107		1107		
methanol	1034		1034							
ethylene	950	950	950	950	950	950	950	950	950	950
1,3-butadiene	908	908				908	908	908	908	
p-xylene								794		794
furan			745	745	745	745				
chlorobenzene	741	741					741	741	741	741
HCN							712	712	712	712
benzene	674	674								

* "H" prefix means the fast heating rate. "News" and "Cell" represent newspaper and cellulose, respectively.

Table 5. Tentative Identification of FTIR Peaks for Coal 92073 Mixtures (Wavenumber, cm⁻¹).

<u>Name</u>	<u>73PVC</u>	<u>H73PV</u>	<u>73New</u>	<u>H73Ne</u>	<u>73Cell</u>	<u>H73Cell</u>	<u>73P2N2</u>	<u>H73PN</u>	<u>735122</u>	<u>H73122</u>
methane	3018	3016	3016	3016	3018	3016	3016	3016	3016	3016
hydrogen chloride	2798	2798	2798	2798	2798	2798	2798	2798	2798	2798
carbon dioxide	2358	2358	2358	2358	2358	2358	2358	2358	2358	2360
carbon monoxide	2178	2178	2178	2178	2178	2178	2178	2178	2178	2178
carbonyl sulfide	2074	2074	2074	2074	2074	2074	2074	2074	2074	2074
carbonyl group (multiplet)	1800~ 1700	1800~ 1700	1800~ 1700	1800~ 1700	1800~ 1700	1800~ 1700	1800~ 1700	1800~ 1700	1800~ 1700	1800~ 1700
sulfur dioxide	1374	1374	1374	1374	1374	1374	1374	1374	1374	1374
acetic acid	1175	-	1175	1175	1175	-	1175	1176	1176	-
formic acid	1107	-	1107	1107	1107	1107	1107	1107	1107	1106
methanol	-	1034	1034	1033	-	1033	-	1033	-	-
ethylene	950	950	-	950	950	950	950	950	950	950
1,3-butadiene	908	-	-	908	908	-	908	908	906	-
p-Xylene	793	-	-	793	-	-	-	793	-	793
furan	-	-	745	745	745	745	745	745	745	745
chlorobenzene or o-Xylene	741	741	741	741	741	741	741	741	741	741
hydrogen cyanide	712	-	712	-	712	-	712	-	712	712

Tables 6 and 7 summarize the tentative identification of major peaks in the MS spectra of products resulting from the combustion of both the individual components and mixtures at the slow and rapid heating rates. There are more than 20 detectable organic compounds in the evolved gases, most of which are aromatic compounds. It is notable that peak 112 in the spectra of blends appears more often at the fast heating rate than for the slow heating rate. In accordance with the FTIR data, this is probably an indication that chlorinated organic compounds can be formed more easily at the higher heating rate.

B. Studies of the Mechanism for the Formation of PCDD/Fs During the Combustion of MSW

The purpose of this series of experiments was to examine the proposed mechanism for the formation of PCDD/Fs during the combustion of MSW. Before the following study was conducted, a series of experiments was completed to obtain the optimum conditions for the operation of the furnace and establish the detection limits for GC/MS analysis.

1. Studies with Raw Materials.

Four grams of coal 92073 was burned in a tube furnace in an air flow of 1 standard cubic foot per hour. The furnace was preheated to a temperature of 850°C before the sample was introduced. The gaseous products were trapped in chilled CH_2Cl_2 and analyzed by GC/MS. Similar experiments were carried out on PVC, newspaper, cellulose and RDF. In summary of the results of replicated analyses, phenol is one of the major products evolved during the combustion of coal, newspaper, cellulose, and RDF. One of the major products of PVC combustion is HCl. This is in accordance with the TG/MS results and the proposed mechanism for the formation of polychlorinated phenols. From the GC/MS data, chlorophenol is a major product when blends are burned.

A set of experiments to identify the chlorinated species formed from phenol and Cl_2 and the conditions under which they survive was conducted. A 100 mg sample of phenol was burned in the presence of 0.5% Cl_2 in N_2 and the evolved gases were trapped in methylene chloride and

Table 6. Tentative Parent Structures of MS Peaks for Raw Materials*

Name	PVC	HPVC**	News**	HNews	Cell**	HCell	90003	H90003	92073	H92073
methylpyrene	216									
methyldibenzofuran	182									
1,4-naphthoquinone		158								
dimethylnaphthalene		156								
vinyl naphthalene		154								
acenaphthene		154								
biphenyl		154								
dichlorobenzene	146	146								
methylnaphthalene		142								
ethylmethylphenol										136
chlorobenzene	112	112						112	112	112
octene	112	112	112					112	112	112
methylfurfural			110			110				
methylphenol									108	
xylene	106	106	106	106				106		106
ethylbenzene	106	106	106	106				106		106
3-methyl-2-furanone	98	98	98	94	98	98	98	98	98	98
furanmethanol	98	98	98	98	98	98	98	98	98	98
furfural	96	96	96	96	96	96		96	96	96

Table 6. (Continued)

Name	PVC	HPVC	News	HNew	Cell	HCell	90003	H90003	92073	H92073
phenol	94	94	94	94	94					
toluene	92	92	92	92		92	92	92	92	92
hexene	84	84	84	84		84	84	84	84	84
thiophene							84	84	84	84
methylfuran			82	82	82	82	82	82		
benzene	78	78	78	78	78	78	78	78	78	
furan			68	68	68	68	68	68		
sulfur dioxide							64	64	64	
naphthalene	128	128								
chlorotoluene	126	126								
propylbenzene	120	120	120	120				120	120	
ethylmethylbenzene	120	120	120	120				120	120	
trimethylbenzene	120	120	120	120				120	120	
benzofuran				118	118					

* The numbers in the table represent the m/z values in the mass spectra.

** "H" prefix means the fast heating rate. "News" and "Cell" represent newspaper and cellulose, respectively. The compounds in bold type indicate those also detected by the GC/MS technique.

Table 7. Tentative Parent Structures of MS Peaks*

Name	73PVC	H73PV	73New	H73Ne	73Cell	H73Cell	73P2N2	H73PN	735122	H73122
dimethylnaphthalene		156								
vinyl naphthalene		154								
acenaphthene		154								
biphenyl		154								
methylbenzothiophene	148						148	148	148	
phthalic anhydride	148						148	148	148	
dichlorozene	146						146	146	146	
indan-1,3-dione	146						146	146	146	
methyltetrahydro-naphthalene	146						146	146	146	
methylnaphthalene		142					142	142	142	
chlorobenzaldehyde		140					140	140	140	
chlorobenzaldehyde-H		139					139	139	139	
benzodihydrofuran	134	134	134				134	134	134	
naphthalene	128	128	128				128	128	128	
trimethylcyclohexane	126	126					126	126	126	
benzodihydrofuran	120	120	120				120	120	120	120
propylbenzene	120	120	120				120	120	120	120
acetophenone	120	120	120				120	120	120	120
methylbenzaldehyde	120	120	120				120	120	120	120
trimethylbenzene	120	120	120				120	120	120	120
chlorobenzene	112	112	112	112		112	112	112	112	112
xylene	106	106	106	106	106	106	106	106	106	106
benzaldehyde	106	106	106	106	106	106	106	106	106	106
ethylbenzene	106	106	106	106	106	106	106	106	106	106
xylene-H	105	105	105	105	105	105	105	105	105	105
benzaldehyde-H	105	105	105	105	105	105	105	105	105	105
3-methyl-2-furanone	98	98	98	98	98	98	98	98	98	98
methylthiophene	98	98	98	98	98	98	98	98	98	98
furfural	96	96	96	96	96	96	96	96	96	96
toluene	92	92	92	92	92	92	92	92	92	92
toluene-H	91	91	91	91	91	91	91	91	91	91
hexene	84	84	84	84	84	84	84	84	84	84
thiophene	84	84	84	84	84	84	84	84	84	84
benzene	78	78	78	78	78	78	78	78	78	78
furan	68	68	68	68	68	68	68	68	68	68
sulfur dioxide	64	64	64	64	64	64	64	64	64	64

* The numbers represent m/z values for peaks in the mass spectra of products.

analyzed using GC/MS. The temperature of the reaction was varied, yet the results seemed fairly consistent. It was possible to identify phenol, chlorophenol and dichlorophenol. The same reaction performed in the solution phase seemed to occur readily at room temperature. It then remained to resolve the issue of a vapor phase or solvent phase reaction. Therefore NaHSO_3 , a reducing agent for molecular chlorine, was used to solve this problem. Chlorine can be immediately reduced on reaching the solvent, as a result, the reaction in the solution phase is forestalled. The resulting aqueous solution (in the gas trap) was then extracted using 10 mL aliquots of methylene chloride to partition aqueous and organic phases. This greatly minimized the possibility of reaction in aqueous phase, so it would be reasonable to conclude that the compounds identified in subsequent analyses were formed due to reaction of vapors. The results from the above experiments provide a reliable prediction of the practical chemical reactions occurring in the AFBC system. It confirms the possibility of the formation of chlorophenol through the vapor phase reaction which readily takes place under the conditions of the AFBC.

2. Studies of the Deacon Reaction

As revealed in the previous work, the major combustion product of PVC is HCl, which in turn may be converted to molecular chlorine through the thermal Deacon Reaction. To examine the possibility of producing molecular chlorine via the Deacon reaction over temperatures ranging from 400-800°C, a mixture of air and 10% HCl in nitrogen (air: HCl volume ratio of 2:1) was introduced into the quartz tube preheated to different temperatures in the furnace. The product gases were trapped in a phenol-methylene chloride solution and the solution was analyzed for chlorophenols by the means of GC/MS.

Phenol has proven to be an effective absorbent for chlorine gas, therefore, the production of molecular chlorine through the Deacon Reaction can be monitored by the production of chlorinated phenol in the trapped solution. Figure 16 shows the GC/MS results from the experiments performed at different temperatures. As illustrated in the chromatograms the

Figure 16. Chromatograms of the products from the Deacon Reaction experiments.

production of chlorophenols is enhanced as the temperature increases. This indicates that the Deacon Reaction is favored at higher temperatures, which is consistent with thermodynamic calculations that shows the Deacon Reaction is favored at 590°C. The results are summarized in Table 8.

As already reported, the Deacon Reaction readily occurs, even at the room temperature, in the presence of catalyst such as Cu compounds. Cu is one of the more abundant elements in MSW, consequently, under the co-firing conditions the Deacon Reaction may take place much easier than under our test conditions.

3. Studies of the Chlorination of Phenol

To examine the gas phase chlorination of phenol, as expressed in the equation (2), 100 mg portions of phenol were placed in a heated tube and evaporated in the presence of a constant flow of 0.5% Cl₂ in nitrogen. Chlorination occurred in the gaseous phase and the products were cooled by liquid nitrogen and condensed upon exiting from the combustion tube, carefully washed by methylene chloride, and analyzed using the GC/MS system.

The gas-phase chlorination of phenol experiments produced 2-chlorophenol, 4-chlorophenol and 2,4-chlorophenol, which were identified by NIST library matches and GC retention times of the pure materials. The results are listed in Table 9. The chlorination of phenol began at temperature around 250°C. At higher temperatures, dibenzofuran was produced.

4. Studies of the Condensation of Chlorophenols

The combustion of chlorinated phenols, which may lead to the reaction illustrated in equation (3), was examined by heating 100 mg portions of 2,4-chlorophenol in the presence of air in the tube furnace. The combustion products were absorbed by CH₂Cl₂ and identified using the GC/MS system. The reaction was also studied in a series of experiments in which 3 mg portions of 2,4-dichlorophenol were heated in air at a rate of 20°C/min in the TGA and the evolved gases

Table 8. Results from the Study of The Deacon Reaction

<u>Temperature (°C)</u>	<u>Tentative Product Identification</u>
Room temperature	None
400	2-chlorophenol and 4-chlorophenol
600	2,4- dichlorophenol, 3-chlorophenol 4-chlorophenol, 2-chlorophenol
800	2,4-dichlorophenol, 3-chlorophenol 4-chlorophenol, 2-chlorophenol

Table 9. Chlorination and Condensation Reactions of Phenol

<u>Run</u>	<u>Temperature (°C)</u>	<u>Time (min)</u>	<u>Tentative Product Identification</u>
1	600	15	Dibenzofurans, no chlorophenols
2	800	15	Dibenzofurans, no chlorophenols
3	600	30	Dibenzofuran, mono, di and trichlorophenols
4	800	30	Dibenzofurans, mono, di and trichlorophenols
5*	700	30	Dibenzofuran, mono, di and tri chlorophenols
6*	250	30	Dibenzofuran, mono, di and trichlorophenols
7*	425	30	Chlorinated phenols and dibenzofuran.

* The trap used for the last three runs contained aqueous sodium bisulfite.

were monitored (on-line) using FTIR and MS. The MS profiles for the combustion products of 2,4-dichlorophenol are shown in Figure 17. Figure 18 is its 3D FTIR spectrum.

The GC/MS results shows the condensation products from the combustion of 2,4-dichlorophenol include 2,4,6-trichlorophenol, tetrachlorodibenzofuran, and dichlorodibenzodioxin. Figure 19 shows the chromatograms of the reaction products. Tetrachlorodibenzofuran and dichlorodibenzodioxin began to be formed below 400°C. Table 10 summarizes the experimental results.

Based on the above information, the proposed mechanism seems to be a possible chemical pathway for the production of PCDD/Fs during the combustion of MSW under the specific temperature ranges studied.

5. Studies of the Reaction Between PVC and Phenol

In order to gain a more comprehensive understanding of the formation of the chlorinated organic compounds during the combustion of MSW, the reaction between PVC and phenol in a tube furnace was studied. As confirmed by the previous study, combustion of newspaper and cellulosic stocks will yield phenol, and the thermal decomposition of PVC will produce Cl_2 , the necessary chlorination agents.

To minimize the heat up time of the reactants in these tests, the furnace was preheated to the desired temperature, then the reactor tube with phenol and PVC was inserted. Two different reagent combinations were tested, Cu/phenol/PVC and PVC/phenol.

The results showed that the presence of Cu facilitate the formation of chlorinated organics. Copper works as a catalyst to facilitate the Deacon Reaction and, as a result, more chlorinated organic compounds are produced in the presence of copper wire. Also, compared with the yield of mono-, and dichlorinated organics at 400°C, fewer of these compounds were detected at 800°C from the reaction of phenol and PVC under the testing conditions, as shown in Figure 20.

Figure 17. Mass spectra profiles for the combustion products of 2,4-dichlorophenol.

Figure 18. 3D FTIR spectra of the combustion products of 2,4-dichlorophenol.

Figure 19. Chromatograms of the reaction products from the combustion of 2,4-dichlorophenol.

Table 10. Products from the Study of The Condensation Reactions of Chlorophenols.

<u>Sample</u>	<u>Temperature (°C)</u>	<u>Tentative Product Identification</u>
2,4-dichlorophenol	700	Tetrachlorodibenzodioxin, tetrachlorofuran, dibenzodioxin, 2-chlorophenol, 2,6-dichlorophenol, 2,4,6-trichlorophenol, dichlorobenzene, trichlorobenzene, dichlorodibenzofuran.
2,4-dichlorophenol	400	Tetrachlorodibenzofuran, trichlorodibenzodioxin, dichlorodibenzodioxin.
4-chlorophenol	700	Dichlorodibenzofuran, benzene, chlorobenzene.
2-chlorophenol	700	Dichlorodibenzofuran, phenol.

Figure 20. The reaction products from PVC and phenol heated in the tube furnace.

These results seem to contradict the conclusions obtained from the previous study, in which the gas-phase reaction between phenol and chlorine gas was tested. However, there are some differences between these two test systems. Unlike the former study, in which the chlorine gas was introduced into the furnace directly, Cl_2 is produced in-situ from the thermal decomposition of PVC through the Deacon Reaction in this set of experiments.

Through the previous thermal analysis studies of raw materials, the decomposition process of PVC begins around 200°C , and reaches its maximum at 400°C with the heating rate at $100^\circ\text{C}/\text{min}$. Chlorine gas may be generated through the Deacon Reaction with the release of a large amount of HCl . From the thermodynamic evaluation of the Deacon Reaction, increasing combustion temperatures would appear to suppress the equilibrium formation of Cl_2 . However, when kinetics are taken into account, high temperature tends to increase Cl_2 formation and oxychlorination reaction rates. Theoretically, there is an optimum temperature for the formation of chlorine from the thermal decomposition of PVC through the Deacon Reaction. As a consequence, there may be an optimum temperature for the reaction of PVC with phenol to produce chlorophenol.

C. The Effect of Sulfur Species on the Deacon Reaction

The following tests were designed to explore the negative effect of SO_2 upon the chlorine formation through the Deacon Reaction, subsequently, minimizing possible PCDD formation. In the previous studies, it was found that combustion of the chlorine-containing polymer PVC may produce chlorinated organic compounds. The most important of these compounds were chlorinated benzenes (the major products), naphthalenes, styrenes, and biphenyls. There are several possible mechanisms for the formation of chlorinated organic compounds during combustion of chlorine-containing polymers. In some cases, thermal rearrangements and elimination reactions may give rise to a group of simple structures. In other cases, fragmentation of the polymer to small organic free radicals and either Cl_2 or atomic Cl may result in new combinations of cyclic materials.

As is known, coal contains both inorganic and organic sulfur. The inorganic sulfur is largely in the form of pyrite, a mineral whose composition approximates FeS_2 . The organic constituents include aliphatically bound sulfur, such as thio ethers, and a wide variety of aromatic sulfur compounds. Aliphatic sulfur is more important in low-rank coals such as lignite; however, high-sulfur bituminous coals contain more aromatically bound sulfur. Many of these compounds are very easily oxidized, consequently, one of the major products from the combustion of coal is SO_2 .

Tests conducted by Gullet and coworkers showed that the homogeneous reaction of Cl_2 with SO_2 to form HCl (a less likely chlorinating agent than Cl_2) is not measurable below 800°C . This is not apparent from thermodynamic calculations of the free energy change. Although equilibrium calculations suggest that the reaction is favored over the full range of temperatures tested, the kinetics of reaction may prevent observation of measurable product until the higher temperatures are reached.

Therefore, the possible effect of SO_2 upon the formation of Cl_2 through the Deacon Reaction was examined. To simulate the conditions used in an AFBC system, the quartz tube was preheated to the desired temperature, then the gas was introduced. The flow rate of HCl (1% in nitrogen), SO_2 (4.86% in nitrogen) and air were adjusted by the calibrated teflon flow meters. The evolved gas was trapped by a carefully chosen absorbent, which was prepared by dissolving 50 mg phenol in 25 mL methylene chloride. Then the trapped solution were concentrated to 1 mL and injected into the GC/MS system for analysis. In the quantitative study, the concentration of HCl and O_2 in the gaseous mixtures was fixed, and only changed the fraction of SO_2 . At each condition, the results presented were based on at least three runs.

As pointed out in the previous studies, phenol was confirmed to be an effective organic sorbent for chlorine. In the case of any chlorine produced, it reacted with phenol and subsequently, chlorinated phenols are formed. The amount of phenol in the trapping solution was accurately controlled to within $\pm 0.0001\text{g}$. The production of molecular chlorine was measured by

comparing the relative amount of chlorinated phenol and phenol in the methylene chloride solution. The results show that once SO_2 is introduced the production of chlorophenol decreased. The relationship between the S/Cl ratio and the production of chlorophenol is shown in Figure 21.

Griffin⁶, in a study of co-incineration of coal and municipal solid wastes, postulated that dibenzodioxins would not form when the S/Cl ratio was greater than 10, and proposed increasing the sulfur of the wastes in co-combustion with coal in order to decrease dioxin formation. However, in our experiments in which the S/Cl was less than 2.5/1, dramatic decreases in the major chlorine-containing products of combustion were observed. This could indicate that quenching effects of sulfur are even greater than calculated by Griffin.

D. AFBC Results

1. Preliminary Laboratory-Scale Fluidized Bed Combustion Test

The main purpose of these preliminary AFBC runs was to determine the compatibility of coal and pelletized wood in blends. The first two tests were made on April 25, 1995, using WKU coal No. 95010, and wood pellets provided by Jim C. Hamer Co. Evolved gases were analyzed by GC and FTIR analyses. In addition, gas samples for IC and fly ash samples were collected.

Evolved gases from the combustor were analyzed by gas chromatography. It was found that when the system was running under stable combustion conditions CO and CH_4 were not detected in the flue gases. In addition, gas samples were collected for IC analysis to measure chloride and sulfate. The IC data showed that sulfate was not detected, in agreement with FTIR data. Thus limestone appears to be an effective sorbent, absorbing almost all of the sulfur dioxide evolved from the coal and coal/wood combustion. Chlorine occurs in the range of 1,000 ppm in coal and wood samples, and it was found in the range 0.1-0.5 ppm in IC samples.

Figure 21. Production of chlorinated phenol as a function of S/Cl ratio.

The fly ash samples were used to measure the carbon content, in order to calculate the combustion efficiency. Combustion efficiencies greater than 97% and frequently around 98-99% were achieved without employing char recycle. Thermal efficiency is calculated by the thermal balance and during the combustion run the thermal efficiency values ranged from 69.6% to 83.5%.

In summary, this six-hour burn started with coal, with gradual switching to sawdust pellets. No difficulty was encountered in using a mixture of 95% sawdust and 5% coal to maintain the bed temperature around 1500°F. Some conclusions from these experiments are as follows:

- Combustion efficiencies greater than 97% were achieved without employing char recycle. Generally, the combustion efficiencies of mixtures of coal and wood were greater than those of pure coal.
- Thermal efficiencies from 69.6% to 83.5% were realized in each of the tests conducted.
- By using limestone as the bed material, a sulfur capture efficiency of more than 90% was achieved.

2. Two 1000-Hour Runs

Two 1000-hour test runs were completed to test for the emission of chlorine, sulfur and organic compounds from the combustion of two coals. The results serve as the baseline for the AFBC system and were compared to those from the addition of RDF during combustion processes. The first coal (KY#9) was a high sulfur (2.8%) and low chlorine (0.012%) coal, whereas the second coal (IL#6) was a high sulfur (2.1%) and high chlorine (0.28%) material. The principal operating parameters were as follows:

Excess air level:	approximately 1.3
Ca/S ratio:	near 3
Bed temperature	near 1500°F
Oxygen in the flue gas	4-6%
Unburned carbon in the fly ash	6-15%

Figures 22 and 23 show the effect of different coals on the emission of sulfate and chloride from the AFBC system. The rate of sulfation is the rate determining step for complete desulfurization. If the sulfation step is limited, the conversion efficiency is drastically reduced. This concept is a balance between the rate of sulfation and the amount of available surface area from calcium oxide. The results indicate the temperature ranges for maximum desulfurization in our AFBC experimental conditions are between 1120 to 1170 K. Poor desulfurization was observed above 1170 K. Higher concentrations of HCl were measured from the combustion of the high-chlorine content coal. The reaction between HCl and CaO is generally not favored at the higher temperature (1073 K) except with higher concentrations (400 ppm) of HCl. Also, no chlorine was identified in the absorbent solution. Naphthalene was the only organic compound identified in the flue gases from the combustion of both coals.

3. Co-firing PVC with Coal in the AFBC System

The objective of this set of experiments was to evaluate the combustion performance when co-firing the coal with MSW. The objectives were to determine the emission of inorganic acid gases (HCl and SO₂), the extent of chlorinated organic compound formation, as well as to examine the effect of using coal as a co-combustion energy source with MSW.

The fuel used in this test was switched from coal alone to the mixture of coal, PVC and wood pellets. The experimental conditions are as follows:

- Fuel compositions:
- (1) 100% coal
 - (2) 89% coal, 1% PVC and 10% wood pellets
 - (3) 86.7% coal, 3.3% PVC and 10% wood pellets
- Fuel feed rates: ~17.5 lb/hr
- Limestone feed rates: ~1.26 lb/hr for coal 95010, ~4.48 lb/hr for coal 95031
- Ca/S ratio: ~3.0
- Air flow rate: ~3.25 lb/hr

Figure 22. The effects of different coals on the emission of SO₂ during combustion in an AFBC system.

Figure 23. The effects of different coals on the emission of HCl during combustion in an AFBC system.

The IC data showed that with the increase of PVC in the fuel mixture, the HCl emission increased and the SO₂ emission decreased, as shown in Figures 24 and 25. Compared with the results from the combustion runs of 100% coal, no chlorinated organics and PAHs were detected under our experimental conditions. These results indicate a promising future for co-firing MSW with coal.

X. CONCLUSIONS

Based on the data and diagrams presented in the above sections the following statements and observations can be made.

- Thermal analysis is a useful method to study the combustion behavior of different fuels
- The major combustion product of PVC is HCl. With the release of large amounts of HCl, molecular chlorine can be generated through the thermal Deacon Reaction
- The TG/FTIR/MS results indicate that under high heating rates, there are more hydrocarbons released from the combustion of coal and other raw materials. Moreover, the concurrent evolution of HCl and the large amount of hydrocarbons may facilitate the formation of chlorinated organics.
- The proposed four-step mechanism involving the Deacon Reaction appears to be a possible chemical pathway for the formation of PCDD/Fs during the co-combustion process within specific temperature ranges.
- SO₂ is an effective inhibitor for the formation of molecular chlorine through the Deacon Reaction.
- No PAHs and chlorinated organics were detected in the fly ash and flue gas when co-firing PVC with coal in our AFBC system.

Figure 24. The emission of HCl as a function of the composition of the fuel.

Figure 25. The emission of SO_2 as a function of the composition of the fuel.

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