

# STUDIES OF THE MECHANISM FOR THE FORMATION OF CHLORINATED ORGANICS DURING THE COMBUSTION OF MSW AND COAL

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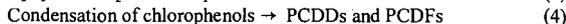
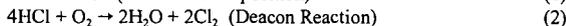
## ABSTRACT

Several kinds of coals and the major combustible components in MSW, such PVC and cellulose, were tested in this project. TGA/MS/FTIR analyses were performed on the raw materials and their blends, and the combustion profiles collected indicated various types of thermal behavior. The results indicated greater possibilities for the formation of organic compounds during co-firing at fast heating rates than at slow heating rates. Experiments in a tube furnace showed that molecular chlorine is a key intermediate for the formation of chlorinated organics during the combustion of MSW. A mechanism proposed for the formation of chlorinated organics includes the Deacon Reaction. Experiments conducted using pure organic compounds verified this reaction as a possible pathway. The effect of sulfur dioxide on the formation of molecular chlorine during combustion processes was examined. The results indicate the introduction of SO<sub>2</sub> does minimize the formation of molecular chlorine and subsequently chlorinated organics.

## INTRODUCTION

The amount of municipal solid waste produced in the United States each year has risen to more than 200 million tons. According to a prediction by the Environmental Protection Agency (EPA) this amount will rise to 216 million tons by the year 2000.<sup>1</sup> Landfilling, 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. However, due to the concern over emissions of hazardous chlorinated organics, especially the harmful polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs), the development of technology for the incineration of MSW has slowed significantly.

Despite reports of significant amounts of PCDDs and PCDFs being found in the emissions of municipal waste combustors, they were not detected in the effluents from a combined coal/municipal waste plant, nor were noteworthy amounts found in the fly ash.<sup>2</sup> Several mechanisms have been proposed to explain the formation of PCDD or PCDFs during the combustion of MSW, and 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.<sup>3</sup> This synthesis involves the Deacon Reaction and is represented by the following steps:

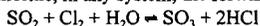


From the Deacon reaction, molecular chlorine is produced and subsequently chlorinates aromatic compounds through substitution reactions. In our study, the source of HCl has been confirmed as the thermal decomposition of chlorine-containing plastics. Chlorine gas may be generated in-situ from HCl and oxygen in the combustion gases of MSW incinerators via the Deacon Reaction.

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<sub>2</sub> 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.<sup>4</sup> Based on the thermodynamic evaluation 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.<sup>5</sup> Gullett and co-workers reported that high concentrations of a sulfur species (sulfur dioxide) are responsible for the apparent lack of PCDDs and PCDFs in the emissions from coal-fired combustors.<sup>6</sup> Lindbauer showed that co-firing MSW with 60% coal drastically reduced the formation of PCDD/PCDF.<sup>7</sup> Co-firing coal and MSW seems to have 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 involving sulfur species proposed for limiting PCDD production, 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 the project reported in this paper, this reaction was examined in a tube furnace. The results indicated an apparent inhibiting effect of sulfur on the Deacon reaction.

Municipal solid waste (MSW) varies considerably in composition. The noncombustibles of MSW, such as metals and glasses, were excluded from this study. Refused-derived fuels (RDF) are made from the combustible components of MSW. The combustion and thermal decomposition process of these individual materials and their blends were examined in this study using TGA/FTIR/MS and GC/MS techniques. The combination of TGA/FTIR and TGA/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.

## EXPERIMENTAL

### 1. TGA/FTIR/MS System

Small amounts of tested materials were placed in the TGA and heated to 1000°C at different heating rates in a dynamic air atmosphere. The spectra and profiles of gas species flowing out of the TGA were 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 TGA is also interfaced to the mass spectrometer using a fused silica capillary sampling inlet that is heated to approximately 170°C.

### 2. 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. To study the combustion performance of the materials of interest, the furnace was preheated to the desired temperature before the sample was introduced. 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 a cold 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 helped confirm the identification of the unknowns. Standard materials were tested to establish the detection limits of the experimental set-up.

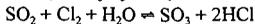
### 3. Laboratory Fluidized Bed Combustion Tests

The laboratory scale (12-inch) atmospheric fluidized bed combustor at Western Kentucky University was used in this study. The active bed area is 125 in<sup>2</sup>. 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. The fuel is injected into the fluidized bed by using pneumatic injectors. The injectors used for these tests are located about 9 in above the air distributor of the combustor. The bed temperature is controlled by the fuel feed rate adjustment.

Evolved gases from the combustor were analyzed by gas chromatography and FTIR spectroscopy. 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.

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## RESULTS AND DISCUSSION

### 1. Characterization of Raw Materials and Their Blends

The thermal behavior of the raw materials of interest were investigated at a heating rate of 10°C/min. The purpose of these 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 used to assess the relative thermal stability and temperature relationships of the materials. These results are important to the analysis of materials and control of the performance of an AFBC.

As observed from the FTIR and MS analyses, a common decomposition product from newspaper and cellulose was furfural. Upon interpretation of the MS spectrum obtained from the combustion of PVC one finds a very notable result. As shown in Figure 1, it appears that the production of molecular chlorine accompanies the release of a large amount of HCl during the combustion of PVC. Materials with masses 36 and 38 are formed at the same time, and strongly suggest the presence of isotopes of  $H^{35}Cl$  and  $H^{37}Cl$ . The integrated ratio is close to the chlorine isotopic ratio. Furthermore, three additional m/z peaks appear at exactly the same point, with apparent masses of 70, 72, and 74 corresponding to  $^{35}Cl_2$ ,  $^{35}Cl^{37}Cl$ , and  $^{37}Cl_2$ . This is strong evidence suggesting that some fraction of the abundant HCl may be undergoing a thermal Deacon Reaction to produce molecular chlorine. Following the in-situ generation of  $Cl_2$ , the aromatic compounds can be readily attacked to form chlorinated organics such as chlorobenzene, which correspond to masses of 112 and 114. 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 attributed to the absence of oxygen, a necessary reactant in the Deacon Reaction. However, although there is no  $Cl_2$  formed, HCl is still the major product from the combustion of PVC, even in air.

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. The decomposition reactions of fuels occur at a much faster rate and at higher temperatures as the heating rate increases. As shown in the TGA/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. In fact, the heating rate in an AFBC system is much higher than 100°C/min, whereby one can expect there are greater possibilities for yielding chlorinated organic compounds during co-firing coals with RDF in an AFBC system.

### 2. 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.

Four gram samples of different raw materials were burned in air in a tube furnace. 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. As a summary of the results of replicated analyses, phenol is one of the major products that 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 TGA/MS results and the proposed mechanism for the formation of polychlorinated phenols. It was shown in the GC/MS data that chlorophenol is a major product when blends are burned.

To examine the possibility of producing molecular chlorine via the Deacon Reaction over a temperature range of 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 analyzed for chlorophenols by 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. The results showed that the production of chlorophenols is enhanced as the temperature increases. This indicates that the Deacon Reaction is favored at higher temperatures.

The Deacon Reaction readily occurs, even at the room temperature, in the presence of a 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 more readily than under our test conditions.

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% Cl<sub>2</sub> in nitrogen. 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 chlorination of phenol began at temperatures around 250°C and produced 2-chlorophenol, 4-chlorophenol and 2,4-chlorophenol. At higher temperatures, dibenzofuran was produced.

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 GC/MS results show that the condensation products from the combustion of 2,4-dichlorophenol include 2,4,6-trichlorophenol, tetrachlorodibenzofuran, and dichlorodibenzodioxin. The latter two compounds began to be formed below 400°C.

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.

### 3. The Effect of Sulfur Species on the Deacon Reaction

The following tests were designed to explore the negative effect of SO<sub>2</sub> 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.

Tests conducted by Gullet and coworkers showed that the homogeneous reaction of Cl<sub>2</sub> with SO<sub>2</sub> to form HCl (a less likely chlorinating agent than Cl<sub>2</sub>) is not measurable below 800°C.<sup>8</sup> 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<sub>2</sub> upon the formation of Cl<sub>2</sub> through the Deacon Reaction was examined at 800°C. The quartz tube reactor was preheated to the desired temperature before the gas was introduced. The flow rate of HCl (1% in nitrogen), SO<sub>2</sub> (4.86% in nitrogen) and air were adjusted by the calibrated teflon flowmeters. The evolved gas was trapped by a carefully chosen absorbent, which was prepared by dissolving 50 mg phenol in 25 mL methylene chloride. The amount of phenol in the trapping solution was accurately controlled to within +/-0.0001g. 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<sub>2</sub> in the gaseous mixtures was fixed, and only changed the fraction of SO<sub>2</sub>. At each condition, the results presented were based on at least three runs. It was shown that once SO<sub>2</sub> was introduced the production of chlorophenol decreased. The relationship between the S/Cl ratio and the production of chlorophenol is shown in Figure 2.

Griffin, 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.<sup>5</sup> 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 those calculated by Griffin.

### 4. Co-combustion of PVC with coal in the AFBC system

The objective of this set of experiments was to evaluate the combustion performance when co-firing coal with MSW. PVC was selected for this study, since it is the major source of chlorine during the MSW incineration. The objective was to determine the emission of inorganic acid gases (HCl and SO<sub>2</sub>), 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 were 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

Analytical data for the raw materials used in this study are shown in Table 1. The IC data showed that with the increase of PVC in the fuel mixture, the HCl emission increased and the SO<sub>2</sub> emission decreased. Compared with the results from the combustion runs of 100% coal, no chlorinated organics and PAHs were detected under our experimental conditions.

## CONCLUSIONS

From the results of the study reported in this paper, the following statements and observations can be made:

- 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 TGA/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.
- SO<sub>2</sub> 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 the WKU AFBC system.

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**Table 1. Analytical Data for Raw Materials**

<u>Parameter</u>	<u>95010</u>	<u>95031</u>	<u>PVC</u>
Coal Seam	Blend	IL#6	
Rank of Coals	A	B	
% Moisture*	2.32	8.32	0.00
% Ash	7.22	10.78	0.36
% Vol. Matter	39.97	37.21	99.64
% Fixed Carbon	52.82	52.02	0.00
% Carbon	79.38	72.61	38.71
% Hydrogen	5.31	4.82	4.2
% Nitrogen	1.63	1.54	0.07
% Sulfur	0.67	2.38	0.22
% Oxygen	5.69	7.57	0
Chlorine, ppm	1,039	3,065	56.45**
Cal. Value (Btu/lb)	14,077	12,842	8,556

\* 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.

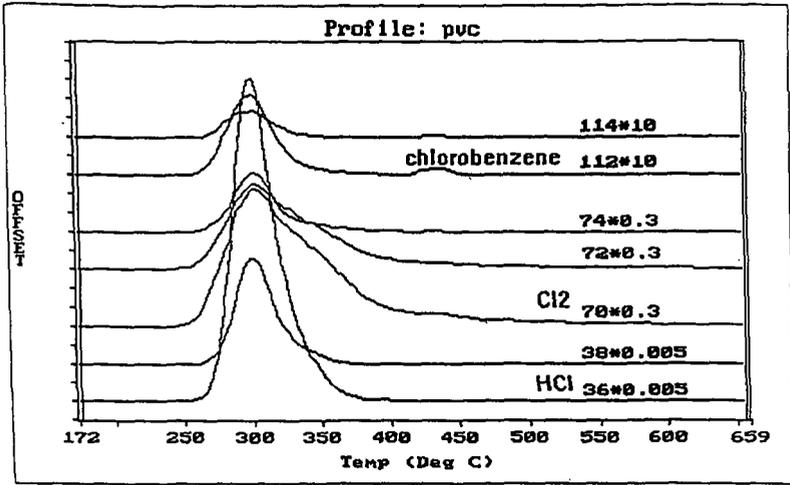


Figure 1. Mass profiles of HCl and Cl<sub>2</sub> evolved during the combustion of PVC.

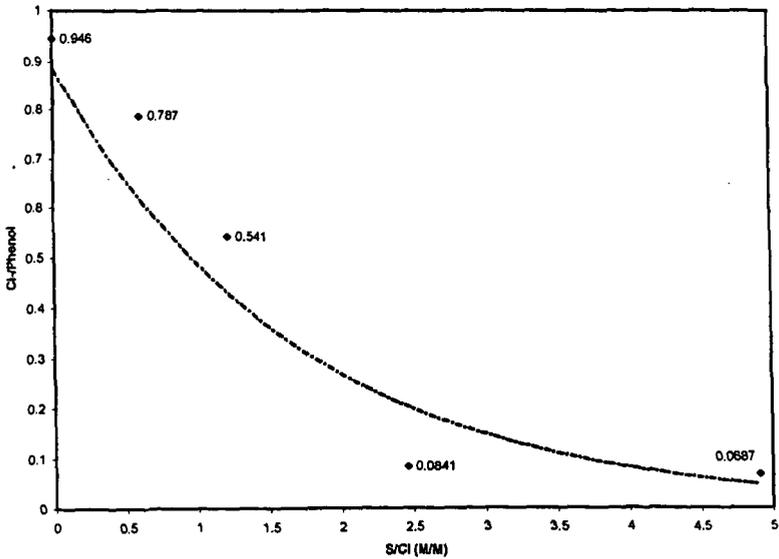


Figure 2. Production of chlorinated phenol as a function of the S/Cl ratio.