The Effects of SO2 on the Formation of Cl2 During Co-Firing Municipal Solid Waste With Coal

Ying Xie
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THE EFFECT OF SO$_2$ ON THE FORMATION OF Cl$_2$

DURING CO-FIRING MUNICIPAL SOLID WASTE WITH COAL

A Thesis Presented to
the Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
of the Requirement for the Degree
Master of Science

by
Ying Xie

August, 1998
THE EFFECT OF SO\textsubscript{2} ON THE FORMATION OF Cl\textsubscript{2}

DURING CO-FIRING MUNICIPAL SOLID WASTE WITH COAL

Date Recommended: July 13, 1998

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Ying Xie
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THE EFFECT OF SO$_2$ ON THE FORMATION OF Cl$_2$

DURING CO-FIRING MUNICIPAL SOLID WASTE WITH COAL

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August 1998

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Department of Chemistry

Western Kentucky University

The Deacon Reaction was proposed as a mechanism for the formation of molecular chlorine during the combustion of municipal solid waste (MSW):

$$4\text{HCl} + \text{O}_2 \leftrightarrow 2\text{Cl}_2 + 2\text{H}_2\text{O}$$

As suggested by some researchers, co-firing high sulfur coal with MSW may reduce the emission of toxic chlorinated organics, resulting from the reaction between SO$_2$ and Cl$_2$:

$$\text{SO}_2 + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_3 + 2\text{HCl}$$

The effect of sulfur dioxide on the formation of chlorine through the Deacon Reaction is investigated in this study. A Lindberg Furnace was utilized and preheated to 800°C to simulate the conditions in the AFBC system. The results indicated that SO$_2$ is an effective inhibitor for Cl$_2$ formation. In addition, the optimum S/Cl ratio to reduce the toxic emission for co-firing is proposed. Tests regarding the AFBC system were also carried out to evaluate the combustion performance when co-firing coal with PVC pellets.
I. INTRODUCTION

A. Background

One of the big issues challenging environmental management and pollution control at present is the disposal of the tremendous amount of municipal solid waste (MSW). According to the forecast of Environmental Protection Agency (EPA) the amount of MSW generated in United States every year will rise to 216 million tons in the year 2000.\(^1\) Landfilling, the traditional approach to dealing with the waste, becomes more expensive and impractical owing to the growing societal concern over land use, the rapidly declining availability of sanitary landfills and stringent environmental regulations.

Incineration is one of the alternative waste management strategies to replace landfilling, and such waste-to-energy technologies have already displayed a few advantages over the conventional method. There are several MSW incinerators in the United States and Europe constructed for burning municipal wastes alone or combined with wood wastes.\(^2\) The energy recovery from these plants is attractive to state and local governments, and in addition, composting effectively reduces the volume of MSW. However, the development of such facilities has slowed significantly in recent years, resulting from apprehension over possible emissions of hazardous chlorinated organics, especially the harmful polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated
dibenzofurans (PCDFs). The emissions of PCDD/Fs from incineration processes were first reported in 1977 by Olie and co-workers. A number of measurements and evaluations have been carried out in a variety of combustion sources thereafter, and trace quantities of PCDD/Fs emissions have been detected in most combustion sources involving the burning of organic materials, such as waste incineration, the paper industry, motor vehicle exhausts, etc. MSW incineration has been identified as one of the serious PCDD/Fs emission sources by some scientists, based on the relatively high dioxin concentrations in flue gas and fly ash discharged from incinerators. Researchers have suggested various pathways to rationalize the formation of PCDD/Fs from MSW combustion and proposed several technical control measures to diminish the production of PCDD/Fs. The focus of this work is the study of one remedial strategy, in which coal is co-fired with MSW to reduce the emission of chlorinated organic compounds. This work is of special importance in improving the performance of the incineration technology, in order to make it reach its full potential in an environmentally acceptable manner.

B. Formation of PCDD/Fs during the Combustion of MSW

Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans are a group of chlorinated tricyclic aromatic compounds with similar physical, chemical and biological properties. They are sometimes present in off-gases from several industrial processes and can be formed during some human activities. The structures of these compounds are illustrated as follows:
Various degrees and positions of chlorination on the aromatic ring structures possibly take place, leading to 135 PCDFs and 75 PCDDs in total. In the environment PCDDs and PCDFs are detected in trace amounts as a mixture of the isomers and are usually referred as “dioxin” collectively.

Although the level of PCDD/Fs that results in negative health effects in human beings is still under debate, it is believed that these compounds, even in trace quantities, exhibit high toxicity and show carcinogenic and mutagenic effects. In a recent United States EPA review, the noncancer health effects of dioxin in humans, such as disruption of immune and reproductive systems have also been proposed.\textsuperscript{6, 7} Therefore, minimization of such species in the effluents of combustion systems is essential to optimize the incineration conditions. PCDDs and PCDFs are chemically stable in general and usually in small amounts. As a consequence, a feasible measure to reduce their emissions is to prevent their formation during the combustion rather than to capture or destroy them thereafter.

Theoretical calculations indicated that PCDD/Fs are formed through a heterogeneous mechanism at lower temperatures ($<600^\circ$C) rather than via homogeneous
gas phase reactions.\textsuperscript{8} Such a temperature regime exists in the post-combustion zone of the incinerator. The off-gas from the combustion chamber passes the part of an incineration plant in which these gases are cooled down and passed through an air pollution control device before being emitted from the stack. Residue particles (fly ash) present in the off-gas may act as an active surface for the formation of PCDD/Fs.

Several potential mechanisms have been advanced to explain the PCDD/Fs formation in the municipal solid waste incinerator. The first involves the incomplete combustion of trace levels of PCDD/Fs already present in the feed.\textsuperscript{9} The second theory suggested that at low temperatures, such as 250-350°C, PCDD/Fs could be engendered from native carbon in MSW fly ash, i.e., unburned, unextractable carbon present in the fly ash matrix. This route is often referred as de novo synthesis. Experimental evidence verified that in the presence of a metal catalyst, the particle bound carbon on the fly ash would react with oxygen, water and inorganic chlorides via a copper (Cu\textsuperscript{2+}) catalyzed reaction to form aromatic structures including chlorinated organics and PCDD/Fs.\textsuperscript{10} At present the mechanism of de novo synthesis is still unclear, and none of the proposals regarding the de novo synthesis render a mechanism explicit enough to be simulated and tested under laboratory conditions.

Another alternative pathway is associated with chemically similar precursors, such as chlorophenols, which may be formed initially as the products of incomplete combustion (hereafter collectively referred to as “precursor mechanism”). Laboratory evidence demonstrated that transition metal ions like Cu and Fe are capable of catalyzing formation reactions, which take place on the fly ash particles. The small organic molecules can be adsorbed onto the fly ash from the off-gas and subsequently converted
to PCDD/Fs. All theories referred to offer plausible pathways for the formation of PCDD/Fs, and they may be valid and cooperative under different circumstances. Extensive characterization of the mechanism of PCDD and PCDF formation is made difficult by the inability to accurately simulate the combustion/fly ash environment and to control the experiment parameters that influence PCDD and PCDF formation.

However, as indicated from Dickson’s study, in the presence of sufficient phenol and chlorine sources, the fly ash catalyzed formation of PCDDs using chlorophenol as precursors is more prevalent than de novo synthesis using carbon. In their very recent report, it was shown that the octachlorodibenzo-p-dioxin (OCDD) yield from pentachlorophenol precursors were 2-4 orders of magnitude greater than those from the de novo synthesis of combined particulate C, inorganic chlorides and a Cu catalyst. It appears that the precursor mechanism is most important in the presence of substantial amounts of phenol and chlorine.

A thorough understanding of the mechanism of dioxin formation will facilitate a search for dioxin sources in the environment and provide a better guidance for devising technical control strategies and improving the performance of practical combustion facilities in order to reduce dioxin emissions. Based on a literature review, the following mechanism is proposed for the formation of PCDD/Fs during the combustion of MSW:

1. Chlorinated aliphatics, in particular plastics containing vinyl chloride or vinylidene dichloride units (PVC, Saran) are well known to undergo thermal decomposition with the elimination of large quantities of HCl;
2. HCl is partially converted to Cl$_2$ via the Deacon Reaction

$$4\text{HCl} + \text{O}_2 \leftrightarrow 2\text{H}_2\text{O} + 2\text{Cl}_2$$ (1)
(3) Molecular chlorine reacts with aromatic compounds such as phenols, to produce chlorinated aromatic compounds including chlorophenols and polychlorophenols.

(4) Polychlorinated phenols then undergo nucleophilic aromatic substitution, catalyzed by base, or by copper (I) surface species, by a homogeneous free radical reaction sequence, or by a heterogeneous de novo synthesis.

This mechanism has been proven to be a possible chemical pathway in certain temperature ranges by Lu’s\textsuperscript{14} and Yang’s\textsuperscript{15} work. Molecular chlorine is deemed a key intermediate in the foregoing mechanism. Molecular chlorine can be generated from the Deacon Reaction and subsequently form chlorinated aromatic compounds through aromatic substitution reactions, as implicated by Griffin\textsuperscript{16} and verified by others\textsuperscript{17,18}.

From previous studies, the phenol source is identified as the combustion product of newspaper, cellulose or other related matters in MSW\textsuperscript{14}.

The oxidation of HCl to Cl\textsubscript{2} has been known as a catalyzed reaction for the past century. CuCl\textsubscript{2}, Cu\textsubscript{2}Cl\textsubscript{2} and other transition metal salts were utilized as catalysts in most of the earlier studies\textsuperscript{19}. In agreement with the JANAF Thermochemical Tables, most thermodynamic measurements and calculations for the reversible Deacon Reaction show that the forward reaction dominates up to 600°\textdegree{}C under standard conditions. The Deacon Reaction has a standard free energy of reaction of $-76$, $-49$, $-9.2$ and $+4.4$ kJ at 298, 500, 800 and 900K, respectively\textsuperscript{20}. However, laboratory evidence confirmed that this reaction is able to be proceeded homogeneously in the gas phase at increased temperatures\textsuperscript{21,22}. In the event of a short retention times, which means that the reaction is more likely kinetically governed rather than thermodynamic controlled, the Deacon Reaction is favored at higher temperatures.
The occurrence of the Deacon Reaction in the MSW incineration process can also be supported by numerous studies with regard to the effect of oxygen on the PCDD/Fs production. There is a consensus in the literature among the laboratory-, pilot- and field-scale researchers that the formation of PCDD/Fs is dependent upon the $O_2$ concentration. Vogg and his co-workers found that a greater production of PCDDs and PCDFs resulting from the increase of $O_2$ concentration from 0 to 10%. Researchers also reported that an elevated air-to-fuel ratio (0.8-1.2) led to higher levels of PCDD/F during fluidized bed combustion of model waste materials. This dependency of $Cl_2$ formation from HCl through reaction 1 has been shown on the bench-scale to be linearly dependent on the $O_2$ concentration up to 3%, after which conversion remains constant to 10%. The above experimental phenomena can be construed as the effect of oxygen on the Deacon Reaction, from which molecular chlorine is generated and subsequently incorporated in the organochloride formation and PCDD/Fs. A recent paper reports the Deacon Reaction is also catalyzed at about 400°C by iron compounds, which are abundant in eastern and mid-continent coal ashes. It is reasonable to conclude that the Deacon Reaction plays an important role during the co-combustion of coal and MSW.

Based on the laboratory results above, scientists have suggested a few practical strategies to minimize the emission of PCDD/Fs from the combustion of MSW. One of these strategies concerns the use of sulfur or nitrogen compounds as an inhibitor. The compounds which may either alter the acidity of the fly ash surface, or are likely to form some kind of complex with transition metal ions that catalyze PCDD/F formation, are capable of inhibiting the formation of toxic chlorinated organics, such as $NH_3$, ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA) or $Na_2S$. A study
was conducted to evaluate the influence of combustion, absorption and adsorption in the synthesis of PCDD/Fs during the waste combustion.\textsuperscript{27} Four models were utilized to predict the effect of three different operational parameters. As revealed from the regression analysis results, the formation of PCDD/Fs can be remarkably reduced by means of using sorbent injection, limiting the excess air and increasing the quench rate in the combustion process. Another recommended measure to control the formation of PCDD/Fs is the co-firing of high sulfur coal and MSW, in which coal displays its dual usage to be a desirable co-combustion energy source and a practical inhibitor in the meantime.

C. Co-firing MSW with Coal

Even though parts-per-billions to parts-per-trillion of PCDD/Fs have been reported in the flue gas as well as fly ash from municipal waste combustors,\textsuperscript{28,29} they were not detected in the gaseous effluents from a combined coal/municipal waste plant,\textsuperscript{30} nor were significant amounts found on coal fly ash.\textsuperscript{31} From a combustion chemistry viewpoint, the presence of molecular chlorine and the basic organic structures in both systems above would render the initial aromatic compounds necessary for the formation of triple ring structures of dioxins and furans, which in turn are the basic structures for the highly toxic polychlorinated species. The possible variance in copper concentrations between coal- and MSW-fired boilers is not sufficient to reflect the resulting PCDD/F levels. However, there is a distinct difference in the level of sulfur species, or the sulfur-to-chlorine ratio, between coal-fired utility power plants and municipal waste incinerators. A sulfur-to-chlorine ratio in a power plant burning a typical 2% sulfur coal
is about 2, which is an order of magnitude higher than that found in a typical municipal waste combustor (MWC). Such a high S/Cl ratio in the coal combustor is believed to be the cause of the reduced emission of toxic organics.\textsuperscript{32}

Municipal solid waste varies considerably in composition.\textsuperscript{33} Many organic materials present in the MSW possess a chemical structure capable of releasing chlorinated organic compounds under pyrolysis and combustion condition, especially the plastics. Most plastics used as household applications are disposable and nonbiodegradable. Plastics account for 8% of the total amount of municipal solid wastes and up to 20% by volume.\textsuperscript{34} As their usage is anticipated to grow in the future, the amount of plastics discarded will also increase. PVC is one of leading plastics in total production. In 1990, 0.5 million tons of polyvinyl chloride (PVC) found its way to the waste stream in the United States. The existence of PVC plastic, and other chlorine-containing organics such as pesticides, flame retardants, etc. in the waste, is responsible for the formation of corrosive or toxic substances like HCl, other halogenated acids, chlorinated organic matters and further PCDD/Fs, in the incineration exit gases and particles from waste incinerators.

Thermal degradation of PVC has been studied by numerous researchers since 1960. Its decomposition has been investigated from 185\textdegree{}C to 650\textdegree{}C, and the major volatile product in all cases is HCl. Other decomposition products that have been reported included polychlorinated benzene, as well as aliphatic and aromatic hydrocarbons. The decomposition process is slow prior to 200\textdegree{}C, but quite rapid above 400\textdegree{}C. It has been reported by Hawley-Fedder and his co-workers. that major component of combustion products of a mixture of polyethylene, polystyrene, and PVC burning at a
temperature over 800°C were alkylbenzenes and aliphatic and polynuclear aromatic hydrocarbons, with the release of a large amount of HCl. The contents of chlorinated compounds were very low.\textsuperscript{35} Since the MSW in the United States generally consists of a notable quantity of PVC, Saran and other chlorinated polymers, the yield of HCl from combustion of MSW will be significant.

Besides inorganics such as SO\textsubscript{x}, NO\textsubscript{x}, HCl and residues from the combustion of coal, the organic pollutants released from coal have increasingly drawn the attention of scientists. There are more than 300 organic compounds identified from the decomposition productions of coal combustion,\textsuperscript{36,37} and some of them are chlorinated organic compounds. However, through an exhaustive literature search, no evidence of PCDD/Fs emissions from the combustion of coal has been found.

Compatibility is one of the problems encountered when co-firing various 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 parameters used to evaluate the rate of burning of a fuel is the volatile matter. For bituminous coals, the volatile matter is about 36%, whereas the volatile matter for RDF or MSW is about 55-85%. The meaning is that coal burns much slower and release about 50-150% more energy than MSW, RDF or wood waste. Large variances exist in the combustion profiles of coal, RDF, MSW and wood waste, but blends of these fuels, when co-fired under the proper conditions, can exhibit satisfactory performance as boiler fuels.\textsuperscript{14}

Coal as a co-firing energy source for municipal solid wastes is able to suppress the formation of chlorine-containing organic compounds. Scheidle and his 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.\textsuperscript{38} Similar results can be inferred from Lindbauer’s study which showed that co-firing MSW with 60% coal drastically reduced the formation of PCDD/Fs.\textsuperscript{39} Banaee and co-workers studied the co-combustion of Saran wrap with high-sulfur coals and other polymeric materials, and the results show the promising ability of coal to inhibit the formation of chlorinated benzenes.\textsuperscript{40} Bonfanti and his co-workers investigated the environmental aspects relevant to the co-firing of pulverized coal and RDF in a slag forming combustor, and the results show that the micro pollutant emission was very low.\textsuperscript{41} Ohlsson and coworkers observed that despite the enhancing level of HCl due to the addition of RDF, no PCDD/Fs have been detected when co-firing high-sulfur coal and RDF pellets.\textsuperscript{42} All the studies previous mentioned verified that the addition of coal, especially high-sulfur coal, to municipal solid wastes would result in an appreciably lower PCDD/F level. Thus, co-combustion of high sulfur coal and MSW has the dual advantages of being a source of energy and having the potential of suppressing the formation of chlorinated species in combustor emissions.

D. Effect of Sulfur Species on the Formation of Chlorine

The effect of coal to inhibit the formation of chlorinated organics has been attributed to its high-sulfur content. As is well-known, coal consists of both inorganic and organic sulfur. The inorganic sulfur is largely in the form of pyrite, a mineral whose composition approximates FeS\textsubscript{2}. The organic constituents include aliphatically bound sulfur, such as thio ethers, and a wide variety of aromatic sulfur compounds. Aliphatic
sulfur is dominant in low-rank coals such as lignite. In contrast, high-sulfur bituminous coals contain more aromatically bound sulfur. Most of these compounds are very readily oxidized; therefore one of the major products from the combustion of coal is SO₂.

On the basis of 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. However, in the presence of considerable amounts of sulfur, chlorine formation and consequently, PCDD/Fs formation is decreased. Gullet and his co-workers revealed that high concentrations of sulfur species (sulfur dioxide) were liable for the apparent lack of PCDD/Fs in the emissions from coal-fired combustors. Frankenhaeuser and co-workers also addressed the adverse effect of SO₂ in the formation of organic chlorine during the co-combustion of plastics with coal.

There have been several different mechanisms advanced with respect to the inhibiting effect of sulfur species on the formation of PCDD/Fs, one of which suggested that in coal combustion the critical role of sulfur is depleting the Cl₂ through the following reaction then, subsequently, rendering less PCDD/Fs. When sulfur is present in excess over chlorine, in any system, the forward reaction predominates:

\[ \text{SO}_2 + \text{Cl}_2 + \text{H}_2\text{O} \leftrightarrow \text{SO}_3 + 2\text{HCl} \]  

(2)

Thus the chlorinating agent, chlorine, is converted into HCl. In principle, organochlorine species produced during the combustion process could be formed by mechanisms involving either HCl, Cl₂ or atomic Cl. However, as revealed by Gullett and co-workers, Cl₂ gas when introduced into a furnace together with phenol produced a fairly large amount of chlorinated organic compounds that were approximately three orders of
magnitude greater than when HCl was used. Comparing with Cl₂, HCl is very unlikely to undergo aromatic substitution reactions to yield PCDD and PCDF precursors.

Another postulated role of sulfur in the formation of chlorinated organics is to poison the copper-based Deacon Reaction catalyst. It has been shown that Cu species such as CuCl, CuO are effective catalysts for the Deacon Reaction. In the presence of these copper-based catalysts, the Deacon Reaction is able to be processed easily in room temperature. Under specific circumstances, sulfur dioxide may react with CuO to produce CuSO₄ through the following reaction:

\[ \text{CuO} + \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{CuSO}_4 \]

It has been observed that around the peak PCDD formation temperature of about 350°C, CuSO₄ is a less active catalyst for both the Deacon Reaction and the biaryl synthesis of chlorinated precursors in the PCDD production. Gullet and co-workers conducted experiments to distinguish between two possible sulfur effects on reducing the Cl₂ availability - reduced Deacon Reaction activity by catalyst poisoning versus depletion of Cl₂ through homogeneous gas-phase reaction. The results revealed that a lesser amount of Cl₂ results from the depletion by SO₂ rather than from the inactivity of the Deacon Reaction catalysts, although the catalyst poisoning by sulfur species can still affect the PCDD/F biaryl synthesis step significantly.

A third possibility is that the presence of SO₂ gas discourages the formation of PCDD/Fs by either sulfonating the phenolic precursors, thereby preventing subsequent chlorination and biaryl synthesis, or replacing the oxygen links with S and form polychlorodibenzothiophene and polychlorothianthrenes, the S analogs of PCDD/Fs. However, those high-temperature gas-phase reactions between S species and organic
precursors have been reported to be an unlikely occurrence under the co-combustion conditions.\textsuperscript{45}

E. Objectives of this Study

Published experimental data with respect to the mechanism of sulfur species reducing the formation of chlorinated organics during combustion is scarce. As indicated in the proposed four-step mechanism mentioned in Section B, molecular chlorine is a key intermediate for the formation of PCDD/Fs. Theoretically, the emissions of chlorinated organics can be effectively inhibited if the molecular chlorine yield is reduced as far as possible. The objectives of this study are to examine the possible effect of sulfur species on the formation of molecular chlorine via the Deacon Reaction and to determine the optimum sulfur-to-chlorine ratio in preventing the emissions of chlorinated organic materials.

Atmospheric fluidized bed combustion (AFBC) tests were also carried out, for the purpose of evaluating the performance of and emissions from an AFBC system during the co-firing of mixtures of coal and PVC pellets. Fluidized bed combustion (FBC) systems are desirable in dealing with MSW incineration. Other alternatives include semi-suspension stoker-fired boilers and co-firing with pulverized coal in a cyclone fired combustor. FBC systems are commonly mid-size utility boilers that find applications in institutional power plants for heating purposes and in many industrial applications for steam generation. An AFBC system is particularly suitable for waste fuels due to its capability to burn low grade and variable fuels as well as absorbing sulfur dioxide through the sorbents.
II. EXPERIMENTAL

A. Chemicals and Gases:

Chemical reagents used in this study are as follows:

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

Specialty gases used included:

- 1% HCl in nitrogen (Specialty gases, Louisville, KY)
- 4.86% SO₂ in nitrogen (Specialty gases, Louisville, KY)
- Compressed Air (Kentucky Airgas Inc.)
- Nitrogen (Gateway Airgas, St. Louis, MO)

B. Experimental Setup

A trapping solution followed by GC-MS detection was utilized in this work. The schematic of the trapping solution set-up is shown in Figure 1.

In order to simulate conditions used in an AFBC system, experiments were conducted in a twelve-inch concentric tube, quartz reactor inserted into a horizontally mounted electric Lindberg furnace. The reactor was preheated to 800°C, and the temperature readings were obtained by means of chromel-alumel thermocouples inserted into the lower part of the furnace and displayed on a digital meter.
Figure 1. Cold trap setup.
The composition of the process gases can be adjusted using the calibrated teflon flow meters before being introduced into the reaction system. A chamber containing ceramic pellets was used to mix the gases before being introduced into the reactor. Prior to performing the experiments, the temperature of the furnace was calibrated to ensure the reaction conditions would be reproducible.

The reaction products were swept into a cooled trap containing a chosen absorbent, which was prepared by dissolving 50 mg phenol in 25 mL methylene chloride. The amount of phenol was controlled in a range of +/- 0.0001 g.

Upon the completion of the reaction, the solution was concentrated to 1 mL and subjected to the GC/MS analysis. A Shimadzu QP5000 system equipped with a NIST/EPA/NIH 62,000 compound database was employed in this study. The gas chromatography has connections with two parallel GC columns and a digital splitter. A computer handles the carrier gas flow rate through each of these columns. Since the viscosity of a gas will change with a change in temperature, it is essential that the gas pressure be specifically programmed, for the purpose of maintaining the same flow rate throughout the duration of analysis. One of the two columns is interfaced to the MS and the other column to an electron capture detector (ECD), which will eventually be used to perform on-line analysis of the gaseous emissions from the AFBC. The electron impact (EI) mode of the mass spectrometer operates in the range of 10-700 amu with a standard 70 eV source and is equipped with a 151 L/sec turbo molecular pump; the high capacity of this pump facilitates the use of a 0.32 mm capillary column for analysis. The column in the gas chromatography system is 0.32 mm in diameter and 60 m in length. The stationary phase consists of Restek RTX-1 (bonded dimethylpolysiloxane) and has a
phase coating with a thickness of 1 μm. The component capacity of this column is approximately 500 ng with a resolution almost as high (84%) as a 0.25 mm diameter column of the same length. Depending on operating conditions the sensitivity of this system may vary.

The identification of compounds was accomplished by using a computerized library search and by comparison with the literature mass spectra. Furthermore, a comparison between the GC retention time of the standard compounds with that of sample is helpful in verifying the identification of the unknowns.

The detailed GC parameters for GC/MS analysis are summarized in Table 1.

C. Experimental Procedure

Different sulfur-to-chlorine (S/Cl) ratios were tested in this study, in order to semi-quantitatively examine the effect of SO₂ on the formation of chlorine through the Deacon Reaction. The process gas consists of HCl, SO₂, air, and nitrogen as well. The total gas flow rate was fixed at 180 mL/min, for the purpose of establishing the comparable reaction conditions. The volume of the quartz reactor is approximately 150 mL, thus a retention time of 50 seconds was obtained. The flow rate of HCl and air was set as 60 mL/min in each experiment, and nitrogen gas was used as balance gas. Various S/Cl ratio can be provided by modifying the flow rate of SO₂.

At least three repeat runs were conducted under each different reaction condition. The various test conditions are shown in Table 2. The experimental errors mainly arose from the fluctuation of furnace temperature, control of flow rate, cleanup method and distillation process.
Table 1. GC Parameters for GC/MS Analysis

<table>
<thead>
<tr>
<th>Component</th>
<th>Parameter Description</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Injector</strong></td>
<td>Temperature (°C)</td>
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</tr>
<tr>
<td><strong>Oven</strong></td>
<td>Initial Temperature (°C)</td>
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</tr>
<tr>
<td></td>
<td>Temperature Program:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Rate (°C/min)</td>
<td>Temp. (°C)</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>150.00</td>
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<td>5.00</td>
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<td>250.00</td>
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<td></td>
<td>6.00</td>
<td>310.00</td>
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<tr>
<td><strong>Flow Controller</strong></td>
<td>Carrier Gas Pressure (kPa):</td>
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<tr>
<td></td>
<td>Carrier Gas Pressure Time (min):</td>
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<td>Pressure Program:</td>
<td>Rate (kPa/min)</td>
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<td></td>
<td>1.60</td>
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<td></td>
<td>1.30</td>
<td>135.50</td>
</tr>
<tr>
<td></td>
<td>1.20</td>
<td>147.50</td>
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<tr>
<td></td>
<td>1.20</td>
<td>159.50</td>
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<tr>
<td></td>
<td>Total Flow (mL/min):</td>
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<tr>
<td></td>
<td>Split Ratio:</td>
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<tr>
<td><strong>Interface</strong></td>
<td>Temperature (°C):</td>
<td>230.00</td>
</tr>
</tbody>
</table>
It is essential to point out that the experiments hereafter were carried out under laboratory conditions, and only the natural gases were involved.

Table 2. Different Sulfur-to-Chlorine Ratios for Tests

<table>
<thead>
<tr>
<th>S/Cl (Mole/Mole)</th>
<th>Flow Rate (mL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SO2</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.614</td>
<td>7.5</td>
</tr>
<tr>
<td>1.227</td>
<td>15</td>
</tr>
<tr>
<td>2.455</td>
<td>30</td>
</tr>
<tr>
<td>4.909</td>
<td>60</td>
</tr>
</tbody>
</table>

D. Laboratory Fluidized Bed Combustion Tests

The laboratory scale atmospheric fluidized bed combustor at Western Kentucky University was built by the University with support from TVA, EPRI and the United States Department of Energy. The schematic drawing of this AFBC system is illustrated in Figure 2. The active bed area is 0.08 m² (125 in²). The freeboard zone of the combustor is 3.05 m (10 feet) high, providing adequate residence time for the combustion of fine fuel particles which may be entrained in the gases leaving the bed. Such design also ensures sufficient time for 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 rendering a stable bed height.
Figure 2. Schematic drawing of the AFBC combustor.
In this project, an under-bed continuous feed fuel/limestone system was installed. The system consists of an auger feed under positive pressure, which is located about 0.29 m (9 inches) above the air distributor of the combustor. This modification improved combustion efficiency to approximately 95%. Six movable bed heat exchangers in the bed area were added to the AFBC system. Typical operation includes setting the correct coal/limestone feed and air flows and then using the movable tubes to adjust the bed temperature to the desired setting. Another sixty-six gas heat exchanger tubes were in fixed position located approximately one meter from the top of the combustor. The hot gases from the combustor were allowed to enter a wet cyclone where they were met with a wall of water (which keeps the cyclone cool), which subsequently took almost all solids to the bottom of the cyclone into a holding tank. The operating parameters of the combustor (air/water flow, coal/limestone feed, fuel bunker weight, temperatures, and pressure) were controlled and logged to file with a Zenith 150 MHz computer utilizing the LABTECH software version 3.0. During the combustion runs any required alternations in the parameters can be readily entered into the computer, by accessing the correct control screen and making the necessary corrections on line.

Two coals were utilized in this study, an Illinios #6 coal (95031) and an eastern Kentucky coal (95010). The limestone was commercially obtained from Kentucky Stone in Princeton, Kentucky. Detailed analytical data for the two coals, limestone and PVC pellets used in the study are presented in Table 3. The coal and limestone both were air-dried before being crushed to -4 mesh (4.75 mm). PVC was mixed with coal in 0.1% by weight and 0.33% by weight ratios for the tests.
Table 3. Analytical Data* for the Coals and Limestone Used in this Study

<table>
<thead>
<tr>
<th></th>
<th>Coal 95010</th>
<th>Coal 95031</th>
<th>Limestone</th>
<th>PVC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture (%)</td>
<td>2.32</td>
<td>8.32</td>
<td>0.19</td>
<td>0.00</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>7.22</td>
<td>10.78</td>
<td>57.93</td>
<td>0.36</td>
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<td>Volatile Matter (%)</td>
<td>39.97</td>
<td>37.21</td>
<td>18.90</td>
<td>99.64</td>
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<tr>
<td>Fixed Carbon (%)</td>
<td>52.82</td>
<td>52.02</td>
<td>22.98</td>
<td>0.00</td>
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<tr>
<td>Carbon (%)</td>
<td>79.38</td>
<td>72.16</td>
<td>11.18</td>
<td>38.71</td>
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<tr>
<td>Hydrogen (%)</td>
<td>5.31</td>
<td>4.82</td>
<td>0.16</td>
<td>4.2</td>
</tr>
<tr>
<td>Nitrogen (%)</td>
<td>1.63</td>
<td>1.54</td>
<td>0.00</td>
<td>0.07</td>
</tr>
<tr>
<td>Sulfur (%)</td>
<td>0.67</td>
<td>2.38</td>
<td>0.00</td>
<td>0.22</td>
</tr>
<tr>
<td>Oxygen (%)</td>
<td>5.69</td>
<td>7.57</td>
<td>30.73</td>
<td>0.00</td>
</tr>
<tr>
<td>Chlorine (ppm)</td>
<td>1039</td>
<td>3070</td>
<td>36</td>
<td>56.45**</td>
</tr>
<tr>
<td>Btu/Pound</td>
<td>14077</td>
<td>12842</td>
<td>--------</td>
<td>8,556</td>
</tr>
</tbody>
</table>

*Moisture is as-determined, all other values are reported on a dry basis

** The unit for chlorine in PVC is percent
During the duration of the tests, limestone was fed into the system at a constant rate depending upon the fuel used. The major operating parameters for the experiments were as follows: excess air level - around 1.3, Ca/S ratio - approximate 3; bed temperature was controlled in the range of 1140 to 1160 K.

A full description of the flue gas sampling system and procedure, as well as the fly ash and bed ash sampling procedures, has been reported elsewhere.\textsuperscript{47,48} During combustion runs the flue gases at the gas heat exchanger region were analyzed continuously using on-line Fourier Transform Infrared Spectroscopy (FTIR) and gas chromatography (GC). To determine if any chlorinated organic compounds were formed during the combustion runs, the gaseous compounds evolved from the combustor were collected in Tenax adsorption tubes. The collected samples were extracted separately with hexane (99.9\%) for 24 hours using a soxhlet extraction apparatus, then subjected to GC/MS analysis. The principle objective of the GC/MS analysis of the combustion gases and leachates of residues and fly ash was to determine the presence of organic compounds and the classes of organic compounds formed, with particular emphasis on chlorinated organic compounds and PCDD/Fs.
III. RESULTS AND DISCUSSION

A. Effect of Sulfur Dioxide on the Deacon Reaction

As described in the experimental section, the trapping solution used to capture the molecular chlorine evolved from the reactor was prepared by dissolving a carefully controlled amount of phenol into methylene chloride. Phenol was chosen as the sorbent for molecular chlorine, resulting from the significant difference between its capability of reaction with Cl\textsubscript{2} and that with HCl. The reaction between phenol and molecular chlorine is a well-known organic chemistry reaction. In a textbook published in 1936, Hickinbottom stated \(^{49}\)

\[ \text{H-Ar-OH} + \text{Cl}_2 \rightarrow \text{Cl-Ar-OH} + \text{HCl} \]

that “alone or diluted by an anhydrous solvent such as glacial acetic acid, carbon tetrachloride or chloroform, mono-, di- or tri- substituted phenols are obtained from phenol in the presence of Cl\textsubscript{2}.” Phenols are readily chlorinated by Cl\textsubscript{2}, in both polar organic solvents and nonpolar solvents. Previous work proved that the heterogeneous reaction between phenol and Cl\textsubscript{2} could take place easily at room temperature without catalyst.\(^{14}\) In contrast, the reaction between HCl and Phenol is much more difficult to achieve under the same condition.

In case any molecular chlorine is generated from the combustion reaction, it will be released from the reactor and react with phenol present in the trapping solution and be converted to chlorophenol. The complete (100%) absorption of molecular chlorine by
phenol is not a certainty; however, the absorption efficiency can be deemed similar in each experiment, provided that the absorption condition was kept identical as far as possible. In fact, when interpreting the GC/MS analysis data, it was found that the amount of phenol present in the trapping solution exceeds the quantity of chlorinated phenols produced, which means another possible deviation resulting from the adsorption is excluded. Therefore, the chosen trapping method is capable of capturing the evolved Cl\(_2\) from the reaction, and sufficient to render reliable data for semi-quantitative analysis.

The molecular chlorine yield is in conformance with the production of chlorinated phenol, which can be obtained from the GC/MS analysis regarding the trapping solution. Since the quantity of phenol used in each test was kept at the same value, the Cl\(_2\) yield in each test can be evaluated by the ratio of the concentration of chlorinated phenol and phenol in the trapping solution, which can be computed from the corresponding GC peak area in the GC chromatogram of the trapped solution. A typical GC chromatogram is shown in Figure 3. Figures 4, 5, and 6 illustrate the identification of phenol, o-chlorophenol, p-chlorophenol from the MS fragments, respectively.

The results of tests under varying reaction conditions are summarized in Figure 7. As clearly reflected from this plot, without SO\(_2\) in the reaction system, the relative yield of chlorinated phenol (represented by Chlorinated Phenol/Phenol) is significant. In the absence of SO\(_2\) (S/Cl = 0), HCl reacts with oxygen in the reaction system to form molecular chlorine. The Deacon Reaction is exothermic at 298 K (\(\Delta H = -114 \text{ KJ/mol}\), \(\Delta G = -76 \text{ KJ/mol}\)), and the equilibrium will shift to the reactants with the increase of temperature, thereby resulting in the lower conversion of HCl to Cl\(_2\). However, before equilibrium is reached, the reaction is predominantly kinetically controlled.
Figure 3. A typical GC chromatogram of the trapping solution.
Figure 4. Library search for phenol from the MS fragments.
Figure 5. Library search for 2-chlorophenol from the MS fragments.
Figure 6. Library search for 4-chlorophenol from the MS fragments.
Figure 7. Relative yield of chlorinated phenols as a function of S/Cl ratio.
Yang also reported that in the event the reaction takes place in a steadily moving gas flow and no catalyst is present, the reaction shall be far away from equilibrium. Consequently, a higher temperature will result in a high reaction rate for the Deacon Reaction, associated with a higher chlorine yield. As shown in Figure 7, in the absence of SO\textsubscript{2} in the reaction system, the relative yield of chlorinated phenols is high. Then with the addition of SO\textsubscript{2} into the reactor, the production of molecular chlorine decreased. Especially, when the S/Cl ratio approached 2.5/1, the chlorinated phenol production decreased to less than 8% of the original, as inferred from the Figure 7.

The conversion factor of HCl to Cl\textsubscript{2} can be deduced from the GC/MS results. Since the quantity of phenol used in the trapping solution for each test is similar, which is 50 mg corresponding to 5.32 \times 10^{-4} mole, the GC peak area of phenol in each trapped solution is comparable. The amount of chlorinated phenol in the trapped solution can be calculated on the basis of its relative ratio to phenol, according to their GC peak area. As mentioned above, the trapping time is 4 hrs. with a steadily moving gas flow, in which 1% HCl is mixed, so as to obtain a total HCl introduction as 6.23 \times 10^{-3} mole. Regarding the tests without the addition of SO\textsubscript{2}, the relative ratio of chlorinated phenol to phenol in the trapped solution is around 0.94/100. This would lead to a conversion factor of around 0.15% for HCl to Cl\textsubscript{2}, assuming the absorption of Cl\textsubscript{2} by phenol is complete. This result is consistent with other studies. Actually, fly ash does produce Cl\textsubscript{2} through the Deacon Reaction, when passing HCl over the fly ash bed 1.3% is converted to Cl\textsubscript{2}. This variance can be ascribed to the transition metal compounds present in the fly ash, which may act as the catalyst of Deacon process.

As indicated in Figure 7, before sulfur-to-chlorine ratio approaching 2.5/1,
yield of relative chlorinated phenols versus S/Cl ratio exhibits a good linear relationship. However, after the sulfur-to-chlorine ratio exceeds 2.5/1, extra addition of sulfur species, even doubled, has no apparent influence on the relative yield of chlorinated phenols, showing as a platform in the experimental curve in Figure 7. As shown in Table 2, the amount of HCl and air in the reaction system is fixed during the experiments, only the flow rate of SO\textsubscript{2} was changed in order to change the S/Cl ratio. Therefore, it is reasonable to conclude that when the S/Cl ratio is about 2.5/1, the Cl\textsubscript{2} generated from Deacon Reaction is depleted by the SO\textsubscript{2} in the reaction system completely. After that, even more SO\textsubscript{2} is introduced in the reactor, no significant difference is shown in the relative yield of chlorinated phenols. The resulted sulfur-to-chlorine ratio of 2.5/1 is higher than that proposed by Raghunathan and Gullet\textsuperscript{5} However, it is much lower than the suggested value of 10 from thermodynamic calculation.\textsuperscript{16} Despite Figure 7 showing that the emission of molecular chlorine declined with an increased sulfur-to-chlorine ratio, it cannot be unequivocally said that adding much more sulfur species into the combustion system is recommendable. It is well-known that SO\textsubscript{2} is another major air pollutant source and a direct cause for acid rain. Therefore, our work is important in helping co-firing plants to choose a practical S/Cl ratio in order to optimize the MSW incineration in an environmentally acceptable manner.

With respect to the inhibiting mechanism of sulfur on the formation of Cl\textsubscript{2}, the reaction between SO\textsubscript{2} and Cl\textsubscript{2} should be taken into account. Smith performed the equilibrium calculation toward reaction 2, according to the free energy and enthalpy data of the species involved in the reaction system. The result showed that the Cl\textsubscript{2}-SO\textsubscript{2} reaction is strongly favored over the entire temperature range, and the amount of Cl\textsubscript{2}
reacted was limited only by the available SO₂. However, this homogeneous reaction is not measurable below 800°C, due to the kinetics of reaction that may prevent observation of appreciable product until testing at a higher temperature. Raghunathan and Gullet conducted a series of experiments to examine the reaction between SO₂ and Cl₂. They reported that HCl formation in the presence of SO₂ was consistent with reaction 2, although the maximum Cl₂ conversion or HCl concentration achieved was less than the theoretical value of nearly 100% conversion.

Upon closer analysis of the reaction system involved in our study, HCl-SO₂-O₂, considering the initial concentration of each gas, either O₂ or SO₂ is in excess compared to HCl. In the presence of SO₂, Cl₂ generated from the Deacon Reaction would be converted back to HCl, a much weaker chlorine agent compared with Cl₂. In the view of Le Chatelier Principle, the reaction between SO₂ and Cl₂ will facilitate the production of Cl₂ via reaction 1. On the other hand, the presence of a large amount of O₂ in the system may cause a negligible effect. Consequently, as illustrated in Figure 7, the production of molecular chlorine, which is monitored by the relative yield of chlorinated phenol, exhibits a linear relationship with the sulfur-to-chlorine ratio until the S/Cl ratio reaches 2.5/1, and such dependency illustrates the occurrence of reaction 2.

B. Results from Co-firing Coal with PVC in an AFBC System

Co-firing coal with PVC tests were conducted in the AFBC system at Western Kentucky University. The fuels used in the tests were switched from coal alone to mixtures 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 rate: approximately 7.94 kg/hr

Limestone feed rates: approximately 0.57 kg/hr for coal 95010
2.03 kg/hr for coal 95031

Ca/S ratio: approximately 3.0

The varying limestone feed rate was used for coals with different sulfur content, in order to maintain a similar Ca/S ratio. The combustion temperatures of the tests are kept at 800°C, much lower than the recommended combustion temperature of 980°C or greater, for minimizing the organic emissions. Requirements for maintaining high and uniform temperature is one of the difficulties faced in the use of incineration for waste with chlorine-materials. The presence of mixing nonhomogeneities and temperature fluctuations within the combustion chamber can lead to a higher of incomplete combustion products than normally expected. These ultimately end up as hazardous emissions in the effluent stream. However, no difficulty was encountered in our study upon switching the fuel from coal to coal mixtures to maintain the bed temperature around 800°C.

As depicted in Figure 8, addition of PVC into the combustor led to a dramatic decrease in the emission of SO$_2$ in the flue gas. Moreover, as illustrated in Figures 9 and 10, the amount of SO$_2$ captured in the bed ash and fly ash was enhanced as the PVC ratio in the fuel mixture was increased. One explanation of the increased capture by the
limestone is that the transient formation of liquid calcium chloride phase can modify the
surface on the partially sulfated sorbent particles, resulting in the elevated sulfur
capture.\textsuperscript{51} However, a more complex mechanism including the possibility of the reaction
between SO\textsubscript{2} and Cl\textsubscript{2} may be involved. Such experimental phenomena verified the
occurrence of reaction 1 and reaction 2 in the co-firing process.

Limestone is widely utilized as bed material in the AFBC system to capture the
SO\textsubscript{2} emissions from the coal combustion process. This effect is associated with the
following two-step process:

\begin{align*}
\text{CaCO}_3 & \rightarrow \text{CaO} + \text{CO}_2 \quad \text{(3)} \\
\text{CaO} + \text{SO}_3 & \rightarrow \text{CaSO}_4 \quad \text{(4)}
\end{align*}

The limestone injected into the combustor first undergoes decomposition to
release CaO, and in the presence of oxygen, CaO subsequently reacts with SO\textsubscript{2} to form
CaSO\textsubscript{4}. It is believed that sulfur species are absorbed by limestone in the form of SO\textsubscript{3}
rather than SO\textsubscript{2}. As has been revealed, a large amount of HCl will release from the
thermal degradation of PVC in the fuel mixture, and then convert to Cl\textsubscript{2} through the
Deacon Reaction. In accordance with reaction 2, the reaction between SO\textsubscript{2} and Cl\textsubscript{2} would
promote the conversion of SO\textsubscript{2} to SO\textsubscript{3}, thus the amount of sulfur captured by limestone is
increased. In addition, the utilization of limestone as bed material and the feeding of
limestone mixtures into the combustor during the burning will keep excess CaO present
in the combustion system; therefore, reaction 4 is favored with a consequence of
promoting the conversion from SO\textsubscript{2} to SO\textsubscript{3} through reaction 2.
Figure 8. Effect of PVC/Fuel ratio on the concentration of SO$_2$ in the flue gas.
Figure 9. Effect of PVC/Fuel ratio on the concentration of sulfur in the bed ash.
Figure 10. Effect of PVC/Fuel ratio on the concentration of sulfur in the fly ash.
Dougherty and Callazo-Lopez utilized solid calcium oxide (CaO) in a fluidized bed placed above the combustion zone as a scavenger for chlorine-containing radicals. They experimentally demonstrated a significant decrease in the levels of organochlorine emissions in a laboratory reactor. Takeshita and co-workers revealed that the effect of dolomites limestone (CaCO_3-MgCO_3) added to a fluidized bed waste combustor led to PCDD and PCDF yield reductions in proportion to the decline in HCl concentration. Gullet and Nielsen also suggested a technology named “lime injection” that depends on removing HCl and/or Cl_2 gases from incinerator emissions by scrubbers and spray dryers. However, such an effect from limestone is not observable in our study because the presence of limestone makes no noticeable difference, either in the emission of HCl in the flue gas, or in the concentration of chloride in the bed ash and fly ash, as shown in Tables 4 and 5. According to the tests conducted during the previous study, it was proved that limestone can be used to effectively absorb the HCl emission in a temperature of around 600°C. However, the decomposition temperature of CaCO_3, the major component of limestone, is approximate 720°C in an oxygen-rich atmosphere. That means at the peak temperature for the absorption of HCl, the decomposition of limestone is not sufficient.
Table 4. The Effect of Limestone on the Distribution of Sulfur

<table>
<thead>
<tr>
<th></th>
<th>Coal 95010 with 3.3% PVC</th>
<th>Coal 95031 with 3.3% PVC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>with limestone</td>
<td>no limestone</td>
</tr>
<tr>
<td>SO₂ in flue gas (ppm)</td>
<td>0.126</td>
<td>3.125</td>
</tr>
<tr>
<td>Sulfur in fly ash (%)</td>
<td>0.739</td>
<td>n/a</td>
</tr>
<tr>
<td>Sulfur in bed ash (%)</td>
<td>4.319</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Table 5. The Effect of Limestone on the Distribution of Chloride

<table>
<thead>
<tr>
<th></th>
<th>Coal 95010 with 3.3% PVC</th>
<th>Coal 95031 with 3.3% PVC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>with limestone</td>
<td>no limestone</td>
</tr>
<tr>
<td>HCl in flue gas (ppm)</td>
<td>168.58</td>
<td>160.39</td>
</tr>
<tr>
<td>Chloride in fly ash (%)</td>
<td>0.347</td>
<td>0.343</td>
</tr>
<tr>
<td>Chloride in bed ash (%)</td>
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<td>n/a</td>
</tr>
</tbody>
</table>

Under our testing and sampling conditions, no chlorinated organics and PCDD/Fs were detected from the co-combustion tests. Such results may promote the co-combustion techniques.
IV. CONCLUSIONS

1. Sulfur dioxide is an effective inhibitor that can be used to suppress the formation of molecular chlorine via the Deacon Reaction during AFBC combustion processes.

2. When the sulfur-to-chlorine ratio in fuels approaches 2.5/1, a dramatic decrease in chlorine production is observed during AFBC combustor.

3. The presence of PVC in the fuel mixture improves the effectiveness of limestone to capture the $SO_2$ emissions during AFBC combustion.

4. No PCDD/Fs were detected in the fly ashes and flue gases when coal was co-fired with PVC pellets in an AFBC system.

In summary, sulfur enhancement of MSW by co-firing with coal followed by $SO_2$ emission controls may be the most practical strategies for minimizing chlorinated organics emissions.
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