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CHLORINATED ORGANIC COMPOUNDS EVOLVED DURING THE COMBUSTION OF BLENDS OF REFUSE-DERIVED FUELS AND COALS

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Abstract

The objective of this study was to examine the possible formation of chlorinated organic compounds during the combustion of blends of refuse derived fuels (RDF) and coal under conditions similar to those of an atmospheric fluidized bed combustion (AFBC) system. A series of experiments were conducted using a TG interfaced to FTIR. Additional experiments using a tube furnace preheated to AFBC operating temperatures were also conducted. The combustion products were cryogenically trapped and analyzed with a GC/MS system. The chlorination of phenols and the condensation reactions of chlorophenols were investigated in this study. A possible mechanism for the formation of chlorinated organic compounds such as dibenzodioxins and dibenzofurans, by chlorination and condensation reactions involving phenols, was proposed.

Keywords: evolved gas analysis, refuse derived fuels, thermal analysis

Introduction

The amount of municipal solid waste (MSW) generated in the United States each year has risen to nearly 200 million tons. The amount of waste generated and the rapidly declining availability of landfill space has forced municipalities to evaluate alternative waste management technologies. Incineration of unprocessed MSW is an area of concern since polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have been reported as products of MSW combustion [1].

Lindbaurer and coworkers [2] reported that co-firing MSW with 60% coal drastically reduced PCDD/PCDF levels. Gullett and Raghunathan [3] found that sulfur hindered PCDD and PCDF formation even at a sulfur/chlorine ratio of 0.64. The mechanism thought to be responsible for the inhibition is as follows:

$$SO_2+Cl_2+H_2O \rightarrow SO_3+2HCl \qquad (1)$$

This mechanism, and several others that have been proposed, recognize the existence of molecular chlorine (and not HCl) as an important precursor to the formation of chlorinated hydrocarbons during combustion. Although the presence of molecular chlorine is thought to be a key starting material, the conclusive reports in

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the literature about the possible formation of PCDDs and PCDFs in combustion systems are often contradictory and confusing [4].

In previous work TG/FTIR/MS studies of the organic compounds evolved during combustion of blends of coal and refuse derived fuels revealed the production of phenols, furans, and various other organic materials during the combustion of paper and other cellulosic materials blended with coals [5, 6]. The production of molecular chlorine during the combustion of polyvinyl chloride was also observed. Phenol, furan, and molecular chlorine could provide the important precursors for the formation of PCDDs and PCDFs in combustion processes. TG/FTIR/MS studies done by Lu [5] showed that more hydrocarbons are evolved at a fast heating rate due to incomplete combustion. These studies indicated there is a greater likelihood for the formation of chlorinated organic compounds at the fast heating rates, due to the concurrent evolution of HCl (which may be converted to molecular chlorine) and hydrocarbons, especially aromatics. Thus, 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.

A mechanism being proposed for the formation of chlorinated organics and possibly PCDDs and PCDFs is given in Eqs (2–4):

$$4HCl + O_2 \rightarrow 2H_2O + 2Cl_2 \text{ (Deacon reaction)} \tag{2}$$

$$C_6H_5OH + Cl_2 \rightarrow \text{chlorophenols} \tag{3}$$

$$\text{condensation of chlorophenols} \rightarrow \text{PCDDs and PCDFs} \tag{4}$$

This paper reports results from a series of studies designed to prove, or disprove, this proposed mechanism.

Experimental

Apparatus and reagents

The TG/FTIR system consisted of a TA Instruments TGA-951 system interfaced with a Perkin-Elmer 1650 Fourier Transform Infrared Spectrometer. A Shimadzu QP 5000 system with a NIST/EPA/NIH 62000 compound database was used for the GC/MS analysis. A twelve-inch Sola Basic Lindberg tube furnace was used for the preheated tube experiments. Reagents used include MC&B reagent grade phenol, EM Scientific HPLC grade dichloromethane, while 2,4-dichlorophenol, 4-chlorophenol, 2-chlorophenol and dibenzofuran were 99+% grade from Aldrich.

To closely simulate conditions in an AFBC combustor, studies were conducted using a preheated quartz tube in the Lindberg tube furnace. The evolved gases were trapped in methylene chloride, concentrated, and analyzed using the GC/MS system. Combustion products of phenol and chlorophenols were also investigated. The detailed experimental conditions are outlined in the following paragraphs.

To examine the possibility of producing molecular chlorine via the Deacon reaction, as illustrated in Eq. (2), a mixture of air and 10% HCl in N_2 (air:HCl volume ratio of 2:1) was introduced into the quartz tube preheated to different temperatures in the tube furnace. The product gases were trapped in a phenol-methylene chloride solution and the solution analyzed for chlorophenols using the GC/MS system.

To examine the gas phase chlorination of phenol, as illustrated in Eq. (3), 100 mg portions of phenol were placed in a heated tube and evaporated in the presence of a constant flow 0.5% Cl_2 in N_2. Chlorination took place in the gaseous phase and the products were cooled down by liquid N_2, condensed in the exit part of the tube, carefully washed by CH_2Cl_2, and analyzed using the GC/MS system.

The combustion of chlorinated phenols, which may lead to the reaction illustrated in Eq. (4), was examined by heating 100 mg portions of 2,4-dichlorophenol in the presence of air in the tube furnace. The combustion products were adsorbed by CH_2Cl_2 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^{-1} in the TG and the evolved gases were monitored (on-line) using the FTIR.

Results and discussion

The production of molecular chlorine by heating HCl in air followed by the chlorination of phenol in solution is an indication that the Deacon reaction (Eq. (2))

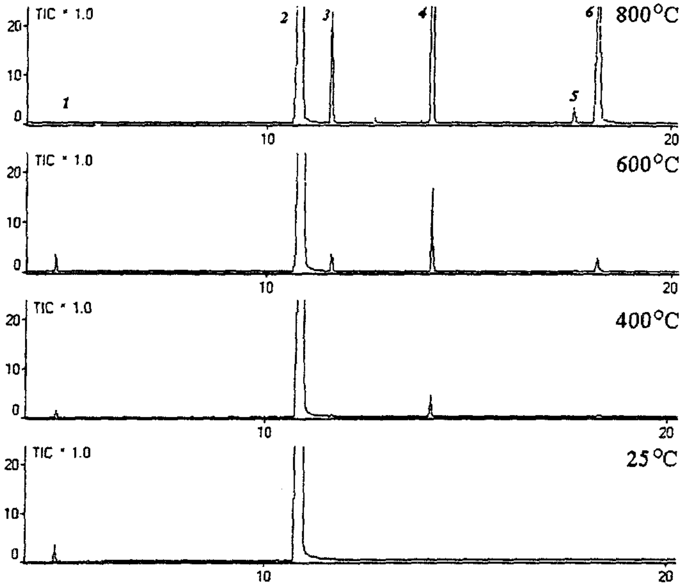

Fig. 1 Chromatograms of the products from the reaction of HCl heated in the presence of air and trapped in a phenol-CH_2Cl_2 solution, concentrated, and analyzed by GC/MS. The mass assignments (NIST library matches) are as follows: 1 – cyclohexene (impurity in CH_2Cl_2), 2 – phenol, 3 – 2-chlorophenol, 4 – *trans*-1,2-dichlorocyclohexane, 5 – 2,4-dichlorophenol, and 6 – 4-chlorophenol. The identifications were confirmed by matching the GC retention times of the pure compounds

takes place in the heated tube. Figure 1 shows the GC/MS results from these experiments conducted at different temperatures. The chromatograms indicate that the higher temperatures favor an increase in the production of chlorophenols. This indicates the Deacon reaction is favored at higher temperatures, which is consistent with thermodynamic calculations that show the Deacon reaction is favored above 590°C.

The gas phase chlorination of phenol (Eq. (3)) experiments produced 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol, as identified by NIST library matches and GC retention times of the pure materials. The chlorination of phenol began at temperatures around 250°C. At higher temperatures, dibenzofuran was produced.

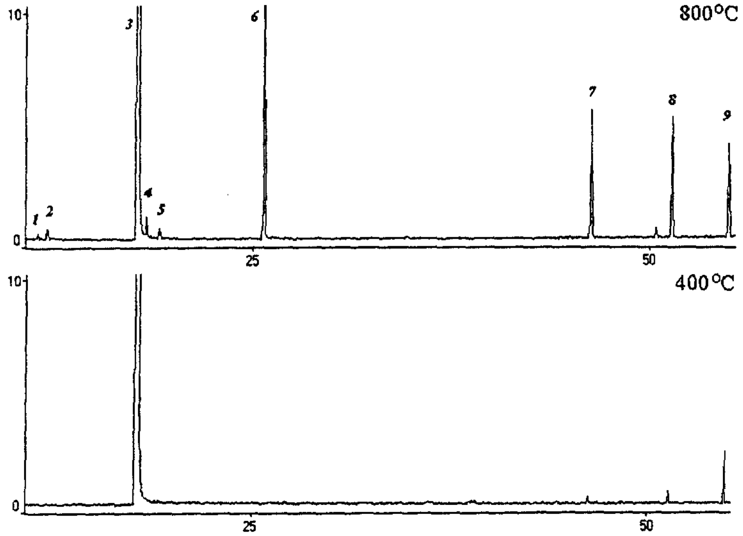

Fig. 2 Chromatograms of the products from the combustion of 2,4-dichlorophenol and trapped in a CH_2Cl_2 solvent, concentrated, and analyzed by GC/MS. The mass assignments (NIST library matches) are as follows: 1 – 2-chlorophenol, 2 – 1,3-dichlorobenzene, 3 – 2,4-dichlorophenol, 4 – 1,3,5-trichlorobenzene, 5 – 2,6-dichlorophenol, 6 – 2,4,6-trichlorophenol, 7 – dichlorodibenzodioxin, 8 – trichloro-dibenzodioxin, 9 – tetrachlorodibenzofuran. The identifications except for the last three were confirmed by matching the GC retention times of the pure compounds

To examine the possible condensation of chlorophenols during combustion reactions, as is illustrated by Eq. (4), the compound 2,4-dichlorophenol was heated in air inside the tube furnace. The combustion products were trapped in methylene chloride, concentrated, and analyzed by GC/MS. Figure 2 shows examples of chromatograms for the combustion products. The products are indicated to be mainly 2,4,6-trichlorophenol, tetrachlorodibenzofuran, and dichlorodibenzodioxin, as identified by NIST library searches. Tetrachlorodibenzofuran and dichlorodibenzodioxin began to be formed below 400°C. Combustion of 2,4-dichlorophenol was also investigated by TG (Fig. 3). TG/FTIR on-line analysis of the evolved gases indicated the emission of CO_2, CO and H_2O, and HCl, as labeled on the three dimensional plot in Fig. 4 (60 seconds per file). The thermal decomposition of 2,4-dichlorophenol to CO_2; CO and H_2O, and HCl began around 500°C.

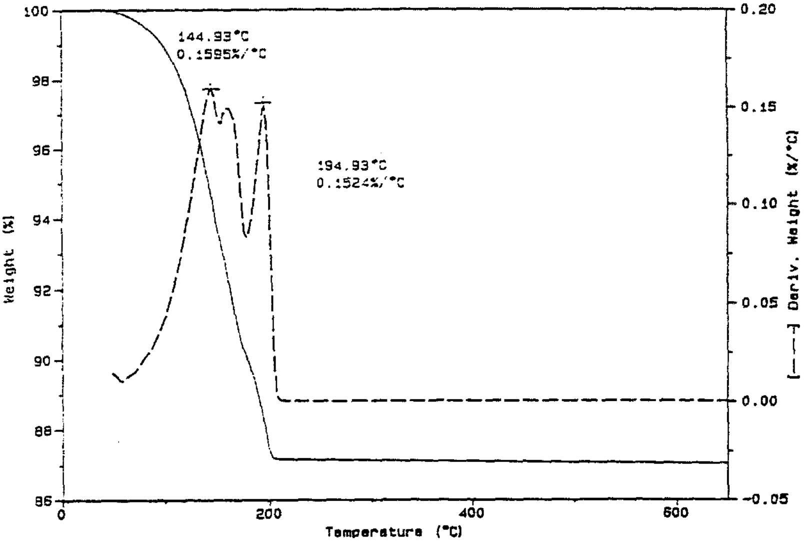

Fig. 3 TG curve for combustion of 2,4-dichlorophenol

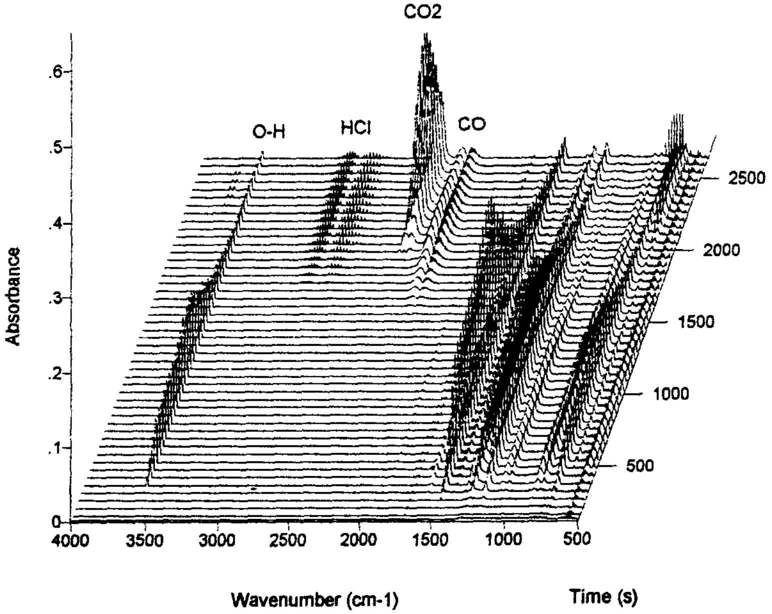

Fig. 4 Three-dimensional FTIR spectra of the combustion products of 2,4-dichlorophenol

Conclusions

Based on the information presented in this paper summary statements that can be made include:

- The Deacon reaction for the production of molecular chorine is generally favored at temperatures over 600°C.
- The gas phase chlorination of phenol is generally favored at temperatures over 600°C.
- Tetrachlorodibenzofuran, dichlorodibenzodioxin, and other chlorinated organic compounds are formed during the combustion of 2,4-dichlorophenol.
- The proposed three-step mechanism appears to be a possible pathway for the production PCDDs and PCDFs in combustion processes.

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