

TG/MS STUDY OF ORGANIC COMPOUNDS EVOLVED DURING THE CO-FIRING OF COAL AND REFUSE DERIVED FUELS

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INTRODUCTION

The Environmental Protection Agency reported that the total municipal solid waste (MSW) produced in the U.S. increased from 179 million tons in 1988 to 195 million tons in 1990.¹ It is predicted that the country will produce about 216 million tons of garbage in the year 2000.² Waste-to-energy conversion of MSW appears to be most attractive because of the energy recovered, economic value of the recycled materials, and the cost saving derived from reduced landfill usage. However, extra care needs to be taken in burning MSW or Refuse Derived Fuel (RDF) to optimize the operating conditions of a combustor so that the combustion takes place in an environmentally acceptable manner. For instance, polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have been found in the precipitator fly ash and flue gas of a number of incinerator facilities in the United States and Europe. Though the amount of PCDDs and PCDFs is only in the parts-per-billion to parts-per-trillion range, these chlorinated organics exhibit very high toxicity ($LD_{50} < 10 \mu\text{g/Kg}$) and 2,3,7,8-tetrachlorodibenzodioxin has been found to be acenegenic, carcinogenic, and teratogenic. This has slowed or even stopped the construction and operation of waste-to-energy plants. In previous work,³ the study of single materials has given us a good understanding of the characteristics and thermal behavior of these materials, their relative thermal stability and temperature relationships, their decomposition products and the evolution profiles of different gaseous products. The formation of molecular chlorine during combustion processes could be a key step for the formation of chlorinated organic compounds. The production of phenol and furan during the combustion of newspaper and cellulose could provide the important precursors for the formation of polychlorinated dibenzodioxin (PCDD) and polychlorinated dibenzofuran (PCDF).

EXPERIMENTAL

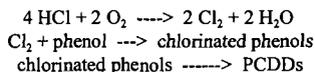
Materials used in this study include two coal samples (92073 - a KY #9 coal and 90003 - an IL #6 coal), PVC (OxyChem Corporation), cellulose (Whatman Corporation), and newspaper. The TG/MS system consists of a DuPont Instruments Model 951 Thermogravimetric Analyzer interfaced with a VG Thermolab Mass Spectrometer. The detection range of the TG/MS system is 1-300 atomic mass units (amu). Electron impact ionization energy is 70 eV. A sample size of ~20 mg was heated in air (50 mL/min) at a slow heating rate of 10°C/min to 700°C and a fast heating rate of 100°C/min to 900°C then held at the maximum temperature for five minutes. The MS system can automatically sample the gases evolved from the TG system, analyze them with its quadrupole analyzer, and save the spectra. The detailed experimental conditions are discussed in Lu's thesis.⁴

RESULTS AND DISCUSSION

Comparing the TG curves for the five raw materials (coals 92073 and 90003, PVC, cellulose, and newspaper) shows that the coals have a higher decomposition temperature and slower weight loss rates compared to the other materials. PVC, newspaper and cellulose show three distinct weight loss stages. At the fast heating rate similar results were obtained except that the weight loss shifts to higher temperatures (T_{max}) and the rate of maximum weight loss (R_{max}) increases. This indicates that the decomposition reactions of fuels occur much faster and at higher temperatures as the heating rate increases. The decomposition at the slow heating rate was studied in order to understand the mechanism of each stage. The study at the fast heating rate was done to approach the firing conditions of an atmospheric fluidized bed combustor (AFBC) unit. The heating rates in an AFBC system are much faster than those of the TGA experiments. Thus it is expected that the decomposition reactions occur at higher T_{max} and R_{max} values in the AFBC systems.

The evolved gases were identified using two analytical systems, TG/FTIR and TG/MS. The TG/FTIR system can be used to identify compounds with different functional groups and similar masses. The TG/MS can be used to identify species such as Cl_2 , O_2 , and N_2 which cannot be detected using FTIR techniques. The results show that at a fast heating rate the decomposition reactions are

compressed into a narrow time range. Hence the decomposition stages cannot be separated as is done with the slow heating rate. The FTIR data indicate that more hydrocarbons are produced at fast heating rates whereas more oxidation products are obtained at slow heating rates. Mass spectrometric results indicate that chlorine molecules are produced concurrently with HCl during the decomposition of PVC. The ratio of HCl/Cl₂ produced is around 150. This suggests that some of the abundant HCl could undergo a thermal Deacon reaction. This reaction is favored up to 600°C at atmospheric pressures. The Deacon reaction (given below) could provide a plausible starting point for the formation of chlorinated dioxins from the combustion of chlorine rich fuel mixtures.⁴ The suggested mechanism is as follows:



The study of single materials gives a good understanding of the characteristics and thermal behavior of these compounds, their relative thermal stability, and the evolution profiles of different gaseous decomposition products. This will help in the analysis of thermal decomposition products of blends and in the evaluation of their combustion kinetics and interactive mechanisms.

A series of experiments on blends (containing different amounts of coal, PVC, newspaper and cellulose) was conducted at both heating rates. PVC, which is a major source of chlorine, accounts for only 1% of MSW. A greater amount was used in these studies to investigate the conditions and mechanism for the formation of the chlorinated species. At a slow heating rate it is possible to evaluate kinetic and dynamic changes occurring during combustion. The studies at a fast heating rate will provide a better picture of combustion performance in an AFBC system.

The blends used in this study were manually prepared and labeled as follows:

- Blend 1: 03PVC is a mixture of coal 90003 and PVC (50% each);
- Blend 2: 03NEW is a mixture of coal 90003 and newspaper (50% each);
- Blend 3: 03Cell is a mixture of coal 90003 and cellulose (50% each);
- Blend 4: 03PN is a mixture of coal 90003 (50%), PVC (25%), and newspaper (25%);
- Blend 5: 035122 is a mixture of coal 90003 (50%), PVC (10%), newspaper (20%), and cellulose (20%);
- Blend 6: 73PVC is a mixture of coal 92073 and PVC (50% each);
- Blend 7: 73NEW is a mixture of coal 92073 and newspaper (50% each);
- Blend 8: 73Cell is a mixture of coal 92073 and cellulose (50% each);
- Blend 9: 73PN is a mixture of coal 92073 (50%), PVC (25%), and newspaper (25%);
- Blend 10: 735122 is a mixture of coal 92073 (50%), PVC (10%), newspaper (20%), and cellulose (20%).

1. TG/DTG Results

Table 1 is a summary of the TG/DTG results at both heating rates for all the blends. It can be seen that the maximum rates of major weight loss (R_{\max}) at the fast heating rate are much higher than those at the slow heating rate. For example, decomposition increases from 10%/min to 62%/min for blend #35122. This indicates that the decomposition reactions of fuels occur at a faster reaction rate as the heating rate increases. Since the heating rates in an AFBC system are much faster than those in TGA experiments it can be expected that decomposition reactions will occur at greater R_{\max} in AFBC systems.

On comparison with data for single materials, there is an important difference. For most blends, the combustion profiles are compressed into a continuous stage of weight loss at the fast heating rate. This means that the different decomposition stages for most blends can be separated from each other only at a slow heating rate. It is difficult to distinguish each decomposition stage in the combustion profiles at the fast heating rate, except for the moisture loss stage. Unlike those at the slow heating rate, the profiles of decomposition reactions for most blends display only one continuous weight loss at the fast heating rate. Also, the T_{\max} in the compressed profiles are in between the two T_{\max} values at the slow heating rate. For example, T_{\max} for H73PN is 344°C but T_{\max} for 73PN is 336°C and 432°C.

Figure 1 is a comparison of TG curves for blend 035122 and its components, coal 90003, PVC, cellulose, and newspaper; at the slow heating rate. The blend has a much lower decomposition temperature than the coal because of mixing with the easily decomposing components, (with high

volatile matter content), newspaper, cellulose, and PVC. This indicates that there are some mutual chemical interactions among the components during the combustion process. For the blend curve, the first weight loss is due to moisture. The second weight loss comes from the decomposition of PVC, newspaper and cellulose. The third weight loss is due to combustion of coal and carbon residues from PVC. It is possible that the combustion of newspaper, cellulose and PVC induce the shift of the coal combustion to a much lower temperature. The temperature at 50% weight loss ($T_{1/2}$) for coal is about 500°C and 370°C for the blends.

At the fast heating rate, the same trend is observed, the blend decomposes at much lower temperatures than the coal ($T_{1/2}$ for coal is ~750°C and ~450°C for blend). Compared with the blend curve at the slow heating rate the combustion profile of the blend becomes more continuous so that the second and third weight losses, which were clearly seen previously, cannot be definitely separated, indicating that combustion behavior is different at different heating rates.

2. Mass Spectrometry Results

Table 2 summarizes the tentative identification of some peaks in the MS spectra of blends 1 to 10 at the slow and fast (with a prefix "H-") heating rates. The compounds in bold type are also detected by the gas trap and GC/MS techniques. It is difficult to clearly interpret the complicated spectra obtained from the combustion of all the blends and attention was given to the sulfur and chlorine species in the evolved gases.

Figure 2 shows some mass profiles at the slow heating rate for blend 9(73PN). There are two major decomposition stages shown in this figure. The first stage occurs around 300°C. In this stage, HCl (36 and 38) and chlorine (70, 72 and 74) from PVC, furan (68) and furfural (96) from newspaper are major products. The second stage is at around 340°C. In this stage, larger molecules, toluene (92), methyl thiophene (98), xylene (106), chlorobenzene (112), and naphthalene (128) start evolving, which indicates that the coal begins to decompose. Phenol is also identified from the decomposition of newspaper. These two stages correspond to the second weight loss in the TGA curve.

There are similar results in Figure 3 (blend 5, file 035122). The peaks 60 (carbonyl sulfide) and 64 (sulfur dioxide) display the same changes as observed in coal 92073, i.e., sulfur dioxide has three decomposition phases and carbonyl sulfide has only two. In the profiles for HCl and molecular chlorine there are some differences. The HCl and molecular chlorine show two peaks at about 300°C and 340°C. The first peak may be attributed to the decomposition of PVC. The second peak is due to the decomposition of coal 90003 (high chlorine, low sulfur) and newspaper. An important fact is that molecular chlorine, phenol and furan are released at the same temperature range. This indicates that there is some possibility for the formation of chlorophenol at this temperature. However, it is difficult to identify chlorophenol from TG/MS studies due to two reasons. First, the amount of phenol ($m/z = 94$) present in the gas phase is very small. Secondly, chlorophenol has the same mass, 128, as naphthalene. These two species cannot be distinguished from each other in the TG/MS system. This problem can be resolved using a separation system. In tubular furnace studies more sample can be loaded, increasing the amount of phenol produced. Also the GC/MS system can separate the components prior to identification. The results from 10 grams of blend sample show that naphthalene is a major product and small amounts of chlorophenol is also identified. The results using 100 mg phenol as sample and 0.5% chlorine in nitrogen as purge gas and the same heating rate show that mono-, di-, and tri-chlorophenols can be formed. This indicates that during co-firing coal with MSW, either the amount of phenol produced is too small to form chlorophenol, or the amount of the produced chlorophenol is too small to be detected by the TG/MS system.

Comparison of the evolved gases at slow and fast heating rates show trends very similar to those of the individual raw materials. More hydrocarbons and chlorinated species are formed during the same time span at the fast heating rate whereas they evolve at different times at the slow heating rate.

CONCLUSIONS

- The TG/FTIR/MS system was used to identify molecular chlorine, furan, phenol and other aromatic compounds, along with HCl, CO, CO₂, and H₂O in the gaseous products of the combustion of coal, PVC resin, newspaper, and cellulose in air. This is a significant finding that will lead us to study this combustion step further to look for the formation of chlorinated organic compounds.
- The TG/MS techniques allow the study of reaction pathways for the formation of gaseous products during combustion.

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Table 1. Summary of TG/DTG Results for Blends

Sample	$\Delta W_2(\%)$	T_{max}	R_{max}	$\Delta W_3(\%)$	T_{max}	R_{max}
03PVC	30	307	6	64	457	6
H03PVC	42	354	71	55	435	32
03New	30	340	19	59	463	8
H03New	93	349	41			
03Cell	43	341	17	48	442	18
H03Cell	92	361	67			
03PN	27	302	7	64	419	13
H03PN	94	345	81			
035122	49	300	10	44	444	7
H035122	51	324	62	39	595	13
73PVC	37	306	7	51	437	5
H73PVC	82	347	57			
73New	51	337	33	24	444	14
H73New	73	374	99			
73Cell	53	346	23	30	423	19
H73Cell	82	383	99			
73PN	52	336	31	29	432	12
H73PN	85	344	98			
735122	40	300	6	42	418	8
H735122	49	331	70	43	538	12

Note: R_{max} is maximum rate of weight loss, %/min; T_{max} is the temperature at R_{max} , °C; ΔW is the weight loss.

Table 2. Tentative Parent Structures of MS Peaks for Coal 92073 Blends

Name	B6	HB6	B8	HB8	B9	HB9	B10	HB10
dimethylnaphthalene		156						
vinyl naphthalene		154						
acenaphthene			154					
biphenyl			154					
methylbenzothiophene	148			148	148	148		
dichlorobenzene	146			146	146	146		
indan-1,3-dione	146			146	146	146		
methylnaphthalene		142		142	142	142		
decene		140		140	140	140		
ethylxylene		134	134		134	134	134	
tetrahydronaphthalene	132			132	132	132		
naphthalene		128	128		128	128	128	
chlorotoluene	126	126		126	126	126		
propylbenzene	120	120		120	120	120	120	
ethylmethylbenzene	120	120		120	120	120	120	
trimethylbenzene	120	120		120	120	120	120	
indene		116	116			116		116 116
chlorobenzene	112	112		112	112		112	112 112
octene	112	112		112	112		112	112 112
xylene	106	106	106	106	106		106	106 106
ethylbenzene	106	106	106	106	106		106	106
3-methyl-2-furanone	98	98	98	98	98		98	98 98
methylthiophene	98	98	98	98	98		98	98 98
furfural	96	96	96	96	96		96	96 96
phenol	94	94	94		94		94	94 94
toluene	92	92	92	92	92		92	92 92
thiophene	84	84	84	84	84		84	84 84
benzene	78	78	78	78	78		78	78 78
furan/1,3-pentadiene	68	68	68	68	68		68	68 68
SO₂/1,3-pentadiene	64	64	64	64	64		64	64 64

"H-" prefix means the fast heating rate was used. "B + number" means the blend + number. The compounds in bold type indicate those also detected by the GC/MS system.

COMPARISON FOR BLEND AND ITS COMPONENT TGA CURVES
 File: 035122.018 80003.006 PVC.002 NEWSPAPER.020 CELLULOSE.003

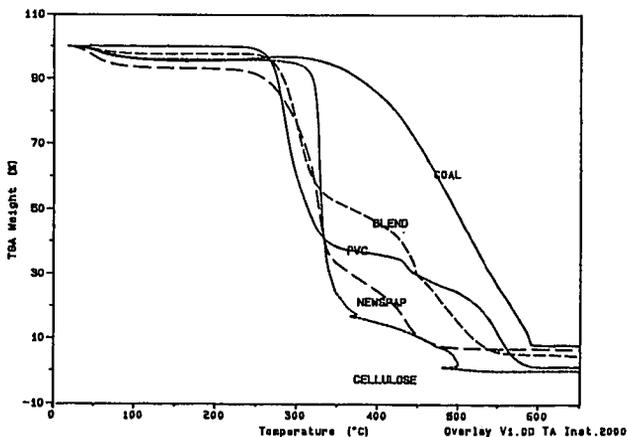


Figure 1. TG curves for blend 035122 and the four components of the blend.

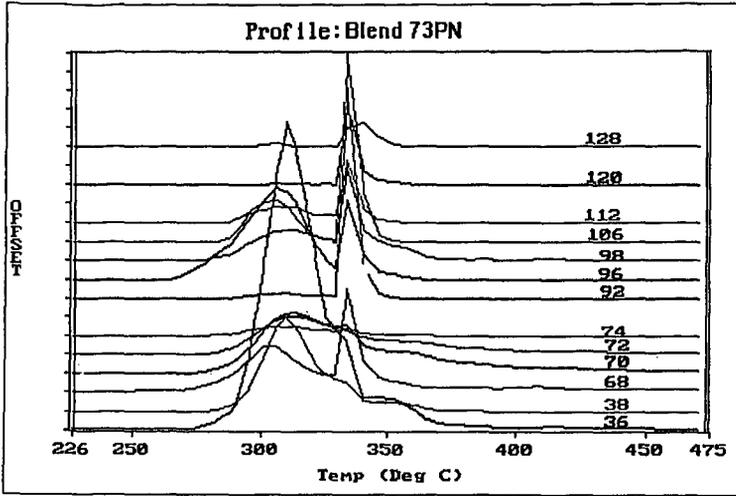


Figure 2. Profiles of m/z values for combustion products of blend 9(73PN).

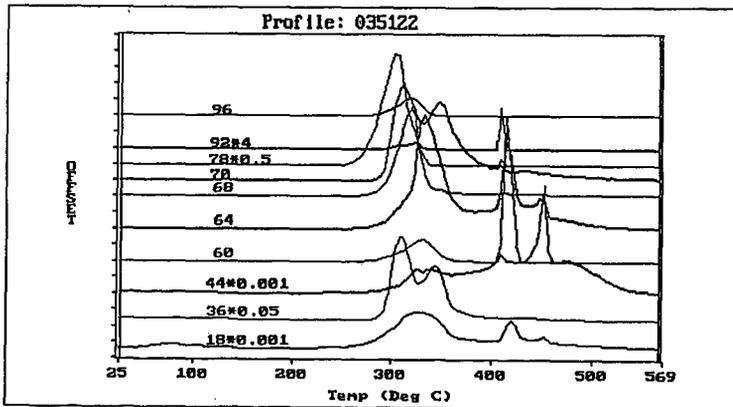


Figure 3. Profiles of m/z values for combustion products of blend 5(035122).