

SULFUR AND NITROGEN EVOLUTION IN THE ARGONNE COALS

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INTRODUCTION

In a previous study (1), the major volatile products evolving from the Argonne Premium coals were investigated using TG-FTIR temperature programmed pyrolysis and combustion. The focus of this study is on the evolutions of two minor volatile products, sulfur and nitrogen, using the same TG-FTIR technique. Although sulfur and nitrogen are small contributors to the mass loss from coal during pyrolysis, their oxides are a major cause of environmental pollutants during coal combustion.

EXPERIMENTAL APPARATUS

Details on the TG-FTIR system appear elsewhere (1,2,3). Its components are as follows: a DuPont 951 TGA, a hardware interface, an Infrared Analysis 16 pass gas cell with transfer optics, and a Michelson 110 FT-IR (resolution, 4 cm^{-1} ; detector, MCT). A helium sweep gas (250 cm^3/min) is employed to bring evolved products from the TGA directly into the gas cell. The system is operated at atmospheric pressure.

PROCEDURE

A 50 mg sample loaded in the platinum sample pan of the DuPont 951 is taken on a 30°C/min temperature excursion in helium first to 150°C to dry for 4 minutes and then to 900°C at 30°C/min for pyrolysis. Upon reaching 900°C and holding the temperature for 3 minutes, the sample is immediately cooled to 250°C over a 20 minute period. After cooling, a small flow of O₂ (20 cm^3/min) is added to the helium sweep gas and the temperature is ramped to 900°C in order to combust the remaining char. Infrared spectra are obtained once every 41 seconds.

A post-oxidation method was employed to collectively study sulfur evolution. In this procedure, heat (approximately 900°C) and oxygen (10 cm^3/min) is added to the volatile product stream after the furnace but before the analysis cell. This added step allows detection of H₂S, a very weak infrared absorber; elemental sulfur; and tar sulfur by monitoring SO₂ evolution rate. Details of this post-oxidation method appear elsewhere (1).

RESULTS AND DISCUSSION

Sulfur Evolution - The total sulfur evolution from pyrolysis of the Argonne Premium coals is presented in Figure 1. Sulfur was studied collectively by post-oxidizing the pyrolysis products and monitoring the SO₂ evolution rate. The SO₂ evolution curves exhibit two main evolution peaks. For each peak, the temperature of the maximum evolution rate (T_{max}) increases with increasing rank. Similar rank dependence has been reported by Kelemen et al. (4) and Oh et al.(5). Furthermore, the low temperature SO₂ evolution peak coincides with the coal's tar evolution peak.

To determine the pyritic sulfur contributions to the SO₂ evolutions, Illinois #6 and Pittsburgh #8 coals were subjected to ASTM D-2492 (6) under a nitrogen atmosphere. In this method, sulfate sulfur is extracted from the coal with dilute hydrochloric acid and pyrites (FeS₂) are removed using dilute nitric acid. Results from temperature programmed pyrolysis and combustion of raw and ASTM D-2492 modified Illinois #6 coal are presented in Figures 2 and 3 respectively. Figures 2a and 3a are the balance and thermocouple curves and Figures 2b and 3b are the SO₂ evolution and weight curves. The tar evolution curve for the raw Illinois #6 coal (obtained with out the post-oxidizer in line) is included in Figure 2a to demonstrate how the tar peak overlays the low temperature SO₂ peak. The ASTM D-2492 procedure removed a substantial amount of the low temperature SO₂ peak, the entire high temperature SO₂ peak and the "sharp" portion of the combustion cycle SO₂ peak. These results indicate that pyritic sulfur evolves during the low and the high temperature SO₂ peak, an observation that has been reported by others (5,7). Temperature programmed pyrolysis and combustion of raw and ASTM D-2492 modified Pittsburgh #8 coal showed similar trends as the Illinois #6 coal.

Table 1 compares the TG-FTIR's pyritic and organic sulfur values with those provided by Argonne National Laboratory (8) and also gives the pyrolysis and oxidation contributions to the pyritic and organic sulfur amounts. For Illinois #6 coal, 53 percent of the pyritic sulfur and 62 percent of the organic sulfur along with 47 (ash-free) weight percent of the volatiles evolved during pyrolysis while for Pittsburgh #8 coal, 64 percent of the pyritic sulfur and 48 percent of the organic sulfur along with 43 (ash-free) weight percent of the volatiles evolved during pyrolysis. Consequently, both coals are preferentially evolving sulfur during pyrolysis.

To compare coal pyrite with pure pyrite, a pure pyrite sample from Custer, South Dakota was subjected to temperature programmed pyrolysis and combustion and the evolution curve is presented in Figure 4. The pyrite sample shows no low temperature SO₂ and has a high temperature SO₂ T_{max} (609°C) slightly higher than that of Illinois #6 coal in Figure 2b (578°C).

What causes the low temperature pyrite decomposition in coals during pyrolysis? Since for each Argonne Premium coal the tar evolution and the low temperature SO₂ evolution have similar T_{max}'s, it is feasible that the tars are responsible for the low temperature pyrite decomposition in coal. In support of this possibility, presented in Figures 5a and b are Arrhenius plots comparing the mean reaction rates (\bar{r}) for tar evolution and low temperature SO₂ evolution for Illinois #6 and Pittsburgh #8 coals respectively. The Arrhenius parameters were generated using the method of evaluating the T_{max} shift with heating rate as described by Braun et al. (9). In this method, a plot of $\ln H_r/T_{max}^2$ versus $1/T_{max}$, where H_r is the experimental heating rate, produces a line with the slope equal to $-(E_r/R)$. The Arrhenius plots show that the mean tar and low temperature SO₂ reaction rates differ by a factor of 4 for the Illinois #6 coal and are virtually identical for the Pittsburgh #8 coal.

As noted from Figure 1, the high temperature SO₂ T_{max} which is a result of pyrite decomposition demonstrates rank dependence. The SO₂ T_{max} increases from 564°C in the case of Zap coal, to 674°C in the case of Upper Freeport coal. It is unclear as to why pyrite in coal is rank dependent. Pyrolysis experiments are presently being done with pyrite/model compound mixtures and with pyrite in the presence of various gases, added to the helium sweep gas in an attempt to address this issue.

Nitrogen Evolution - The NH₃ and HCN evolutions from pyrolysis of the Argonne Premium coals are presented in Figures 6 and 7. The NH₃ evolution curves exhibit two main evolution peaks.

For each peak, the T_{max} increases with increasing rank although the majority of the shift in T_{max} for the high temperature NH_3 peak occurs between Wyodak and Illinois #6 coals. The HCN evolution curves exhibit only one main evolution peak and, with the exception of Zap and Wyodak coals, the HCN evolution curves overlay the high temperature NH_3 evolution curve suggesting that a common source is responsible for their formation. In the cases of Zap and Wyodak coals, HCN evolves at a lower temperature than the high temperature NH_3 evolves.

Table 2 compares that TG-FTIR weight percents for NH_3 and HCN to previously obtained values generated during rapid heating rate pyrolysis in an entrained flow reactor (EFR) (10). For each coal, the total amount of nitrogen evolved in of the each pyrolysis systems is similar. The ratio of HCN to NH_3 , however, differs significantly. The dominant product during slow heating rate pyrolysis in the TG-FTIR is NH_3 while the only product during rapid pyrolysis in the EFR is HCN. These results can be explained by the following possibilities: 1) A competitive reaction process leads to the formation of NH_3 at the expense of HCN at low pyrolysis heating rates; 2) in the entrained flow reactor, secondary pyrolysis reactions especially tar cracking, lead to the formation of HCN and the destruction of NH_3 ; 3) NH_3 is removed in the collection system in the entrained flow reactor (e.g., dissolution into water which condenses on the walls of the gas collection bag).

In an attempt to increase the tar cracking in a slow heating rate pyrolysis run, Utah Blind Canyon coal was pyrolyzed in the TG-FTIR and the pyrolysis products were passed through a hot quartz tube heated to approximately 900°C just prior the gas analysis cell. This post-pyrolysis method utilizes the same apparatus as the post-oxidization method; however, helium is added to the sample stream rather than oxygen. The post-pyrolysis results are presented in Figure 8. Figure 8a displays the HCN evolution curves while Figure 8b shows the NH_3 evolution curves. In the post-pyrolysis experiment, the HCN evolution peak at the 20 minute mark indicates a significant increase in tar cracking. This supports item 2 in the latter paragraph although post-pyrolysis does not show significant reductions in NH_3 evolution.

SUMMARY AND CONCLUSIONS

Sulfur Evolution - The total sulfur evolution during pyrolysis measured by post-oxidation of volatile products demonstrated two main evolution peaks which had consistent rank variations. The first SO_2 peak is from organic and pyritic sulfur while the second SO_2 peak is from pyritic sulfur only. Arrhenius plots showed that tar evolution and low temperature SO_2 evolution had similar mean reactions rates. And, sulfur was found to be preferentially released during pyrolysis.

Nitrogen Evolution - NH_3 evolution exhibited two main peaks whose T_{max} 's showed rank dependence although the majority of the shift in the high temperature NH_3 peak occurred between Wyodak and Illinois #6 coals. HCN evolution curves coincided with the high temperature NH_3 evolutions except in the cases of Wyodak and Zap coals where lower HCN T_{max} 's were observed. Finally, the dominant product during slow heating rate pyrolysis was NH_3 , while during rapid heating rate pyrolysis HCN was the only product.

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Table 1. TG-FTIR and Argonne Values for Pyritic and Organic Sulfur in Illinois No. 6 and Pittsburgh No. 8.

	TG-FTIR (AF Wt.%)						Argonne Values (AF Wt.%)	
	Pyritic			Organic			Pyritic	Organic
	Pyrolysis	Oxid.	Total	Pyrolysis	Oxid.	Total	Total	Total
Illinois	1.73	1.53	3.26	1.17	0.73	1.90	3.02	2.16
Pittsburgh	1.12	0.64	1.76	0.42	0.46	0.88	1.48	0.88

Table 2. NH₃ and HCN Weight Percents from Pyrolysis in TG-FTIR and Entrained Flow Reactor.

	TG-FTIR		EFR 1100°C, 24'	
	(as-received wt.%)		(ash free wt.%)	
	HCN	NH ₃	HCN	NH ₃
Pocahontas	0.034	0.27	0.28	0
Upper Freeport	0.028	0.42	0.78	0
Pittsburgh	0.038	0.47	0.84	0
Stockton	0.051	0.45	0.55	0
Utah Blind Canyon	0.101	0.53	1.21	0
Illinois	0.065	0.45	---	---
Wyodak	0.035	0.28	0.60	0
Zap	0.082	0.40	---	---

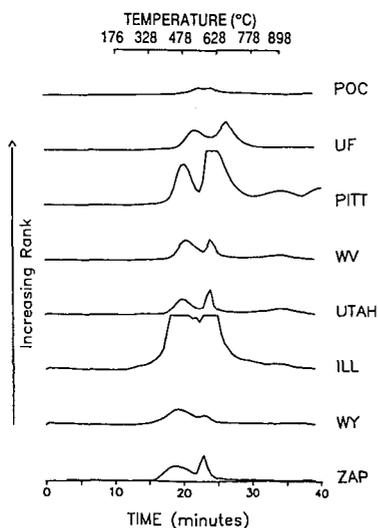


Figure 1. SO₂ Evolution Curves from Pyrolysis of the Argonne Coals with Post-Oxidation of Volatile Products.

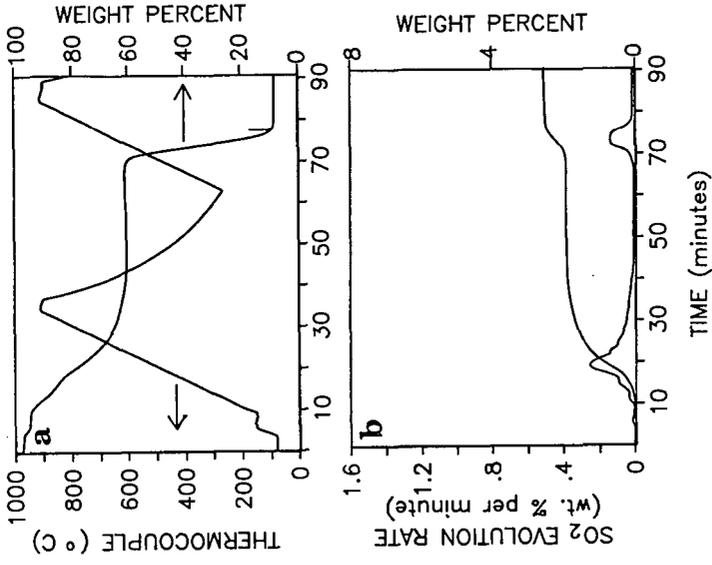


Figure 2. Results from Pyrolysis of Illinois No. 6 Coal with Post-Oxidation of Volatile Products. a) Balance, Thermocouple and Tar Evolution Curves and b) SO₂ Evolution and Weight Curves.

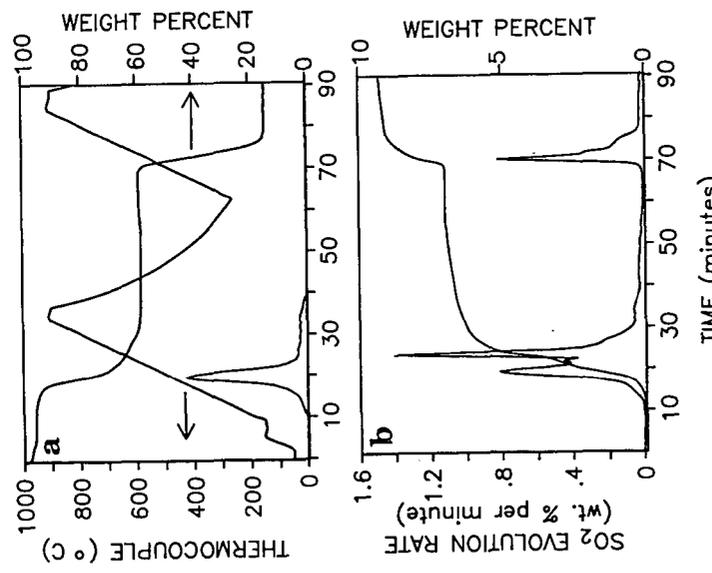


Figure 3. Results from Pyrolysis of ASTM D-2492 Modified Illinois No. 6 with Post-Oxidation of Volatile Products. a) Balance and Thermocouple Curves and b) SO₂ Evolution and Weight Curves.

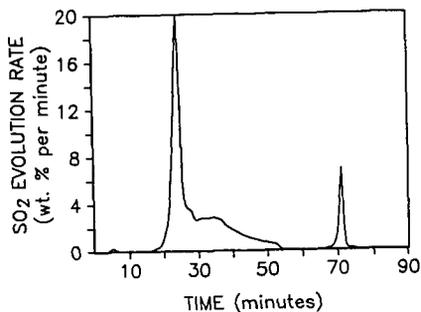


Figure 4. SO_2 Evolution Curve from Pyrolysis of Pyrite with Post-Oxidation of Volatile Products.

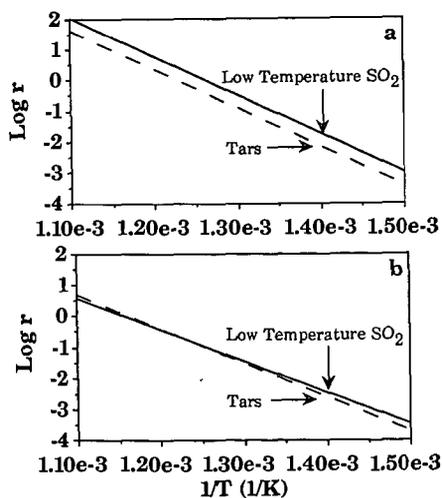


Figure 5. Arrhenius Plots Comparing Mean Reaction Rate (r) of Tar Evolution and Low Temperature SO_2 Evolution for a) Illinois No. 6 and b) Pittsburgh No. 8.

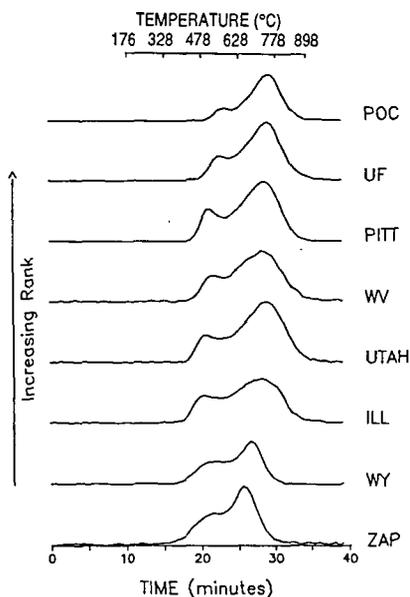


Figure 6. NH_3 Evolution Curves from Pyrolysis of the Argonne Coals.

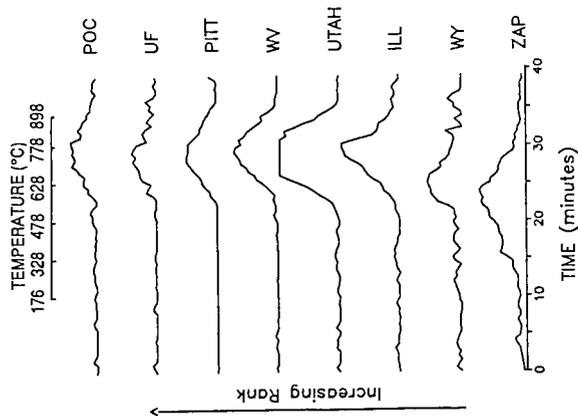


Figure 7. HCN Evolution Curves from Pyrolysis of the Argonne Coals.

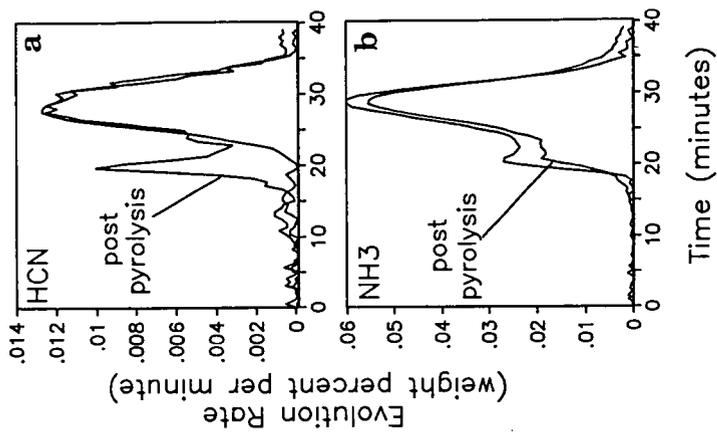


Figure 8. Results from Pyrolysis and Post-Pyrolysis of Utah Blind Canyon. a) HCN Evolution Curves and b) NH_3 Evolution Curves.