Report Title: DETERMINATION OF THE FORMS OF NITROGEN RELEASED IN COAL TAR DURING RAPID DEVOLATILIZATION

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DISCLAIMER

ABSTRACT

The primary objective of this work is to determine the **forms of nitrogen in coal that lead to nitrogen release during devolatilization.** Experiments are to be performed in two existing **laminar flow reactors** available at Brigham Young University, which are both capable of temperatures (up to 2000 K), particle heating rates (10^4 to 10^5 K/s), and residence times (up to 500 ms) relevant to conditions commonly encountered in industrial pulverized coal combustors. The forms of nitrogen in coal, char, and tar samples will be analyzed using state-of-the-art techniques, including nuclear magnetic resonance (**NMR**), X-Ray photoelectron spectroscopy (**XPS**), and high resolution **nitrogen-specific chromatography**. These sophisticated analysis techniques will be performed in collaboration with other researchers at BYU, the University of Utah, and industrial organizations. Coals will be obtained as a function of rank, including eight coals from the University of Utah that are to be used in pilot scale tests in support of the DOE Coal-2000 HiPPS (High Performance Power Systems) and LEBS (Low-Emission Boiler Systems) programs. Anticipated results from the proposed research will be (a) nitrogen release parameters during devolatilization for specific coals pertinent to the HiPPS and LEBS projects, (b) better fundamental understanding of the chemistry of nitrogen release, and (c) a nitrogen release submodel based on fundamental chemistry that may be more widely applicable than existing empirical relationships.

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EXECUTIVE SUMMARY

The primary objective of this work is to determine the forms of nitrogen in coal that lead to nitrogen release during devolatilization. Several moderate temperature coal pyrolysis experiments have been performed in a drop tube reactor in nitrogen, generating char and tar samples from 5 different coals (Zap lignite, NM subbituminous, Illinois #6 hvb bituminous, Pittsburgh #8 hva bituminous, and Pocahontas #3 lv bituminous). Initial ^{13}C NMR analysis of the low temperature (900 K) experiments was reported in the previous report and published at the 26th International Symposium on Combustion. These data indicated that the carbon per cluster in the tar, and hence the nitrogen per cluster in the tar, was much different than observed in the parent coal or corresponding char. These results contradicted the most recent models of nitrogen evolution during coal pyrolysis.

Additional experiments were performed at higher temperatures (1050 K and 1200 K) in order to determine if tar from more severe pyrolysis experiments exhibited these same features. The tars from these experiments analyzed to date (mainly some of the 1050 K samples) were not dissolved in CD_2Cl_2 prior to analysis, and indicate higher numbers of carbon per cluster (and nitrogens per cluster) than in the 900 K samples. This indicates that the 900 K samples should be repeated and analyzed without dissolution in CD_2Cl_2.

The Argonne Premium Coals (APC) were analyzed with ^{15} NMR for the first time, and then additional acid-washed APC samples were also analyzed with ^{15}N NMR. The noisy signals (due to low nitrogen concentrations) were analyzed qualitatively, and indicate the presence of pyridinic structures only in the acid-washed samples. The pyridinic structures can only be viewed with ^{15}N NMR as quaternary nitrogen, and the acid wash converts the pyridinic form to quaternary.

Preliminary nitrogen specific gas chromatography was performed on a few coal samples. This analysis showed that there are extremely complex mixtures of nitrogen-containing compounds in coal tar. Only about 30 compounds were identified in the low molecular weight portion of the tar that was able to pass through the gas chromatography.

INTRODUCTION

Control of emissions of nitrogen oxides (NO_x) from coal combustion systems is becoming a major design and retrofit consideration. Most NO_x in coal combustion systems comes from nitrogen in the fuel, rather than from nitrogen in the air. Practical emission control strategies include burner design strategies (e.g., low NO_x burners), overfire air, reburning, selective non-catalytic reduction (SNCR) using reduction agents such as NH_3 or urea, and selective catalytic reduction (SCR). The order listed also reflects the order of increasing costs for implementation. It is therefore most economically desirable to perform burner modifications to reduce NO_x emissions rather than other control measures.

Low-NO_x burners work on the principle that devolatilized nitrogen species will form N_2 rather than NO_x under locally fuel-rich conditions with sufficient residence time at appropriate temperatures. The amount and form of nitrogen released during devolatilization influence the degree of NO_x reduction attainable using burner design strategies for a given coal. Nitrogen in the char following devolatilization is released by heterogeneous oxidation, and may not be controlled by aerodynamic burner modifications.

The use of comprehensive computer modeling is becoming an efficient screening method in the design of new systems, when based on sound fundamental understanding of the systems to be modeled. Although several empirical relationships for nitrogen evolution from coal during devolatilization have been developed, the fundamental chemistry of coal nitrogen evolution is still not fully understood, and is a weak link in comprehensive coal combustion models used for screening of new systems.

The objectives this work are to perform detailed chemical measurements of the forms of nitrogen in coal, char, and tar. Questions to be answered by this research fall into two categories:

1. Why do low rank coals (i.e., lignites) release as much nitrogen during devolatilization as hva bituminous coals when the tar yields are markedly different?
2. Why do coals of similar rank and elemental composition release different amounts of nitrogen during devolatilization?

Seven tasks are proposed to help answer these two questions:

1. Obtain representative coals being used or considered for use by industry. This includes eight coals from Dr. Pershing at the U. of Utah that will be used in his research for the DOE-HiPPS and DOE-LEBS programs.

2. Analyze parent coals for:
   - elemental nitrogen content
   - extract yield
   - elemental composition of extracts
   - XPS nitrogen form (5-member, 6-member, etc.)
   - ^{15}N NMR spectra

3. Collect char samples in the FFB under 0% post-flame O_2 conditions. Determine the fraction of nitrogen released during pyrolysis at high heating rates and temperatures in the FFB. Also perform XPS and ^{15}N NMR experiments on selected FFB chars.

4. Perform HPCP pyrolysis experiments to collect tar and char samples as a function of residence time and temperature. Determine the fraction of nitrogen released during pyrolysis at high heating rates and temperatures. Also perform XPS and ^{15}N NMR experiments on selected HPCP chars and tars.

5. Perform solvent extractions on parent coals and partially-devolatilized coal chars, saving both extract and residue samples. Analyze residues and extracts for elemental composition. Perform ^{15}N NMR and high resolution chromatography experiments on extracts to look for changes in the forms of nitrogen as a function of coal type and extent of devolatilization.

6. Perform new NMR experiments (i.e., DNP) to better characterize forms of nitrogen in coal, coal char, and tar.

7. Develop a model of nitrogen release as a function of coal type based on chemical forms of nitrogen in coal.

EXPERIMENTAL APPARATUS

This research focuses on the solid and liquid products produced during coal devolatilization. These include coal chars, tars and solvent extraction products of char. To produce the devolatilized products two systems were used: a drop tube reactor (HPCP) and a flat flame burner (FFB). The HPCP has been used to perform moderate temperature experiments (800 to 1200 K) at atmospheric pressures to provide char and tar samples as a function of residence time during devolatilization. The FFB experiments provide char and soot samples from a high temperature, high heating rate environment with products of methane combustion present.

RESULTS AND DISCUSSION

The cost-shared part of this project started on May 1, 1995, and the DOE part started on August 1, 1995. Accomplishments from May 1, 1996 to October 31, 1996 include:

- Determination of chemical structure features with the use of ^{13}C NMR techniques of matching samples of coal, char and tar that were produced in the HPCP.
- Completion of a set of experiments in the FFB that included 17 coals. These experiments provided char and soot which will be used to determine degree of nitrogen evolution under high temperature, high heating rate environments.
- Development of technique to measure the fractional conversion of fuel nitrogen to hydrogen cyanide in the HPCP.
- Completion of solvent extractions of chars generated in the HPCP for a set of 5 coals at 2 conditions.
- Analysis of the Argonne Premium Coal (APC) samples and acid-washed APC samples using ^{15}N NMR spectroscopy.
- Completion of a preliminary nitrogen-specific chromatography analysis of coal tars. This work is being done under the direction of Dr. Milt Lee at BYU.
- Further collaborative work has been conducted with Dr. Simon Kelemen at Exxon Research to analyze char and tar samples produced in the HPCP using XPS.

HPCP Pyrolysis Experiments

Chars and tars were collected in HPCP drop tube reactor experiments at temperatures ranging from 900 to 1200 K for five coals during the previous reporting period. Elemental (CHN) analysis has been performed on all the chars and tars produced to date. Some of the ^{13}C NMR analysis of these fifteen sets of samples (char, tar, and coal from 5 coals and 3 pyrolysis conditions) was completed during this reporting period. Also, during this reporting period, the HPCP collection system was modified to allow for

the analysis of gas phase pyrolysis products. An on-line hydrogen cyanide detector (HCN) was used to perform initial experiments to determine fractional conversion of fuel nitrogen to HCN. It is anticipated that ^{13}C NMR analysis of liquid and solid pyrolysis products, in combination with these gas phase measurements, will provide additional insight into the nitrogen evolution process.

^{13}C NMR Analysis of Coal, Char, and Tar Samples

The technique used to analyze tar samples was mentioned in the last semi-annual report and presented at the International Combustion Symposium.[1] This technique involved partially dissolving the tar sample in deuterated methylene chloride (CD_2Cl_2). The soluble portion was analyzed with a recently-developed high resolution liquid ^{13}C NMR technique. The non-soluble portion of the tar was analyzed with standard solid state ^{13}C NMR techniques. Three tar samples from the high volatile bituminous coals at the 900 K condition were analyzed with this technique, and the results were published.[1] Recently, a method was developed that enables accurate determination of tar structural parameters with standard solid state ^{13}C NMR techniques. This method was used to analyze 4 tars and 1 char at the 1050 K condition. Similar ^{13}C NMR analysis of the remaining pyrolysis tar and char samples is currently underway and completion is expected shortly.

The results of the previous ^{13}C NMR analysis of the 900 K tars are shown in Table 1. The data from the low temperature (900 K) condition include the combined tar values, calculated as a weighted average of the dissolved tar and tar residue. As seen in Table 1, 12 to 42% of the tar sample collected at the 900 K condition was insoluble in CD_2Cl_2 and was deposited on the filter as residue.

The preliminary data from the medium temperature (1050 K) condition can be seen in Table 2. The preliminary data from the medium temperature (1050 K) condition permits comparison of the tar structure at two different stages of pyrolysis for the Pittsburgh #8 and Illinois #6 coals. As shown in Tables 1 and 2, the B.L. parameter increases greatly with pyrolysis temperature for both coals while the opposite trend is observed for the S.C. parameter. For the Pittsburgh #8 coal, the MW_{cl} of the tar increases with pyrolysis temperature while the opposite trend is seen for the Illinois #6 coal. Also, the number of nitrogens per cluster in the tar increases with pyrolysis temperature and is closer to the level seen in the parent coal.

As previously mentioned, the low temperature tars were analyzed with a different method than the medium temperature tars. A portion of the low temperature tars was analyzed after being dissolved in CD_2Cl_2. It is difficult to conclude that a changes in NMR parameters are due solely to changes in pyrolysis conditions and are not influenced by the dissolution process. For this reason, we are currently planning to repeat the ^{13}C NMR analyses of the low temperature (900 K) tars with the new solid-state technique.

^{15}N NMR Analysis

The Argonne Premium Coal (APC) samples were analyzed using ^{15}N NMR (see Fig. 1); these are the first published ^{15}N NMR data on the APC samples. The large amount of noise present in these spectra is due to the small concentration of nitrogen (<2 wt.%) in the samples. The ^{15}N NMR spectra of the pristine coals only show evidence of the presence of protonated nitrogens in five-member rings. A diversity of these pyrrolic type nitrogens is noted in the higher rank coals, as evidenced by the split peaks for the

Pocahontas coal. This observation is attributed to increasing ring size with rank, although no model compound data exist to verify this assumption. Pyridinic nitrogens are not observed in the NMR spectra, which is not surprising considering the spinning speeds employed and the unfavorable cross polarization dynamics for these types of nitrogens. Details justifying this statement are included in two papers that have recently been submitted for publication.[2,3]

Treating the coals with strong acid (see Figure 2) results in an increase in the signal from the pyridinium (quaternary) type nitrogens, thus implying that pyridine type nitrogens are present in the coal but are undetectable by standard solid state NMR techniques.[3] Note the increase in intensity in the -175 ppm chemical shift region following acid treatment. This change presumably arises from the appearance of pyridinium (quaternary) type nitrogens as pyridinic nitrogens are converted into pyridinium species. The reasons are explained in reference 2 as are the experimental conditions. The vertical reference lines are placed to guide the eye to the chemical shift frequencies of pyridine, pyridinium ion, pyrrole, and carbazole as fiducial marks.

These experimental results are now in general agreement with the XPS data which indicate that approximately 25% of the nitrogens are present as pyridine types. The shifts in the peaks and nature of the peaks in the ^{15}N NMR spectra for different coals indicate differences in the nitrogen structures present, which may lead to reactivity differences. It is hoped that improvements in ^{15}N NMR techniques can help quantify these differences.

Nitrogen-Specific Chromatography Analysis

A preliminary nitrogen-specific chromatography analysis of coal tars was completed in this reporting period. This initial investigation was limited in scope and was directed at developing the techniques required to apply nitrogen-specific gas chromatography/mass spectrometry to coal tars. Illinois #6 coal was pyrolyzed in the HPCP at three temperature conditions. The resulting tars were analyzed with nitrogen-specific gas chromatography/-mass spectrometry under the direction of Dr. Milt Lee at BYU. This analysis showed that there are extremely complex mixtures of nitrogen-containing compounds in coal tar. Due to this extreme complexity, the quantitative resolution of the resulting chromatograms was poor. However, despite the lack of good resolution, thirty nitrogen-containing polycyclic aromatic compounds were tentatively identified in these tars. These compounds were mainly pyridinic and pyrrolic, with numbers of fused aromatic rings ranging from 2 to 5. These results are in agreement with previous investigations of coal tar.[4] Further work in this area will continue into the next reporting period.

Flat Flame Burner Pyrolysis Experiments

Flat flame burner (FFB) experiments were performed on 12 additional coals of broadly differing rank, nitrogen content and total volatiles yield, as shown in Table 3. Previous experiments were performed on the five coals used in the HPCP experiments. These FFB experiments were performed under 0% post-flame O_2 conditions with a maximum gas temperature of 1650 K and 15 ms residence time. The analysis of the resulting pyrolysis products is currently underway. The results of this study will be used to identify coals which have similar total volatiles yield while releasing significantly

different amounts of nitrogen. Once identified, the HPCP will be used to perform moderate pyrolysis experiments on these coals. It is expected that these pyrolysis experiments, in combination with NMR, GC/MS, solvent extraction and XPS analyses will permit further insight into the nitrogen evolution process.

FUTURE PLANS

Future plans include performing pyrolysis experiments on selected coals from the FFB study. This will permit examination of samples from earlier stages of devolatilization and should provide insight into why these coals release similar amounts of total volatiles while releasing different amounts of nitrogen. Additional experiments will be performed in the HPCP using the five standard coals. These experiments will be aimed at determining the fractional conversion of fuel nitrogen to HCN for these coals and to provide additional char and tar samples for ^{13}C NMR, XPS, and GC/MS analysis. The HCN analyzer will be used in conjunction with the FFB in an effort to determine the amount of HCN formed under more severe pyrolysis conditions. Elemental (CHNS) determination of solvent extraction products of HPCP chars will be performed. The documentation of all samples and analyses performed to date will be organized and examined in order to determine discrepancies and need for additional experiments and/or analyses. Initial modeling ideas will also be initiated during the next reporting period.

CONCLUSIONS

The primary objective of this work is to determine the forms of nitrogen in coal that lead to nitrogen release during devolatilization. During this reporting period, major progress was made in developing the analytical techniques necessary to identify the forms of nitrogen in coal and coal pyrolysis products. The first ^{15}N NMR spectra of the Argonne Premium Coal (APC) samples were obtained. Also, ^{15}N NMR spectra of acid-washed APC samples enabled the identification of pyridinic type nitrogens in coal, bringing the experimental results of ^{15}N NMR in agreement with XPS data. A preliminary nitrogen-specific chromatography analysis of coal tars completed. A new technique for solid-state ^{13}C NMR analyses of coal tars was developed. These advances in analytical techniques will permit further insight into the nitrogen forms in coal and the nitrogen evolution process.

REFERENCES

1. Watt, M., T. H. Fletcher, S. Bai, M. S. Solum, and R. J. Pugmire, "Chemical Structure of Coal Tar During Devolatilization," in press, Twenty-Sixth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA (1996).

2. Solum, M. S., Anderson-Altman, K. A., Strohmeyer, M., Berges, D., Zhang, Y., Facelli, J. C. Pugmire, R. J., Grant, D. M., "^{15}N Chemical Shift Principal Values in Nitrogen Heterocycles," submitted for publication, Journal of the American Chemical Society (1996).

3. Solum, M. S., Pugmire, R. J., Grant, D. M., Kelemen, S. R., Gorbaty, M. L., Wind, R. A., "^{15}N CPMAS NMR of the Argonne Premium Coals," submitted for publication, Energy and Fuels (1996).

4. Nelson, P. F. and Tyler, R. J., "Formation of light gases and aromatic species during the rapid pyrolysis of coal," *25th Symposium (Int.) on Combustion*; The Combustion Institute, pp. 427 (1986).

PUBLICATIONS/PRESENTATIONS RELATED TO THIS CONTRACT

1. Watt, M., T. H. Fletcher, S. Bai, M. S. Solum, and R. J. Pugmire, "Chemical Structure of Coal Tar During Devolatilization," in press, Twenty-Sixth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA (1996).

Table 1
Derived Properties of Coal, Tar, and Char from the ^{13}C NMR analysis[b] (160 ms at 900 K)

Coal	Sample	X_b	C_{cl}	$\sigma+1$	P_o	B.L.	S.C.	MW_{cl}	MW_{att}	tar res.
Pitt #8	coal	0.29	14	4.8	0.48	2.3	2.5	323	32	
Pitt #8	char	0.366	18	5.4	0.76	4.1	1.3	315	18	
Pitt #8	tar dis.	0.134	8	2.4	0.45	1.0	1.4			
Pitt #8	tar res.	0.25	12	3.9	0.73	2.8	1.1			0.25
Pitt #8	tar	0.163	9	2.8	0.52	1.5	1.3	178	25	
Illinois #6	coal	0.30	15	5.5	0.52	2.9	2.6	368	35	
Illinois #6	char	0.314	15	5.3	0.64	3.4	1.9	326	29	
Illinois #6	tar dis.	0.144	9	2.5	0.47	1.2	1.3			
Illinois #6	tar res.	0.27	13	4.6	0.69	3.2	1.4			0.42
Illinois #6	tar	0.197	11	3.4	0.56	2.0	1.3	228	30	
Blue #1	coal	0.27	13	5.0	0.48	2.4	2.6	371	42	
Blue #1	char	0.344	17	5.8	0.64	3.7	2.1	402	34	
Blue #1	tar dis.	0.09	7	3.0	0.58	1.7	1.3			
Blue #1	tar res.	0.273	13	4.7	0.54	2.5	2.2			0.12
Blue #1	tar	0.112	8	3.2	0.58	1.8	1.4	205	35	

Table 2
Derived Properties of Coal, Tar, and Char from the ^{13}C NMR analysis[b] (210 ms, 1050 K)

Coal	Sample	X_b	C_{cl}	$\sigma+1$	P_o	B.L.	S.C.	MW_{cl}	MW_{att}
Beulah Zap	tar	0.250	12	3.6	0.76	2.7	0.9	223	22
Pitt #8	coal	0.290	14	4.8	0.48	2.3	2.5	320	32
Pitt #8	tar	0.330	16	4.4	0.79	3.5	0.9	256	14
Illinois #6	coal	0.300	15	5.5	0.52	2.9	2.6	373	35
Illinois #6	tar	0.253	12	3.8	0.82	3.1	0.7	203	15
Pocahontas #3	char	0.398	20	4.5	0.90	4.1	0.4	286	10
Pocahontas #3	tar	0.322	16	3.9	0.76	3.0	0.9	245	14

[a]Percentage carbon (error): f_a = total sp^2-hybridized carbon (±3); f_a' = aromatic carbon (±4); f_a^C = carbonyl, d > 165 ppm (±2); f_a^H = aromatic with proton attachment (±3); f_a^N = nonprotonated aromatic (±3); f_a^P = phenolic or phenolic ether, d = 150-165 ppm (±2); f_a^S = alkylated aromatic d = 135-150 ppm(±3); f_a^B = aromatic bridgehead (±4); f_{al} = aliphatic carbon (±2); f_{al}^H = CH or CH_2 (±2); f_{al}^* = CH_3 or nonprotonated (±2); f_{al}^O = bonded to oxygen, d = 50-90 ppm (±2), tar dis. = tar that dissolved in CD_2Cl_2

[b]X_b = fraction of bridgehead carbons, C_{cl} = aromatic carbons per cluster, s+1 = total attachments per cluster, P_o = fraction of attachments that are bridges, B.L. = bridges and loops per cluster, S.C. = side chains per cluster, MW_{cl} = the average molecular weight of an aromatic cluster, MW_{att} = the average molecular weight of the cluster attachments, Tar = tar collected on filters and corrected for the tar deposited on sampling apparatus, tar dis. = tar that dissolved in CD_2Cl_2

Table 3
Additional Coals Examined in the Flat Flame Burner

Coal	Rank	Sample Number
Bottom	lignite	DECS 1
Adaville #1	subbituminous A	DECS 7
Beulah	lignite	DECS 11
Sewell	mv bituminous	DECS 13
Kentucky #8	hvB bituminous	DECS 18
Elkhorn #3	hvA bituminous	DECS 20
Lykens Valley #2	anthracite	DECS 21
Deadman	subbituminous A	DECS 27
Penn. Anthracite C	semianthracite	PSOC 1515
Lower Kittanning	lv bituminous	PSOC 1516
Smith Roland	subbituminous C	PSOC 1520
Lower Hartshorne	lv bituminous	PSOC 1521

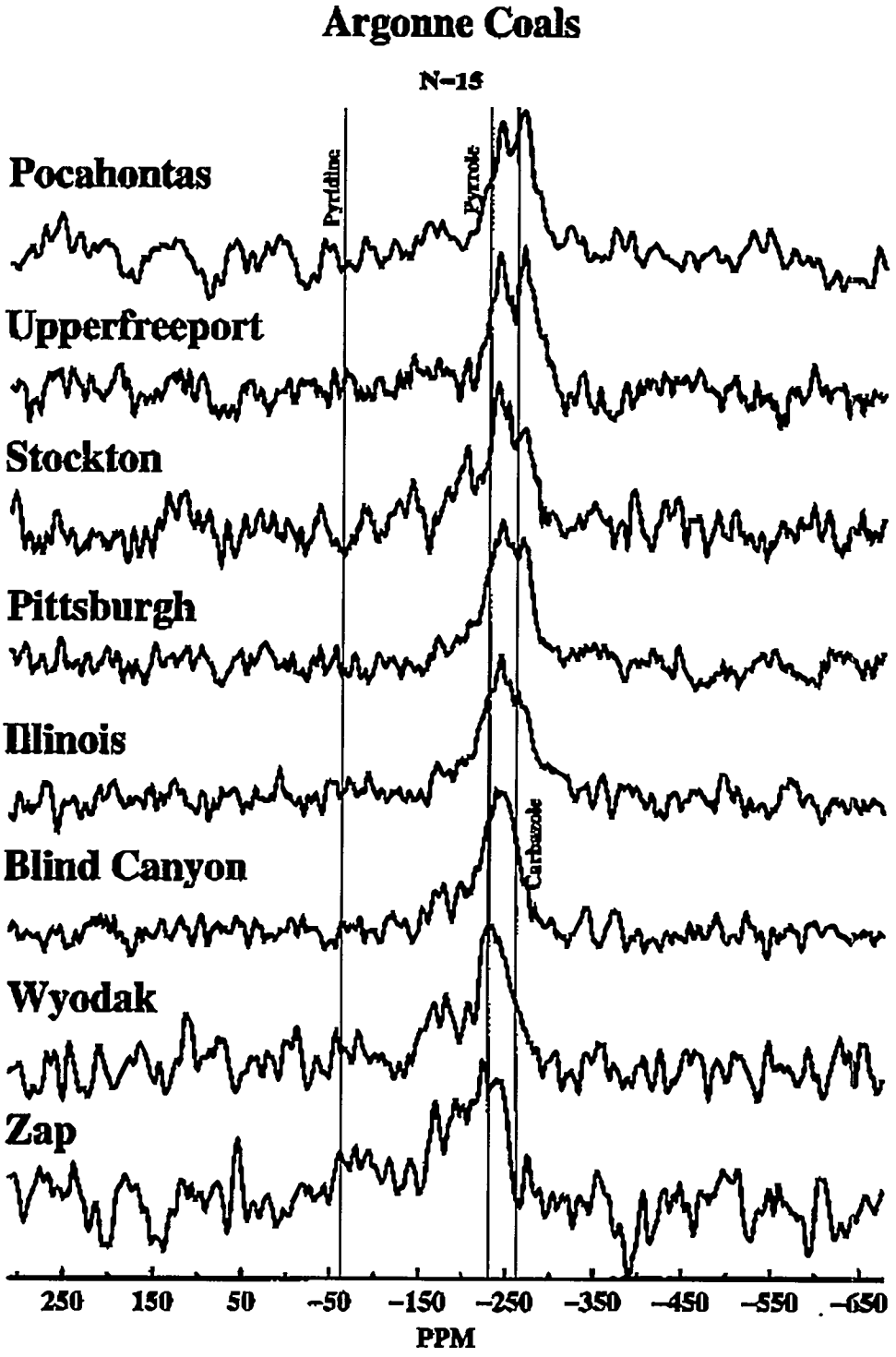

Figure 1. Natural abundance ^{15}N CPMAS spectra of the Argonne Premium Coals. The vertical reference lines are placed to guide the eye to the chemical shift frequencies of pyridine, pyrrole, and carbazole as fiducial marks.

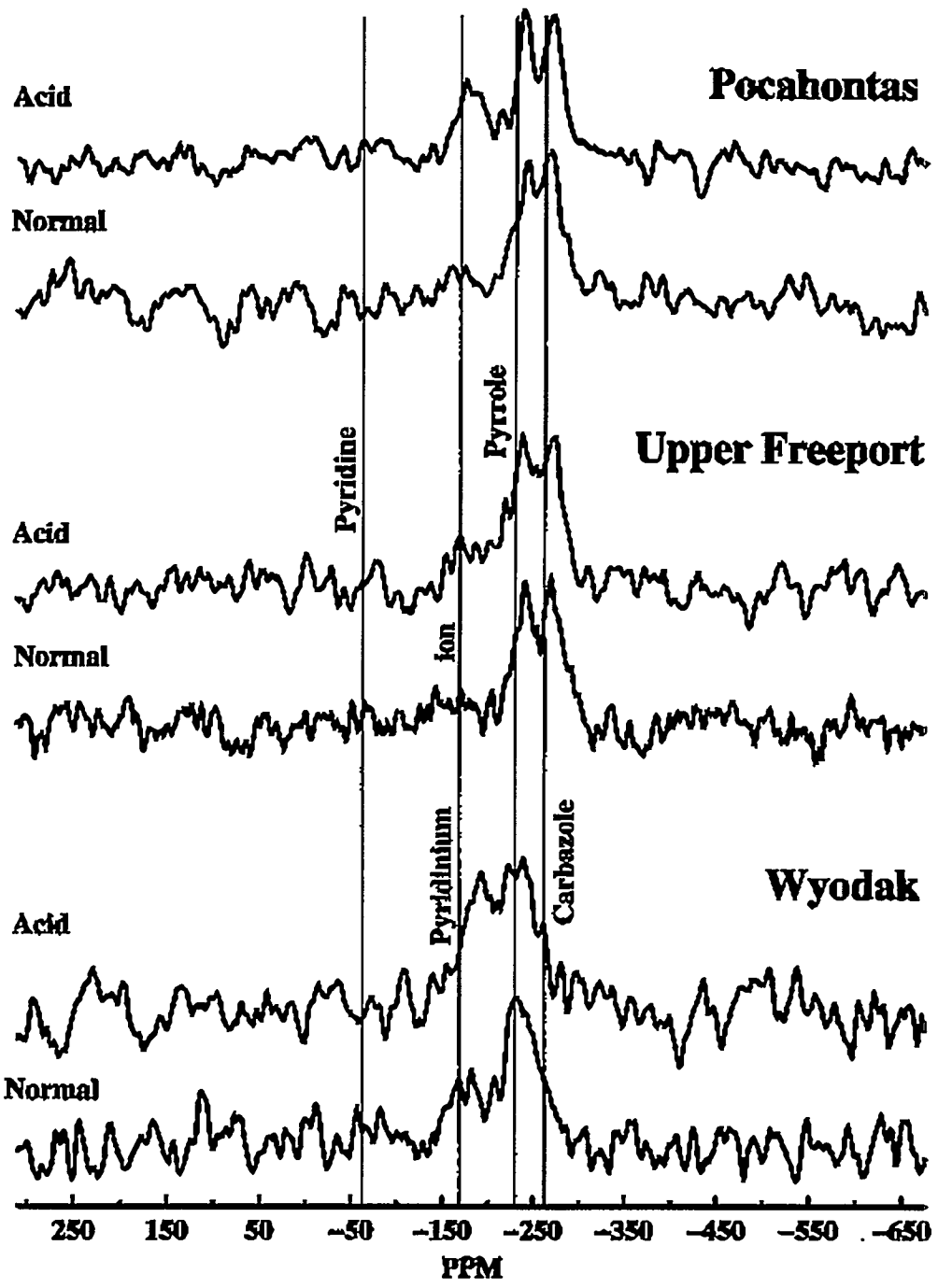

Figure 2. Stacked ^{15}N CPMAS spectra of the pristine and acid (p-toluenesulfonic acid) treated pairs of three of the Argonne Premium Coals.