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

_____ Semi-Annual Report

Principal Investigator: Thomas H. Fletcher

Grant No. DE-FG22-95PC95215

Chemical Engineering Department
Brigham Young University
Provo, UT 84602

October 31, 1997

Date of Grant: August 1, 1995
Anticipated Completion Date: July 31, 1997

Government Award: $50,000 for second year

Program Manager: Philip Goldberg

Contracting Officer Representative (COR): Philip Goldberg

Reporting Period: May 1, 1997 to October 31, 1997

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 are 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 are being performed in collaboration with other researchers at BYU, the University of Utah, and industrial organizations. Coals have been 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 are (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.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

EXECUTIVE SUMMARY

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. Techniques were developed to improve the resolution of pyridinic type nitrogens with ^{15}N NMR. This advance will permit further insight into the nitrogen forms in coal and the nitrogen evolution process.

A detailed set of mild pyrolysis experiments was completed. These experiments provided char and tar samples for analysis by various techniques. These experiments involved five coals and three pyrolysis conditions. Solid-state ^{13}C NMR analyses of the coal tar samples from the 1088 K condition have now been performed for the first time without dissolving the tar samples. These data indicate that the average number of aromatic carbons per cluster (C_{cl}) in the coal tar is similar to that found in the parent coal. Previous ^{13}C NMR analyses of tar samples dissolved in deuterated methylene chloride (CD_2Cl_2) had indicated that the value of C_{cl} in the tar was much lower than in the coal. This is an example of unexpected errors arising from the use of solvents when analyzing coal tars. The solid-state ^{13}C NMR analyses of tar have also shown other interesting trends. The NMR analyses of additional tar and char samples will provide an improved understanding of nitrogen chemistry of coal pyrolysis.

More work has been performed to determine the spectral response obtained from the standard cross polarization magic angle spinning experiments carried out on various model compounds and coal samples. Experiments were performed to determine the effects of varying the cross polarization time on a model compound that contained both pyridinic- and pyrrolic-type nitrogens. These experiments indicate that if care is not taken in selecting the experimental conditions employed in acquiring ^{15}N NMR data, the relative contributions from pyrrolic and pyridinic species will always be in error. Additionally, the ^{15}N CP/MAS spectra of Pocahontas and Pittsburgh coals and their matched char-tar pairs have been obtained.

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, 1997 to October 31, 1997 include:

- Completion of HPCP reactor modifications
- Completion of a set of experiments in the HPCP that included 5 coals at three pyrolysis conditions. These experiments provided tar, char and gaseous samples for analysis.
- Completion of ^{13}C NMR analyses of 5 tars at one pyrolysis condition.
- Completion of ^{15}N NMR analyses of 2 coal/char/tar sets.

HPCP Reactor Modifications

The High Pressure Controlled Profile (HPCP) reactor modifications mentioned in the previous semi-annual report (i.e., heater modifications) were completed, and the reactor is now performing extremely well. No unexpected heater-related shutdowns were experienced after these modifications were completed, which has permitted a large number of experiments to be performed, resulting in a relatively large number of char, tar, and gas samples.

HPCP Pyrolysis Experiments

A detailed set of mild (900 to 1220 K) pyrolysis experiments has been completed in the HPCP. These experiments focused on the five U.S. coals listed in Table 1. These coals have been crushed and aerodynamically classified to the 65 to 73 μm size range.

Pyrolysis experiments were performed on these five coals under the conditions listed in Table 2. These experiments were designed to provide insight into the chemical structure of tar and char during pyrolysis. These experiments provided tar, char and gaseous samples for analysis by various techniques. The resulting tars and chars are currently being analyzed with standard solid state ^{13}C and ^{15}N NMR techniques. The elemental compositions of these samples are currently being determined. ICP analysis is being used to help confirm the mass release. During these experiments, the gas phase concentration of hydrogen cyanide (HCN) was determined with an on-line HCN toxic gas monitor.

Several of the NMR analyses from these experiments have been completed. ^{15}N NMR analyses have been completed for two coal/tar/char sets. These spectra are shown in Figures 3 and 4 and will be discussed below. The solid-state ^{13}C NMR analyses of the tars from the 1088 K condition have been completed; these are the first known data on solid tar samples that have been scraped from filters rather than washed with a solvent. These results are presented in Tables 3 and 4. For comparison, the ^{13}C NMR structural and lattice parameters of the parent coals are also provided in Tables 3 and 4. As can be seen in Table 4, the number of aromatic carbons per cluster (C_{cl}) in the tars is quite similar to that of the parent coals. Previous ^{13}C NMR analyses of tar samples dissolved in deuterated methylene chloride (CD_2Cl_2) had indicated that the value of C_{cl} in the tar was much lower than in the coal, even when combined with data from the tar residue.[1] This is an example of unexpected errors arising from the use of solvents when analyzing coal tars. It is believed that the current solid-state data on undissolved tars provide a more accurate picture of the structure of tars than was previously available. As can be seen in Table 4, the average molecular weight of cluster attachments (MW_{att}) parameter is much lower in the tars than in the coals. It is also interesting to note that the MW_{att} does not appear to be a function of coal type for these coals, whereas large changes in MW_{att} were observed in the parent coals. For all coals, the attachments per cluster (σ+1) in the tars is less than in the coals. The same trend is seen for the side chains per cluster (S.C.). These are recent data, and interpretation will continue in the next few months.

In the next reporting period, the tars and chars from all fifteen experiments will be analyzed with both ^{13}C and ^{15}N NMR. When completed, these analyses will represent the first detailed ^{13}C NMR and ^{15}N NMR analyses of matched tar and char sampled from five coals and three degrees of pyrolysis. These analyses will provide a greatly enhanced knowledge of the chemical structure of char and tar during primary pyrolysis. Additionally, a great deal of information will be gained about the chemical environment of the fuel nitrogen during pyrolysis. As can be seen in Table 1, the Illinois #6 and Blue #1 coals are identical in rank and similar in nitrogen content. Previous experiments have indicated that these coals release markedly different amounts of nitrogen during pyrolysis. It is anticipated that, chemical structural information gained from the ^{13}C NMR analyses of char and tar samples from these coals will help determine why coals of similar rank and elemental composition release different amounts of nitrogen during devolatilization.

^{15}N NMR Analysis

During this reporting period, major progress has been made in developing the analytical techniques necessary to identify the forms of nitrogen in coal and coal pyrolysis products. More work has been done to determine the spectral response obtained from the standard cross polarization magic angle spinning experiments carried out on various model compounds and coal samples. Previous studies on model nitrogen heterocycles demonstrated the wide variation in the cross polarization parameters observed in different types of compounds.[2] The large values for the nitrogen cross polarization time constant in pyridine-type compounds, compared to those observed in pyrrolic compounds, where a proton is directly attached to the nitrogen, assures that the spectral response will not be linear for the two types of nitrogen species. Furthermore, the large chemical shift anisotropy of the nitrogen atoms in heterocycles presents another challenge to correct

interpretation of the ^{15}N NMR spectra. The spinning side bands that accompany any magic angle spinning experiment are particularly troublesome in the case of nitrogen heterocycles. The intensity of the signal is spread between the various side bands and at relatively low spinning speeds the majority of the signal intensity is moved from the center band into the side bands. By increasing the spinning speed, more of the signal intensity can be transferred from the side bands into the center band. However, at the high magnetic fields utilized to optimize the overall spectral sensitivity, spinning speeds in excess of 4 KHz create additional problems with the cross polarization process. A careful discussion of these competing effects has been given by Solum, et. al.[3] in the analysis of the ^{15}N NMR spectra of the Argonne Premium Coals. Hence, under normal conditions, only the pyrrolic nitrogens will be observed because they contain directly bonded protons and also exhibit a much smaller chemical shift anisotropy.

Previous experiments concentrated on obtaining ^{15}N data on a 400 MHz spectrometer in order to take advantage of the inherent sensitivity associated with a high magnetic field. However, the problems associated with loss of signal intensity from the center band into the side bands at this field strength prompted a move to an alternative field strength, e. g., 200 MHz. Two examples of the effects of different field strength can be observed in Figure 1 which contains the ^{15}N CP/MAS spectra of pitch samples prepared from quinoline (Q-Pitch) and isoquinoline (IQ-Pitch). The spectra were obtained under comparable conditions for each pitch at the two different field strengths. A Toss pulse sequence was employed in an effort to move the spinning side bands (which are not visible in the 400 MHz spectra) back into the center band. Two major peaks are observed for each sample, one at approximately -80 ppm (representing a pyridinic-type nitrogen) and another approximately -250 ppm (representing a pyrrolic-type nitrogen). By visually comparing the spectra at the two field strengths it is immediately apparent that the data taken at 400 MHz under estimates the amount of pyridinic nitrogen present for both pitches.

Model compound experiments[2] prompted investigation of the effects of varying the cross polarization time on a model compound that contained both pyridinic- and pyrrolic-type nitrogens. For this experiment, 7-azaindole was selected. Two spectra are given in Figure 2. Again, the TOSS pulse sequence was utilized to minimize loss of signal from the center band into the spinning side bands. Cross polarization times (CT) of 1 and 5 ms were employed. The proton $T_{1\rho}$ for this compound is long and, hence, a variable contact time experiment up to 5 ms is possible. The relative intensities of the pyridinic nitrogen signal (compared to the pyrrolic nitrogen signal) is 0.2 at a contact time of 1 ms and 0.94 at a contact time of 5 ms. These data provide a useful starting point for evaluating the relative amounts of pyridinic nitrogen observed in earlier data. Since the proton $T_{1\rho}$ values in coals are usually short, a contact time in the range of 1-2 ms is normally used in cross polarization experiments. The azaindole data suggest that, under the conditions normally used in obtaining CP/MAS data in coals, as little as 20% of the pyridinic nitrogen may be observable just from the cross polarization dynamics. Another factor of 2-3 in loss of signal intensity may be lost into the spinning side bands due to the large chemical shift anisotropy of the pyridinic compounds. These findings indicate that if care is not taken in selecting the experimental conditions employed in acquiring ^{15}N NMR data, the relative contributions from pyrrolic and pyridinic species will always be in error.

In spite of the experimental difficulties described above, there is merit in examining the ^{15}N NMR spectra of coals due to the subtle differences that have previously been mentioned.[3] Recently, tar/char pairs from different coals have been examined in an effort to gain insight into the transformations that occur during pyrolysis.[4] The ^{15}N CP/MAS spectra of Pocahontas and Pittsburgh coals and their matched char-tar pairs are given in Figures 3 and 4. As can be seen in the figures, the signal to noise observed in the tar and char samples is not very high but it is sufficient to demonstrate that differences exist in the types of nitrogen species present in the coal/tar/char samples of Pittsburgh and Pocahontas coals. Future work in the area will focus on companion ^{13}C NMR studies on the tar and char samples as well as additional ^{15}N NMR experiments on coal pyrolysis products.

FUTURE PLANS

Future plans include performing mild pyrolysis experiments on two coals from the FFB study mentioned in the previous report. These coals are very similar in rank and differ greatly in total volatiles and nitrogen release. Additionally, ^{13}C and ^{15}N NMR analyses will be performed on all tars and chars resulting from the HPCP pyrolysis experiments. These analyses will provide a greatly enhanced knowledge of the chemical structure of char and tar during primary pyrolysis. Additionally, a great deal of information will be gained about the chemical environment of the fuel nitrogen during pyrolysis. Initial modeling ideas have been initiated and will continue during the next reporting period. The majority of the Dynamic Nuclear Polarization (DNP) equipment has been assembled, and the final amplifier is scheduled to arrive this month. The DNP experiments will commence as soon as possible on the tar and char samples already collected.

SUMMARY AND CONCLUSIONS

Modifications to the HPCP drop tube reactor were completed, facilitating much-improved operation. Three sets of samples on five coals at three reactor conditions were collected. For the first time, solid-state ^{13}C NMR analyses was performed on undissolved coal tar samples, showing marked differences with previous data from dissolved tar samples. In particular, the number of aromatic carbons per cluster in the solid-state analyses was similar to that found in the coal. This is an example of unexpected errors arising from the use of solvents when analyzing coal tars. The solid-state ^{13}C NMR analyses of tar have also shown other interesting trends. 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. Techniques were developed to improve the resolution of pyridinic type nitrogens with ^{15}N NMR. Preliminary ^{15}N data for two coals and their corresponding tars and chars were presented, indicating that nitrogen functionalities seem change with coal type. This advance 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," *Twenty-Sixth Symposium (International) on Combustion,* The Combustion Institute, Pittsburgh, PA, 3153-3160 (1996).
2. Solum, M. S., K. A. Anderson-Altman, M. Strohmeyer, D. Burges, Y. Zhang, J. C. Facelli, R. J. Pugmire, D. M. Grant, ^{15}N Chemical Shift Principal Values in Nitrogen Heterocylces, J. Am. Chem. Soc., 1997 (in press).
3. Solum, M. S., R. J. Pugmire, D. M. Grant, S. R. Kelemen, M. L. Gorbaty, and R. A. Wind, ^{15}N CPMAS NMR of the Argonne Premium Coals, Energy Fuels, **1997**, 11, 491.
4. ^{15}N NMR Spectroscopy of Coals and Pyrolysis Products, R. J. Pugmire, M. S. Solum, D. M. Grant, T. H. Fletcher, and R. A. Wind, International Conference on Coal Science, Essen, Germany, 7-11 Sept. **1997**, pp. 417-420.

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," *Twenty-Sixth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, PA, 3153-3160 (1996).
2. Genetti, D. and T. H. Fletcher, "Predicting ^{13}C NMR Measurements of Chemical Structure of Coal Based on Elemental Composition and Volatile Matter Content," ACS Division of Fuel Chemistry Preprints, **42**:1, 194-198 (April, 1997).
3. Baxter, L. L., R. E. Mitchell, T. H. Fletcher, and R. E. Mitchell, "Nitrogen Release during Coal Combustion," *Energy and Fuels*, **10**, 188-196 (1996).
4. Baxter, L. L., R. E. Mitchell, and T. H. Fletcher, "Release of Inorganic Material During Coal Devolatilization," *Combustion & Flame*, **4**, 494-502 (1997).
5. Hambly, E., D. Genetti, S. Perry, and T. H. Fletcher, "Nitrogen Release During Coal Devolatilization," poster presented at the 11th Annual ACERC Conference, Provo, Utah (March 12-13, 1997).
6. Fletcher, T. H. and D. Genetti, "Predicting ^{13}C NMR Measurements of the Chemical Structure of Coal Based on Proximate and Ultimate Analysis," oral and poster presentation at the 11th Annual ACERC Conference, Provo, Utah (March 12-13, 1997).

Table 1
Experimental Coals and Properties

Coal	PSOC #	Rank	%C(daf)	%H(daf)	%N(daf)	%Ash(mf)
Beulah Zap	1507 D	ligA	69.99	5.59	1.17	15.31
Illinois #6	1493 D	hvCb	76.65	4.93	1.47	15.13
Blue #1	1445 D	hvCb	77.29	5.69	1.27	3.62
Pittsburgh #8	1451 D	hvAb	84.70	5.40	1.71	4.11
Pocahontas #3	1508 D	lvb	90.52	4.60	1.60	11.65

Table 2
Conditions of Mild Pyrolysis Experiments

Condition	Max Gas Temperature, K	Residence Time, ms
Condition 1	840	168
Condition 2	1088	282
Condition 3	1215	408

Table 3
^{13}C NMR Analysis of Coals and Tars[a] (282 ms at 1088 K)

Coal	Sample	f_a	f_a^C	$f_{a'}$	f_a^H	f_a^N	f_a^P	f_a^S	f_a^B	f_{al}	f_{al}^H	f_{al}^*	f_{al}^O
Beulah Zap	coal	65	8	57	19	38	7	14	17	35	24	11	11
Beulah Zap	tar	88	7	81	36	45	11	22	12	12	7	5	2
Blue #1	coal	60	5	55	19	36	8	13	15	40	29	11	7
Blue #1	tar	88	4	84	35	49	8	18	23	12	6	6	1
Illinois #6	coal	66	3	63	21	42	7	16	19	34	24	1	8
Illinois #6	tar	88	2	86	36	50	7	19	24	12	6	6	1
Pitt #8	coal	65	3	62	23	39	5	16	18	35	24	11	7
Pitt #8	tar	86	2	84	36	48	5	18	25	14	7	7	2
Poc #3	coal	78	1	77	32	45	2	15	28	22	15	7	7
Poc #3	tar	89	1	88	38	50	3	18	29	11	7	4	2

[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 apparatus, tar dis. = tar that dissolved in CD_2Cl_2

Table 4
Derived Properties of Coal and Tar from the ^{13}C NMR analysis[b] (282 ms at 1088 K)

Coal	Sample	X_b	C_{cl}	$\sigma+1$	P_o	B.L.	S.C.	MW_{cl}	MW_{att}
Beulah Zap	coal	0.246	14	5.2	0.48	2.4	2.8	440	52
Beulah Zap	tar	0.148	9	3.7	0.85	3.2	0.5	170	16
Blue #1	coal	0.270	13	5.0	0.48	2.4	2.6	371	42
Blue #1	tar	0.274	13	4.0	0.77	3.1	0.9	222	15
Illinois #6	coal	0.300	15	5.5	0.52	2.9	2.6	368	35
Illinois #6	tar	0.279	13	3.9	0.77	3.0	0.9	213	13
Pitt #8	coal	0.290	14	4.8	0.48	2.3	2.5	323	32
Pitt #8	tar	0.298	14	3.8	0.70	2.7	1.1	228	14
Poc #3	coal	0.364	18	4.0	0.59	2.3	1.7	316	23
Poc #3	tar	0.330	16	3.8	0.81	3.1	0.7	237	10

[b] X_b = fraction of bridgehead carbons, C_{cl} = aromatic carbons per cluster, $\sigma+1$ = 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

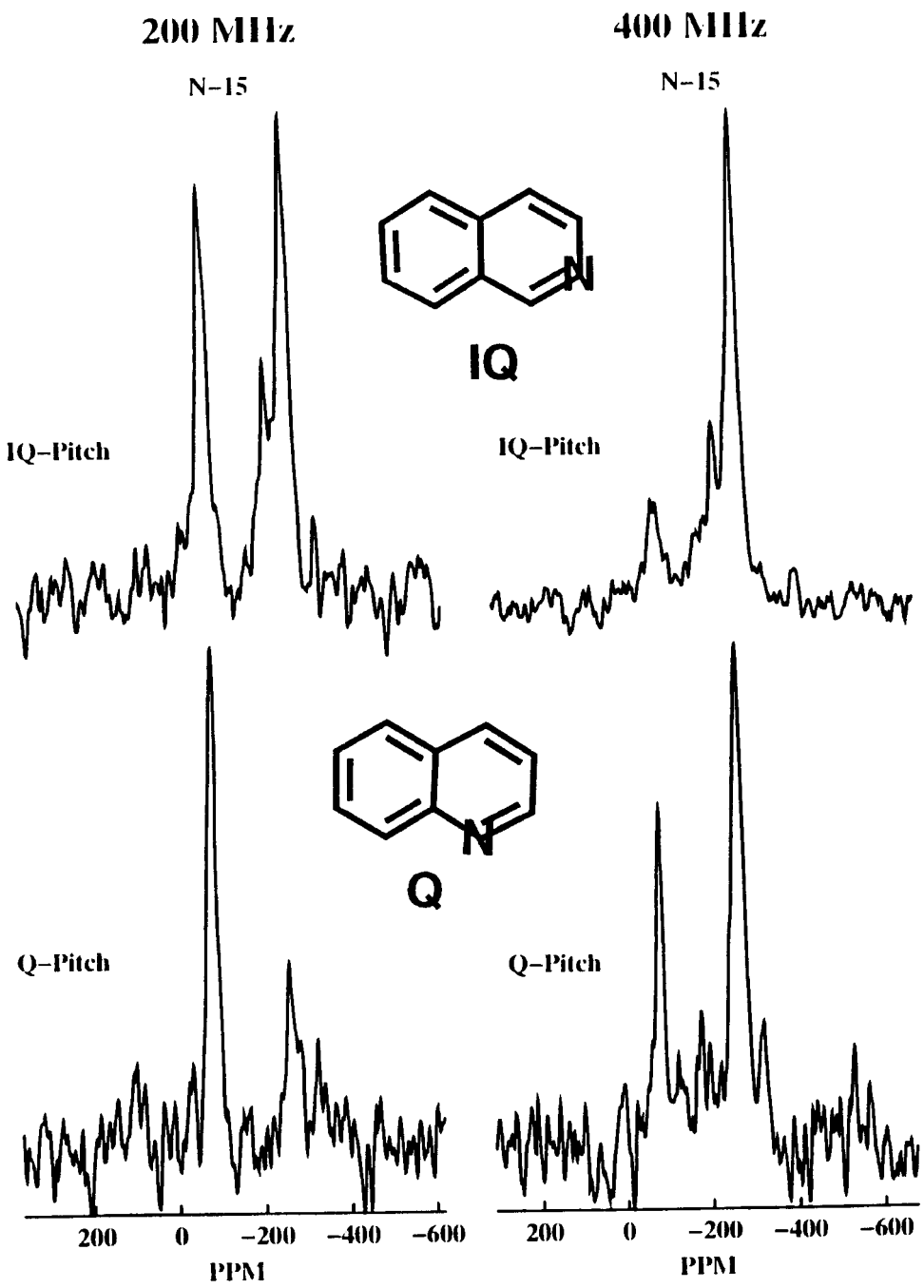

Figure 1. ^{15}N CP/MAS spectra of pitch samples obtained from isoquinoline (IQ) and quinoline (Q). Samples were obtained at magnetic field strengths of 200 and 400 MHz.

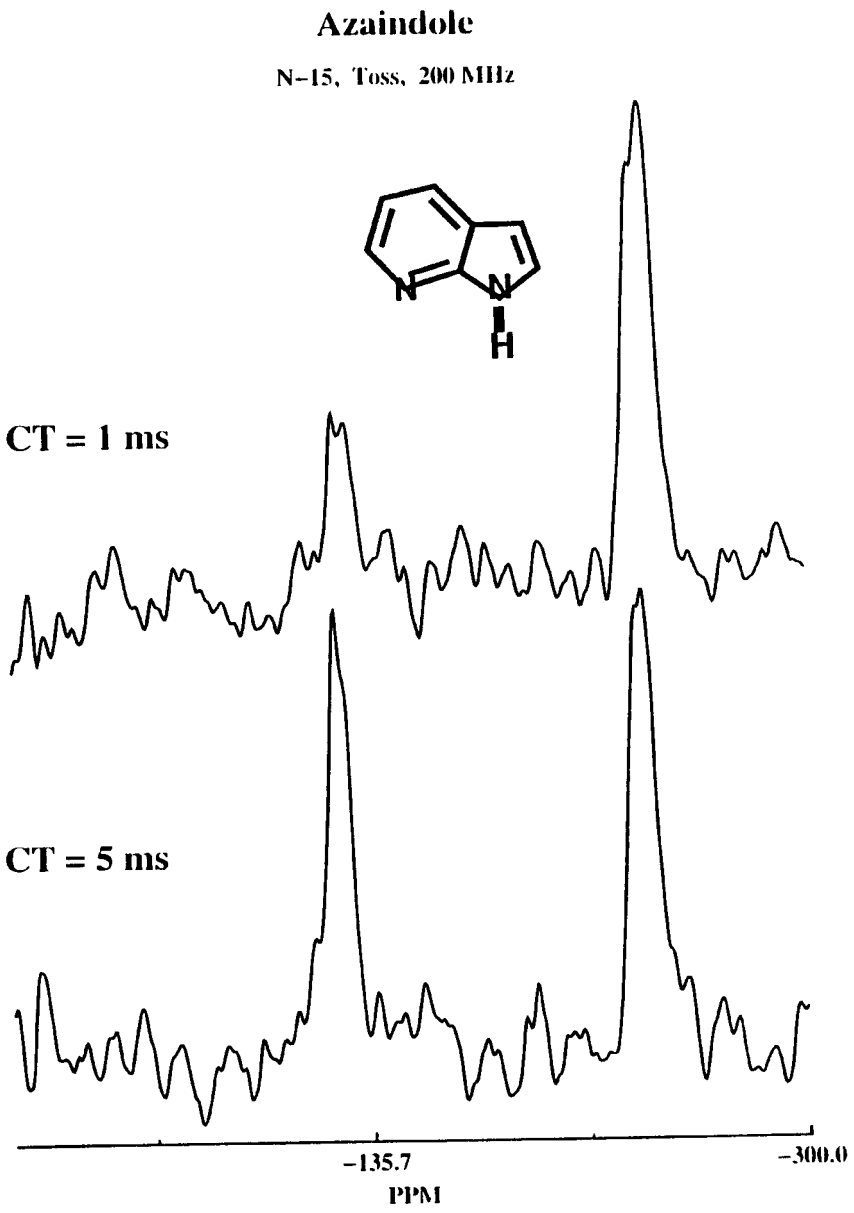

Figure 2. ^{15}N CP/MAS spectra of 7-azaindole obtained with contact times (CT) of 1 and 5 ms. The relative intensities of the pyridinic and pyrrolic nitrogens are 20/100 and 94/100. A TOSS pulse sequence was used for both experiments.

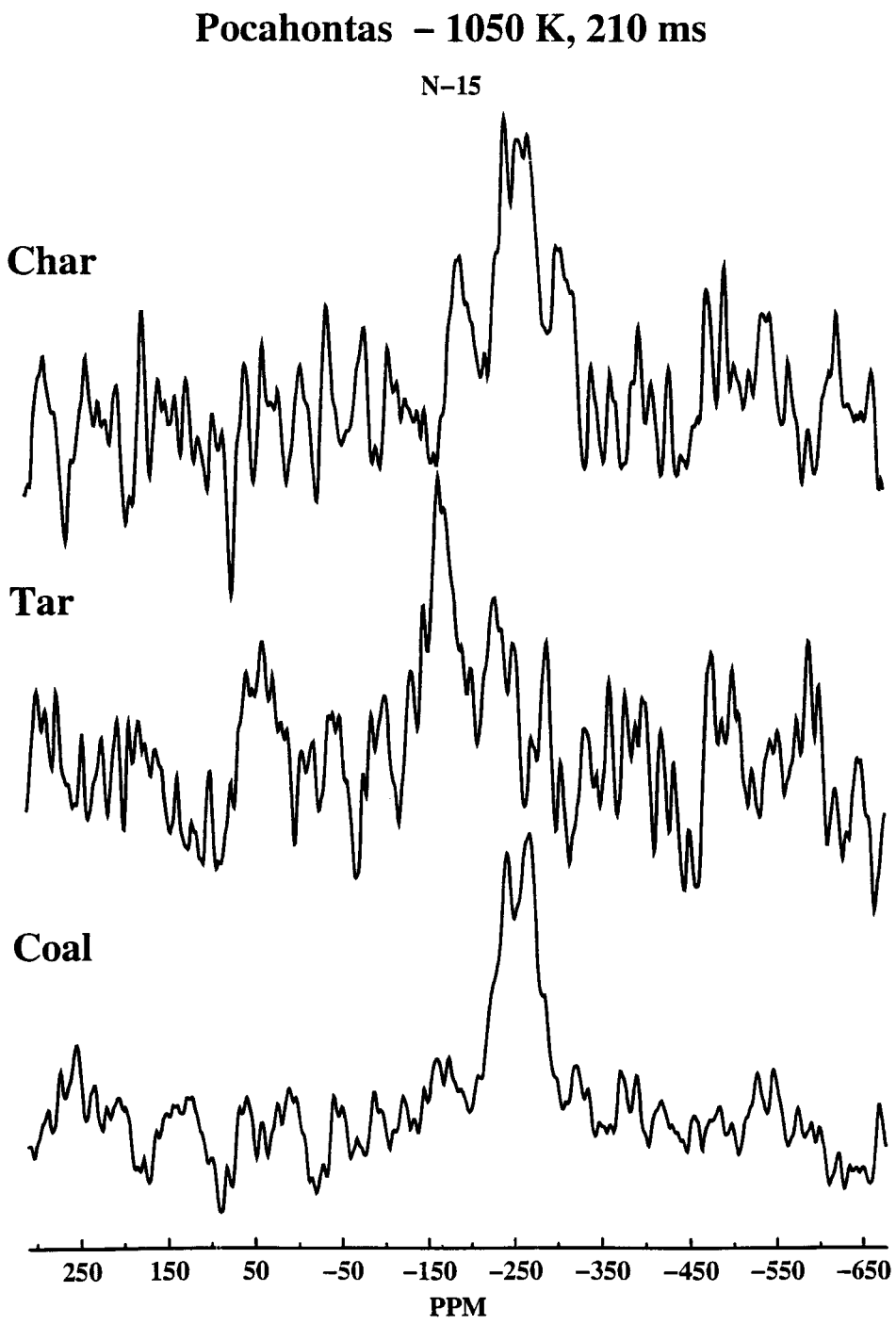

Figure 3. ^{15}N CP/MAS spectra of a Pocahontas coal and its matched char-tar pair.

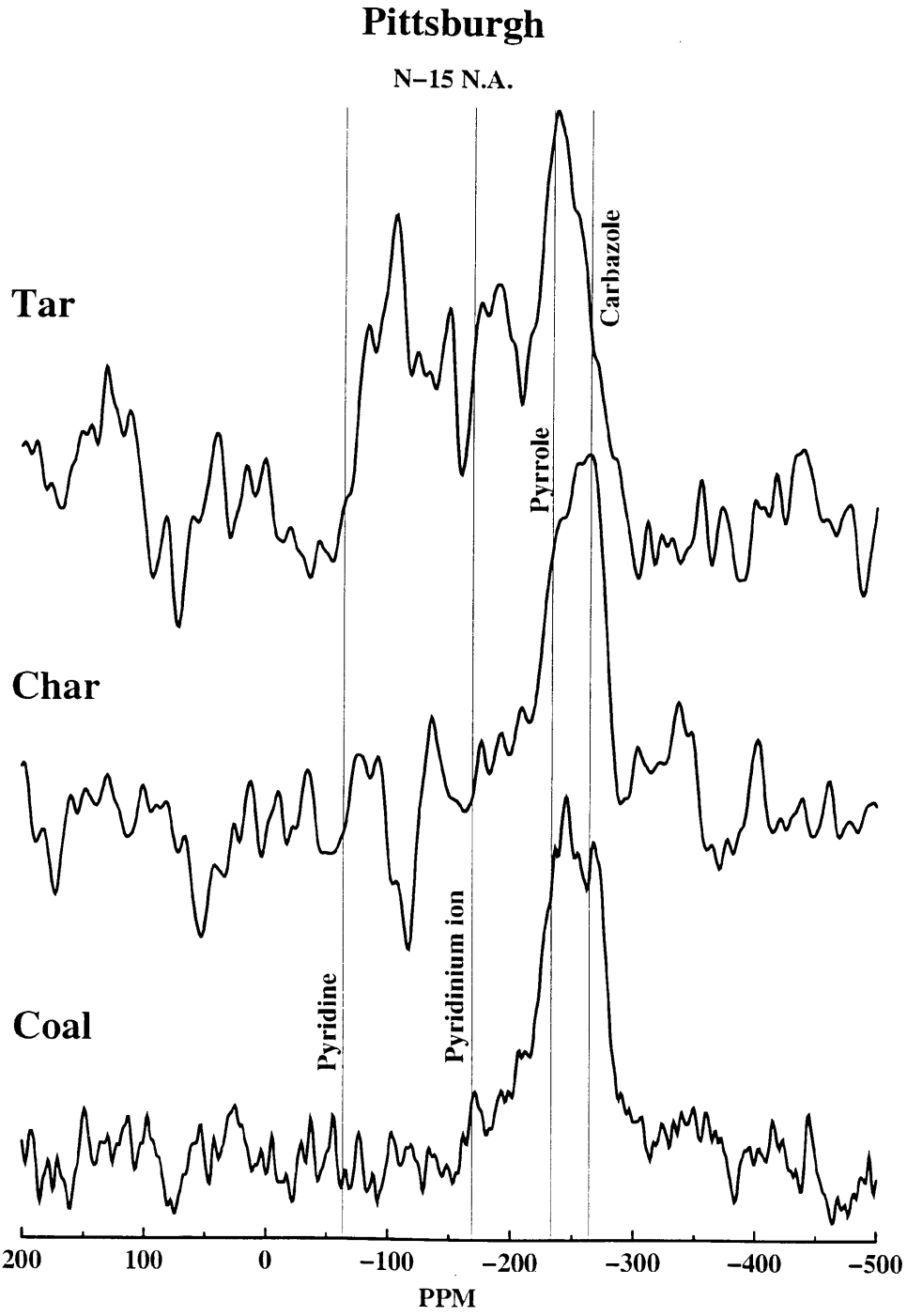

Figure 4. ^{15}N CP/MAS spectra of a Pittsburgh coal and its matched char-tar pair.