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

Draft Semi-Annual Report

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Grant No. DE-FG22-95PC95215

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April 30, 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: October 31, 1996 to May 1, 1997

(U.S. DOE Patent Clearance is not required prior to the publication of this document)

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.

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 high temperature, high heating rate pyrolysis experiments was completed. These experiments provided char which was used to determine degree of nitrogen evolution. These experiments successfully identified several coal pairs which exhibit similar total volatiles yield and markedly different nitrogen evolution. These coal pairs will be used in future temperature pyrolysis experiments to determine how nitrogen release is related to the forms of nitrogen in the coal structure.

Five Pacific Rim coal samples were analyzed with ^{15}N NMR spectroscopy. These analyses idicated that some coals contain a wider range of pyrrolic-type compounds than the others. As mentioned in the previous report, 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. Future quantitative analyses may provide insight into how these different forms lead to varying levels of nitrgoen release during devolatilization.

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 October 31, 1996 to May 1, 1997 include:

- Completion of a set of experiments in the FFB that included 15 coals. These experiments provided char which was used to determine degree of nitrogen evolution under high temperature, high heating rate environments.
- Identification of several coal pairs which exhibit similar total volatiles yield and markedly different nitrogen evolution.
- Commenced modification of entrained flow reactor.
- Analysis of five Pacific Rim coal samples using ^{15}N NMR spectroscopy.
- Developed techniques to improve resolution of pyridinic type nitrogens with ^{15}N NMR.
- 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.

Flat Flame Burner Pyrolysis Experiments

During the previous reporting period, flat flame burner (FFB) experiments were performed on 15 additional coals of broadly differing rank, nitrogen content and total volatiles yield, as shown in Table 1. 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 has been completed. The conversion of the fuel nitrogen to volatiles nitrogen has been determined for these experiments. This was accomplished by determining the total volatiles release and the elemental composition of the parent coal and the resulting char. The results of this analysis can be seen in Figure 1 which is a plot of fractional nitrogen release versus total volatiles release. The 45° line indicates the same amount of nitrogen release as total volatile release. As seen in the figure, these experiments were sucessful in identifying several sets of coals that exhibit similar total volatiles yield and markedly different nitrogen release. For example, the two coals at ~52% total volatiles release exhibited nitrogen release values of 55% and 30%! Figure 2 is a plot of fractional nitrogen release versus coal rank (where % carbon is used as an indicator of rank). These data indicate that these experiments were also successful in identifying coals of broadly differing rank that released similar amounts of nitrogen. For example, some coals in the 70-75% carbon range exhibited 55% nitrogen release, while one coal exhibited ~25% nitrogen release. Other pairs of coals with 75-80% carbon and 87% carbon seem to exhibit widely differing nitrogen release behavior. These coals are therefore candidates for further study.

Two of the data points in Figure 1 seem unreasonable: (I) the high nitrogen release for the 20% volatile release sample; and (ii) the 85% volatile release sample. These data points will be repeated by performing duplicate experiments in the flat flame burner, with subsequent particle analysis.

Under the conditions used in these experiments, the coal is almost totally pyrolyzed. These experiments, therefore indicate the total amount of nitrogen evolution during pyrolysis. It is not clear from these experiments why some coals of similar rank and elemental composition evolve markedly different amounts of nitrogen during devolatilization. However, these experiments do identify which coals should be examined more closely with less severe pyrolysis experiments. Less severe pyrolysis experiments will provide char and tar samples at varying degrees of devolatilization. These tar and char samples will then be analyzed with standard solid state ^{13}C NMR techniques. The resulting chemical strucural features, will provide insight into the nitrogen chemistry during devolatilization.

HPCP Modification

The High Pressure Controlled Profile (HPCP) reactor has been plagued with issues pertaining to the reliability of the Super Kanthal heating elements. The current heating elements have been failing at a rate of approximately one every two weeks (at a cost of ~$400 each). This instability has limited the time available to perform experiments to about two days every two weeks. For this reason, it was decided that the current heating elements should be replaced with more conventional and reliable heating elements. In the reactor section of the HPCP, the twelve Kanthal, horizontally oriented heating elements will be replaced with two semi-cylindrical heating elements. In the preheater section of the HPCP, the one Kanthal element will be replaced with two semi-cylindrical heating elements. The new heating elements are limited to 1200°C operating temperatures, but this temperature limitation is still higher than typical pyrolysis temperatures. Due to the nature of the heating element changes, the temperature control system of this apparatus also requires modification. The current IBM computer based control system will be replaced by microprocessor based temperature/power controller unit. This modification has commenced and should be completed in May, 1997. Once these modifications are completed, a detailed set of moderate pyrolysis experiments will be performed with this reactor.

Future HPCP Pyrolysis Experiments

Mild (900 to 1200 K) pyrolysis experiments will be performed in the HPCP. These experiments will focus on the five U.S. coals listed in Table 2. These coals have been crushed and aerodynamically classified to the 65 to 73 μm size range. These experiments are designed to provide insight into the chemical structure of tar and char during pyrolysis. The purpose of these experiments is to provide tar, char and gaseous samples for analysis by various techniques. Experiments will be performed at three temperature/residence time conditions coresponding to three different degrees of devolatilization. The resulting tar and char will be analyzed with standard solid state ^{13}C and ^{15}N NMR techniques. The elemental composition of the tars and chars will also be determined. ICP analysis will be used to help confirm the mass release. During these experiments, the gas phase concentration of hydrogen cyanide (HCN) will be monitored on-line with an HCN toxic gas monitor.

The primary objective of these experiments is to determine the chemical strucural features of char and tar during pyrolysis. These experiments will represent the first detailed ^{13}C 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 2, the coals Illinois #6 and Blue #1 are identical in rank and nearly identical 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 nitrgon duringn devolatilization.

^{15}N NMR Analysis

A series of Pacific Rim coals (listed in Table 3) were recently analyzed using ^{15}N NMR and the spectra are given in Figure 3. The Yallourn and Hunter Valley are Australian brown and HV bituminous coals, respectively. The Banko is an Indonesian subbituminous coal while the Taiheiyo and Miike are Japanese coals. As can be seen in Figure 3, the Yallourn coal is distinctive from the other samples by virtue of the width of the spectral band. This coal contains a wider range of pyrrolic-type compounds than the other coals. The other samples exhibit similar line shapes and span a similar isotropic chemical shift range suggesting the presence of similar types of pyrrolic nitrogen species.

As mentioned in the previous report, 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. In order to quantify these differences, improvements in ^{15}N NMR techniques are necessary. Much of the effort during this reporting period has focused on improving these techniques.

Initial work on model nitrogen heterocycles demonstrated a wide variation in the cross polarization parameters observed in different types of compounds. It was determined that 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.[1] 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 which 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.[2] in the analysis of the ^{15}N NMR spectra of the Argonne Premium Coals. Hence, under normal conditions, one will only observe the pyrrolic nitrogens because they contain directly bonded protons and also exhibit a much smaller chemical shift anisotropy.

Recently, ^{15}N experiments have been performed in which a side-band suppression pulse sequence (known as a Toss sequence) has been employed. Use of this pulse sequence reduces the amount of signal intensity dispersed into the side-band pattern of a spinning sample. Preliminary results indicate that a portion of the signal associated with the pyridinic nitrogens can be recovered in the center band thus raising the possibility that it may be possible to directly observe (in a non-quantitative way) the presence of pyridinic nitrogens in coal samples. The effectiveness of the Toss sequence in recovering intensity from the spinning side-bands into the center-band will be evaluated.

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. As detailed above, 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. 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. 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.

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Table 1
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

Table 2
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 3
Pacific Rim Coals Used for ^{15}N NMR Studies

Coal	PSOC #	Rank	%C(daf)	%H(daf)	%N(daf)	%Ash(mf)
Yallourn	Australia	brown	65.9	3.97	0.63	1.6
South Banko	Indonesia	sub	72.3	4.61	1.36	2.7
Taiheiyo	Japan	n.a.	78.7	6.22	1.17	12.5
Miike	Japan	n.a.	79.9	6.12	1.20	16.0
Hunter Valley	Australia	hv bit	88.2	5.40	2.10	9.2

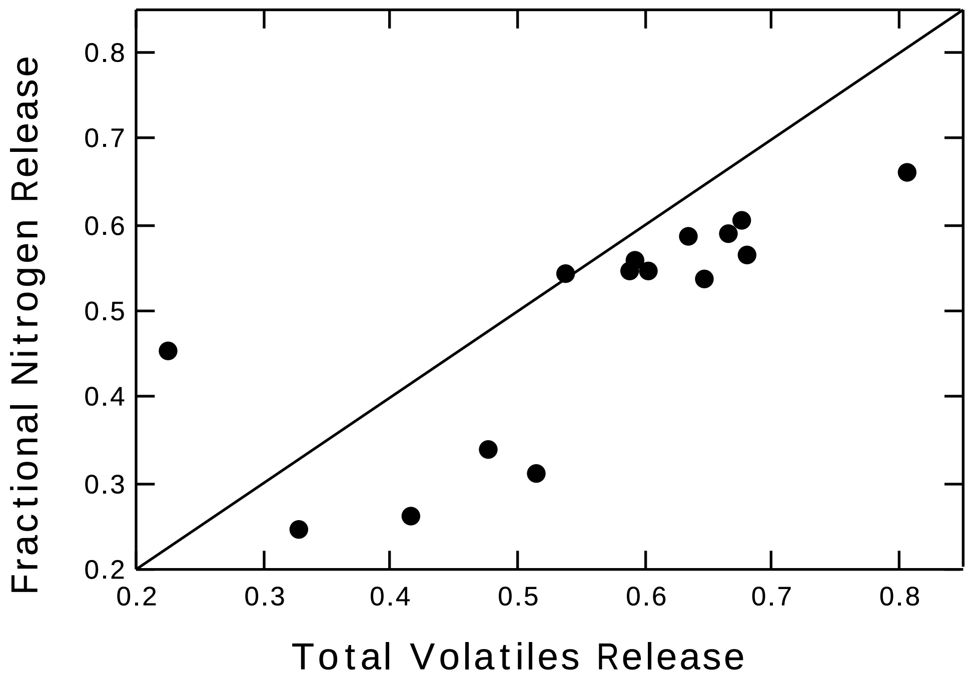

Figure 1. Fractional nitrogen release vs. total volatiles release for the FFB experiments for the coals listed in Table 1.

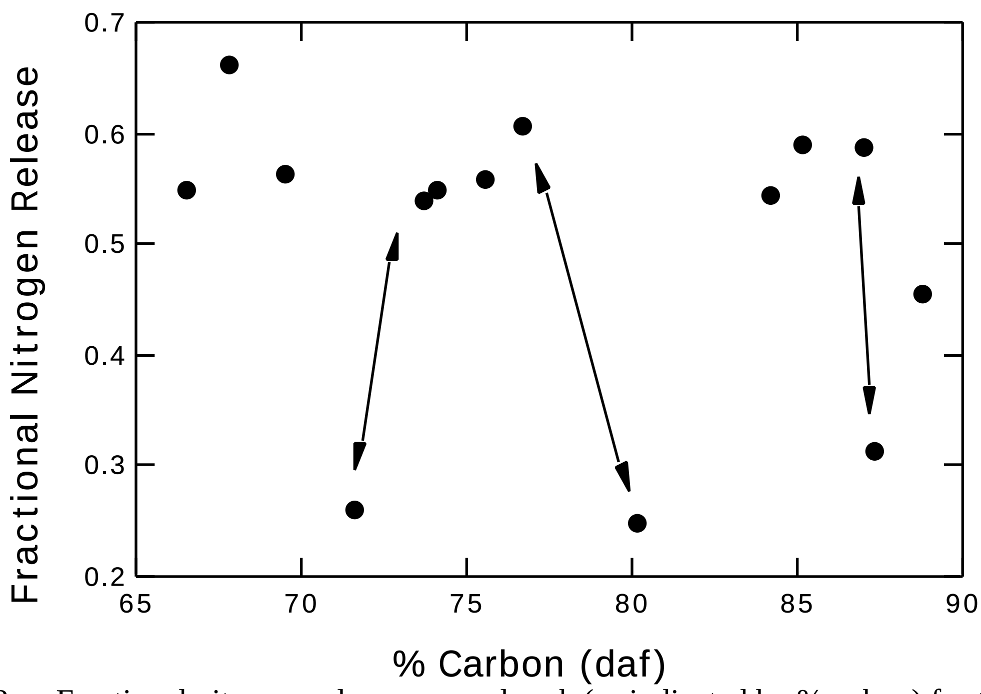

Figure 2 Fractional nitrogen release vs. coal rank (as indicated by %carbon) for the FFB experiments for the coals listed in Table 1. Lines indicate possible pairs of coals of similar rank exhibiting markedly different nitrogen release behavior.

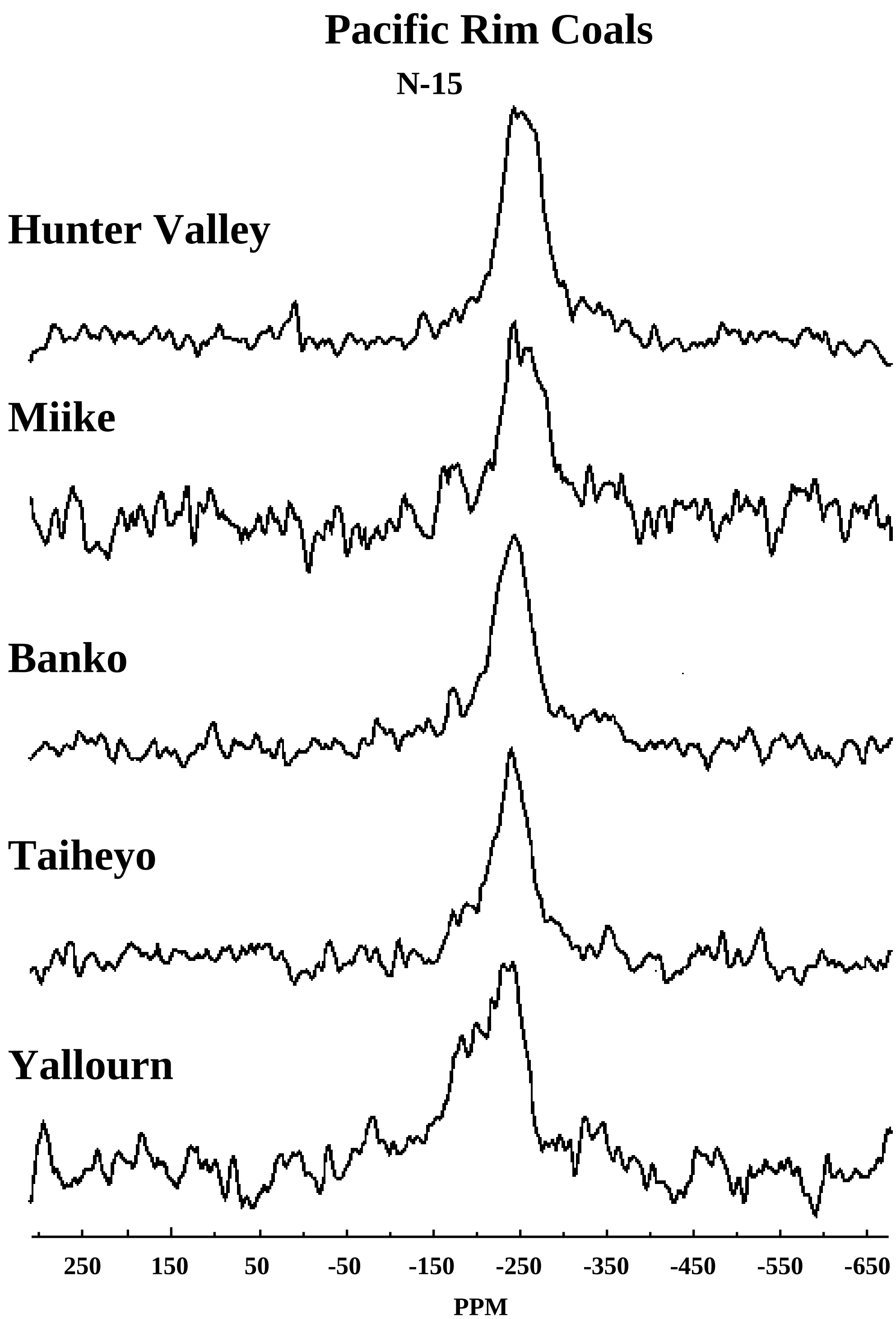

Figure 3. Natural abundance ^{15}N CPMAS spectra of a series of Pacific Rim coals provided by Professor M. Nomura as part of a joint international coal study.