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

Draft Semi-Annual Report

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Grant No. DE-FG22-95PC9521 55

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April 30, 1998

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: November 1, 1997 to April 30, 1998

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.

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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. 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. Dynamic nuclear polarization (DNP) techniques were developed and applied to model compounds and coal samples in an effort to improve the signal to noise ratio observed during ^{15}N NMR analyses of coal. The enhancements gained using the DNP technique were measured for model compounds and an Argonne Premium Pocahontas #3 coal sample. These enhancements are currently on the order of 30 times that seen in standard (CP/MAS) ^{15}N NMR experiments. Current work is focusing on optimizing probe design so that larger enhancements will be observed.

A detailed set of moderate temperature pyrolysis experiments was completed during the previous reporting period. These experiments provided char and tar samples for analysis by various techniques. These experiments involved five coals and three pyrolysis conditions. The results of the solid-state ^{13}C NMR analyses of the coal tar samples from the 1080 K condition were reported previously. The solid-state ^{13}C NMR analyses of the matching char samples have now been performed. These char NMR data, together with the solid-state NMR data reported previously on tar and coal, represent the first matched set of coal/char/tar data obtained using *solid-state* ^{13}C NMR. These data serve to increase the understanding of the chemical structure of pyrolysis products during devolatilization. These NMR data were used to show that several assumptions that are commonly made in coal nitrogen devolatilization models may be reasonable. Specifically, (1) the average number of aromatic carbons per cluster (C_{Cl}) in the tar is similar to that found in the parent coal, and (2) the mass of nitrogen per cluster (MW_N) in the tar is equal to the mass of nitrogen per cluster in the char at any time during the pyrolysis process.

During this reporting period, initial work has begun on the development of a model of nitrogen release as a function of coal type based on chemical forms of nitrogen in coal. Initial model formulation and evaluation has been completed. Additional work will be performed in this area during the next reporting period.

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 ^{13}C NMR analyses of 5 chars at one pyrolysis condition.
- Completion of ^{15}N NMR (DNP) analysis of Pocahontas #3 coal.
- Completion of initial nitrogen devolatilization model formulation and evaluation.

Solid-State ^{13}C NMR Analysis of HPCP Pyrolysis Samples

As described in the previous semi-annual report, a detailed set of moderate temperature (900 to 1220 K) pyrolysis experiments was completed in the HPCP. 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 results of these experiments are summarized in Table 1. Mass, tar and nitrogen release are reported as a fraction of dry, ash-free (daf) coal. The mass release is calculated by comparing the mass of daf coal fed to the mass of daf char collected. As expected, the mass release increases with pyrolysis temperature for all coal. For all coals, the tar release increases with pyrolysis temperature, reaching a maximum at the 1080 K condition and decreasing slightly at the 1220 K condition. This decrease in tar yield is due to secondary reactions in which part of the released tar is broken down into smaller molecules that are able to pass through the reactor collection system as gases. Tar release is also a function of coal rank; at each temperature condition, the tar yield increases with rank, reaching a maximum at the Pittsburgh #8 high volatile A bituminous coal and decreasing for the Pocahontas #3 low volatile bituminous coal. The elemental compositions of the chars and tars from the HPCP pyrolysis experiments have been determined. These results can be found elsewhere.[1] The elemental compositions of the chars and tars from these experiments are similar to those seen by other researchers.[2-5]

The results of the solid-state ^{13}C NMR analyses of the tars from the 1080 K condition were reported in the last semi-annual report. The solid-state ^{13}C NMR analyses of the chars from the 1080 K conditions have now been completed; this data set represents the first matched coal/char/tar chemical structural data obtained using solid-state ^{13}C NMR. The results of the char NMR analyses are reported in Tables 2 and 3, along with the matching coal and tar data.

Comparing the solid-state NMR data for the coal, char and tar provides insight into the nature of the structural changes that occur during pyrolysis. As shown in Table 2, the carbon aromaticity (f_a') of the tar is 14 to 53 percent higher than in the parent coal (on a relative basis). In general, the aromaticity of the tars seems to increase slightly with coal rank. For all coals, the aromaticity of the char is higher than the corresponding tar. With exception of the lignite, the aromaticity of the char appears to remain relatively constant with rank. The values of C_{Cl} in the coal range from 13 to 18, which corresponds to structures with 3 to 5 aromatic rings. These values are in agreement with previous data[2] that showed values of C_{Cl} ranging from 10 to 18 for coals with rank ranging from lignite to low volatile bituminous. The values of C_{Cl} in the tar range from 9 to 16 (see Figure 1). With the exception of the lignite, the value of C_{Cl} in the tar is similar to that of the corresponding parent coal (within 13 % on a relative basis). These new solid-state NMR data on tar help to confirm the assumption that the values of C_{Cl} in the tar are comparable to those in the parent coals, an assumption that is used extensively in the network coal pyrolysis models.[6] The values of C_{Cl} in the char range from 13 to 18. With the exception of the char produced from the subbituminous coal, Blue #1, the value of C_{Cl} in the char is similar to that of the corresponding parent coal. These char data are consistent with those of Watt[5, 7]. However, these char data differ slightly from other previous work[2, 8-10] that indicated that the number of aromatic carbons per cluster in the char does not increase substantially during pyrolysis. The previous data showed values of C_{Cl} generally staying in the range of 12 to 16, whereas the current data show slight increases in range (13 to 18), but these data are within experimental error. For all coals, the values of C_{Cl} in the char are larger than the corresponding tar. This is the first set of data in which matched sets of char and tar have been analyzed with *solid-state* ^{13}C NMR techniques, so comparisons with previous data are not available. The fact that the char contains more aromatic carbons per cluster than the tar is consistent with general theories of coal pyrolysis.

The average cluster molecular weight (MW_{Cl}) in the coal, char and tar are shown in Table 2. This cluster molecular weight contains the weight of the aromatic rings, side chains and half of the bridges of a cluster. For all coals, the average cluster molecular weight in the char and tar are lower than in the parent coal. The values of MW_{Cl} in the coals decrease from 440 to 316 with increasing rank; this trend is not seen in the chars or the tars due to the loss side chain material. Except for the Beulah Zap lignite, MW_{Cl} in the tars is relatively constant with rank. In the chars, MW_{Cl} is relatively constant with rank, except for the Blue #1 char. As seen in the table, for the bituminous coals (Illinois #6, Pittsburgh #8 and Pocahontas #3), the values of MW_{Cl} in the chars are very similar to that of the tars. Several sets of data indicate that tar molecular weight distributions peak in the range of 250 to 400 daltons.[3, 11, 12] The tars in this study have molecular weights per cluster in the range of 170 to 240 daltons. These results seem to indicate the presence of species in the tars that contain more that one cluster per molecule (i.e., dimers and trimers rather than monomers).

Several of the derived ^{13}C NMR structural parameters provide information about the number (σ+1, B.L., S.C.) and size (MW_{δ}) of attachments to clusters. Additional insight into the pyrolysis process is gained by observing the changes in these parameters in the pyrolysis products. As seen in Figure 2, the number of side chains per cluster (S.C.) in the chars and tars are much lower than in the corresponding coals. In the parent coals, the values of S.C. decrease with rank, while this trend is not seen in the resulting chars and tars. This change in trend was first reported by Fletcher et al.[8] For all coals, the number of side chains per cluster observed in the char is smaller than in the corresponding tar. The fact that the number of aromatic carbons per cluster are similar for coal, char and tar, and that the number of side chains per cluster are greatly lower in the char and tar, is consistent with the increased aromaticity in the chars and tars as compared to the parent coals.

The total number of attachments per cluster (σ+1) in the coal, char and tar are shown in Table 3. As seen in the table, σ+1 varies with coal type in the coals and chars. For all coals, σ+1 in the char is similar to the parent coal. The number of attachments per cluster in the tar is less than in the parent coal. Interestingly, while σ+1 varies with coal type in the parent coals, σ+1 in the tars is nearly constant with coal type. The number of bridges and loops per cluster (B.L.) in the char are generally much higher than in the parent coals, as shown in Table 3. Values of B.L. in the tars are only moderately higher than in the corresponding coals, except for the Illinois #6 coal, where the values of B.L. in the tar and coal are similar. The marked increase in B.L. in the chars is consistent with previously reported data.[2, 8, 9] The slight increase in the number of bridges and loops per cluster (B.L.) in the tar may indicate that some form of polymerization may have occurred in the tars. This result would be consistent with the presence of dimers in the tar, and helps rationalize the difference between the measured value of MW_{Cl} and the reported values of the average tar molecular weight.[3, 11, 12]

The average molecular weight of attachments (MW_{δ}) in the tar and char are much lower than that found in the parent coals (see Figure 3). While MW_{δ} decreases steadily with rank in the coals, the values of MW_{δ} in the tars change only slightly with rank, with no distinguishable trend. In the chars, a slight decrease in MW_{δ} may be see with rank, which is similar to the trend reported by Fletcher et al.[8]

The chemical structure of the tars from the 1080 K experiments, as determined from solid-state ^{13}C NMR spectroscopy, do not vary greatly with coal rank. The greatest differences seem to be in the tar from the lignite. However, large differences in tar yield are seen as a function of coal rank, as expected. The similarity in chemical structure of the coal tars is somewhat surprising since large differences are seen in both the elemental composition of these tars and the chemical structural features of the parent coals.

Several attempts have recently been made to model the release of nitrogen during devolatilization with network devolatilization models.[5, 13] The following assumptions are commonly made in these devolatilization models:

1. The number of aromatic carbons per cluster (C_{Cl}) in the tar is equal to the number of aromatic carbons per cluster in the coal.
2. The carbon aromaticity (f_a') of the tar is equal to the carbon aromaticity of the coal.
3. The mass of nitrogen per cluster (M_{Cl}^{N}) in the tar is equal to the mass of nitrogen per cluster in the char at any time during the pyrolysis process.

The results of the NMR analyses reported here allow the validity of these devolatilization model assumptions to be analyzed. The solid-state ^{13}C NMR data presented here, on tars generated during nearly complete devolatilization, indicate that assumption 1 (i.e., that $C_{Cl, tar} \quad C_{Cl,coal}$) may be reasonable for all but the lignite (see Figure 1). The aromaticity data reported above indicates that assumption 2, that the carbon aromaticity of the tar is equal to the carbon aromaticity of the coal, is *not* accurate for nearly complete devolatilization. It has been shown previously[5, 7] that the mass of nitrogen per aromatic cluster (M_{Cl}^{N}) in coal, char or tar may be calculated as follows:

$$M_{Cl}^{N} = MW_{Cl}\, x_N$$

The number of moles of nitrogen per cluster (N_{Cl}) may be obtained by dividing M_{Cl}^{N} by the molecular weight of nitrogen (MW_N). The number of moles of nitrogen per cluster was determined for the coals, chars and tars of this study and the results are presented in

Figure 4. For all coals, the moles of nitrogen per cluster in the char and tar are lower than in the parent coal. Additionally, the values of N_{Cl} in the char are larger than in the tar for the low rank coals (Beulah Zap and Blue #1). For the three higher rank coals (Illinois #6, Pittsburgh #8 and Pocahontas #3) the values of N_{Cl} in the char and tar are very similar (most likely within the combined experimental error of the analysis techniques). These data indicate that for the higher rank coals, assumption 3 above may be reasonable; namely that the mass of nitrogen per cluster in the tar is equal to the mass of nitrogen per cluster in the char at any time during the pyrolysis process. This assumption does not seem to hold true for the two low rank coals.

^{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. Specifically, recent work in this area has focused on fundamental dynamic nuclear polarization (DNP) NMR experiments, which incorporate the principals of electron spin resonance with NMR experiments. The DNP experiments take advantage of the enhanced NMR sensitivity obtained by irradiating the target nucleus (nitrogen-15) at the NMR Larmor frequency while simultaneously irradiating the free electrons present in coals, chars, and tars. The maximum theoretical enhancement that one can obtain for nitrogen in this DNP/NMR experiment is 6,500 while enhancements for protons and carbon-13 are 650 and 2,600, respectively. Even if a sensitivity enhancement of only 5-10% of the theoretical maximum is achieved, the results will be sufficient to permit determination of the various types of nitrogen species that are distributed in the coal, char, and tar samples. It is thought that a fundamental understanding of the early pyrolysis and subsequent char oxidation stages will provide critical data for refining models for predicting nitrogen release into the gas phase at different stages of combustion.

Construction of the new DNP/NMR spectrometer is largely completed. This spectrometer utilizes a small imaging magnet (free-bore diameter of 31 cm) operating at 1.4 tesla. A Chemagnetics CMX-100 console provides the NMR transmitters, receivers, etc. needed for the NMR frequencies and the console computer is also used to control the microwave frequency generator to a 10W traveling wave tube amplifier. Probe design is currently being optimized and the system is being calibrated with model compounds that have been doped with stable free radicals, as discussed below.

Recently, the nitrogen-15 enhancement in carbazole was measured. These data, given in Figure 5, indicate that the N-15 DNP enhancement mechanism for carbazole is due to a solid state effect. A single pulse experiment was employed to measure the direct nitrogen enhancement factor in a N-15 labeled sample of carbazole. Multiple measurements gave enhancement values of 900-1000. Work has now begun on obtaining DNP data on coals. Coal samples present a special challenge due to their “lossey” nature (e.g., they are highly conducting). Hence, it is difficult to focus the microwave power efficiently in the sample. The design of the microwave horn antenna and reflector are critical in order to maximize the efficiency of the microwave power. Efforts are now being devoted to optimizing the probe design in order to minimize these difficulties. The proton enhancement data on Pocahontas coal (Figure 6) was obtained and illustrates an enhancement value of 30. This enhancement value is probably sufficient to enable N-15 data on coals to be obtained. However, current efforts are focusing on revising the probe design in an effort to increase the proton enhancement value by a factor of two.

Modeling Nitrogen Release

During this reporting period, initial work has begun on the development of a model of nitrogen release as a function of coal type based on chemical forms of nitrogen in coal. It is thought that nitrogen release during primary devolatilization occurs via two mechanisms:[13, 14] (i) nitrogen atoms contained in the aromatic clusters are transported away as heteroatoms in the aromatic clusters of tar molecules (thought to be the primary mode of nitrogen release during devolatilization); and (ii) nitrogen atoms can be released from the char as HCN and NH_3 during thermal rupture of aromatic rings structures. The detailed chemistry of HCN and NH_3 formation has not yet been determined. However, it is believed that nitrogen is first released as HCN; then NH_3 is formed from subsequent reactions with hydrogen.[14]

Nitrogen release models have been developed by Bassilakis *et al* [14] and Niksa[13] based on the following simplifying assumptions: (i) nitrogen atoms are randomly distributed through the coal's aromatic clusters; (ii) nitrogen atoms contained in the aromatic clusters of the metaplast are transported from the infinite matrix during tar evolution; and (iii) ring opening and condensation reactions are negligible (cluster size is constant). Both models use first order kinetics with a distributed activation energy to describe the rate of release of nitrogen from the char.

Niksa has extended the FLASHCHAIN model of devolatilization to predict nitrogen release by monitoring, η, the change in the average moles of nitrogen per mole of aromatic clusters.[13] The rate of nitrogen evolution by tar transport is directly proportional to the evolution rate of tar molecules which accounts for the largest fraction of nitrogen release during devolatilization. As explained above, additional nitrogen is released from char as HCN. HCN release was modeled by the first order rate equation:

$$\frac{dY_{HCN}}{dt} = k_{HCN}\,\eta$$

where Y_{HCN} is the molar yield of HCN, and k_{HCN} is the first-order rate constant which is calculated from an Arrhenius expression with a distributed activation energy. The pre-exponential factor, A_{HCN}, was correlated with the O/N ratio to account for lower HCN yields for high rank coals (which generally contain less oxygen than higher rank coals). No attempt was made to describe the actual mechanism for HCN release. The rate constants were simply empirically fit to match experimental nitrogen release data. The nitrogen release model developed by Bassilakis and coworkers[14] for the FG-DVC model is similar to that used in FLASHCHAIN. The nitrogen release models used by Niksa and Bassilakis appear to give good first order approximations of nitrogen release, but a more mechanistic approach to nitrogen release from char would be useful.

The following steps are being carried out to develop a nitrogen release model based on the chemical structure of nitrogen to be applied in the Chemical Percolation Devolatilization (CPD) model:[15] (i) develop a nitrogen release model based on the approach used by Niksa and Bassilakis which will involve developing an accounting scheme for nitrogen released with the tar, and a first order rate expression with a distributed activation energy to model the release of nitrogen from the char as HCN (the pre-exponential factor and activation energy will be fit using nitrogen release data from devolatilization experiments performed as Sandia National Laboratories[2] and from recent devolatilization experiments carried out at Brigham Young University in the flat flame burner (FFB) and the HPCP); (ii) evaluate the simplifying assumptions of the model using ^{13}C NMR measurements of coal and char structure; (iii) explore other possible char nitrogen release mechanisms and rate expressions, compare prediction capabilities of the different models, and draw conclusions as to which model is best suited for use in the CPD (as ^{15}N NMR of coal and char becomes feasible, it is hoped that a mechanism based on nitrogen functionality can be developed); and (iv) couple the “best suited” model with the CPD code.

FUTURE PLANS

Future plans include performing solid-state ^{13}C (CP/MAS) and ^{15}N (DNP) NMR analyses on the char and tar samples already obtained at the 820 K and 1220 K conditions in the HPCP. 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, as detailed above.

SUMMARY AND CONCLUSIONS

Solid-state ^{13}C NMR analyses were performed on chars produced in the HPCP at 1080 K maximum gas temperature and 285 ms residence time. These char NMR data, together with the solid-state NMR data reported previously on tar and coal, represent the first matched set of coal/char/tar data obtained using solid-state ^{13}C NMR. This data serves to increase the understanding of the chemical structure of pyrolysis products during devolatilization. These NMR data were used to show that several assumptions that are commonly made in coal nitrogen devolatilization models may be reasonable. 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. Major advances were made with the DNP NMR experiments that are crucial to increasing the understanding to nitrogen forms in coal and its pyrolysis products. The first ^{15}N NMR data were obtained for Pocahontas #3 coal; an enhancement of 30 was obtained using the DNP technique. Additional ^{15}N NMR (DNP) analyses of coal and its pyrolysis products will provide further insight into the nitrogen forms in coal and the nitrogen evolution process.

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PUBLICATIONS/PRESENTATIONS RELATED TO THIS CONTRACT

A. Publications

Sponsored by Contract

Genetti, D., T. H. Fletcher, and R. J. Pugmire, “Predicting ^{13}C NMR Measurements of the Chemical Structure of Coal Based on Elemental Composition and Volatile Matter Content,” submitted to Energy and Fuels (April, 1998).

Hambly, E. M., T. H. Fletcher, M. S. Solum, and R. J. Pugmire, “Chemical Structure of Coal Tar during Devolatilization Using Solid-State ^{13}C NMR,” submitted to the *27th Symposium (International) on Combustion* (December, 1997).

Kelemen, S. R., M. L. Gorbaty, P. J. Kwiatek, T. H. Fletcher, M. Watt, M. S. Solum, and R. J. Pugmire, "Nitrogen Transformations in Coal during Pyrolysis," *Energy and Fuels,* **12**, 159-173 (1998). (partially sponsored by contract)

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).

Related to Contract

Brown, A. L. and T. H. Fletcher, “Modeling Soot Derived from Pulverized Coal,” accepted for publication in *Energy and Fuels* (1998).

Fletcher, T. H., J. Ma, J. R. Rigby, A. L. Brown, and B. W. Webb, "Soot in Coal Combustion Systems," *Progress in Energy and Combustion Science,* **23**, 283-301 (1997).

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B. Presentations

Sponsored by Contract (or cost-sharing on contract)

Hambly, E. M., Fletcher, T. H., Pugmire, R. J., “Solid-State ^{13}C NMR Analysis of Coal Tar and Char,” accepted for presentation at the National ACS Meeting, Dallas, TX (March, 1998).

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Table 1
Summary of HPCP Pyrolysis Experiments

Coal	Condition	Mass Release (daf)	Tar Release (daf)	Nitrogen Release (daf)
Beulah Zap	820 K	0.294	0.008	0.217
	1080 K	0.519	0.033	0.352
	1220 K	0.495	0.016	0.306
Blue #1	820 K	0.107	0.010	0.085
	1080 K	0.512	0.145	0.372
	1220 K	0.577	0.096	0.476
Illinois #6	820 K	0.106	0.009	0.049
	1080 K	0.592	0.180	0.485
	1220 K	0.570	0.147	0.435
Pittsburgh #8	820 K	0.103	0.010	0.073
	1080 K	0.479	0.225	0.372
	1220 K	0.558	0.200	0.456
Pocahontas #3	820 K	0.051	0.002	0.091
	1080 K	0.271	0.096	0.224
	1220 K	0.241	0.092	0.128

Table 2

^{13}C NMR Analysis of Coal, Char and Tar - 1080 K Condition[a]

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
	char	91	7	84	29	55	9	23	23	9	8	1	6
	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
	char	94	4	90	32	58	7	19	32	6	4	2	3
	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	10	8
	char	94	6	88	29	59	9	25	25	6	4	2	2
	tar	88	2	86	36	50	7	19	24	12	6	6	1
Pittsburgh #8	coal	65	3	62	23	39	5	16	18	35	24	11	7
	char	93	2	91	37	54	6	20	28	7	5	2	2
	tar	86	2	84	36	48	5	18	25	14	7	7	2
Pocahontas #3	coal	78	1	77	32	45	2	15	28	22	15	7	7
	char	92	2	90	40	50	3	17	30	8	5	3	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).

Table 3
Derived Structural Parameters from ^{13}C NMR - 1080 K Condition[b]

Coal	Sample	χ_b	C_{Cl}	σ+1	P_0	B.L.	S.C.	MW_{Cl}	MW_δ
Beulah Zap	coal	0.246	14	5.3	0.48	2.5	2.8	440	50
	char	0.274	13	4.9	0.97	4.8	0.1	228	14
	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	384	45
	char	0.356	18	5.2	0.92	4.8	0.4	283	12
	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	402	39
	char	0.284	14	5.4	0.94	5.1	0.3	222	9
	tar	0.279	13	3.9	0.77	3.0	0.9	213	13
Pittsburgh #8	coal	0.290	14	4.8	0.48	2.3	2.5	329	33
	char	0.308	15	4.3	0.92	4.0	0.3	220	8
	tar	0.298	14	3.8	0.70	2.7	1.1	228	14
Pocahontas #3	coal	0.364	18	4.0	0.59	2.3	1.7	316	23
	char	0.333	16.5	3.6	0.85	3.1	0.5	228	6
	tar	0.330	16	3.8	0.81	3.1	0.7	237	10

[b] χ_b = fraction of bridgehead carbons, C_{Cl} = aromatic carbons per cluster, σ+1 = total attachments per cluster, P_0 = 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_δ = the average molecular weight of the cluster attachments.

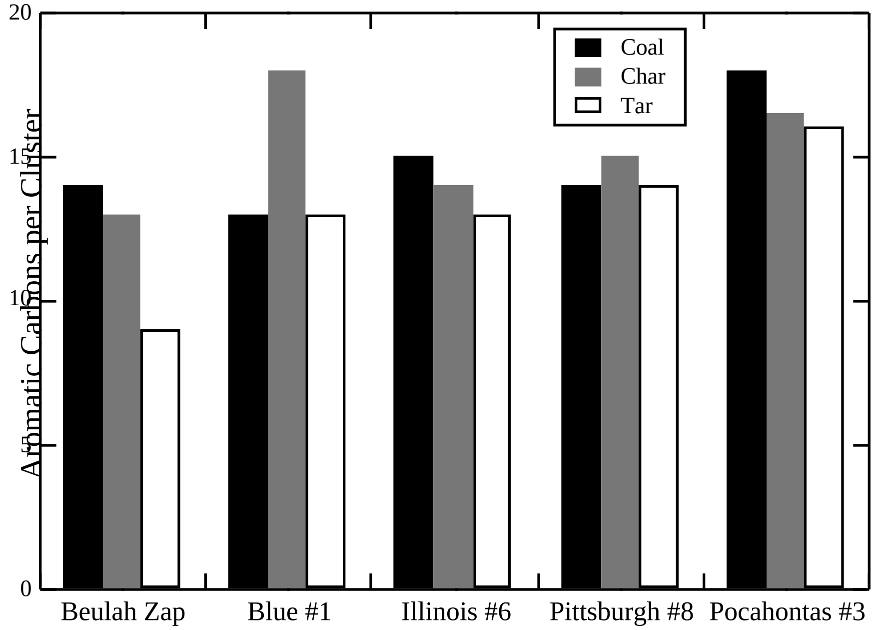

Figure 1. Aromatic Carbons per Cluster in Coal, Char and Tar. Results of solid-state ^{13}C NMR analysis of char and tar produced at 1080 K condition in the HPCP.

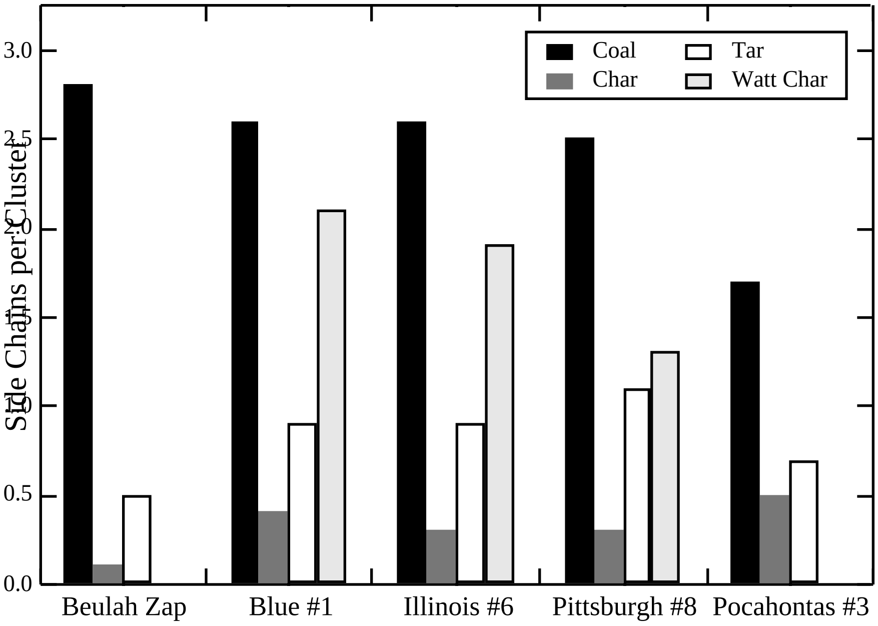

Figure 2. Side Chains per Cluster in Coal, Char and Tar. Results of solid-state ^{13}C NMR analysis of char and tar produced at 1080 K condition in the HPCP.

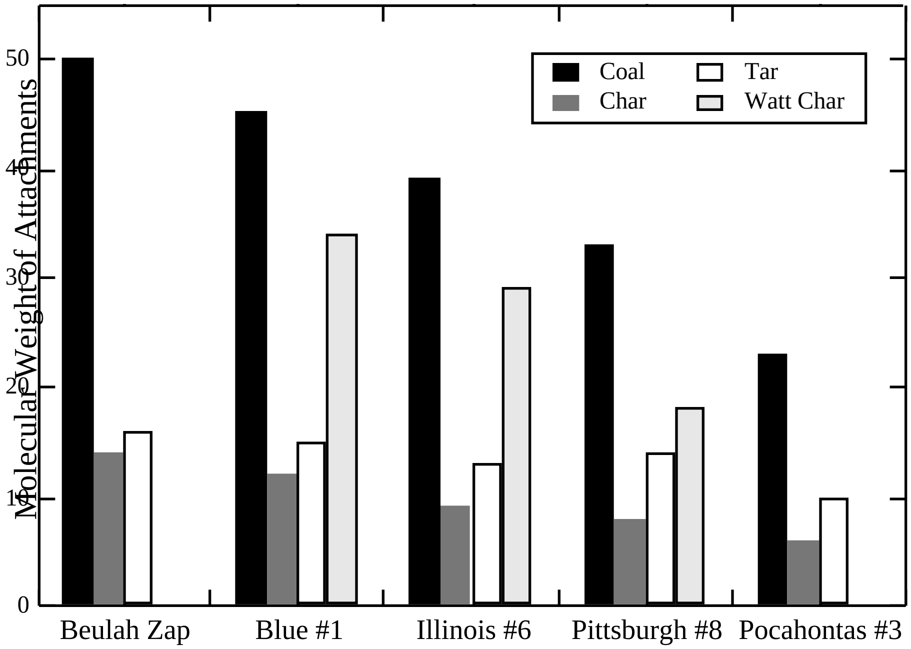

Figure 3. Molecular Weight of Attachments in Coal, Char and Tar. Results of solid-state ^{13}C NMR analysis of char and tar produced at 1080 K condition in the HPCP.

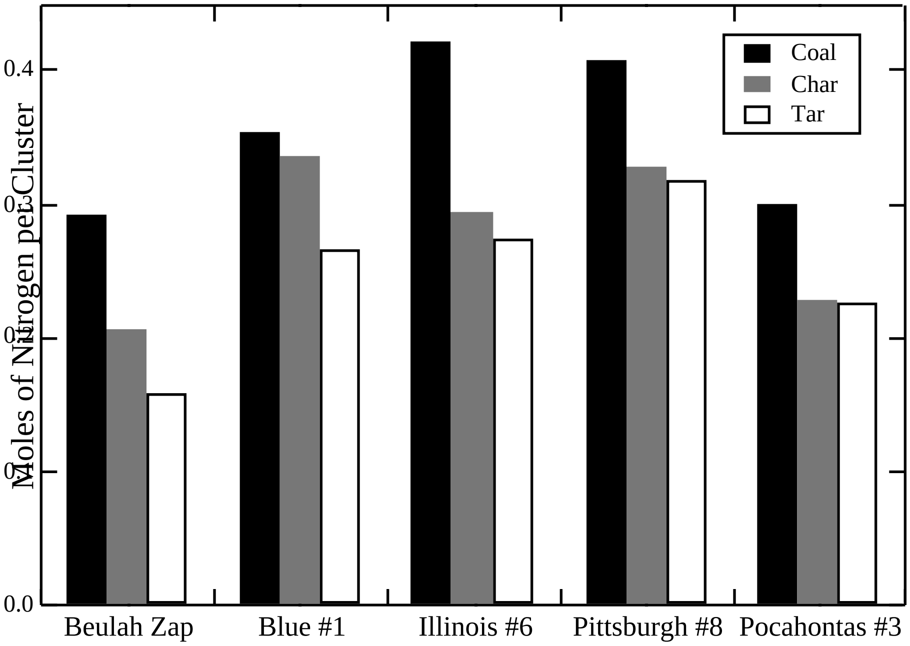

Figure 4. Moles of Nitrogen per Cluster in Coal, Char and Tar.

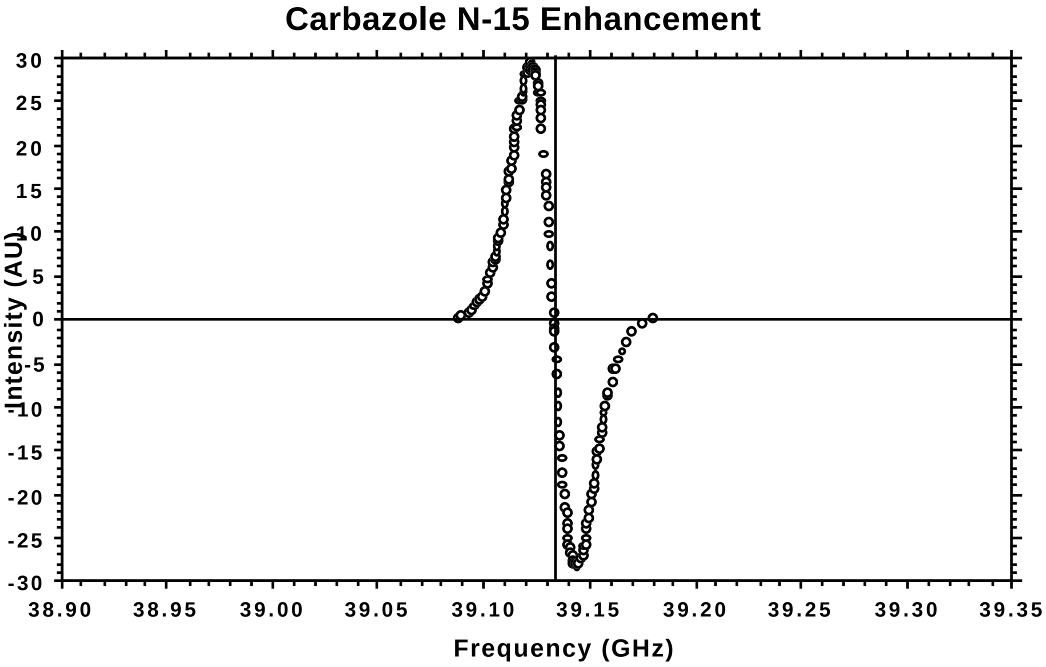

Figure 5. Nitrogen-15 enhancement curve for carbazole. The antisymmetric pattern is characteristic of the solid state enhancement mechanism.

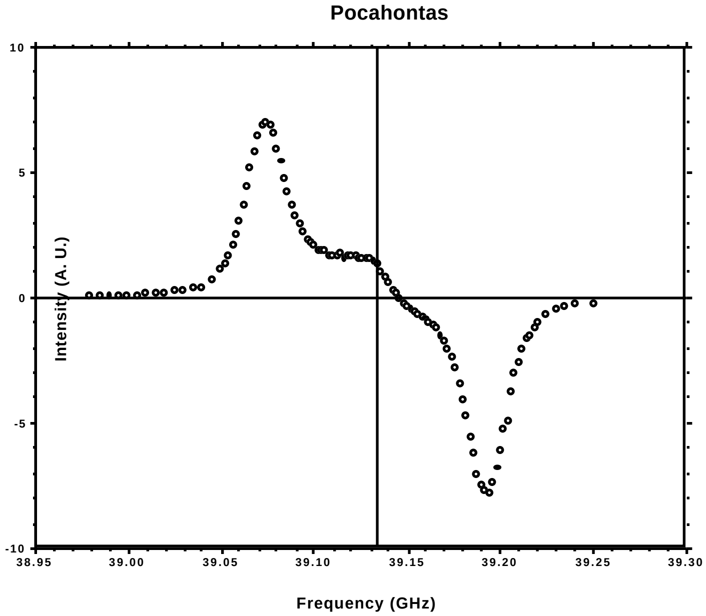

Figure 6. Proton enhancement curve for the Pocahontas coal sample from the Argonne Premium Coal Sample Bank. The maximum proton enhancement obtained is 30.