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Characterization of the Argonne premium coals by using NMR of 1H and 13C and FTIR spectroscopy

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Characterization of the Argonne premium coals by using NMR
of hydrogen and carbon-13 and FTIR spectroscopy

dela Rosa, Luisita Caberto, Ph.D.

Iowa State University, 1991

Characterization of the Argonne premium coals by using

NMR of ^{1}H and ^{13}C and FTIR spectroscopy

by

Luisita Caberto dela Rosa

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of the

Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Physical Chemistry

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Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1991

To my children,

Femi

Misi

Joe

Lara

whose loving support permitted the

realization of this degree.

TABLE OF CONTENTS

SYMBOLS AND ABBREVIATIONS

$A_G(t)$ Amplitude of Gaussian component of FID at time t, with t = 0 at the top of an echo

$A_L(t)$ Amplitude of Lorentzian component at time t, with t = 0 at the top of an echo

APCSP   Argonne Premium Coal Sample Program

AR   As received

ASTM   American Society for Testing Materials

C_{al} Aliphatic carbon weight % concentration (MAF) as measured by FTIR

C_{ar} Aromatic carbon weight % concentration (MAF), $C_{ar} = C_t - C_{al}$ as measured by FTIR

CP   Cross-polarization

CP/MAS   Cross-polarization combined with magic-angle spinning

CRAMPS   Combined rotation and multiple pulse NMR spectroscopy

C_t Weight % carbon (MAF) in the coal as measured by FTIR

dmmf   Dry, mineral-matter free

ESR   Electron spin resonance

FID   Free induction decay

FTIR	Fourier Transform infrared
f_a	Carbon aromaticity measured by NMR
$f_a(IR)$	Carbon aromaticity of coal calculated from FTIR spectra
H_a	Hydrogen aromaticity measured by NMR
$H_a(IR)$	Hydrogen aromaticity of coal calculated from FTIR spectra
H_{al}	Aliphatic hydrogen weight % concentration (MAF) of coal calculated from FTIR spectra
H_{ar}	Aromatic hydrogen weight % concentration (MAF) of coal calculated from FTIR spectra
H_{oh}	Weight % concentration (MAF) of OH group of coal calculated from FTIR spectra
H_t	Total hydrogen weight % concentration (MAF) of coal calculated from FTIR spectra
H/C	Atomic hydrogen to atomic carbon ratio in the coal sample
$(H/C)_{al}$	Aliphatic hydrogen to aliphatic carbon ratio in the coal sample as measured by NMR
$(H/C)_{ar}$	Aromatic hydrogen to aromatic carbon ratio in the coal sample as measured by NMR
HVB	High volatile bituminous
L	Lignite

LVB	Low volatile bituminous
MAF	Moisture and ash free
MAS	Magic-angle spinning
M_{al}	Amplitude of the aliphatic peak in a CRAMPS spectrum
M_{ar}	Amplitude of the aromatic peak in a CRAMPS spectrum
$M_\rho(\tau)$	Longitudinal magnetization in the rotating frame at time τ after the spin-locking pulse
$M(\tau)$	Longitudinal magnetization at time τ after the 180° pulse
$M(\tau_{cp})^i$	Integrated area of each peak (i = al, ar) of ^{13}C CP/MAS spectrum
M_0^{al}	Initial aliphatic magnetization of ^{13}C CP/MAS spectrum
M_0^{ar}	Initial aromatic magnetization of ^{13}C CP/MAS spectrum
MVB	Medium volatile bituminous
N_c	Number of ^1H spins exhibiting short and medium T_2's per gram of coal
N_e	Number of free radicals per gram sample as measured by ESR
N_T	Total number of ^1H spins per gram of coal sample
N_w	Number of ^1H spins with the longest T_2's per gram of coal

NMR	Nuclear magnetic resonance
P	MAF weight percent of oxygen in the coal sample
PAH	Polycondensed aromatic hydrocarbon
rf	Radio frequency
SB	Subbituminous
TGA	Thermogravimetric analysis
T_{CH}^i	time constant for polarization transfer during a CP experiment (i = al, ar)
T_1	Longitudinal relaxation time constant in the laboratory frame
T_1^{av}	Mean longitudinal relaxation time constant in the laboratory frame
$T_{1\rho}$	Longitudinal relaxation time constant in the rotating frame
$T_{1\rho}^{av}$	Mean longitudinal relaxation time constant in the rotating frame
T_{2G}	Transverse relaxation times of the Gaussian component of the FID
T_{2L}	Transverse relaxation time of the Lorentzian component of the FID
vct	Variable contact time

α	Fraction of the magnetization characterized by the long time constant T_1^l
$(1-\alpha)$	Fraction of the magnetization characterized by the short time constant T_1^S
β	Fraction of the magnetization characterized by the long time constant $T_{1\rho}^l$
$(1-\beta)$	Fraction of the magnetization characterized by the short time constant $T_{1\rho}^S$
χ_b	Mole fraction of aromatic bridgehead carbon atoms in the coal sample
δ	Chemical shift anisotropy
ν_r	MAS spinning speeds
$\tau, \Delta\tau$	Pulse separation time, separation time increment
τ_c	Homonuclear decoupling pulse sequence cycle time
τ_{cp}	Contact time between ^{1}H and ^{13}C rotating frames during a CP experiment
$\omega_{al}, \Delta\omega_{al}$	Position and second moment of the aliphatic peak in a CRAMPS spectrum
$\omega_{ar}, \Delta\omega_{ar}$	Position and second moment of the aromatic peak in a CRAMPS spectrum
ω_o	Larmor frequency

GENERAL INTRODUCTION

Visual inspection of a piece of coal shows it to be a heterogeneous mixture of solid organic matter called macerals and inorganic mineral matter. The dark brown to black highly combustible piece of "rock" was formed as a result of severe geological events acting on plant remains such as those of great ferns that grew in swampy regions that existed on earth about 350 million years ago (1), and had metamorphosed into the forms we know today. The complex physical and chemical changes during the decomposition of the vegetable matter led to a gradual loss of moisture, oxygen, and hydrogen, leaving behind a material that is rich in carbon. The degree of metamorphosis of the deposit determined its rank which is measured in the laboratory by the amount of fixed carbon (2) in a sample. Peat formation is the initial stage of coal formation. The lowest ranking coal with the lowest fixed carbon content is lignite. It also contains a high percentage of moisture and oxygen. Next come the bituminous coals. The highest ranking coal is anthracite which is recognized by its glossy black color, dryness, and rock-like hardness. There are no clear boundaries between coal ranks. As a solid fuel, the higher the coal rank, the higher is its heating value.

With the advent of petroleum, the demand for coal went down. However, during the 1975-76 energy crisis, the United States turned to its vast coal reserves for the commercial production of synthetic fuels (3) to augment the nation's supply of clean energy. The economic value of a given

coal is dependent on its composition and its properties which are used to predict its response to a specified process. Washing coal, for example, to separate undesirable constituents depends on physical properties such as density and porosity, which in turn depend on the chemical makeup of the specific coal. Destructive distillation of coal yields coke, tar, coal gas and ammonia. Coke is an essential ingredient in the steel industry. Tar is a source of aromatic hydrocarbons. Coal gas is used basically as fuel. Percentage yields, composition and quality of the products vary even for coals of the same rank but containing different lithotypes (2). The diversity of origin and geological history of coal present special problems in its analysis and utilization. To quote Gerstein (4), " Current technologies for processing coal might be described as subjecting a poorly characterized, heterogeneous material to a series of mysterious transformations to produce only slightly more recognizable products...Efforts to clarify the nature of coal are important if we are to utilize coal to replace needs satisfied in the past by petroleum."

The reliability of any quantitative technique as applied to coals is clouded by a very basic problem, namely, sampling. There are as many varied sampling techniques and laboratory sample preparation methods as there are publications about coal. For a material as heterogeneous as coal, adherence to standardized procedures is essential for obtaining repeatable and reproducible results (5). The laboratory sample is prepared from a gross sample by following the American Society for Testing Materials (ASTM) method D2013. This method specifies that the variance of sampling,

division, and analysis should not be more than 20% of the total variance (if known) of these steps.

From the moment a coal block is removed from the mine until a representative sample reaches the laboratory, it usually losses moisture and gets oxidized (6-7) because of its exposure to the atmosphere. To build a coherent picture of coal from independent studies in various laboratories, there is a need (8) to study coal samples that are carefully chosen, collected, prepared and preserved. This led to the development of the Premium Coal Sample Program (9) in 1981 under the supervision of the Argonne National Laboratory, Argonne, Illinois. Eight coal seams, representative of the type of coals available in the United States, were chosen and carefully sampled. The analytical samples, prepared in small glass ampuls, were made available to the coal research community. With the use of these samples, analytical techniques and their limitations (10) as applied to coal could be standardized and factors that would elucidate the structure of coal could be examined without bias because of these samples' documented history.

The development of two powerful analytical techniques in recent years allowed the direct examination of solid fuels. The first is high resolution solid state nuclear magnetic resonance (NMR) spectroscopy which is a nondestructive qualitative and quantitative technique (11-12) for the detection of hydrogen and carbon. The second is Fourier transform infrared (FTIR) spectroscopy (13), a technique which has all the advantages of an interference spectroscopy in terms of signal averaging and removal of baseline artifacts. The quantitative reliability of both spectroscopic

techniques as applied to coals was investigated by using the Argonne Premium Coal Sample Program coals.

Explanation of the Dissertation Format

This dissertation is presented in the alternate format and consists of a general introduction, two papers, a general conclusion, and an appendix. Literature cited are presented in the style of the journals to which the papers were submitted. References cited in the general introduction are found immediately after the general conclusions and are presented in the style used for the first paper.

Part I

Using ^{1}H NMR spectroscopy as a a technique for quantitation of hydrogen and moisture in coals, implies that (a) all of the protons in the sample are observed by NMR; (b) the time dependence of the FID near t = 0 is known; and (c) the physical meaning of the different components of the FID is well understood. The validity of these assumptions will be examined in this work, using the Argonne premium coals, by determining the "true" lineshape of the whole FID using the solid echo, mathematical analysis of the full FID, and spin counting.

The candidate performed all the experiments described in this paper. This paper was accepted for publication in *Techniques in Magnetic Resonance for Carbonaceous Solids* , Advances in Chemistry Series No. 229,

edited by R. Botto and Y. Sanada, and published by the American Chemical Society. (Status : in press).

Part II

The second paper summarized our use of a variety of transient techniques in NMR of ^{1}H and ^{13}C in solid coals and of FTIR to infer average chemical functionalities of the Argonne premium coals. Proton-relaxation data and hydrogen and carbon aromaticities were measured and the results compared with those reported by other laboratories (14-17). FTIR quantitation results were also evaluated.

The ^{1}H CRAMPS experiments were performed by the candidate, ^{13}C CP/MAS measurements were contributed by Dr. Marek Pruski, and the FTIR work were contributed by Dr. Peter Solomon. The manuscript is in preparation for submission to *Fuel*.

Appendix

A paper (Pruski, M.; Dela Rosa, L.; Gerstein, B. *Energy & Fuels* 1990, *4*, 160) that reported the results of our investigation of the effects of spinning rates and Hartmann-Hahn mismatch during a ^{13}C NMR CP/MAS experiment performed on Argonne coal 401 and coronene as a model compound is included.

All the ^{13}C NMR experiments on Argonne coal 401 and adamantane reported in this paper were contributed by the candidate.

PART I.

QUANTITATION OF PROTONS IN THE ARGONNE
PREMIUM COALS BY SOLID STATE ^{1}H NMR

Quantitation of protons in the Argonne premium coals by solid state ^{1}H NMR

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ABSTRACT

Quantitation of protons and moisture in the eight coals from the Argonne Premium Coal Sample Program by ^{1}H NMR spectroscopy was performed. The solid echo was utilized to determine the true lineshape of the on-resonance ^{1}H free induction decay (FID). A superposition of Gaussian and Lorentzian decay functions was found to adequately describe the FID of dry coals. The Gaussian fraction corresponds to rigid protons in the macrostructure of coal. The Lorentzian fraction is attributed to fragments in the coal exhibiting hindered molecular mobility. For wet coals, an additional slowly decaying Lorentzian fraction must be added to the description of the FID. Identification of the species responsible for the longest decay was made by liquid state NMR of the condensate obtained by heating the sample at 100°C under static vacuum and high resolution solid state NMR of the ^{1}H of the coals before and after removing the matter volatile at 100°C. The NMR quantitation results compared favorably with the results obtained by chemical and thermogravimetric analyses.

INTRODUCTION

The assay of hydrogen by the American Society for Testing and Materials (ASTM) D3178 and of moisture by ASTM D3173 in analysis samples of coal is carried out under carefully controlled conditions ([1]). Since setting up and complying with the requirements of these procedures are tedious and time-consuming, alternative procedures, which most laboratories could perform, are used instead. A fast, analytical procedure for determining the concentration of organic hydrogen in the coal matrix uses an elemental analyzer. However, this analytical method requires very small (<10 mg) samples and may not reflect the inherent heterogeneity of coal. The usual routine moisture analysis used by most laboratories is an indirect determination by mass loss upon heating the sample for one hour at 107 ± 3 °C in a drying oven. Unfortunately, a number of possible sources of errors exist for this method. The loss of mass due to the desorption of gases such as CH_4 and CO is negligible ([2]) but the loss of CO_2 due to decarboxylation at temperatures as low as 60°C, especially for low-rank coals ([3]), may be significant and cause an overestimation of the moisture concentration. On the other hand, when the heating is not carried out in an inert atmosphere, oxidation ([4]) taking place during the drying period will result in underestimating the value of the moisture reported. A serious drawback of this procedure is the readsorption of moisture in the dessicator during the cooling process ([5]). Also, an isotope dilution technique was reported ([6]) in which ^{18}O-enriched water added to the coal sample was

allowed to exchange with the natural abundance water, and the isotope ratio was then analyzed by mass spectrometry. This technique is time-consuming since equilibration required sixteen hours before the exchange was deemed to be complete. The main source of error in this technique results from the assumption that the only exchangeable oxygen present in the coal is that bound in water.

Pulsed nuclear magnetic resonance (NMR) spectroscopy offers an alternative analytical technique for the analysis of hydrogen and moisture in coals. This method is fast and is not subject to the errors of the previously discussed methods. Quantitative elemental analysis by NMR relies on the simple proportionality between the observed signal intensity and the number of spins present in the sample. It has been demonstrated (7) that the initial value of the free induction decay (FID) of the resonant protons observed after a transient radio frequency (rf) pulse excitation can be used as a quantitative measure of the total hydrogen concentration in coals. Since the decay characterized by constants of the order of 10 μs contributes significantly to the ^{1}H NMR in coals, the pulse width used should be $\leq T_2/4$, and the recovery time of the NMR receiver should be of the order of the pulse width. The relative concentration of protons in the sample could be determined by a sample transfer method if the coal sample and the calibration standard were exposed to the same homogeneous rf field and the measurements were made under the same experimental conditions. A plot of the logarithm of the signal amplitude versus the square of time, t, was used to extrapolate the FID to t=0.

Using pulsed NMR, Lynch and Webster (8) studied water associated with brown coal and showed that the observed FID of the protons of coal samples not containing free water could always be resolved into two components: (a) a rapidly relaxing component that was attributed to organic hydrogen atoms and to chemisorbed water and (b) a slowly relaxing component attributed to physisorbed water.

Riley (9) investigated the suitability of a commercial 20 MHz pulsed NMR spectrometer for routine total hydrogen and moisture determination in coals. Instead of measuring the initial amplitude of the FID, the amplitude at 14 µs and at 70 µs after the pulse were measured to determine the total hydrogen and moisture concentrations, respectively. For quantitation, a calibration curve using corresponding amplitudes measured for reference coals was used. The reproducibility of the results obtained was found to be good.

Cutmore et al. (10) investigated the possibility of using NMR for routine on-line analysis of water in coals by studying the effect of rank, particle size, and sample dimensions using ^{1}H NMR at proton resonance frequencies ranging from 6.5 MHz to 60 MHz and found that the NMR results were independent of these factors.

In a most recent study by Graebert et al. (11), ^{1}H NMR was used for quantitative measurements of protons in a series of German brown coals. The water content determined in this study compared favorably with the results obtained using thermogravimetry, near infrared spectroscopy, and titration.

Using ^{1}H NMR spectroscopy as a a technique for quantitation of hydrogen and moisture in coals implies that (a) all of the protons in the sample are observed by NMR, (b) the time dependence of the FID near $t = 0$ is known, and (c) the physical meaning of the different components of the FID is well understood. The validity of these assumptions will be examined in this work using the Argonne Premium Coals by determining the "true" lineshape of the whole FID using the solid echo, mathematical analysis of the full FID, and spin counting.

EXPERIMENTAL

The coals used in this study are from the Argonne Premium Coal Sample Program and are listed in Table I, where the coal identification number, seam, and rank are given (columns 1-3). Only a partial list of the results of proximate and ultimate analyses performed in the laboratory of Commercial Testing and Engineering, Lombard, Illinois, are included in the table (columns 4-9) (12). Moisture concentration was determined by mass loss upon heating the sample in a convection oven at 105°C and 40% relative humidity. Hydrogen concentration was estimated by using an elemental analyzer (Engelke, G., Commercial Testing and Engineering, Inc., personal communication, 1989).

The samples, prepared under humid nitrogen atmosphere, were obtained in brown glass ampuls. Each ampul was opened in a glove box with a dry helium atmosphere; subsequently 50-100 mg of each coal was transferred from the ampuls to pre-weighed 5-mm NMR tubes in <2 minutes. The tubes were sealed off to preserve the samples and weighed. A reference water sample of the same geometry was prepared for ^{1}H spin counting. The sample lengths were approximately 50% of the length of the NMR coil.

All measurements were carried out at room temperature. A home-built solid state NMR spectrometer operating at the ^{1}H resonance frequency of 100.06 MHz was used for lineshape and solid echo determination. A proton-free probe was used to avoid background absorption. A Nicolet 2090 IIIA

Table I. The Argonne premium coals[a]

ID	Seam	Rank	AR H_2O	AR Ash	Dry C	Dry H	MAF C	MAF H
501	Pocahontas 3, VA	LVB	0.65	4.74	86.71	4.23	91.05	4.44
101	Upper Freeport, PA	MVB	1.13	13.03	74.23	4.08	85.50	4.70
401	Pittsburgh 8, PA	HVB	1.65	9.10	75.50	4.83	83.20	5.32
701	Lewiston-Stockton, WV	HVB	2.42	19.36	66.20	4.21	82.58	5.25
601	Blind Canyon, UT	HVB	4.63	4.49	76.89	5.49	80.69	5.76
301	Illinois 6, IL	HVB	7.97	14.25	65.65	4.23	77.67	5.00
202	Wyodak-Anderson, WY	SB	28.09	6.31	68.43	4.88	75.01	5.35
801	Beulah Zap, ND	L	32.24	6.59	65.85	4.36	72.94	4.83

[a]Abbreviatons used in this table include: LVB = Low volatile bituminous; MVB = Medium volatile bituminous; HVB = high volatile bituminous; SB = subbituminous; L = lignite; AR = as received; MAF = moisture and ash free.

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digital oscilloscope recorded 2K data points using a 0.5 μs dwell time. The probe ringdown plus receiver deadtime was 6.5 μs.

Prior to lineshape determination, the longitudinal relaxation time values T_1, were measured by using the inversion-recovery pulse sequence. The 100-point data set for each coal was analyzed by a nonlinear least-squares fitting. The longer of the two T_1 constants extracted was used for the determination of the repetition rate for data averaging. A 90° pulse width of 1.0 μs was chosen for lineshape measurements. The method of spin temperature inversion on alternate pulses, with the subtraction of alternate scans in the averaging process (13), was found necessary to eliminate baseline distortions from the NMR signal. The solid echo was produced by a pulse sequence 90°_x - τ - 90°_y, with τ = 30 μs. Twenty scans were collected in each of the NMR experiments.

The ^{1}H NMR combined rotation and multiple pulse decoupled (CRAMPS) spectra for the as-received and vacuum-dried coal samples were measured by using a Bruker MSL 300 spectrometer. The samples were spun in an alumina rotor at ~3.5 kHz and the MREV-8 multipulse sequence used 90° pulses with widths of 1.5 μs.

Free radical concentrations were determined by using a Bruker ER2000-SRC Electron Spin Spectrometer at a frequency of 9.77 GHz. The coals (~20 mg) were air-dried and placed in 2-mm quartz tubes.

Thermogravimetric analyses (TGA) of the Argonne coals were carried out by using a Perkin Elmer 7 Series Thermal Analyzer System with argon as purge gas. Approximately 50 mg of each coal were transferred to the platinum sample cup. The temperature was ramped from 40°C to 110°C at a rate of 1°C per minute and then held at 110°C for 30 minutes.

RESULTS

The Solid Echo

To measure the number of spins (protons) in a sample by using NMR, it is necessary to know the initial amplitude of the FID signal which occurs at the center of the 90° pulse. However, in a single-pulse experiment, the first few microseconds of the protons' response to a transient rf pulse is always obscured by the probe ringdown and receiver deadtime. This loss of information cannot be completely eliminated but can be minimized by using a low Q probe and a fast recovery receiver. The use of the solid echo ($\underline{14}$), produced by the pulse sequence 90°_x - τ - 90°_y with the shortest possible pulse separation, makes it possible to circumvent the problem ($\underline{11}$, $\underline{15}$). As was shown by Boden et al. ($\underline{14}$), in solids in which dipolar interactions dominate the spectra, an echo is formed following the 90°_x - τ - 90°_y sequence at $t = \tau$ after the second pulse. The τ dependence of the solid echo amplitude, which results from the heteronuclear dipolar interactions (in systems containing two dipolar-coupled spin 1/2 species) or the interpair homonuclear dipolar interactions (in systems of loosely coupled spin 1/2 pairs) was not the subject of the present study. However, the decay of the solid echo, for a fixed and sufficiently short τ, is primarily due to the homonuclear dipolar interactions. Therefore, in coals where the proton-proton dipolar interactions dominate the ^{1}H NMR lineshape, the analysis of the signal following the top of the solid echo can be used to estimate the short time behaviour of the FID.

The solid echo measurements were made by using a pulse separation $\tau = 30 \, \mu s$. Nonlinear least-squares fitting of the echo decay was performed by using one or a superposition of Gaussian and Lorentzian terms:

$$A_G(t) = A_G(0)\exp[-0.5(t/T_{2G})^2], \text{ and} \tag{1}$$

$$A_L(t) = A_L(0)\exp(-t/T_{2L}), \tag{2}$$

where $A_G(t)$ and $A_L(t)$ are the amplitudes at time t, with t = 0 at the top of an echo, T_{2G} and T_{2L} are the transverse relaxation times of the Gaussian and the Lorentzian components, respectively.

The analysis proved that the echoes of most of the coals in the set could be described by the superposition of a Gaussian and two Lorentzian forms. For coal 501, a low volatile bituminous coal, the superposition of two Gaussian forms described the echo best; for coal 101, a medium volatile bituminous coal, however, the superposition of Gaussian and Lorentzian forms was a better fit.

It is noted that only the types of lineshapes as found from this experiment were used in the analysis of the FID of the coals. Although the decay constants describing the solid echo agreed well with those obtained later from the analysis of the FID, the relative fractions of Gaussian and Lorentzian decays, as calculated from the solid echo, changed as a function of τ, perhaps due to the differences in the mobilities of these fractions.

The Components of the FID

The same fitting routine was used in the computer analysis of the on-resonance FID of the studied coals. In Figure 1, the experimentally observed ^{1}H NMR signal and the nonlinear least-squares fit is shown for coal 202. A slowly decaying component can be well fitted with a Lorentzian form [see Equation (2)] by analyzing the tail of the FID starting at 200 μs after the excitation. Here the contribution from the shorter decays is negligible [see Figure 1, curve (a)]. Subsequently, the contribution from the long decay was subtracted from the total FID, and the data were further analyzed for the shorter decays by using superpositions of Gaussian and Lorentzian forms as found from the analysis of the solid echo [Figure 1, curves (b) and (c)]. The resulting decay constants and the corresponding fractions of the FID are compiled in Table II and shown in Figure 1a.

The superposition of the three functions, (a), (b), and (c), is shown in Figure 1 as curve (d). It was compared with the fits for which Gaussian and Lorentzian [curve (e)] or two Gaussian and Lorentzian [curve (f)] decay functions were used. Notice that curve (e) does not match the experimental points in the middle of the decay. However, both curves (d) and (f) well describe the known portion of the FID, and only by the use of the solid echo, could an unambiguous choice of the fitting functions be made. Also, note that because of the negligible intensity of the slowly decaying signal the three-component decomposition of the FID could not be successfully performed for coals 501 and 101. For these two coals only two-component fits could be used.
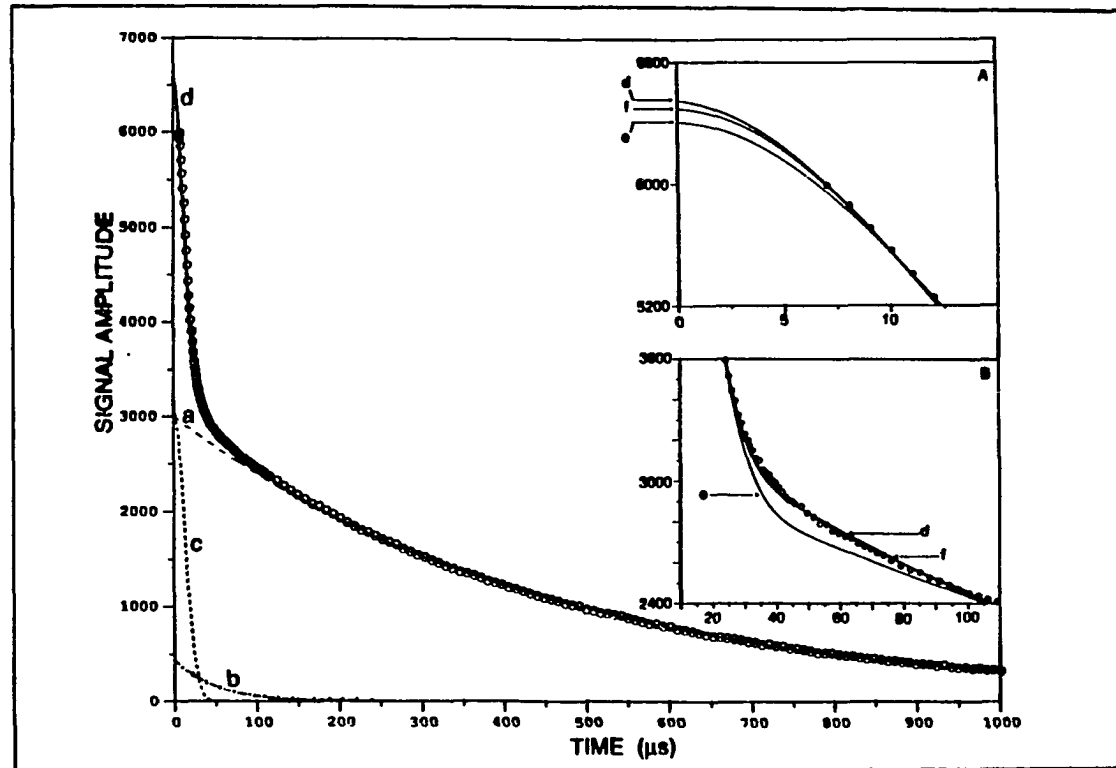
Figure 1.   The numerical nonlinear least squares fit of the ^{1}H FID of Argonne coal #202:   (o)
experimental points;   (a) Lorentzian decay with T_{2L} = 435µs;   (b) Lorentzian decay
with T_{2L} = 29 µs; and   (c) Gaussian decay with T_{2G} = 12.6 µs;   (d) superposition of
(a), (b), and (c);   (e) numerical fit with one Gaussian and one Lorentzian decay
functions;   (f) numerical fit with two Gaussian and one Lorentzian decay functions;
insets A and B are expansions of the initial portion of the FID

Table II. ^{1}H FID parameters obtained for the Argonne coals

Coal ID	T_2 / μs			Fraction of component		
	Fast[a]	Medium	Slow	Fast	Medium	Slow
501	12.7	52(4)[b]	—	0.969	0.031[b]	—
101	12.6	52(4)[b]	—	0.939	0.061[b]	—
401	12.5	28(8)	63(1)	0.912	0.016	0.072
701	12.4	22(1)	76(1)	0.850	0.089	0.061
601	12.2	24(2)	188(2)	0.777	0.138	0.084
301	12.3	37(3)	298(2)	0.778	0.065	0.157
202	12.6	29(1)	435(1)	0.447	0.085	0.468
801	12.7	29(1)	407(1)	0.364	0.092	0.544

[a]Average standard deviation (0.04).

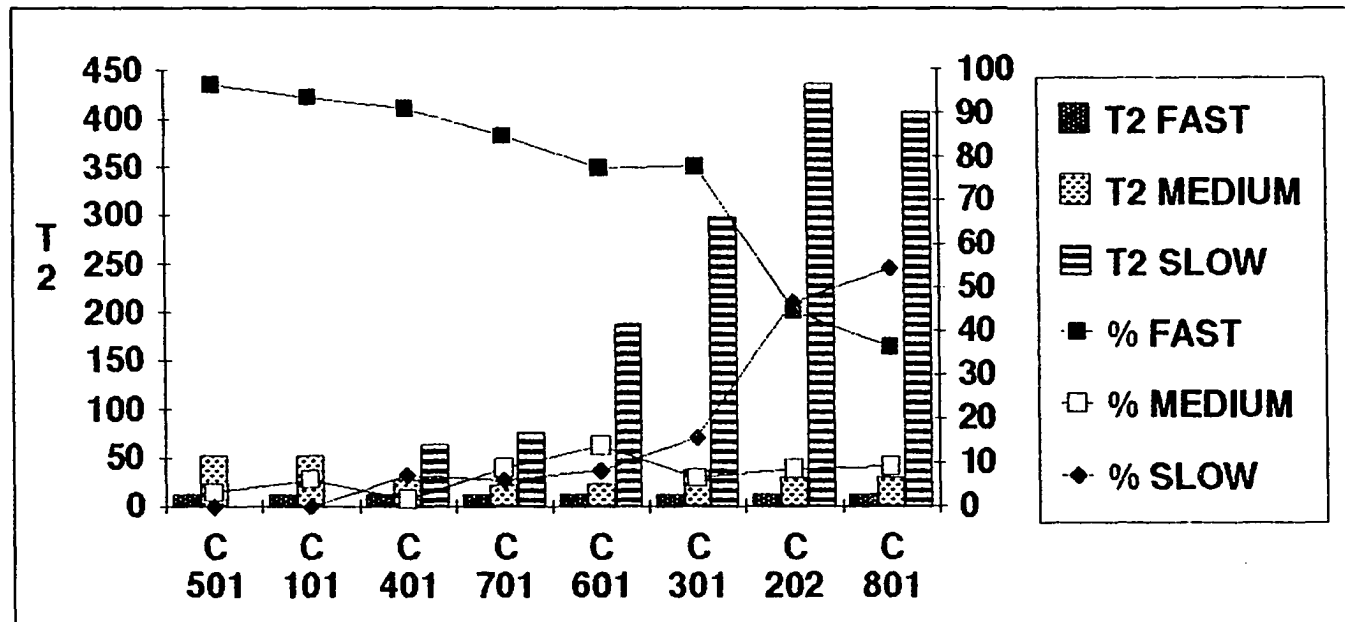[b]Parameters obtained using the superposition of 2 functions only.

Figure 1a. Tabular representation of the T_2's and fractions of the components of the free induction decays of the Argonne premium coals

Spin Counting

The absolute number of proton spins in coals was found by comparing the extrapolated initial intensity of the FID to that of the reference sample that was measured several times during the course of the experiment.The results of the spin counting are presented in Table III, columns 2, 3, and 4, where the total spin concentration per one gram of sample, N_T, the concentration of spins exhibiting short and medium T_2's, N_c, and concentration of spins with the longest T_2's, N_w, are given. From the proximate and ultimate analyses results of Table I (columns 4 and 7), the total concentration of hydrogen atoms, the concentration of organic hydrogen atoms, and the concentration of hydrogen atoms in water present in the coal samples were calculated and listed in Table III, columns 5, 6, and 7, respectively. Columns 8, 9, and 10 in Table III give the ratio of the proton spin counting results obtained by NMR to the corresponding numbers of hydrogen atoms calculated from the proximate and ultimate analyses of the Argonne coals. In addition, the free radical concentrations as measured by electron spin resonance (ESR) are listed in column 11 of Table III. The results of NMR measurements from Table III (columns 2, 3, 4) were used to calculate the weight per cent concentrations of the corresponding hydrogens in coals, and the results were listed in Table IV (columns 2, 5). The total weight loss (in per cent) of the samples during the TGA is listed in Table IV (column 4).

Table III. Hydrogen concentrations from NMR and chemical analyses; free radical concentration from ESR

Coal ID	NMR (10^{-22}/g coal)			Chemical Analysis (10^{-22}/g coal)			$\dfrac{N\,(NMR)\,x100}{N(\text{chem analysis})}$			ESR (10^{-19}/cm^{-3}(dmmf))
	N_T	N_c	N_w	N_T	N_c	N_w	N_T	N_c	N_w	N_e
501	2.5	–	–	2.55	2.51	0.043	97	–	–	1.5
101	2.5	–	–	2.48	2.41	0.074	102	–	–	1.3
401	2.9	2.7	0.2	2.95	2.84	0.11	99	95	(191)	1.4
701	2.6	2.4	0.2	2.63	2.47	0.16	98	98	100	2.2
601	3.6	3.2	0.3	3.44	3.13	0.31	103	104	97	1.8
301	2.8	2.3	0.4	2.87	2.33	0.53	96	100	81	1.1
202	3.6	1.9	1.7	3.97	2.09	1.88	90	92	88	1.7
801	3.4	1.6	1.9	3.92	1.76	2.13	88	89	87	1.5

Table IV. Weight per cent concentration of water and organic hydrogen in the
Argonne premium coals as determined by NMR, by chemical
analyses, and by TGA

| Coal ID | Weight % H_2O | | | Weight % organic H | |
	NMR	Proximate analysis	TGA	NMR	Ultimate analysis[a]
501	–	0.65	0.8	4.1	4.20
101	–	1.13	1.2	4.2	4.03
401	3.1	1.65	1.9	4.5	4.75
701	2.3	2.42	2.9	4.0	4.13
601	4.5	4.63	5.1	5.4	5.24
301	6.5	7.97	7.8	3.9	3.90
202	25.1	28.09	27.1	3.2	3.50
801	28.0	32.24	33.8	2.6	2.94

[a]Weight % organic H (ultimate analysis) = (% H(dry)/100)x(100-%H_2O).

DISCUSSION

The Components of the FID

The analysis of the FID showed that a minimum of three components were present in most of the coals studied. The term minimum is used to indicate that two-component fits are usually not sufficient to fit the data. Assuming an arbitrary number of components to the decay, however, is not regarded as being productive for understanding their nature.

The slowly decaying component of the FID, corresponding to protons with high isotropic rotational mobilities, suggests their complete detachment from the rigid coal framework. Any mobile water (moisture) present in coals would contribute to this component. Additional experiments indicated that there are no significant contributions to the slowly relaxing component from other proton-containing species in the sample. First, the Fourier transform spectra of all the coals studied show only one narrow peak that has the same chemical shift as water (Figure 2). The height of the peak increased and its width decreased for the lower rank, wet coals. Secondly, the identity of the slowly decaying component was established for selected coals (202 and 801) by dry distillation of ~1.5 g of the coal under vacuum at 100°C. Under these conditions, three hours of evacuation were sufficient to completely remove the mobile species from the coal. A distillate, collected in a liquid nitrogen trap, exhibited at room temperature an NMR spectrum identical to that of liquid water. No other peaks were present in its spectrum. A small fraction of distillate, however,
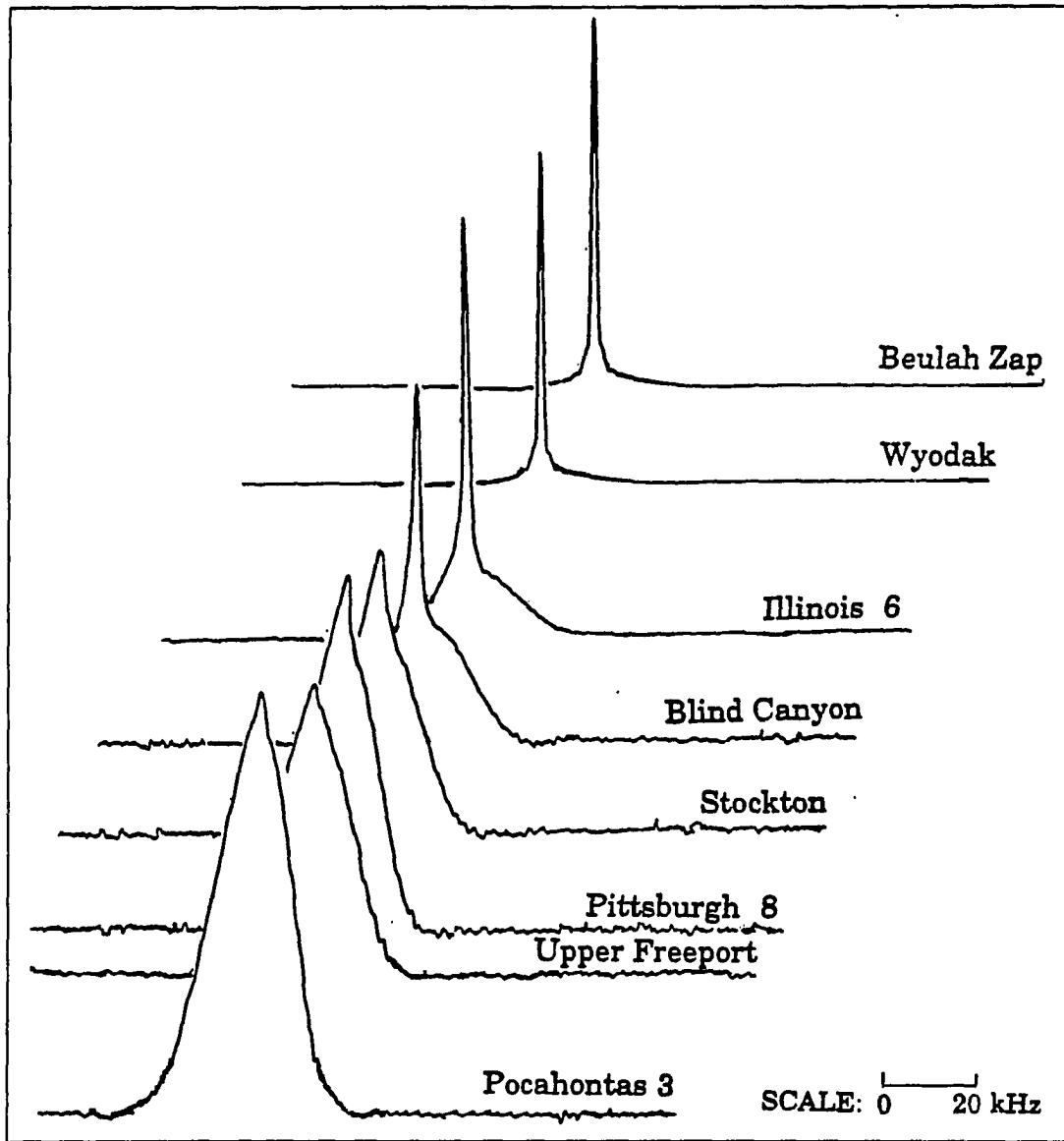
Beulah Zap

Wyodak

Illinois 6

Blind Canyon

Stockton

Pittsburgh 8

Upper Freeport

Pocahontas 3

SCALE: 0   20 kHz

Figure 2.   The ^{1}H NMR spectra of the eight Argonne coals

instantaneously evaporated upon the removal of the liquid nitrogen bath prior to the NMR experiment. Earlier studies by mass spectrometric analysis showed that the only gases evolved from a fresh sample of Illinois 6 coal upon outgassing at a pressure of 10^{-6} torr at room temperature were H_2O and CO_2 (16). The intensities of the rapidly decaying components of the FID remained unchanged upon the above treatment. Also, no detectable hydrogen-containing species besides water were found by using the TGA of the samples in our laboratory.

A further confirming identification of the material present before distillation as being water is found in the proton NMR CRAMPS spectra of the coals. The CRAMPS spectrum of protons in coal 202 before distillation is shown in Figure 3a. A major peak is present at ~5 ppm, (the position characteristic of protons in water) with a shoulder near 7 ppm. Upfield at 2 ppm is a peak identified with aliphatic portion of hydrogen in the coal. After vacuum-drying, the peak centered at 5 ppm disappeared, leaving a peak at 2 ppm and at 7.5 ppm (see Figure 3b), identified with aliphatic and aromatic protons, respectively. Thus, the slowly decaying component of the FID represents water which in coals is mostly physisorbed and trapped in the microcapillary pores (17).

The CRAMPS technique has been used previously to probe chemical functionalities of hydrogen in coals (18 - 20). A following paper (in preparation) from our laboratory will report the results of high resolution solid state NMR of ^{13}C and ^{1}H in the Argonne coals.
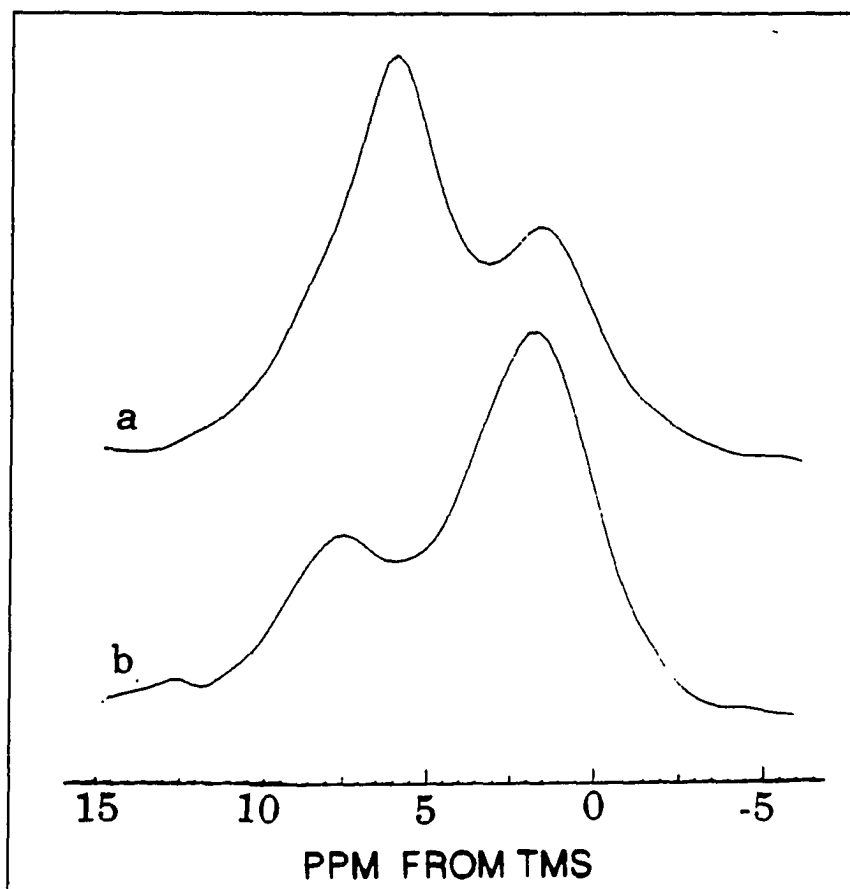
Figure 3. The ^{1}H CRAMPS spectra of Argonne coal #202:
(a) as received; (b) vacuum - dried at 100°C

As indicated earlier, the rest of the FID, representing the "dry" coal,

was fitted with the superposition of Gaussian (T_{2G} ~12 µs) and Lorentzian

(T_{2L} ~20-40 µs) decay functions (Table II). An analysis of these two

components was described for a series of coals of different ranks in earlier

studies by Jurkiewicz et al. (21) and Kamienski et al. (22). Theory (23)

predicts that for spin systems with strongly coupled protons in the rigid-lattice limit and for a correlation time of motion $\tau_c \gg T_2$, the transverse relaxation of protons immediately following a transient excitation can be approximated by a Gaussian function. The rapidly decaying component of the FID, therefore, describes the response of the protons in the rigid macrostructure of coal, e.g., protons attached to polynuclear aromatic rings. Since only 25%-60% of protons in Argonne coals are aromatic (as calculated from the CRAMPS spectra of the dry coals), the macrostructure contains non-aromatic protons that are also "rigid", such as protons in a polyamantane type of structure (24). Thus, the high fraction of the Gaussian component reflects the rigidity of the macromolecular structure of coal. The average interproton distance corresponding to the values of T_{2G} in these samples is ~ 0.18 nm.

The Lorentzian portion of the decay with the medium T_2 represents protons for which anisotropic motion with $\tau_c < 10^{-5}$ s exists. Although some intramolecular mobility, such as the rotation of methyl groups, is expected in coals, it was proposed that this component represents molecules detached from the rigid macromolecular network (21 - 22). It is possible that strongly bound water contributes partially to this signal, so the results contained in the present work may be viewed as a lower limit of the total water content.

Quantitative Measurements

As is evident from Figures 4 and 5 which illustrate the results of Tables III and IV, there is a very good agreement between the results of hydrogen

spin counting by NMR and the hydrogen concentrations obtained via chemical analyses. Only for coals 202 and 801 did the results of the two methods differ by more than 5%. The repeatability of the results obtained by NMR was found to be excellent in our experiments. Five determinations of the initial amplitude of the same sample had a deviation of only 0.5 % while the determination of the initial amplitude of the FID for five different 80 mg samples of the same coal had a deviation of ~4 %. The error estimates for the results of the proximate analysis of moisture and the ultimate analysis for hydrogen were not available.

A comparison of the fraction N_W/N_T as calculated from NMR data and from the proximate analyses for six Argonne coals is shown in Figure 4a. Good agreement exists between the two quantities for most of the coals, which improved as the moisture content increased (especially for coals 202 and 801) despite the discrepancies in the concentrations of hydrogen, N_W and N_T, determined by the two methods for these coals. A similar correlation is presented in Figure 4b, where the weight per cent concentration of the moisture from NMR is compared with the results of the proximate and TGA analyses (see also Table IV, columns 2, 3 and 4). Some discrepancies in the results are now evident, especially for coals 202 and 801. Since the concentrations of carbonyl groups (25) and oxygen are highest in coals 202 and 801, the proximate and TGA analyses results for moisture reported for these two coals may be overestimated because of decarboxylation at temperatures above 60°C. As was mentioned earlier, for coals 501 and 101, which have the lowest moisture content of 0.65% and
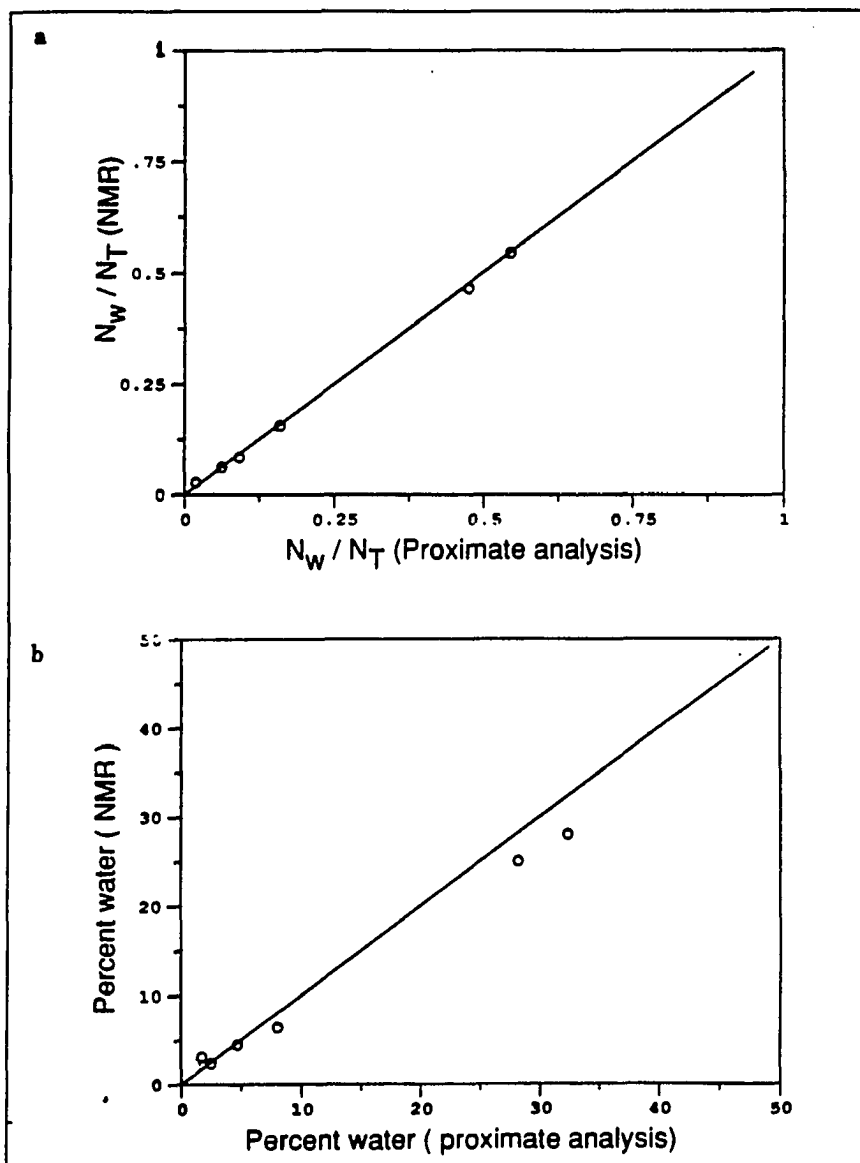
Figure 4. The correlation of the results for moisture analysis by NMR and by mass loss upon heating the sample: (a) The plot of N_W/N_T (NMR) versus N_W/N_T (proximate analysis); (b) The plot of the weight percent of moisture from NMR versus the concentration of moisture from proximate analysis of the coals
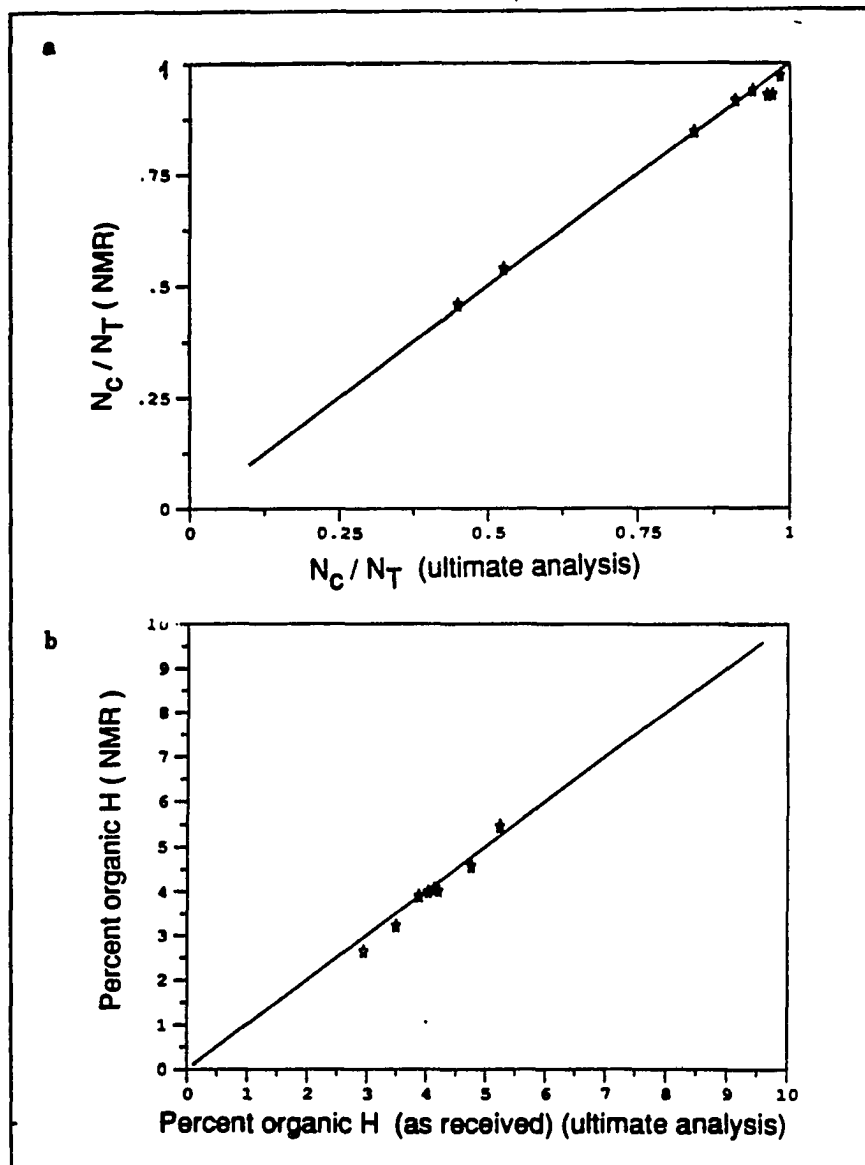
Figure 5. The correlation of the results for quantitation of organic hydrogen in coals by NMR and elemental analysis: (a) The plot of N_C/N_T (NMR) versus N_C/N_T (ultimate analysis); (b) the plot of the weight percent of organic hydrogen from NMR versus the concentration of organic hydrogen from elemental analysis of the coals.
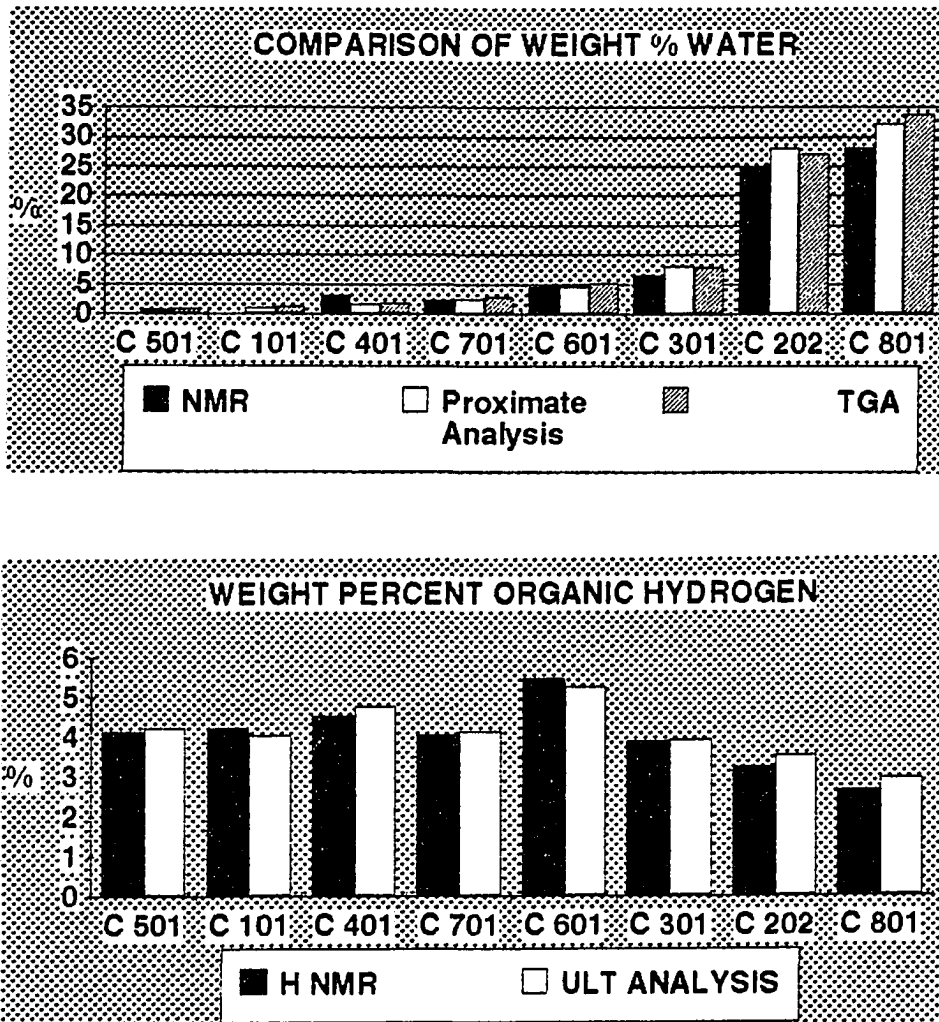
Figure 6.   Comparison of results of quantitation of water and organic
hydrogen in Argonne premium coals by using the techniques of
NMR, ultimate analysis and TGA

1.13%, respectively, the three-component deconvolution of the FID could not be performed. For these two coals, the signals from water are included in the medium components of the decays that consequently have extended values of T_2 (~52 μs).

A similar comparison for the organic hydrogen content of the coal is illustrated in Figures 5a and 5b. Again, the fraction N_C/N_T calculated from NMR data showed very good agreement with the corresponding ultimate analysis data. However, the weight per cent concentrations of hydrogen as inferred from NMR are lower (0-10 %) than the results of elemental analysis (see also Table IV, columns 4 and 5). A possible source of systematic loss of NMR signal is the broadening of the resonance line by the dipolar interaction between protons and unpaired electrons present in organic free radicals in coals. The maximum number of protons made "nonvisible" by the presence of unpaired electrons can be estimated by using the concentration of the free radicals determined by ESR (see column 11, Table III). Assuming the diffusion barrier describing the diffusion of spin polarization to be ~0.8 nm (26) and assuming a uniform distribution of protons and isolated unpaired electrons in the coal, 3% to 6% of protons in the coals were found to be subject to a proton-electron dipolar interaction that would remove their resonance beyond observation. Because of the heterogeneity of coal, a nonuniform distribution of free radicals is likely, which would thus decrease this estimate. However, no correlation exists between the concentration of the free radicals in the coals, as determined by ESR, and the difference observed between the two methods of analysis.

SUMMARY AND CONCLUSION

Solid echo experiments allow the determination of lineshapes and initial intensities of ^{1}H NMR in Argonne coals. A superposition of Gaussian (T_2 ~12 μs) and Lorentzian (T_2 ~20-40 μs) terms adequately described the on-resonance FID of the organic protons in coals. The Gaussian fraction corresponds to rigid protons in the macrostructure of coal. The Lorentzian fraction is ascribed to protons that belong to fragments of the coal framework exhibiting some molecular mobility. For wet coals (>2% moisture content), an additional slowly decaying Lorentzian function must be added to the description of the FID.

The intensities obtained by NMR were compared with concentrations of hydrogen and water obtained via chemical and TGA analyses (see Figure 6). Despite the shortcomings of the methods, the results were found to be in very good agreement. The advantages of NMR are (a) the simplicity of the analysis in which not only the concentrations but also the mobilities of all types of protons in the sample can be analyzed simultaneously; and (b) the possibility of using NMR for on-line measurements where large numbers of samples with considerable volumes are analyzed. The development of a portable ^{1}H NMR spectrometer could combine the above advantages with capability of on-site measurement.

ACKNOWLEDGEMENTS

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PART II.

CHARACTERIZATION OF THE ARGONNE PREMIUM COALS BY USING NMR OF ^{1}H AND ^{13}C AND FTIR SPECTROSCOPY

Characterization of the Argonne premium coals
by using NMR of ^{1}H and ^{13}C and FTIR spectroscopy

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ABSTRACT

Argonne Premium Coal Sample Program (APCSP) coal samples were analyzed by using a variety of transient techniques in solid state NMR of ^{1}H (relaxation measurements, CRAMPS) and ^{13}C (CP/MAS) as well as FTIR spectroscopy. The results of the two techniques were compared and used to infer chemical functionalities of hydrogen and carbon in the APCSP coals. The quantitative validity of the techniques used was evaluated.

Hydrogen and carbon aromaticities of the APCSP coals were measured by using ^{1}H CRAMPS and ^{13}C CP/MAS NMR, respectively, as well as by using FTIR spectroscopy. Hydrogen aromaticity values of the APCSP coals as measured by NMR are consistently higher than the corresponding values obtained from FTIR. Carbon aromaticity values measured by NMR for the bituminous coals corresponded with the FTIR values. However, the carbon aromaticity measured for the younger coals (202 and 801) by using NMR is smaller than the values reported from FTIR measurements. The reproducibility of the values of carbon aromaticity of the APCSP coals measured by NMR was better than 95% for most coals. The use of $(H/C)_{ar}$ and $(H/C)_{al}$ as indicators of coal rank was also evaluated. Hydrogen relaxation time constants reported compared favorably with results from other laboratories.

INTRODUCTION

The major organic constituents of coal are carbon and hydrogen, with oxygen, sulfur, nitrogen and other heteroatoms comprising only a small fraction of the total. Elemental analysis, however, does not give information on the chemical functionalities found in coal. How these atoms are bonded together to make up molecules and how these molecules are linked together to make up the macrostructure[1] of coal is a subject actively pursued by many coal scientists. Various models of coal structure according to rank were proposed, based on the chemical units obtained from mild degradation reactions, that could explain the behaviour of coal during processing. The complexity and heterogeneity[2,3] of coal, however, require that these models portray only an average distribution of chemical functionalities found in coal.[4]

One of the most important compositional parameters describing chemical functionality in coals is aromaticity. The extent to which coal may be described as an aromatic material has been of interest to chemists for many years, even though the concept of aromaticity itself, as applied to coal, has not been clearly defined.[5] The classic textbook definition of an aromatic substance is an organic material whose molecules contain cyclic π-bonding clouds that have a total of six π electrons (the aromatic sextet) and exhibits chemical behaviour similar to that of benzene.[6] X-ray diffraction patterns of high ranking coals showed the presence of graphite-like structures, graphite being the ultimate fused ring aromatic system. Also, chemical degradation

and pyrolysis studies of coals showed that small substituted and unsubstituted aromatic compounds are found in the products. Therefore, by extrapolation, the native coal structure is thought of as a polymeric three-dimensional network of these small aromatic units linked by methylene chains and heteroatoms.[1]

Measures of aromatic character in coals have been considered by van Krevelen[7] who used spacial, optical, electric, magnetic, mechanical, and thermal properties of coal for such considerations, from data compiled prior to 1961. Subsequent to this period, two powerful techniques, namely, high resolution solid state nuclear magnetic resonance (NMR) and Fourier Transform infrared (FTIR) spectroscopy, have been developed which provided analytical information about solid coal that were not available to van Krevelen. NMR is a nondestructive qualitative and quantitative technique which can be used to determine hydrogen and carbon chemical functionalities in organic materials and has been applied to coal and coal products.[8-10] FTIR has all the advantages of an interference spectroscopy in terms of signal averaging and removal of baseline artifacts.[11] It is also a technique that is very sensitive to oxygen functionalities.

The variety of coal sampling techniques, and the complex physical and chemical changes[12,13] that coal undergoes from the moment a coal block is removed from the mine until a representative sample reaches the laboratory, make it difficult to correlate published results of coal studies. There is, therefore, a need[14] to study the same samples in order to compare and collate information and build a coherent picture of coal structure from

independent studies in various laboratories. This led to the development of the Premium Coal Sample Program in 1981 under the supervision of the Argonne National Laboratory (APCSP).[15] The use of these eight APCSP coal samples could permit the standardization of techniques and the examination of factors in the coal itself that would elucidate its nature.

In the present work, the APCSP coal samples were used to investigate quantitative high resolution solid state NMR of ^{1}H and ^{13}C and FTIR spectroscopy in coals. The development of high resolution solid state NMR techniques, such as combined rotation and multiple pulse NMR spectroscopy (CRAMPS),[16] allowed the direct measurement of hydrogen functionalities in coal, thus eliminating the dependence on the results of ^{13}C NMR measurements and assumptions regarding the H/C stoichiometry in coal. CRAMPS overcomes the line-broadening effects of homonuclear ^{1}H-^{1}H dipolar interactions and chemical shift anisotropy in strongly dipolar-broadened solids. CRAMPS experiments provide spectra with the relative intensities of various peaks, even those that are not fully resolved, reliable to within 2 to 3 %, which are useful for quantitation.[17] Also, studies of quantitation of hydrogen by using ^{1}H NMR of the APCSP samples[18] showed that >95% of hydrogen atoms in the sample are observable.

The use of cross-polarization combined with magic-angle spinning (CP/MAS)[19-21] has become the conventional technique for the study of carbon functionalities in organic solids. Much work in recent years addressed the quantitative validity of ^{13}C CP/MAS spectra in solid fuels[22] since a significant fraction (possibly as much as 50%) of carbon may remain

undetected under CP/MAS because of the unfavorable spin dynamics of these materials. The major sources of concern are the high abundance of paramagnetic centers which could shift some of the NMR intensities beyond observation[23] and also result in a broad distribution of relaxation constants involved in polarization-transfer process (T_{CH}, ^1H T_1, ^1H $T_{1\rho}$ and ^{13}C $T_{1\rho}$), and the interference of the rapid sample spinning with the polarization transfer. However, distortion of the ^{13}C CP spectrum at moderate sample spinning rates at or near the vicinity of the Hartmann-Hahn match were observed to be minimal.[24] Recent work[22,24] has also indicated that ^{13}C intensities obtained by using CP/MAS under appropriate conditions agree to within 3% with those obtained under single pulse excitation and strong proton decoupling. "Appropriate conditions" include the use of a static magnetic field which is sufficiently low such that relatively slow spinning eliminates sidebands and reduces the interference of MAS with the CP process, as well as the use of variable polarization-transfer times. The measurement of the carbon aromaticity, f_a, which is the fraction of aromatic sp^2-hybridized carbon atoms, from the ^{13}C NMR spectra of APCSP samples has been carried out by using the CP/MAS technique with the conditions specified above.

This work summarizes our use of a variety of transient techniques in NMR of ^1H and ^{13}C in solid coals and of FTIR to infer average chemical functionalities of the APCSP coals. Proton relaxation data and hydrogen and carbon aromaticities are reported. Aromaticity as a coal rank indicator was explored.

EXPERIMENTAL SECTION

Samples of the eight APCSP coals were obtained from Argonne National Laboratory, Argonne, Illinois. The identification number, source seam, rank, and ultimate analyses[15] of these coals are listed in Table 1. Also presented in the table are the average molecular formula per 1000 carbon atoms that can be calculated from the dry mineral-matter-free (dmmf) composition of the APCSP coals.

Three types of samples, referred to as virgin (as-received), air-dried, and vacuum-dried samples, have been studied in this work. The virgin samples were prepared by transferring coals from the original ampuls to 5-mm NMR tubes (for ^{1}H relaxation studies) or to rotors (for ^{1}H CRAMPS and ^{13}C measurements) under a He atmosphere and sealed. Air-dried samples were obtained from coals which were stored previously at ambient room conditions for several months and studied without further treatment. Vacuum-dried samples were obtained from virgin coals which were evacuated under a static vacuum of 1 millitorr at 100°C for 3 hours.

Most of the NMR spectra were obtained at room temperature by using a home-built spectrometer operating at the Larmor frequencies, ω_0, of 100.06 MHz for ^{1}H and 25.15 MHz for ^{13}C.

Values of T_1 of hydrogen for virgin and air-dried APCSP coals were determined by using inversion-recovery sequence, $180^\circ_y\text{-}\tau\text{-}90^\circ_x$. Two hundred data points were collected for each coal with values of τ incremented between 2 ms and 2000 ms.

Table 1. MAF ultimate analysis of Argonne Premium Coal Sample Program coals[a]

ID	Seam	Rank	AR %H_2O	%C	%H	%N	%S	%O	Ave Formula/1000 C
501	Pocahontas 3, VA	LVB	0.65	91.05	4.44	1.33	0.50	2.47	$C_{1000}H_{581}N_{12}S_2O_{14}$
101	Freeport, PA	MVB	1.13	85.50	4.70	1.55	0.74	7.51	$C_{1000}H_{655}N_{16}S_3O_{40}$
401	Pittsburgh 8, PA	HVB	1.65	83.20	5.32	1.64	0.89	8.83	$C_{1000}H_{762}N_{17}S_4O_{61}$
701	Stockton, WV	HVB	2.42	82.58	5.25	1.56	0.65	9.83	$C_{1000}H_{758}N_{16}S_3O_{59}$
601	Blind Canyon, UT	HVB	4.63	80.69	5.76	1.57	0.37	11.58	$C_{1000}H_{851}N_{17}S_2O_{100}$
301	Illinois 6, IL	HVB	7.97	77.67	5.00	1.37	2.38	13.51	$C_{1000}H_{768}N_{15}S_{11}O_{94}$
202	Wyodak, WY	SB	28.09	75.01	5.35	1.12	0.47	18.02	$C_{1000}H_{849}N_{13}S_2O_{167}$
801	Beulah Zap, ND	L	32.24	72.94	4.83	1.15	0.70	20.34	$C_{1000}H_{788}N_{14}S_4O_{194}$

[a]Abbreviatons used in this table include: LVB = Low volatile bituminous; MVB = Medium volatile bituminous; HVB = high volatile bituminous; SB = subbituminous; L = lignite; AR = as received; MAF = moisture and ash free; % are in weight percent.

Values of $T_{1\rho}$ of hydrogen for virgin and air-dried samples were measured at a radio frequency (rf) field of 50 kHz by using a standard spin-lock sequence. Fifteen to thirty different values of the locking pulse length, varying from 0.01 to 10 ms, were used for each coal. Ten scans at a dwell of 0.5 μs were collected for each free induction decay (FID) observed.

^{1}H CRAMPS experiments at ω_0 of 300 MHz, with virgin and vacuum-dried samples, were performed at room temperature with a Bruker MSL 300 NMR spectrometer. The MREV-8 multiple pulse sequence[25] was used with a 90_x° pulse of 1.5 μs and a cycle time of 42 μs. Each spectrum was a result of 8-36 scans with delay periods of 20 s. T_1's were in fact very short and the 20 s delay was used to protect the spectrometer. The tuning of the spectrometer was controlled prior to each measurement to obtain the same experimental conditions for all spectra. The spinning speeds, v_r, of 3.0-3.5 kHz which were used satisfied the condition $\delta < v_r < (1/\tau_c)$,[26] with δ being the chemical shift anisotropy and τ_c being the cycle time for the homonuclear decoupling pulse sequence.

^{13}C spectra were collected by using quadrature detection with a double-tuned single coil probe equipped with a windmill-type MAS system. The kel-F rotor was filled with ~200 mg sample of air-dried coals and spun at 4-5 kHz with an air drive. The Hartmann-Hahn condition was established at $\omega_1/2\pi$ of 50 kHz and the proton rf field was kept at the same level during the high-power ^{1}H-^{13}C decoupling. CP contact times were varied from 0.05 to 15 ms in the variable-contact-time (vct) experiments. Typically, 5000 to 20000 scans were acquired to obtain a ^{13}C CP/MAS spectrum.

Infrared spectra of the air-dried coals were obtained on a Nicolet model 7199 FTIR spectrometer. The coal samples were further ground in a "Wig-L-Bug" for 20 min. KBr pellets of the coals were prepared by mixing 1 mg of dry, finely ground coal with 300 mg KBr. The 13-mm pellets were pressed in an evacuated die at a pressure of 20000 lbs for 1 min and dried at 110°C for 24 hours to remove water. The spectra were obtained in digital form. Calibration of the infrared spectra of the APCSP coals and corrections for particle scattering and mineral contents were made as described previously.[27]

RESULTS AND DISCUSSION

Hydrogen Relaxation Studies

Relaxation measurements were performed in order to establish appropriate delays for the ^{13}C CP/MAS experiments. However, it is interesting to compare these results with those presented earlier in the literature on the APCSP coals.

$^{1}H\ T_1$ relaxation

Measurements of proton NMR longitudinal relaxation time constants, T_1, were presented and the possible relaxation mechanisms in coals were discussed in a number of papers.[28-33] A detailed examination of the abundant experimental data obtained in this work (one hundred data points for each decay) indicated that a distribution of relaxation times exist in most of the coals studied. Nevertheless, only a two-exponential function, equation (1), was used to analyze the measured decays.

$$M(\tau) = M(\infty)[1 - 2((1-\alpha)\exp(-\tau/T_1{}^s) + \alpha\exp(-\tau/T_1{}^l))] + C, \qquad (1)$$

where $M(\tau)$ is the longitudinal magnetization at time τ after the 180° pulse, $(1-\alpha)$ and α are the fractions of the magnetization characterized by the short and long time constants $T_1{}^s$ and $T_1{}^l$, respectively, and C is a constant. This procedure resulted in reasonable fits (see Figure 1a) and limited the number of parameters involved.
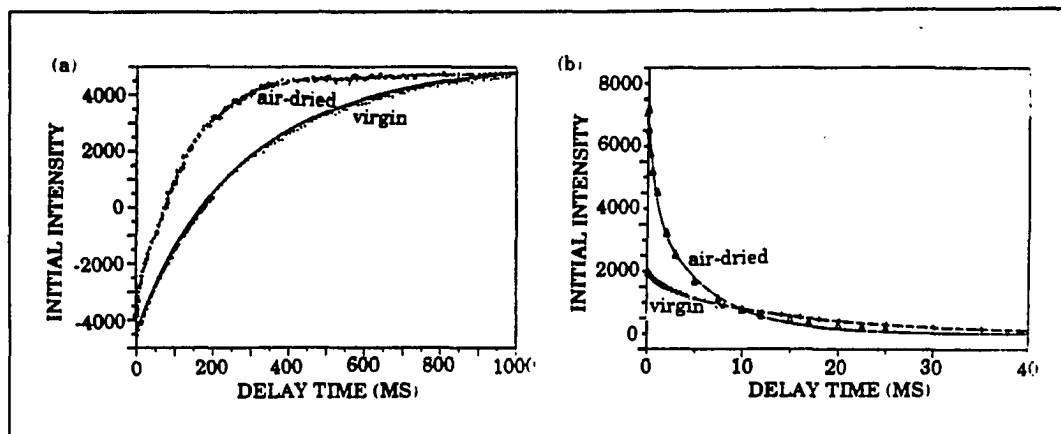
Figure 1. Hydrogen relaxation data and nonlinear least squares fit for virgin and air-dried coal 401 in the (a) laboratory and (b) rotating frame of reference

Since the values of the fractions $(1-\alpha)$ and α scatter considerably among the samples, a mean relaxation time constant, T_1^{av}, defined by

$$(T_1^{av})^{-1} = ((1-\alpha)/T_1^s) + (\alpha/T_1^l), \tag{2}$$

was evaluated, in order to simplify analysis and to make comparison with other literature values easier to accomplish. The results for α, T_1^s, T_1^l, and T_1^{av} are presented in Table 2, columns 3 to 6.

It is evident from Table 2 that the non-exponentiality of the T_1 relaxation in the studied coals increased with decreasing coal rank. The mean relaxation times obtained for the virgin samples are in quite good agreement with the data obtained for the same samples by Solum et al.[34] by using indirect detection of hydrogen by using ^{13}C CP/MAS under proton

decoupling. This agreement seems to indicate that the CP experiments did not significantly prevent the carbon atoms associated with hydrogen atoms which are subject to fast relaxation from being observed. It is also noted that the T_1^{av} values reported in Table 2 are lower than the corresponding values calculated from the ^1H longitudinal relaxation parameters reported for the APCSP coals by Wind et al.[33] at two Larmor frequencies of 60 MHz and 187 MHz. While virgin samples in this work were studied without degassing, Wind's work were on samples that were transferred to NMR tubes under a nitrogen atmosphere and then evacuated to 10^{-3} Torr at room temperature for 24 hours, which sufficed to remove physisorbed H_2O and oxygen.

Although the mechanisms of longitudinal relaxation in coals are not well understood, it seems reasonable to suppose that the non-exponential relaxation in coals is associated with lack of facile spin diffusion between domains of differing T_1. These domains, which could correspond to different macerals, can vary with respect to concentrations and mobilities of hydrogen atoms, as well as concentrations of paramagnetic centers.[35]

Longitudinal relaxation times increased with increasing coal rank. No correlation was found between the relaxation times and the concentration of free radicals as measured by electron spin resonance spectroscopy.[18] However, the relaxation times decreased upon drying the coals in air which is well-illustrated by the mean relaxation times T_1^{av} from Table 2. This effect can be explained by the increase in the concentration of paramagnetic oxygen associated with the samples' exposure to air. These results agree

Table 2. Summary of ^{1}H T_1 and $T_{1\rho}$ of the APCSP coals[a]

Coal ID	Preparation state	α	T_1^s (ms)	T_1^l (ms)	T_1^{av} (ms)	β	$T_{1\rho}^s$ (ms)	$T_{1\rho}^l$ (ms)	$T_{1\rho}^{av}$ (ms)
501	air-dried	0.95	41	345	251	0.49	0.60	4.8	1.05
	virgin	0.87	186	1064	659	0.65	1.96	14.9	4.46
101	air-dried	0.82	116	350	256	0.59	0.47	6.0	1.03
	virgin	0.86	140	621	419	0.77	1.66	17.3	5.43
401	air-dried	0.83	53	147	113	0.58	0.72	6.0	1.46
	virgin	0.70	150	387	263	0.79	1.70	14.9	5.58
701	air-dried	0.40	76	172	98	0.53	0.44	5.5	0.86
	virgin	0.50	96	256	140	0.70	0.76	9.7	2.14
601	air-dried	0.19	34	132	40	0.50	0.44	5.5	0.82
	virgin	0.41	44	111	58	0.71	1.16	11.4	3.19
301	air-dried	0.28	33	94	40	0.51	0.84	6.6	1.52
	virgin	0.38	48	133	64	0.71	1.54	12.7	4.08
202	air-dried	0.38	3.1	14	4.4	0.58	0.44	4.8	0.93
	virgin	0.46	3.1	16	4.9	0.45	0.77	6.8	1.30
801	air-dried	0.46	1.9	12	3.1	0.49	0.27	3.9	0.50
	virgin	0.41	4.3	16	7.0	0.58	0.23	4.6	0.51

[a]Deviations for T_1 and $T_{1\rho}$ range from 3 to 25%; for f^l and f_ρ^l, 3 to 20%.

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with the earlier conclusions of Wind et al.[33] that the presence of
chemisorbed paramagnetic oxygen (not removed by vacuum-pumping) or
unpaired electrons residing in oxygen,[35] provides a relaxation mechanism
that dominates over other mechanisms especially in the lower rank coals.
In higher rank virgin coals (501 and 101), the ^{1}H-^{1}H dipolar coupling and
the interactions of the ^{1}H nuclei with free radicals are the primary
relaxation mechanisms.

^{1}H $T_{1\rho}$ relaxation

To calculate values of $T_{1\rho}$, the longitudinal relaxation time constant in
the rotating frame, the data collected from proton spin-lock experiments
were fitted to an equation of the form,

$$M_\rho(\tau) = M_\rho(0)[(1-\beta)\exp(-\tau/T_{1\rho}{}^S) + \beta\exp(-\tau/T_{1\rho}{}^l)], \qquad (3)$$

where $M_\rho(\tau)$ is the magnetization in the rotating frame at time τ after the
spin-locking pulse, $(1-\beta)$ and β are the fractions of the magnetization
characterized by the time constants $T_{1\rho}{}^S$ and $T_{1\rho}{}^l$, respectively. Figure 1b
illustrates, by using coal 401, a typical set of data points and the nonlinear
least squares fit. An equation similar to equation (2) was used to calculate a
$T_{1\rho}{}^{av}$. Results are collected in Table 2, columns 7 to 10.

Generally, $T_{1\rho}$ relaxation follows a similar trend to that found for T_1.
Again, a close examination of the data indicated the existence of a
distribution of $T_{1\rho}$ values for the coals studied. However, by using equation

(3) satisfactory fits were still obtained. For virgin coals, the values of $T_{1\rho}{}^{av}$ increase with increasing rank from 0.5 to ~5 ms with $T_{1\rho}{}^{s}$ and $T_{1\rho}{}^{l}$ ranging from 0.23 ms to 2 ms and from 4.6 ms to 17 ms for lowest rank and highest rank coals, respectively. For air-dried coals, the relaxation times do not depend very strongly on the coal rank, and are strongly reduced relative to the results on the virgin coals, by a factor of 3 to 5, for all samples except for lower rank coals 202 and 801. It is noted that a significant portion of hydrogen atoms in coals exhibited very fast $T_{1\rho}$ relaxation. Values of $T_{1\rho}{}^{s}$ of 0.3 ms to 0.8 ms with the corresponding fractions of ~50% were found for air-dried coals. This result means that a large fraction of hydrogen atoms cannot contribute to carbon polarization in the ^{13}C CP/MAS NMR experiments at longer contact times. A good agreement between the $T_{1\rho}{}^{l}$ data presented for virgin coals and the $T_{1\rho}$'s obtained from the single exponential analysis of the variable-contact-time CP/MAS spectra of the same coals by Solum et al.[34] supports the last statement. Similarly for air-dried coals, the $T_{1\rho}{}^{l}$ values from Table 2 are in good agreement with the $T_{1\rho}$ data listed in Table 4 for the same coals from vct ^{13}C CP/MAS experiments, discussed later in this work.

NMR Measurements

^{1}H CRAMPS and hydrogen functionalities

The reactivity of coal is a function of the concentration of its aliphatic functionalities. For instance, during the primary stages of coal devolatilization, the depolymerization process consumes hydrogen atoms

donated by the labile aliphatic fraction of the coal. Also, the computer-aided prediction of the tar yield from this process by the DVC model[36] depends on the value of the fraction of aliphatic hydrogen atoms. Another reaction parameter that showed strong correlation to this fraction is the activation energy of the hydroliquefaction of bituminous coals.[37] The fraction of aliphatic hydrogen and its complement, the fraction of aromatic hydrogen, are directly measurable from the CRAMPS spectra of coals.

The resolution in the ^{1}H CRAMPS spectra of fossil fuels is rather limited due to broad distributions of chemical shifts. Since the application of extended pulse sequences, like the BR-24,[37] does not lead to enhanced resolution, the simpler MREV-8 pulse sequence was used in the present studies. The ^{1}H CRAMPS spectra obtained for the virgin and vacuum-dried premium coals are presented in Figure 2. For coals with low water content in the 'as-received' state, the spectra of dried and virgin samples are similar. The two overlapping bands centered at ~2.0 ppm and at ~7.5 ppm are assigned to aliphatic and aromatic hydrogen atoms, respectively.

The presence of physisorbed water in the virgin samples of coals 801, 202, and 301 is strongly manifested in the CRAMPS spectra of these coals. This is in agreement with the results of single pulse NMR experiments, in which sharp peaks with widths ranging from 7 ppm to 11 ppm at a chemical shift identical to that of liquid water (~5 ppm downfield from TMS) were observed.[18] For coal 301, only a small peak at ~5 ppm could be observed in its CRAMPS spectra, but in the spectra of coals 202 and 801 the water peak obscured resolution of the spectrum such that aliphatic and aromatic bands
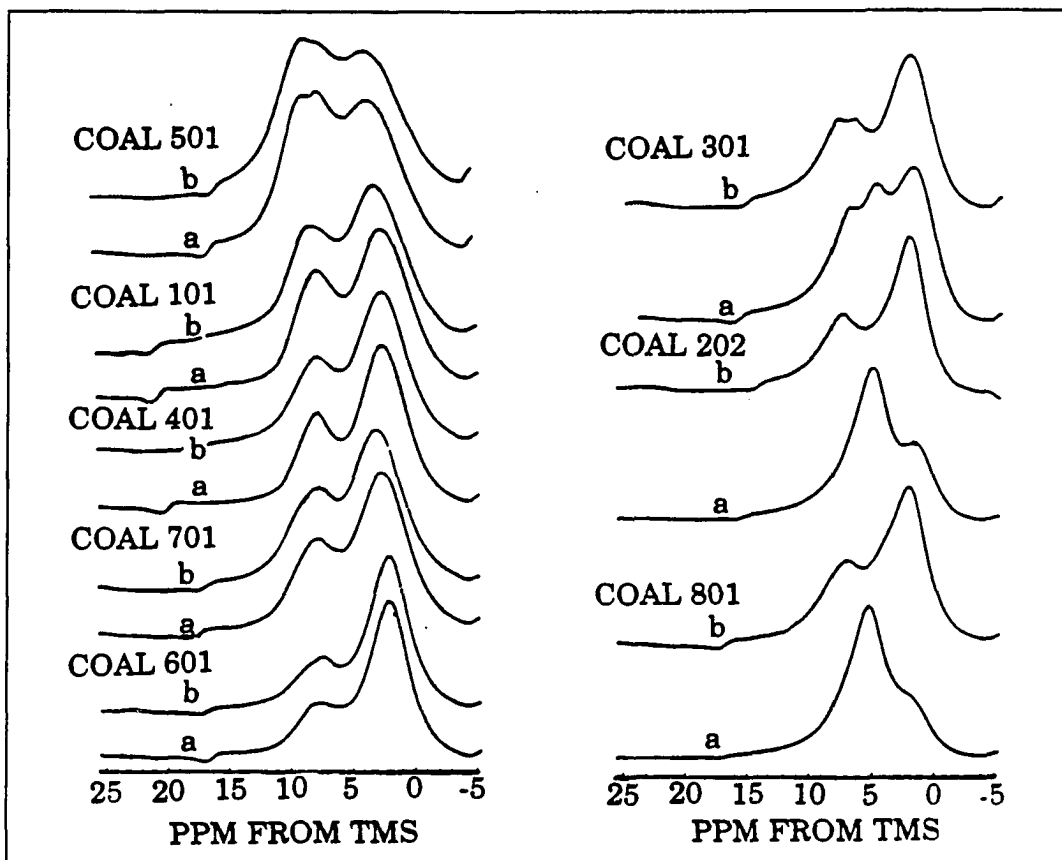
Figure 2. The ^{1}H CRAMPS spectra of the APCSP coals: (a) virgin and (b) vacuum dried

could not be distinguished. The slow isotropic motion of the mobile water molecules adsorbed by these coals, although sufficient to produce a fairly narrow line in single pulse experiments, interfered with the multipulse decoupling. The rate of multiple pulse coherent averaging must be greater than the correlation frequency of the molecular motion before narrowing of the lines can be achieved.[26] It is therefore necessary to examine the spectra

of the vacuum-dried samples in order to determine hydrogen functionalities in coals using CRAMPS. For the computer-aided deconvolution of the spectra, a superposition of two Lorentzian lines were assumed,

$$F(\omega) = M_{ar}/[(\omega-\omega_{ar})^2 + (\Delta\omega_{ar})^2] + M_{al}/[(\omega-\omega_{al})^2 + (\Delta\omega_{al})^2], \quad (4)$$

where M_{ar}, M_{al}, ω_{ar}, and ω_{al} are the amplitudes and positions of the aromatic and aliphatic peaks, respectively, $\Delta\omega_{ar}$ and $\Delta\omega_{al}$ are the second moments of those peaks. Subsequently, the hydrogen aromaticities, H_a, were calculated by using the equation,

$$H_a = (M_{ar}\Delta\omega_{ar})/(M_{ar}\Delta\omega_{ar} + M_{al}\Delta\omega_{al}), \quad (5)$$

The deconvolution-fitted shifts and linewidths for aliphatic and aromatic hydrogen atoms and the hydrogen aromaticities are listed in Table 3, columns 3, 4, 5, 6, and 7. The hydrogen aromaticities (o) are plotted against per cent oxygen (as a rank parameter) as presented in Figure 3. Values of H_a for the bituminous APCSP coals[37] measured by ^{1}H CRAMPS at 187 MHz by using BR-24 pulse sequence at a 90_x of 1.1 μs and a cycle time of 36τ =108 μs are also indicated (□) in Figure 3. There is a fairly good agreement between these two sets of data.

Table 3.   Parameters calculated from the CRAMPS spectra of the APCSP coals and the hydrogen aromaticity[a]

Coal		Aliphatic Hydrogen		Aromatic Hydrogen		H_a
		Shift (ppm)	Width (ppm)	Shift (ppm)	Width (ppm)	
501	dry	2.5	2.8	7.8	3.1	0.57
	virgin	2.3	2.4	7.5	3.0	
101	dry	2.4	2.2	7.6	2.6	0.46
	virgin	2.1	2.2	7.6	2.0	
401	dry	2.4	2.2	7.9	2.3	0.40
	virgin	2.3	2.0	7.8	1.8	
701	dry	2.8	2.3	8.3	2.5	0.39
	virgin	2.4	2.3	7.9	2.3	
601	dry	2.2	1.8	8.0	2.4	0.37
	virgin	2.2	1.8	7.9	2.4	
301	dry	2.4	1.8	7.8	2.8	0.47
	virgin	2.0	1.7	7.5	2.4	
202	dry	2.3	1.5	7.5	2.8	0.47
	virgin[b]	1.8	1.6	7.3	2.4	
801	dry	2.2	1.7	7.1	2.9	0.46
	virgin[b]	2.3	1.7	7.1	1.9	

[a]Band centers and band widths were determined to ±.1 ppm; deviations for hydrogen aromaticity values range from ±0.01 for coal 501 to ±05 for coal 801.

[b]The fitting of these spectra were done with the use of the parameters for the corresponding dry coal spectra.
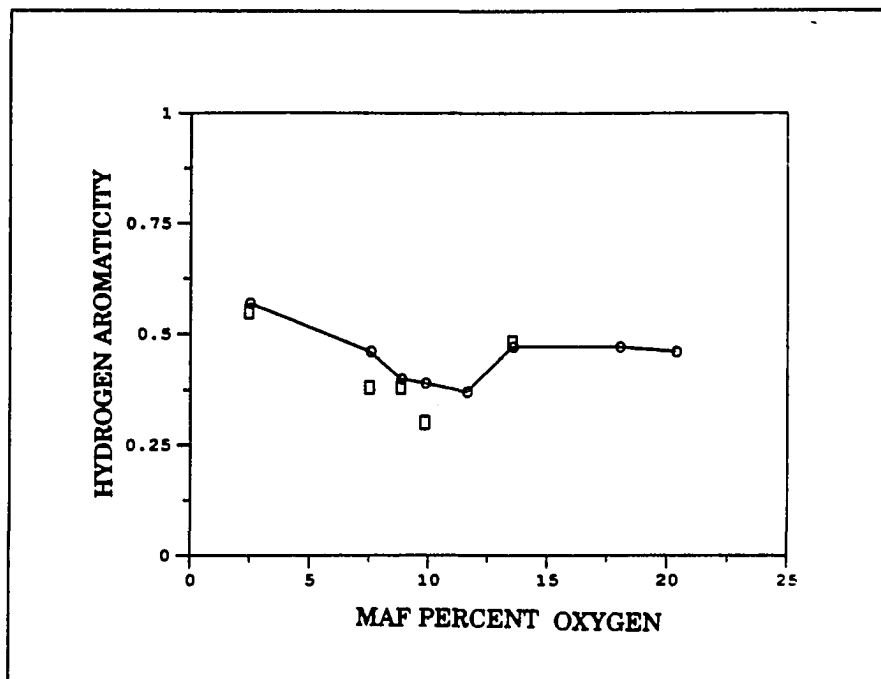
Figure 3.   The hydrogen aromaticity of the APCSP coals measured by
            CRAMPS at 300 MHz by using MREV-8 (o) and at 187 MHz by
            using BR-24 (Shin et al.[38]) (□)

^{13}C CP/MAS measurements and carbon functionalities

Typical CP/MAS spectra of ^{13}C obtained by using a polarization

transfer time of 1.5 ms are shown in Figure 4. As with the ^{1}H CRAMPS

NMR, the heterogeneous nature of coal precludes observation of the type of

relatively sharp ^{13}C NMR spectra appearing in well-defined chemical

structures. Instead, the ^{13}C spectrum obtained with CP/MAS exhibit two

distinct, but rather broad peaks located in the aliphatic and aromatic
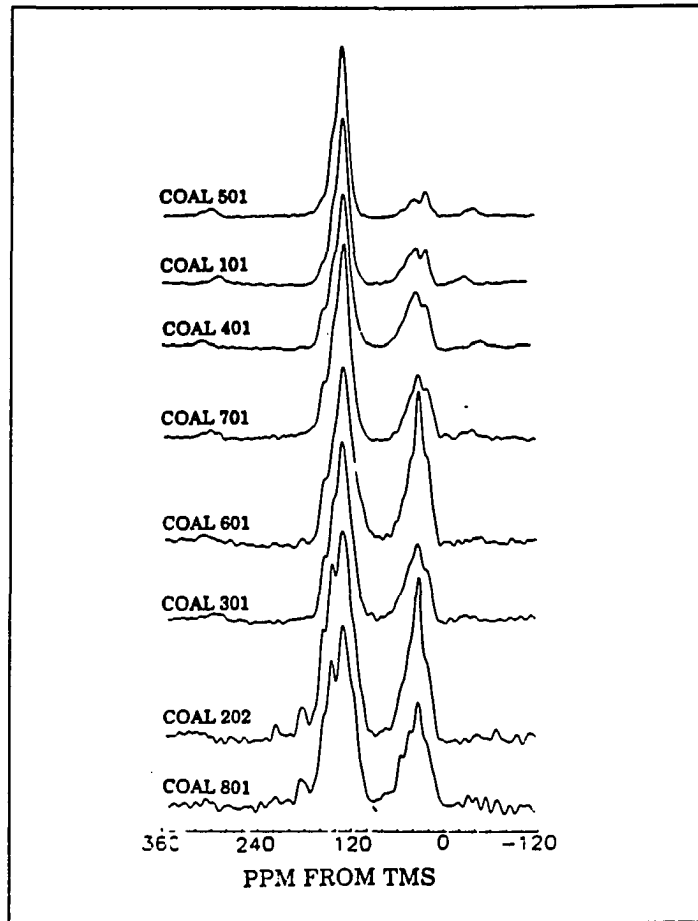
Figure 4. ^{13}C NMR CP/MAS spectra of the APCSP coals at a polarization transfer time of 1.5 ms

regions of the spectrum, representing a wide distribution of various bond types and functionalities. Typical line widths observed are 20-40 ppm. With appropriate signal-to-noise ratios, both aromatic and aliphatic peaks are seen to exhibit some fine structures. The intense and clearly separated resonance at ~20 ppm can be assigned to methyl groups, whereas another

distinct peak at ~33 ppm originates from methylene resonances. In the aromatic region, at least three distinct resonances can be found. A line at ~128 ppm corresponds to benzene-like protonated carbon atoms, lines at ~145 and ~155 ppm are attributed to carbon atoms bonded to other carbon atoms and to oxygen atoms, respectively. In some cases, as in the spectra of coals 202 and 801 (see Figure 5), a distinct peak at 180-200 ppm is observed which represents carbon atoms in carbonyl groups.

A detailed study on the quantitative reliability of ^{13}C CP/MAS NMR conducted recently in the authors' laboratory[18,24] for coal 401 indicated that the carbon aromaticity values of 0.68 and 0.70 obtained at ω_0 of 25.16 MHz for ^{13}C from two independent variable-contact-time (vct) experiments agreed within the experimental error with the value of 0.70 obtained by the use of a time-consuming Bloch decay experiment in which 94% (±5%) of all carbon atoms were detected. With the assumption that these results applied to the other APCSP coals, the carbon aromaticities of the APCSP coal samples were determined from their ^{13}C CP/MAS spectra.

To evaluate carbon aromaticities from the vct experiments,[22] the two broad peaks in each spectrum were divided into the two regions, below (upfield from) and above (downfield from) from 80 ppm (where the signal intensity is almost zero), ascribed to aliphatic and aromatic carbon atoms, respectively. The integrated area of each peak, $M(\tau_{cp})^i$ (i = al, ar) was plotted against contact time, τ_{cp}, and the data were used to extract the initial aliphatic and aromatic magnetizations M_0^{al} and M_0^{ar}, respectively, by extrapolation to $\tau_{cp} = 0$ by using the equation[39]

Table 4. ^{13}C CP/MAS vct experimental parameters and calculated carbon aromaticity values of the APCSP coals

Coal ID	Source seam	$T_{1\rho}^{al}$ (ms)	$T_{1\rho}^{ar}$ (ms)	f_a ±0.01	$f_a(1.5)^a$ ±0.01	f_{co} ±0.01
501	Pocahontas #3	3.1	4.6	0.86	0.87	0.0
101	Upper Freeport	3.8	4.5	0.80	0.79	0.0
401	Pittsburgh #8	3.8	5.2	0.71	0.72	0.0
701	Stockton	2.9	4.0	0.73	0.74	0.01
601	Blind Canyon	4.1	3.9	0.63	0.62	0.01
301	Illinois #6	4.3	5.1	0.70	0.69	0.03
202	Wyodak	2.9	3.5	0.60	0.64	0.06
801	Beulah Zap	2.4	3.7	0.58	0.63	0.08

^{a}Aromaticity calculated from spectra at 1.5 ms contact time.

$$M(\tau_{cp})^i = M_0^i \exp(-\tau_{cp}/T_{1\rho}^i)[1-\exp(-A\tau_{cp}/T_{CH}^i)], \qquad (6)$$

where the initial magnetization is the ^{13}C magnetization that would be observed at long contact times provided the proton polarization is constant, $A = 1 - T_{CH}/T_{1\rho}^i$, and T_{CH}^i is the time constant for polarization transfer. The carbon aromaticity, f_a, is calculated from the ratio

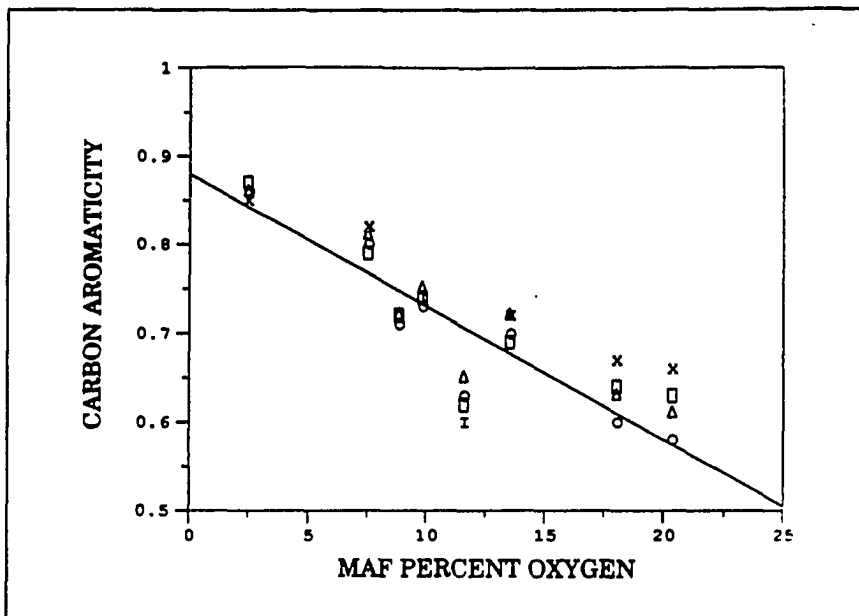$$f_a = M_0^{ar}/(M_0^{ar} + M_0^{al}). \qquad (7)$$

Figure 5.   The carbon aromaticity of the APCSP coals at 25 MHz as
calculated from vct CP/MAS experiments (o) and from CP/MAS
spectra at a single contact time of 1.5 ms (□) is plotted against
% oxygen (MAF) as rank indicator; also indicated are f_a from vct
experiments of Solum et al.[34] (△), from spectra at a single
contact time by Botto and Axelson (X)[40] and by Choi et al. (I)[41];
the least squares fit is for (o)

The $T_{1\rho}$ for aliphatic and aromatic hydrogen atoms, calculated from the vct

experiments for the APCSP coals are presented in Table 4, columns 3 and 4.

The carbon aromaticity calculated from (7) are listed in column 5. Values of

f_a obtained from the spectrum at a contact time of 1.5 ms are also listed

(column 6).

Values of f_a for the APCSP coal samples as measured by using ^{13}C NMR vct CP/MAS under the conditions specified previously from this work (o) and those reported earlier by Solum et al.[34] ($\triangle$) are plotted in Figure 5 versus weight % oxygen (MAF). Also shown in Figure 5 are values of f_a calculated from a CP/MAS spectrum obtained in the present work with a single contact time of 1.5 ms ($\square$). Also included in Figure 5 are values reported by Botto and Axelson[40] for five of the APCSP coals (X), and by Choi et al.[41] for two other APCSP coals (I), calculated from a CP/MAS spectrum with a single contact time of 1.5 ms and 2 ms, respectively. The plot illustrates that the values of f_a derived from ^{13}C CP/MAS spectra measured under the conditions specified previously reported by different laboratories have a reproducibility of more than 95%.

FTIR Measurements

Before discussing the FTIR results we emphasize that NMR counts the nuclei of interest directly with no assumption made about the structure of the sample. The chemical shift identifies the electronic environments of the different nuclei. As such, NMR is an excellent quantitative analytical technique for coal despite the difficulties mentioned previously. It will be used, therefore, to evaluate the quantitation analysis results from FTIR because of FTIR's reliance on assumed average stoichiometry, and with extinction coefficients being rank dependent, and on average extinction coefficients as well.

Qualitatively, FTIR is capable of distinguishing the different
functionalities of carbon, hydrogen and oxygen in a coal sample. Aromatic
hydrogen atoms and their positions in the aromatic ring could be identified
as well as methyl, methylene, and methine hydrogen and carbon atoms.
Oxygen-bearing hydrogen and carbon atoms, such as -OH and -C=O are
easily observed in an infrared spectrum because of their large extinction
coefficients. In contrast, ^{1}H CRAMPS spectra are not well resolved and
unless the -OH concentration in the solid sample is high, there are only two
peaks obtained from a mathematical deconvolution of the bands that are
compatible with the nature of the sample.

The IR spectra (corrected for absorption of mineral matter) in
absorbance units for 1 mg of coal in a 1.33 cm^2 pellet, of the APCSP coals
are presented in Figure 6. The spectra are vertically displaced and
arranged in order of rank with the highest rank coal at the top. It has been
shown that all coals measured in this and previous studies,[42,43] have
spectra which could be synthesized by varying only magnitudes of a set of
Gaussian functions whose widths and positions were held constant. To
obtain quantitative measure of functional group concentrations, a curve
analysis program[11] was used to synthesize the IR spectra by adding forty-
five absorption peaks with Gaussian shapes and variable positions, widths,
and heights. Weight % concentrations of aliphatic and aromatic hydrogen
and carbon functionalities, and hydroxyl hydrogen atoms of the APCSP
coals were obtained from their quantitative infrared spectra using peak
areas determined by the synthesis routine and rank-dependent absorptivity.
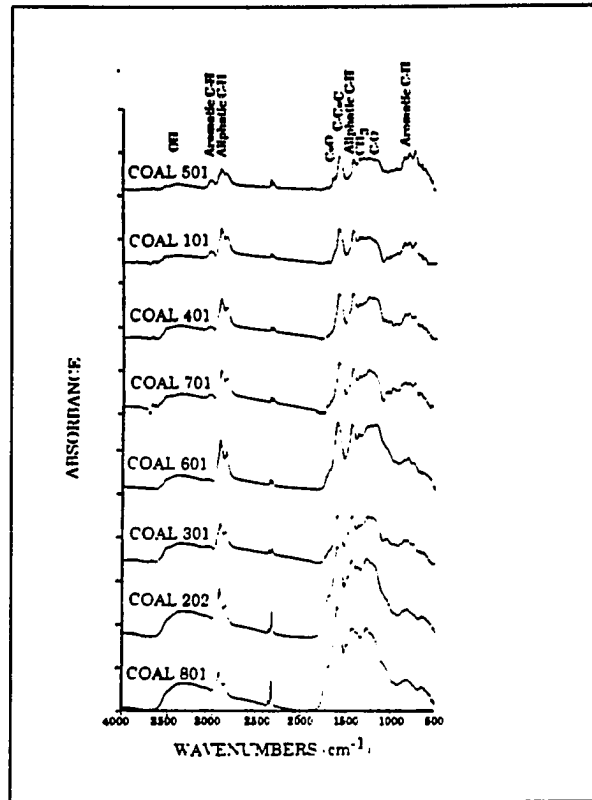
Figure 6. The FT infrared spectra of dry APCSP coals after the removal of the absorption of mineral matter

The weight % concentration of hydroxyl hydrogen atoms, H_{oh}, was estimated directly from the absorption band centered at ~3200 cm^{-1}. The weight % concentrations of aliphatic and aromatic hydrogen atoms, H_{al} and H_{ar}, were obtained from peaks near 2900 cm^{-1} and 800 cm^{-1}, respectively. The results for the MAF weight % concentrations of the functionalities of hydrogen and the total weight % hydrogen, H_t, and the calculated hydrogen aromaticity, $H_a(IR)$, are summarized in Table 5, columns 2-6.

Table 5. Weight % concentration of hydrogen and carbon (MAF) in the APCSP coals as determined by FTIR[a]

	Hydrogen					Carbon					Oxygen	
Coal	H_{al}	H_{oh}	H_{ar}	H_t	$H_a(IR)$	C_{al}	C_{ar}	C_t	$C=O^a$	$f_a(IR)$	O_{oh}	O_{eth}
501	1.97	0.06	2.19	4.22	0.52	14	77	91	1.92	0.85	1.0	1.25
101	3.43	0.11	2.08	5.62	0.37	23	64	87	0.63	0.74	1.75	0.75
401	3.60	0.16	2.07	5.83	0.36	24	59	83	0.86	0.71	2.5	1.88
701	3.48	0.23	2.12	5.83	0.36	23	58	81	3.59	0.72	3.75	1.75
601	4.79	0.16	1.90	6.85	0.28	32	47	79	8.70	0.60	2.5	4.0
301	3.41	0.23	2.07	5.71	0.36	23	54	77	4.48	0.70	3.75	2.25
202	3.03	0.33	1.73	5.09	0.34	20	54	74	23.86	0.73	5.25	5.0
801	2.02	0.34	1.58	3.94	0.40	13	60	73	24.67	0.82	5.5	5.0

[a]Except carbonyl: relative peak area in absorbance units x cm^{-1}.

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The weight % concentrations of aliphatic carbon, C_{al}, were inferred from the corresponding peaks by assuming that the average stoichiometry for aliphatic material in coal is $CH_{1.8}$. This value is the average of values reported in the literature.[11] The weight % concentration of aromatic carbon atoms, C_{ar}, which included carbonyl carbon atoms, was determined by difference, $C_{ar} = C_t - C_{al}$, where C_t is the total weight % concentration of carbon. The results for the MAF weight % concentrations of the carbon functionalities, total weight % carbon, and the calcultated carbon aromaticity are listed in Table 5, columns 7-9 and 11. In addition, the carbonyl and carboxyl relative absorption intensities and the weight percentages of oxygen functionalities that could be calculated from these data are included in the table.

Recent research in quantitative infrared spectroscopy indicates that the weight % concentrations of aliphatic hydrogen, H_{al}, and hydroxyl hydrogen, H_{oh}, can be determined to within ± 10%. The accuracy of the determination of the weight % of aliphatic hydrogen depends on the accuracy of the assumed stoichiometry of aliphatic hydrogen to aliphatic carbon, $(H/C)_{al}$. The weight % of aromatic hydrogen, H_{ar}, can be obtained to an accuracy of ±10% for coals with carbon content above 85 weight %, but variations of up to ±50% arise for coals with lower carbon concentrations.[43]

Quantitation of Hydrogen and Hydrogen Functionalities

In Table 6 and Figure 7, the results of total hydrogen concentration obtained in this work by FTIR are listed and compared with ultimate

Table 6.   Comparison of weight % (MAF) concentration of hydrogen in
            the APCSP coals

Coal ID	Analytical Technique		
	Ultimate analysis[a]	NMR(±0.1)[b]	FTIR(±0.1)
501	4.44	4.2	4.2
101	4.70	4.9	5.6
401	5.32	5.1	5.8
701	5.25	5.2	5.8
601	5.76	6.0	6.8
301	5.00	4.9	5.7
202	5.35	4.7	5.1
801	4.83	4.1	3.9

[a]Data listed are from Table 1, column 6.

[b]Data were calculated from the proton spin counting experiment.[18]

analysis data[15] and with results of ^{1}H spin counting by NMR from our
earlier work.[18] The experimental aspects and the accuracy of quantitation
of hydrogen in coals by NMR were discussed in detail in reference 18. It
was found that despite the shortcomings of NMR and ultimate analysis
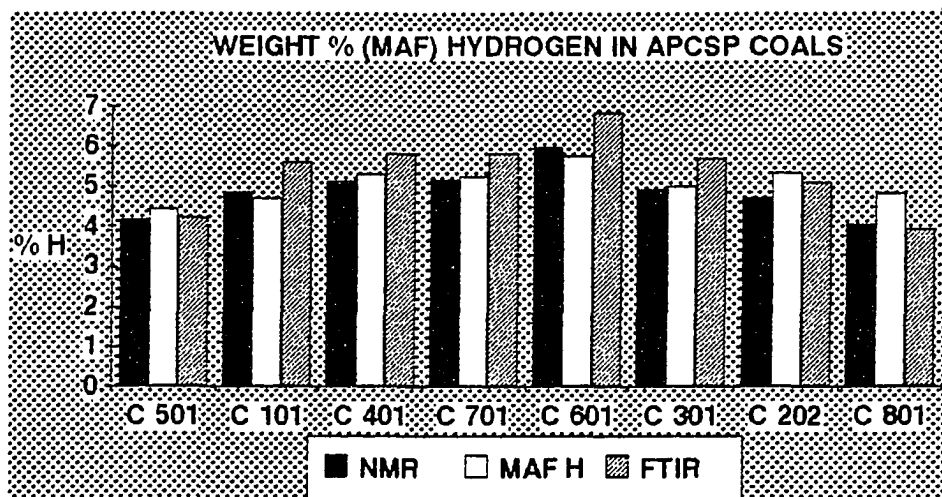procedures, the results obtained by using these two methods differed by less

Figure 7.   Comparison of the results of the quantitation of hydrogen in the APCSP coals by using FTIR spectroscopy, by using elemental analysis[15], and by using ^{1}H NMR[18]

than %5 for all coals except 202 and 801. On the other hand, FTIR yielded H_t values differing by less than 20% from the results of the other two methods. It is noted that for medium and high volatile bituminous coals, the concentrations derived from FTIR were the highest of the three values.

Hydrogen aromaticity of the APCSP coals calculated from the two spectroscopic techniques are presented in Figure 8. Four sets of hydrogen aromaticity values were compared: (a) H_a from CRAMPS (column 7, Table 3), (b) hydrogen aromaticity derived from FTIR with includion of hydroxyl hydrogen contribution, $[(H_{ar} + H_{oh})/H_t]$, (columns 3, 4, and 5, Table 5), (c) H_a from CRAMPS corrected for hydroxyl hydrogen as measured by FTIR
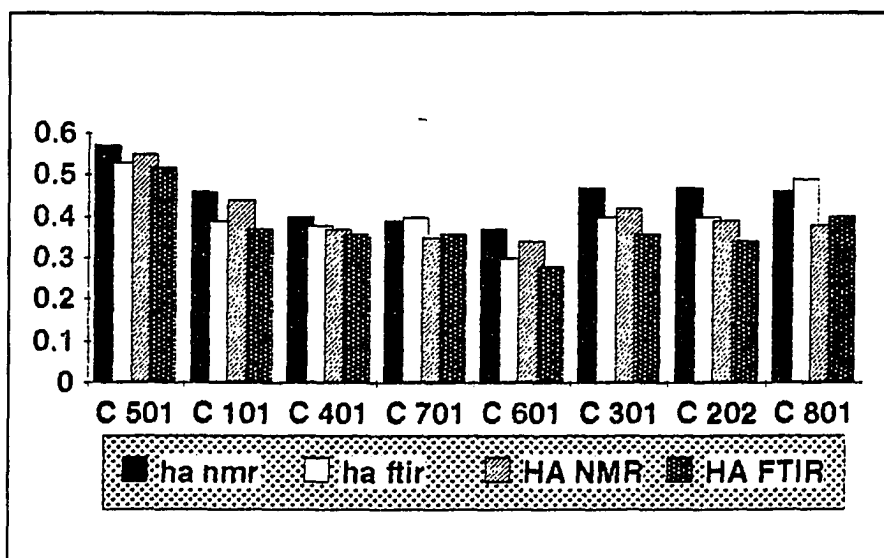
Figure 8.   Comparison of the hydrogen aromaticity values of the APCSP
coals determined by using ^{1}H CRAMPS and FTIR spectroscopy
showing the inclusion of -OH intensities (ha nmr and ha ftir)
and the exclusion of -OH intensities (HA NMR and HA FTIR)

$[H_a \times (H_{ar}/(H_{ar} + H_{oh})]$, and (d) H_a(IR) from FTIR (column 6, Table 5).

There is good agreement between the NMR and FTIR values. The extent of

-OH contribution is negligible for high rank coals, and increases with

decreasing rank. Correcting NMR H_a values for hydroxyl hydrogen

obtained from FTIR results seems to be the most accurate method in

determining the average hydrogen aromaticities of coal. This method

combines the CRAMPS results which are independent of any assumptions

about stoichiometry of hydrogen to carbon and the FTIR's sensitivity to
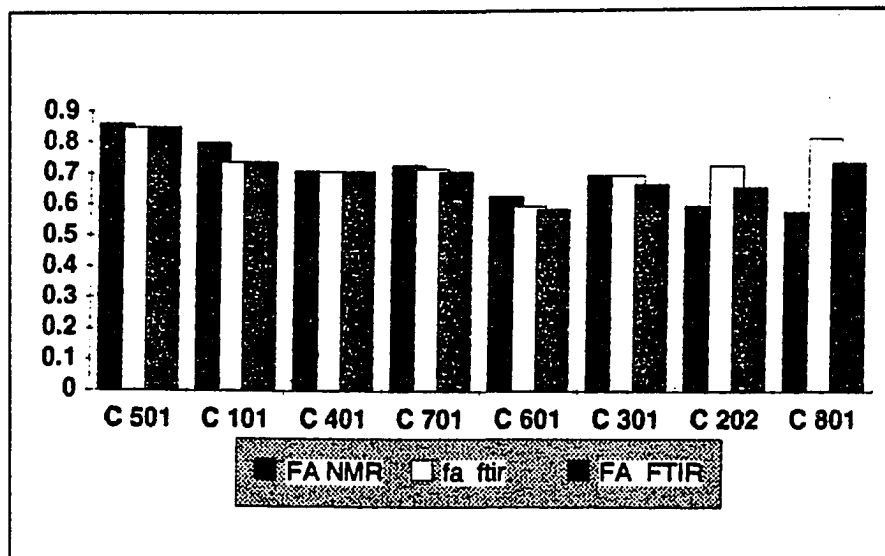
oxygen functionalities.

Figure 9.   Comparison of the carbon aromaticity values of the APCSP coals
as calculated by using FTIR with the values calculated by using
^{13}C NMR CP/MAS

One may also use the ^{13}C intensities at ~165 ppm for >C=O and

-COOH and calculate the concentrations of -OH hydrogen.[34] However, the

resolution of the ^{13}C CP/MAS spectra is not sufficient to do this accurately.

Another method of calculation makes use of ^{13}C NMR dipolar dephasing

experiments[5,44] and ultimate analysis data. The results of hydrogen

aromaticity inferred from this method were in good agreement with the

values for high rank coals but rather in poor agreement with the low rank

coals.

Quantitation of Carbon Functionalities

As indicated earlier, the FTIR calculation of the carbon aromaticity

included >C=O and -COOH intensities to the aromatic carbon absorption

intensities. The FTIR spectra of all APCSP coals showed that the absorption intensities >C=O and -COOH increased with decreasing coal rank (see Figure 6). The strong dependence of the extinction coefficient of these functionalities on coal rank makes quantitation of the absorption peaks difficult. If oxygen functionalities in coal are limited to hydroxyl, carbonyl, carboxyl, and ether linkages, then a rough estimate from weight % oxygen (MAF)[15] and FTIR quantitation of hydroxyl and ether oxygen (Table 5, columns 12 and 13, gives the amount of oxygen present as >C=O and -COOH to be >40% of total oxygen for all coals except for coal 501, where it is <1%. By this method, contributions to the aromatic carbon intensities coming from carbonyl and carboxyl groups to the f_a(IR) were estimated to range from ~0% for coal 501 to ~16% for coal 801.

The fraction of aromatic carbon atoms, C_{ar}, may be directly obtained from the ^{13}C NMR of coals by correcting for the >C=O and -COOH resonances downfield of 170 ppm (see Table 4, column 7). Also, the NMR technique of dipolar dephasing[5,44] may be used to estimate the concentration of carbonyl and carboxyl carbon in these samples. In a manner similar to the correction of hydrogen aromaticity values, the FTIR-derived carbon aromaticity values may be corrected for >C=O and -COOH contributions. Figure 9 shows the comparison of the carbon aromaticity derived from these two spectrophotometric techniques.

$(H/C)_{ar}$ and $(H/C)_{al}$ as Indicators of Rank

The American Society for Testing Materials (ASTM) classifies North American coals into four major groups according to rank (a measure of the degree of maturation). These groups are (from oldest to youngest) anthracitic, bituminous, subbituminous, and lignite. The scheme (ASTM D 388-66) ranks the older coals on the basis of their volatile matter and fixed carbon contents which must be >31% and <69% (on dmmf basis), respectively. The younger coals are ranked on the basis of their heating value expressed in Btu/lb of mineral-matter-free "moist" coal.[45] Note that the APCSP coals from the eastern region of the United States are older than the coals from the western region. Chemical and physical properties of coals vary systematically with rank and can be broadly predicted on the basis of the fixed carbon content and volatile matter, or the ultimate analysis of the whole coal.

NMR offers an analytical technique by which rank can be determined in terms of "aromaticity". Weight % oxygen as a rank parameter was chosen for comparison purposes because of the known correlation between age and oxygen content in coals.[46] Carbon aromaticity as a rank indicator is tested by plotting the values of f_a (o) against weight percent oxygen (MAF), P, (see Figure 5). The data fit the linear regression equation

$$f_a = -0.015P + 0.88 \tag{8}$$

with a coefficient of correlation of -0.93. (A perfect correlation corresponds

Table 7.   Summary of properties of the APCSP coals

Coal ID	H_a	f_a	$(H/C)^a$	$(H/C)_{ar}$	$(H/C)_{al}$	$\chi_b{}^b$	C per ring	No. of rings	No. of subst
501	0.57	0.86	0.58	0.38	1.78	0.40	19-21	5	4-5
101	0.46	0.80	0.65	0.38	1.77	0.36	16-18	4	4-5
401	0.40	0.71	0.76	0.43	1.58	0.31	13-18	3-4	3-4
701	0.39	0.73	0.76	0.41	1.71	0.29	13-14	3	3-5
601	0.37	0.63	0.85	0.50	1.45	0.31	13-14	3	2-3
301	0.47	0.70	0.77	0.52	1.36	0.31	13-14	3	2-3
202	0.47	0.60	0.85	0.67	1.13	0.29	10, 14	2-3	1-2
801	0.46	0.58	0.79	0.63	1.01	0.17	6, 10	1-2	1-2

[a]Ratios are calculated from ultimate analysis data.[15]
[b]Values adopted from Solum et al.[34]

to a coefficient of correlation equal to unity. A negative value corresponds to a negative slope).[47] The deviation of f_a of coal 601 from the line of regression stems from the high fraction of the maceral sporinite[15] found in this coal.

Combining the fractions H_a and f_a with the atomic hydrogen to carbon ratio H/C from the ultimate analysis[15] data (or from NMR spin counting experiments[18,24]) for the APCSP coals yields the aromatic and aliphatic hydrogen to carbon ratios, $(H/C)_{ar}$ and $(H/C)_{al}$, respectively, which can be calculated by using the following equations,

$$(H/C)_{ar} = (H_a/f_a)(H/C), \text{ and} \tag{9a}$$

$$(H/C)_{al} = [(1-H_a)/(1-f_a)](H/C), \tag{9b}$$

The ratio $(H/C)_{ar}$ gives the mole fraction of peripheral protonated carbon atoms in the aromatic clusters, and the ratio $(H/C)_{al}$ gives the stoichiometry of hydrogen to carbon in the aliphatic region of the coals. As a first approximation, the hydrogen aromaticity calculated from ^{1}H CRAMPS and the carbon aromaticity from ^{13}C CP/MAS may be used. The ratios calculated are listed in Table 7, columns 5 and 6. Values of H_a and f_a are included in this table for reference. The ratios $(H/C)_{ar}$ and $(H/C)_{al}$ were plotted against MAF weight percent of oxygen, P, the linear regression lines obtained [see Figure 10, dash lines, (Δ) and ($\square$)] are:
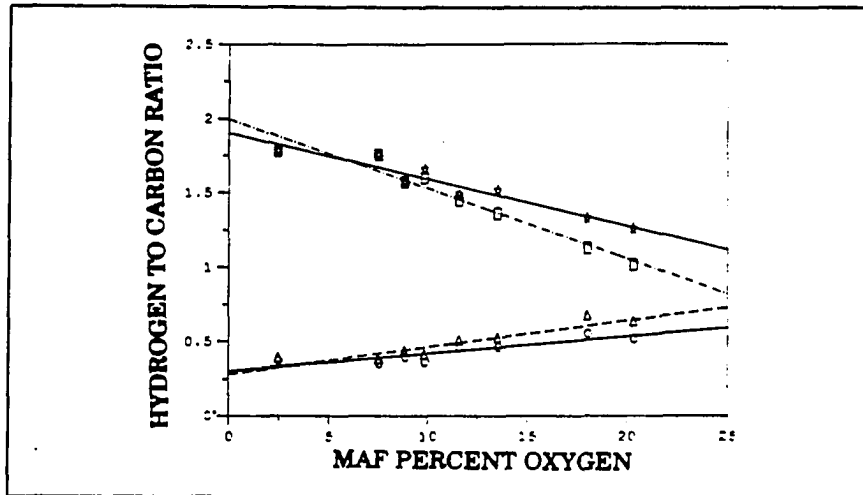
Figure 10. The uncorrected (□) and corrected aliphatic (✶) and the
uncorrected (△) and corrected aromatic (○) hydrogen to carbon
ratio for the APCSP coals as indicators of rank

$$(H/C)_{ar} = 0.018P + 0.29 \tag{10a}$$

$$(H/C)_{al} = -0.048P + 2.0 \tag{10b}$$

with correlations of 0.93 and -0.95, respectively. By using the corrected

hydrogen aromaticity as explained previously, the linear regression lines

[see Figure 10, solid lines, (o) and (✶)] obtained are:

$$(H/C)_{ar} = 0.011P + 0.30 \tag{10c}$$

$$(H/C)_{al} = -0.031P + 1.9 \tag{10d}$$

with correlations of 0.89 and -0.91, respectively. A major result of the present work is that for the first time the ratios $(H/C)_{ar}$ and $(H/C)_{al}$ are directly established via high resolution solid state NMR.

Gross Skeletal Features of Coal

According to Gerstein et al.[48] the average aromatic ring size in coals is a function of $(H/C)_{ar}$ and the number of substituents, or connectivity, to the aromatic ring. Solum et al.[34] suggested that the mole fraction of aromatic bridgehead carbon atoms, χ_b, can be used to estimate the aromatic cluster size because of the strong correlation between χ_b and coal rank. χ_b and $(H/C)_{ar}$ for some model polycondensed aromatic hydrocarbons (PAH) with one to six fused benzene rings and from one to six substitutions, were calculated and the values obtained were compared with the experimental $(H/C)_{ar}$ and χ_b (adopted from Solum et al.[34]) for each of the APCSP coals. The results are summarized in Table 7, columns 8-10.

By this procedure, the largest PAH that can represent an average aromatic unit for coal 501, for instance, is a 5- or 6-fused ring cluster with 4 to 5 substitutions. The infrared spectrum of this coal identified a high fraction of isolated aromatic -CH groups which could indicate that the aromatic clusters found in this coal are predominantly linearly catenated. Also, about 56% of the aliphatic carbon atoms[49] (equivalent to 8 C per 100 C in this sample or 2 to 3 methyl groups per cluster) are present as methyl groups pendant to aromatic rings as indicated by the weak overtone of aromatic $C-CH_3$ at 2732 cm^{-1}. These results correlate with those

found from ruthenium oxidation of this coal,[50] In addition, the oxidation identified 1 C per 100 C atoms in coal 501 to be methine. The average bonding information for carbon in this coal already accounts for all hydrogen atoms. Further accounting for all types of carbon in the sample suggested that an average of 5 C per 100 C are present as aliphatic quaternary carbon, and 11 more aromatic C per 100 C are present as substituted peripheral aromatic carbon atoms, equivalent to 2 to 3 substituted carbon per aromatic cluster. Clearly for this coal, there is not a large fraction of carbon in long chain hydrocarbons. Bridging between aromatic clusters, therefore, can only be achieved through the very few, if any, methylene and methine carbon atoms, with oxygen via ether linkages, with sulfur as disulfides and thio-ethers,[51,52] and with direct C-C bonding to each other, to form larger planar clusters. Perhaps, the quaternary carbon atoms serve as bridges that give the coal its three-dimensional structure. The small fraction of mobile hydrogen atoms observed in single-pulse ^{1}H NMR experiments[18] are most likely due, in part if not in whole, to the hindered rotation of the abundant methyl groups in this coal.

For the high volatile bituminous coals 701, 601, and 301, the average peri-connected aromatic ring condensation index is calculated to be three. But for 401, a mixture of the three- and four-ring clusters could represent its average structure. A model proposed by Shinn[4] for bituminous coals, based on products obtained during coal liquefaction, showed the absence of four-ring aromatic clusters and a relative abundance of benzylic and naphthenic rings. Additional details about the structure of these coals can be surmised

from a combination of $(H/C)_{al}$ and information from infrared spectroscopy.[49]
The fraction of methyl groups pendant to aromatic rings, observed for the
bituminous coals, decreased with decreasing rank. The values of $(H/C)_{al}$
also decreased, just like the aromaticity values, as the rank of the coal
decreased. Since this was accompanied by a decrease in the fraction of
methyl carbon atoms, it follows that the concentrations of the methylene
and methine carbon atoms increased. While coal 101 is similar in structure
to coal 501, but with a smaller aromatic cluster, it has a slightly higher
fraction of protonated aliphatic carbon atoms, other than in methyl groups.
Thus, the hydroaromatic character of the structure increased as the rank of
the coal decreased, as expected.

Single pulse ^{1}H NMR experiments[18] showed that there is a high
fraction of "rigid" hydrogen atoms in coals 202 and 801. Combined with this
information, the low $(H/C)_{al}$ ratio suggested a highly branched, and most
likely, bridged tricycloalkane stucture linked to one and two-ring aromatic
units, as proposed by Whitehurst[1] in 1977. The infrared spectrum also
showed that very few methyl groups were found in this coal.[49] A
depolymerization and solubilization study of coal 202 carried out by
Narayan[53] showed the existence of polymethylene groups with an average
carbon length of 8 as pendant side chains on aromatic rings or as linkages
between aromatic clusters. Narayan also suggested that carboxylate anions
chelated to metal ions serve as bridges in the three-dimensional structuring
of this coal. From the combined chemical, IR, and NMR information
detailed above, it can be concluded that both polymethylenes and

tricycloalkyl structure bridged by quaternary carbon atoms and ether and carboxylate linkages exist in this coal.

Although the detailed bonding structure of (the APCSP) coals can not be inferred from these various studies, the combined results strongly support the hydroaromatic model as a representative average macrostructure of a non-anthracitic coal.

CONCLUSIONS

^{1}H and ^{13}C NMR and FTIR have the capabilities of being the routine tool for quantitatively reliable analysis of coal and coal products, and for following changes in the compositional parameters of coal during processing. Conditions for reliable quantitation results for hydrogen and carbon in coals by using high resolution NMR and FTIR were studied in this work with the Argonne premium coal samples.

Direct determination of the hydrogen aromaticity of coal by using ^{1}H CRAMPS eliminates the calculation of this compositional parameter based on results of ^{13}C NMR and on assumptions about the average stoichiometry of hydrogen to carbon in the sample. Quantitation of -OH concentration in the coal by using FTIR should be performed in order to correct the CRAMPS hydrogen aromaticity data to obtain better average value of the hydrogen aromaticity of younger coals. Knowledge of this parameter permits better prediction of rates and yields for some coal processing, such as hydroliquefaction.[37] However, for some coal processing technology where changes of 3 to 5 H per 100 C atoms across the reactor bed takes place,[54] a >95% accuracy of the results would still be insufficient to make good theoretical predictions.

^{13}C NMR intensities obtained by using CP/MAS at a static field sufficiently low such that relatively slow spinning avoids the problems of sidebands and the interference of magic-angle spinning with the CP

process[24] for calculating carbon aromaticity values for the APCSP coals gave quantitative results that were reproducible to better than 95%. Values of carbon aromaticities calculated from carbon intensities obtained from a single (but optimum) contact time CP/MAS experiment compared favorably to values of carbon aromaticities from variable-contact-time CP/MAS experiments.

Results of quantitation experiments with coals by using NMR of ^{1}H and ^{13}C have a better reliability compared to FTIR spectroscopy because the latter relies on models for computation. The presence of free radicals and strong dipolar interactions in coals, however, limits the accuracy of NMR measurements to ~95%. Where it is possible to measure and set calibration curves for quantitative work with solid coals, high resolution solid state NMR should be the preferred technique because there are no assumptions made about the structure of coal.

One important application of carbon aromaticity is the determination of coal rank and, with the use of the Argonne coals, this parameter correlated with weight percent oxygen (as a rank indicator). A major result of the present work is that for the first time, the ratios of aliphatic hydrogen to aliphatic carbon and of aromatic hydrogen to aromatic carbon in (Argonne) coals are directly established by using high resolution solid state NMR. These ratios correlate with rank as determined by oxygen content with less scatter than the more commonly used carbon aromaticity.

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GENERAL CONCLUSIONS

^{1}H and ^{13}C NMR and FTIR have the capabilities of being the routine tool for quantitatively reliable analysis of coal and coal products, and for following changes in the compositional parameters of coal during processing. Conditions for reliable quantitation results for hydrogen and carbon in coals by using NMR were studied in this work with the Argonne premium coal samples.

I. Solid echo experiments allow the determination of lineshapes and initial intensities of ^{1}H NMR in Argonne premium coals. A superposition of Gaussian (T_2 ~12 μs) and Lorentzian (T_2 ~20-40 μs) terms adequately described the on-resonance FID of the organic protons in coals. The Gaussian fraction corresponds to rigid protons in the macrostructure of coal. The Lorentzian fraction is ascribed to protons that belong to fragments of the coal framework exhibiting some molecular mobility. For wet coals (>2% moisture content), an additional slowly decaying Lorentzian function must be added to the description of the FID.

The intensities obtained by NMR were compared with concentrations of hydrogen and water obtained via chemical and TGA analyses. Despite the shortcomings of the methods, the results were found to be in very good agreement. The advantages of NMR are (a) the simplicity of the analysis in which not only the concentrations but also the mobilities of all types of protons in the sample can be analyzed simultaneously; and (b) the possibility of using NMR for on-line measurements where large numbers of

samples with considerable volumes are analyzed. The development of a portable ^{1}H NMR spectrometer could combine the above advantages with capability of on-site measurement.

II. Direct determination of the hydrogen aromaticity of coal by using ^{1}H CRAMPS eliminates the calculation of this compositional parameter based on results of ^{13}C NMR and on assumptions about the average stoichiometry of hydrogen to carbon in the sample. Quantitation of -OH concentration in the coal by using FTIR should be performed in order to correct the CRAMPS hydrogen aromaticity data to obtain better average value of the hydrogen aromaticity of younger coals. Knowledge of this parameter permits better prediction of rates and yields for some coal processing, such as hydroliquefaction.[37] However, for some coal processing technology where changes of 3 to 5 H per 100 C atoms across the reactor bed takes place,[54] a >95% accuracy of the results would still be insufficient to make good theoretical predictions.

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APPENDIX

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EFFECT OF SAMPLE SPINNING

ON THE

DETECTION OF ^{13}C NMR IN COALS

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Effect of sample spinning on detection of ^{13}C NMR in coals

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ABSTRACT

The effects of sample spinning and of Hartmann-Hahn mismatch on detection of ^{13}C for a Pittsburgh No. 8 coal and coronene (as a model compound) by CP/MAS NMR have been studied. The results on the coal were compared with the "true" ^{13}C intensities under a Bloch decay indicating that reasonable ^{13}C intensities may be obtained using cross-polarization and variable contact time. It is suggested that when CP/MAS is used to obtain NMR of ^{13}C in coals, the most reliable results are obtained at a low enough static fields such that moderate spinning speeds production of sidebands and the interference of spinning with the cross polarization process are avoided.

INTRODUCTION

Techniques for the observation of the dilute ^{13}C spins in organic solids under high resolution by NMR spectroscopy are well developed.[1] By the introduction of line narrowing techniques, heteronuclear dipolar decoupling and magic angle spinning (MAS) for the reduction of chemical shift anisotropy broadening, a resolution necessary to obtain information on individual dilute spins in solids can be achieved. In addition, the signal-to-noise ratio for fixed signal averaging time is greatly enhanced by the use of cross polarization (CP).[2,3] The latter is primarily a result of the T_1 relaxation times being generally much shorter for the abundant than for the rare spins.

A combination of the above techniques (high-power-decoupling-CP/MAS experiment), their further development, and the use of higher magnetic fields enormously widened the capability and applications of solid state NMR. In particular, the ^{13}C CP/MAS experiment and its modification have proved very useful in studies of cokes, coals, and coal-derived products.[4] The problem of quantitative detection of ^{13}C in coals utilizing CP/MAS, however, is still not well resolved. In this work a variety of ^{13}C NMR experiments on a coal sample and coronene are compared and discussed to address this problem.

EXPERIMENTAL SECTION

The coal studied originated from the Pittsburgh No. 8 seam and was obtained from the Argonne National Laboratory Premium Coal Sample Program. The results of elemental analysis as determined in Argonne Laboratory for moisture and ash free sample are C, 83%; H, 5.3%; O, 9%; and S, 2.2%. The coal was exposed to air for several months and was not evacuated to remove oxygen prior to NMR experiments.

Spectra of ^{13}C in the coal were obtained by use of various transient techniques which included CP and CP/MAS with variable contact time or variable ^{13}C rf field as well as direct excitation of ^{13}C. The experiments were carried out on a home-built spectrometer operating at 100.06 and 25.16 MHz for ^{1}H and ^{13}C, respectively. A double-tuned, single coil probe was used with the modified version of Shoemaker-Apple spinning assembly[5] which allowed for MAS of samples placed in 5-mm NMR tubes at rates exceeding 5 kHz (with an air drive). During the CP experiments the proton field of 40 kHz was used both for cross-polarization and decoupling. The spectra were acquired with 2 K quadrature detection and Fourier transformed after zero filling to 8 K.

Coronene was obtained from Aldrich and studied at room temperature as a polycrystalline powder. CP/MAS spectra of coronene were obtained on an MSL 300 Bruker spectrometer. The rf fields of 50 kHz were used during cross-polarization and proton decoupling; the sample was spun at various speeds from 0.83 to 4.81 kHz in an alumina rotor.

All experiments were performed with spin temperature alternation to minimize base-line distortion associated with pulse breakthrough and receiver recovery.[6] The resonance line positions were determined with respect to tetramethylsilane (TMS).

RESULTS AND DISCUSSION

In the simplest case, the behaviour of the dilute spin (S) and the abundant spin (I) spin temperatures during the cross polarization contact in a solid sample can be described by a set of two coupled differential equations, from which the expression for the time evolution for the magnetization $M_S(t)$ of S during the CP experiment is obtained:[7]

$$M_S(t) \cong M_S(0)[1 - \exp(-t/T_{CP})]\exp(-t/T_{1\rho}{}^I), \qquad (1)$$

where $M_S(0)$ is the magnetization of the spin S that would be observed at long contact times providing the proton polarization is constant; T_{CP} is the cross-polarization time constant and $T_{1\rho}{}^I$ is the abundant spins' rotating frame spin-lattice relaxation time.

According to a theory developed by Demco et al.[8] the rate of polarization transfer from abundant to rare spins during the CP experiment in solids can be approximated by

$$(T_{CP})^{-1} = (1/2)\sin^2\theta_S \sin^2\theta_I M_2{}^{IS} J_x(\Delta\omega_e) \qquad (2)$$

where $\theta_S = \tan^{-1}[\omega_{1S}/\Delta\omega_S]$, $\theta_I = \tan^{-1}[\omega_{1I}/\Delta\omega_I]$ with $\omega_{1S} = \gamma_S H_{1S}$, $\omega_{1I} = \gamma_I H_{1I}$, $\Delta\omega_S$ and $\Delta\omega_I$ representing off-resonance frequencies and H_{1S}, H_{1I} being amplitudes of the applied magnetic fields. $M_2{}^{IS}$ is the second moment of the heteronuclear coupling and $J_x(\Delta\omega_e)$ is the real part of the

Fourier transform of the I-I dipolar autocorrelation function with $\Delta\omega_e =$ $[\omega_{1S}^2 + (\Delta\omega_S)^2]^{1/2} - [\omega_{1I}^2 + (\Delta\omega_I)^2]^{1/2}$. The explicit expression for $J_x(\Delta\omega_e)$ involves dipolar fluctuation autocorrelation functions. It was shown[8,9] that T_{CP}^{-1} is a maximum for $\Delta\omega_e = 0$ (Hartmann-Hahn match) and that the most significant terms in the relaxation expression depend on r_{IS}^{-6}, where r_{IS} is the distance between I and S spins. Thus, the process of cross-polarization of ^{13}C (S spins) should be strongly dominated by directly bonded protons (I spins). It also appears that for rigid solids the cross-polarization rate should be proportional to the number of the directly bonded protons. In cases where the dipolar proton- proton (H_{II}) and proton-carbon (H_{IS}) interactions are reduced (cf. by rapid internal motion) the rate of the cross-polarization processes can be slowed considerably. For nonprotonated carbons theoretical predictions are more difficult; generally T_{CP}'s are lengthened significantly for carbons two and more bonds away from nearest proton.

The theoretical expectation is that the values of T_{CP} for rigid solids will follow the order $CH_3 < CH_2 < CH \leq CH_3(\text{rotating}) < C(\text{nonprotonated})$ and is rather well reflected by existing experimental data. For most organic solids, in the absence of molecular motion, the typical experimental values of T_{CP} range from 50 µs for protonated carbons to several hundred microseconds and more for nonprotonated carbons. For example in coronene, which as the simplest compound with hexagonal symmetry and with exterior and interior carbons has been previously studied as a model of a planar aromatic hexagonal net,[10] we obtained (at room temperature) a T_{CP} of 65 ($\pm$ 15) µs for protonated carbons, whereas the most interior

carbons polarize very slowly with a time constant of 5.5 (± 1.5) ms at a sample spinning speed of 4.8 kHz. This change of polarization time is remarkable (still, even in spite of internal mobility, it is less dramatic than expected from (2) if only the intramolecular interactions were present, meaning that interior carbons are cross-polarized predominantly via intermolecular transfer). In typical solid organic compounds $T_{1\rho}^H$ is usually monoexponential with values exceeding 10 ms. Thus, a choice of contact time of 1-10 ms is usually a good compromise between sensitivity and quantitative accuracy of intensities (see (1)).

As was pointed out by Stejskal et al.,[11] the polarization transfer may be additionally modified by high-speed spinning of the sample at the magic angle. Mechanical spinning of the sample introduces additional time dependences to homo- and heteronuclear dipolar Hamiltonians H_{II} and H_{IS}. As a result, the amplitude of the proton-enhanced ^{13}C NMR signal and the cross-polarization rates estimated for different intensities of carbon rf field can exhibit characteristic extrema separated by the spinning frequency.[11] Hence, the proper Hartmann-Hahn match becomes more critical than in a static case. Also, the modulation of both H_{II} and H_{IS} by spinning causes the polarization transfer to occur at a much slower rate, even if the Hartmann-Hahn match is well adjusted. Further complications may take place when molecular motion is present.

In coals which are heterogeneous in nature, the evolution of carbon magnetization is even more complex.[12] First, small, but significant differences in proton spin-lattice relaxation times (T_1^H) associated with

aromatic and aliphatic protons are often observed. Second, in most cases, $T_{1\rho}{}^H$ relaxation in coals is dominated by interactions with unpaired electrons and exhibits a distribution of values with a significant fraction being less than 500 μs.[12] This complicates the polarization transfer, especially those carbons which are far from the nearest proton, e.g., deeply incorporated in polycondensed aromatic rings, cannot be fully polarized before $T_{1\rho}{}^H$ relaxation dominates the proton magnetization. As a consequence, problems with quantitative detection detection of ^{13}C in coals are likely to occur under CP/MAS.

In this work a series of experiments has been performed on a coal sample (Pittsburgh No. 8 Argonne coal) to investigate the quantitative reliability of the cross-polarization technique. From ^1H NMR two values of spin-lattice relaxation time T_1 were found: about 80% of protons in the sample exhibited a T_1 of 147 (± 10) ms and the remainder a T_1 of 53 (± 10) ms. The ^{13}C NMR experiments involved a measurement of CP spectra, with and without magic-angle spinning, as a function of ^{13}C B_1 field (the Hartmann-Hahn matching curve) and the variable contact time CP and CP/MAS experiments performed using an exact Hartmann-Hahn match. Also, a series of Bloch decay ^{13}C spectra were acquired using variable delays between the scans to infer ^{13}C T_1 relaxation times and to find a "true" spectrum of ^{13}C of the coal under study. The intensities and the lineshapes (aromaticities) observed under different experimental conditions were compared.

Figure 1a represents the Hartmann-Hahn matching curve for aliphatic
(+) and aromatic (*), carbon intensities in coal taken under magic-angle
spinning of 4.8 kHz and a fixed contact time of 1 ms. In this experiment the
^{1}H rf field of 40 kHz was established by adjusting the 90° pulse length to
6.25 μs. A set of 80 CP/MAS spectra were than acquired, using the signal
averaging of 2,500 scans per spectrum, for ^{13}C rf field which were varied
from 17.8 to 63.3 kHz using high-accuracy Wavetek step attenuators. The
delay between scans was 0.7 s. Superimposed in Figure 1a is a Hartmann-
Hahn matching curve for CH_2 (solid line) and CH (dashed line) carbons in a
static sample of adamantane taken with a contact time of 5 ms. The 1.14-
kHz shift between the centers of symmetry of the curves representing
carbons in coal and adamantane is a result of probe detuning. The
matching curve (Figure 1a) demonstrates how magic-angle spinning at 4.8
kHz modifies the ^{1}H-^{13}C polarization transfer in this coal. The effect of
spinning is more pronounced for the aromatic intensities but not nearly as
dramatic as in some model compounds with weaker I-I and I-S couplings
(e.g. hexamethylbenzene) studied in our laboratory. It is also seen in Figure
1a that the polarization transfer in the direct neighborhood of Hartmann-
Hahn match ($\omega_{1C} = \omega_{1H}$) occurs at a slower rate than for $\omega_{1C} = \omega_{1H} \pm$
ω_{rot}. This finding agrees with the theoretical predictions of ref 12.

Figure 1b shows the fraction of aromatic carbon in coal f_{ar},
corresponding to the data from Figure 1a, plotted against ^{13}C rf field. It is
assumed that f_{ar} is representing all ^{13}C nuclei with chemical shift values
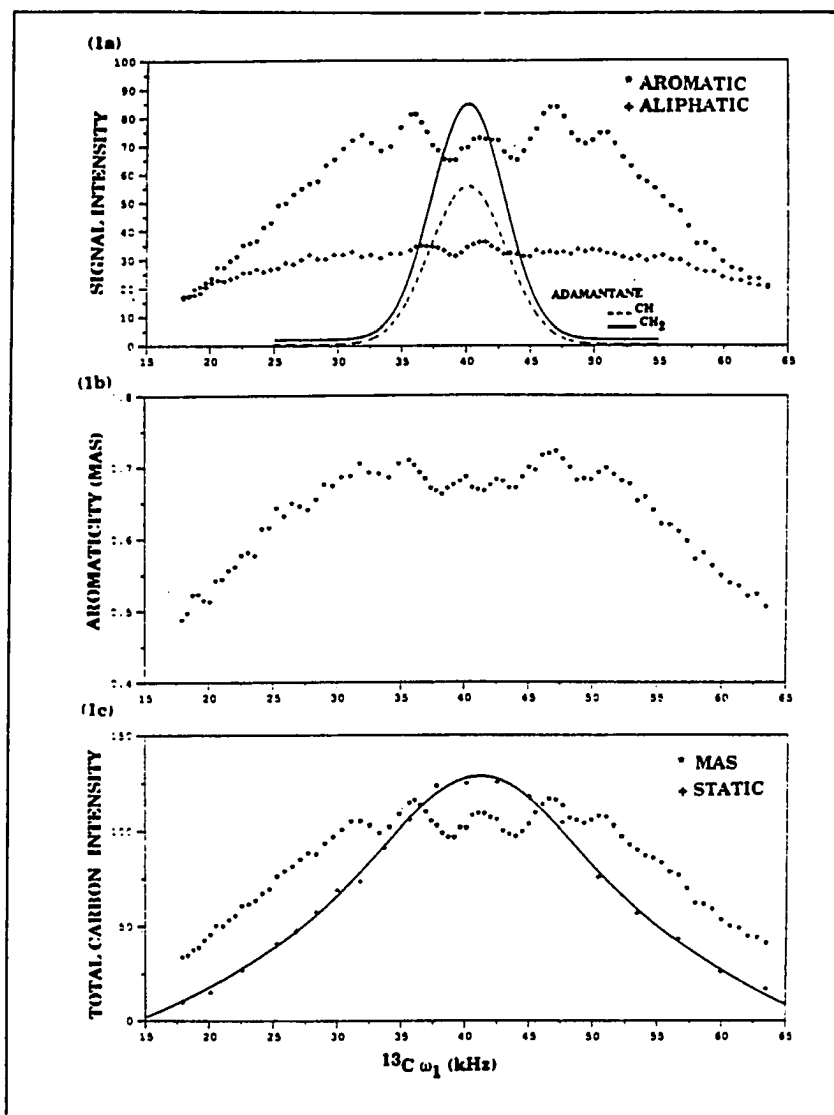greater then 80 ppm. In the vicinity of Hartmann-Hahn match the

Figure 1. (a) CP/MAS intensities of aromatic (*) and aliphatic (+) carbons in Pittsburgh No. 8 coal as a function of ω_{1C} ($\equiv \omega_{1S}$) for a sample spinning speed of 5 kHz and a contact time of 1 ms. Solid and dashed curves represent CH_2 and CH carbons in a static sample of adamantane

(b) Corresponding carbon aromaticities

(c) Total carbon intensities observed for Pittsburgh No. 8 coal in a cross-polarization expriment with sample spinning at 5 kHz as compared with a static sample

distortions of polarization process do not result in markedly different aromaticities. The f_{ar} values varied only between 0.66 and 0.68 within the $\omega_{1C}/2\pi$ range of 40 ± 3 kHz. Since this kind of accuracy of the Hartmann-Hahn match can be easily achieved using static adamantane sample for tuning (see Figure 1a), it may be concluded that sample rotation at 4.8 kHz did not lead to serious line-shape distortions in the studied sample. The distortions are expected to become larger for higher spinning speeds[13] and/or for coals with increased internal mobility (e.g., brown coals).

In Figure 1c the total (aromatic and aliphatic) carbon intensities in coal (*), taken under CP and MAS at 4.8 kHz, are compared with the total carbon intensities as observed for the same sample without MAS (solid curve). The static CP experiment has been performed under unchanged conditions except for the increments of the ^{13}C rf field which were extended four times (to ~2.5 kHz). Each static spectrum was a result of 10 000 scans; the intensities were then normalized to account for the number of accumulations. A comparison of static versus spinning Hartmann-Hahn matching curves (Figure 1c) shows that there is a loss of carbon intensity in the MAS spectra when the Hartmann-Hahn condition is met. An earlier study of the Lewiston-Stockton coal, using cross polarization with a single contact time of 1.5 ms and a fixed ^{13}C rf field adjusted with a static sample of adamantane, yielded losses of 36% and 55% of the total carbon intensities upon magic-angle sample spinning at 4 and 8 kHz, respectively.[14] The intensity in the aromatic region of the spectrum was reduced more than in

the aliphatic region (the f_{ar} values of 0.74 and 0.71 were measured in this experiment using spinning at 4 and 8 kHz).

Since all intensities presented in Figure 1 were measured for only one value of contact time, it was of interest to determine whether the discrepancy between carbon intensities obtained with and without MAS could be corrected by performing variable contact time CP experiments. To accomplish this the ^{13}C rf field was rigorously reestablished at the Hartmann-Hahn match. After spectra have been taken for 16 different contact times ranging from 50 μs to 10 ms, with and without MAS, (1) has been used to infer the initial intensities $M_S(0)$'s as well as T_{CP}'s and $T_{1\rho}$'s for both cases. Again, a loss of carbon intensity (~15%) upon spinning at 4.8 kHz was encountered. The cross-polarization times T_{CP} of 240 μs and 270 μs were obtained for static and spinning samples, respectively. It is noted that these T_{CP} values represent only average behaviour of carbon magnetization during the experiments. Their accuracy is also affected by the transient oscillations due to I-S dipolar interaction[7] which were encountered for short contact times. For the spinning sample T_{CP} values of 310 μs and 80 μs were found for aromatic and aliphatic carbons. The carbon aromaticity f_{ar} of 0.68 (± 0.01) was derived for spinning sample using the $M_S(0)$ values calculated for both aromatic and aliphatic carbons. The reason this value of f_{ar} correlates well with those presented in Figure 1b is simply a matter of choice of the 1-ms contact time. With the use of different single contact time CP/MAS spectra for the evaluation of f_{ar}, values ranging from 0.56 to 0.74 were obtained for contact times ranging between 0.1 and

10 ms. The line-shape changes observed with different contact times reflected differences in the dynamics of the cross-polarization processes for aromatic and aliphatic carbons. Similar trends have been observed previously by Botto et al.[15] The above result indicates the necessity of variable contact time experiments on coals, despite the simplicity of (1), which does not account properly for all relaxation processes in the sample (e.g., how does one deal with the fact that in some coals fractions of protons (>40%) have $T_{1\rho} \leq 500$ μs, as determined by ^1H NMR?).

To conclude the investigation of the quantitativeness of the CP/MAS technique, several Bloch decay experiments were performed with the same sample of Pittsburgh No. 8 coal to obtain a "true" ^{13}C NMR spectrum, i.e., a spectrum of all carbons which are detectable by NMR. To insure the proper experimental conditions the ^{13}C spin lattice relaxation times were measured under high resolution (MAS at 4.8 kHz and proton decoupling) with the progressive saturation method using both direct excitation and cross-polarization to induce nonequilibrium carbon magnetization. With both methods similar results were found: the T_1 relaxation could be approximated by biexponential decay functions with decay constants of T_{1S} ≅ 0.8 s (fraction of ~20%) and T_{1L} ≅ 48 s (~80%) for aromatic carbons and T_{1S} ≅ 0.8 s (~47%) and T_{1L} ≅ 46 s (~53%) for aliphatic carbons. Finally, a spectrum resulting from 10 000 free induction decays was measured under high resolution using direct ^{13}C excitation (Bloch decay) with a delay of 120 s between the scans. The aromatic and aliphatic carbon intensities were then corrected to account for incomplete spin- lattice relaxation to yield the

aromaticity f_{ar} = 0.70 (±0.02). The total carbon intensity was also compared with a reference showing that 94% (+5%) of all carbons were detected in this experiment.

The above results would seem to indicate that the variable contact time CP/MAS experiments in coals can be succesfuly used to determine carbon aromaticity. It is important, however, to use spinning rates, such that the condition v_{rot} << $|H_{II}|$, $|H_{IS}|$ is met for the most possible number of nuclei. If higher spinning speeds are employed the modulation of the Hartmann-Hahn matching curve causes distortions of ^{13}C CP/MAS spectra much stronger than those presented in Figure 1. This has been demonstrated in ^{13}C CP/high-speed-MAS studies of Torlon, a polyamide-imide manufactured by Amoco.[13] In this material the carbon intensity distortions were increasingly severe as the spinning speed increased from 7.3 to 15.6 kHz, whereas no effect of spinning was observed at the low spinning rate of 2.5 kHz. Slow spinning, in turn, will create a problem of spinning sidebands, unless a low magnetic field is used in which v_{rot} > $\Delta v_{\delta}/2$, i.e., the spinning frequency exceeds half of the chemical shift anisotropy. For the aromatic carbons in coals the chemical shift anisotropy is greater than 300 ppm. Consequently, low magnetic fields of less than 2.3 T (~100 MHz for ^{1}H NMR) should be used to avoid sidebands, or, at least, to prevent them from overlapping with other (aliphatic) resonances, if the spinning speed is not to exceed 5 kHz.

It is noted that several techniques have been developed in the recent years to obtain spectra devoid of sidebands in cases when v_{rot} < $\Delta v_{\delta}/2$.

However, the methods developed thus far have disadvantages and are not recommended for quantitative work on coals. The PASS (phase alternated spinning sidebands) experiment, and its later version called TOSS (total sideband suppression), can be used to identify sidebands by coaddition of MAS spectra with systematically phase shifted sidebands.[16] In both techniques the sidebands intensities are not fully recovered in the isotropic peaks causing a severe loss of total intensity and distortions of relative intensities. The role of this effect is demonstrated by the spectrum of ^{13}C in coronene as a function of sample spinning speed. Figure 2a represents a CP/MAS spectrum of coronene taken at a ^{13}C frequency of 75 MHz with a "slow" spinning of 3 kHz. Both isotropic peak and the pattern of sidebands are shown. In Figure 2b are shown the isotropic peaks of ^{13}C in coronene, taken under CP/MAS, with varying sample spinning between 830 and 4810 Hz. The isotropic peak at ~123.5 ppm, which develops at shortest contact times, represents the 12 protonated carbons. The line at 126 ppm corresponds to the intermediate 6 carbons, whereas the inner carbons resonate at ~119.5 ppm. As seen in Figure 2a, the intensities of each group of magnetically equivalent nuclei are distributed among the sidebands in a complicated way, as a function of their respective chemical shift parameters, which may be deduced from those intensities, once the proper association of resonance lines is made.[17] The important aspect of the spectra presented in Figure 2b is that various carbons contribute to the isotropic peaks in different proportions, even upon very small changes in spinning frequency (compare for example the two bottom spectra). Thus the isotropic
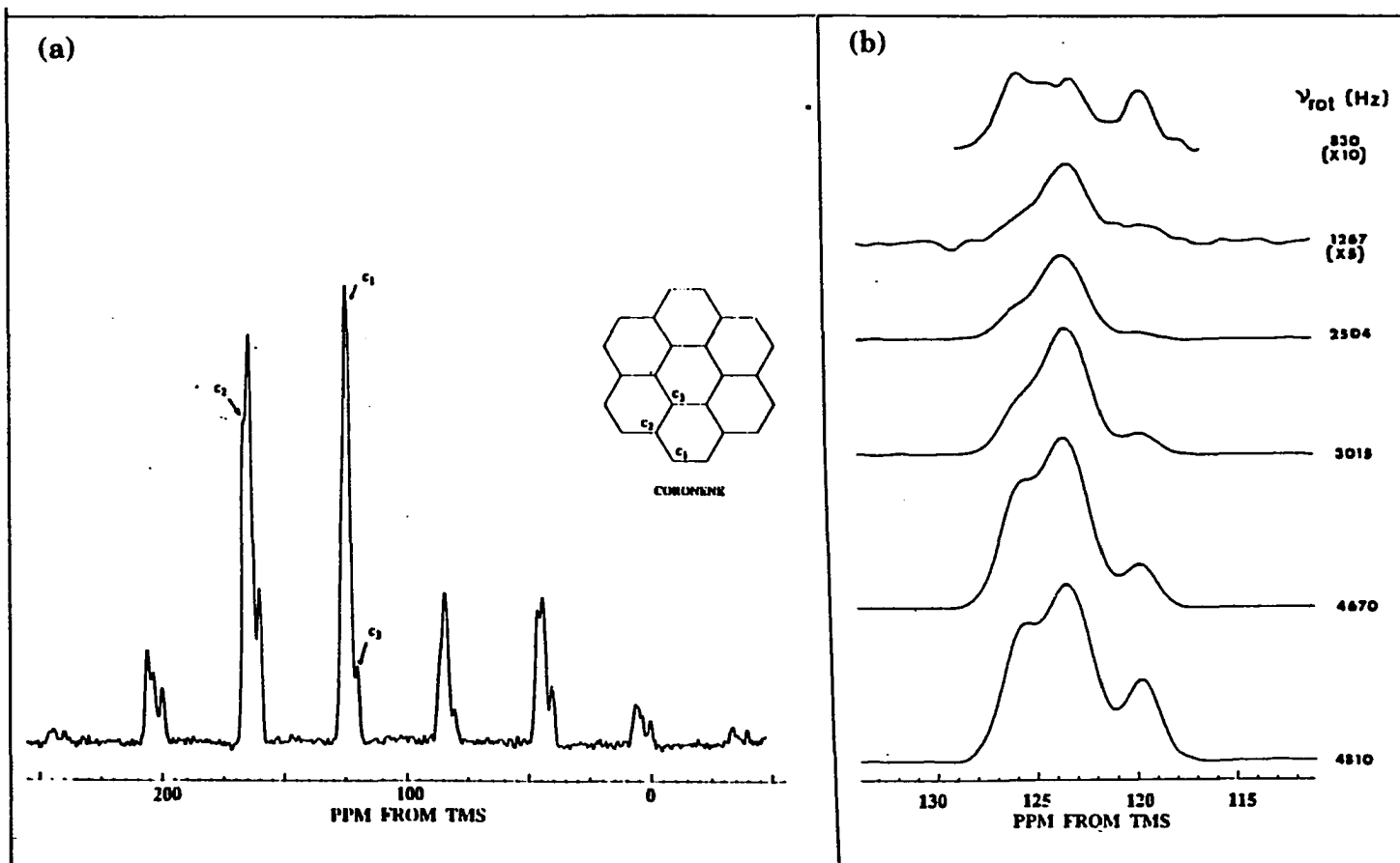
Figure 2.   (a) Proton decoupled ^{13}C CP/MAS spectrum of coronene obtained using sample
spinning of 3.0 kHz. The centerband is located at ~125 ppm
(b) The lineshapes of the isotropic peak (centerband) of ^{13}C in coronene, taken
under CP/MAS, versus sample spinning speed

peaks cannot in general be used for quantitative evaluations in the slow spinning regime unless numerical correction of spectra with sideband suppression is applied.[18] Another technique to reduce the number and intensities of sidebands in high field experiments was proposed by Aue et al.[19] The technique utilizes pulse sequences to reduce the width of the chemical shift anisotropy by 'scaling' such that moderate spinning sufficies to obtain sideband-free spectra. There are, however, several unwanted features that appear in chemical shift scaled MAS spectra, referred to as combination sidebands, combination artifacts, and zero and v_{rot} artifacts. The source of combination sidebands, and artifacts is simultaneous spinning and scaling modulation of the NMR signals at nearly the same frequencies (scaling frequency $v_{sc} = 1/T_{sc}$, where T_{sc} is the time duration of the scaling sequence). Zero and v_{rot} artifacts are very sensitive to small pulse and/or phase changes in the scaling pulse sequence. Although combination artifacts can be considerably reduced by the use of highest possible scaling frequencies, it seems to be practically impossible to avoid artifacts caused by pulse errors.

Finally it has to be pointed out that the usual advantages of higher field experiments, (a) enhanced sensitivity and (b) improved resolution, are of less importance in the studies of coals. (a) For a given sample, the signal-to-noise ratio is proportional to $H_0^{3/2}$ provided the other experimental conditions are not changed. On the other hand, in coals, as well as in many amorphous solids, the residual line width observed under high resolution, is limited by chemical shift distributions, and scales with H_0. Consequently,

the effective gain in signal-to-noise ratio is only proportional to $H_o^{1/2}$. In addition, the T_1 relaxation times of protons are usually longer in higher fields, which slow the acquisition of data. (b) The improvement in resolution at higher magnetic fields is mainly expected due to the proportionality between the external field H_o and the shift in the resonance frequency of a nuclei in a given electronic environment. Both aromatic and aliphatic peaks in ^{13}C NMR spectra of coals represent a wide variety of bond types and functionalities and even though often exhibit some distinct features (methyl or methylene resonances, etc.) the resolution is not improved at higher fields.[18]

SUMMARY AND CONCLUSION

The above results on Pittsburgh No. 8 coal and coronene indicate the double bind in which the spectroscopists wishing to determine quantitative NMR spectra of ^{13}C in coals using CP/MAS find themselves. If the sample in question contains carbon with vastly differing shielding anisotropies, the slow spinning results in sidebands which may not contain equal contributions from all carbons in the sample and overlap with centerbands of adjacent resonances. Using sideband suppression techniques in order to avoid the problem of overlapping sidebands often results in isotropic lines which do not correctly represent contributions from all carbons in the sample. The obvious solution is to spin rapidly enough to avoid sidebands. Rapid spinning, however, results in intensity distorted CP/MAS spectra.

The Hartmann-Hahn matching curve for Pittsburgh No. 8 coal shows that even spinning at 4.8 kHz modified the ^{1}H-^{13}C polarization transfer in this coal. However, in the vicinity of the Hartmann-Hahn match the line-shape distortions were still small at this spinning speed (using a 1 ms contact time the f_{ar} values varied between 0.66 and 0.68 within the carbon rf field range of 40±3 kHz). At a fixed carbon rf field adjusted to match exactly the Hartmann-Hahn condition the f_{ar} values ranging from 0.56 to 0.74 were obtained as the contact time was changed between 0.1 and 10 ms, respectively. From the same data f_{ar} of 0.68 was obtained by use of (1) (variable contact time experiment). This value is in good agreement with a result of a time-consuming Bloch decay experiment (f_{ar} = 0.70) in which

~94% of all carbons in the sample were detected. The above experiments showed that reasonable ^{13}C NMR intensities may be obtained using CP/MAS under appropriate conditions. Those include the use of variable cross-polarization contact times and the use of a static field sufficiently low such that relatively slow spinning avoids the problems of sidebands and the interference of magic-angle spinning with the CP process. Other solutions include (a) avoiding the use of CP and obtaining the spectra of carbon under a single pulse excitation using extra large rotors to obtain desired signal-to-noise ratios, (b) the use of magic-angle hopping[20] in which the CP step is carried out with the sample static, and (c) performing the CP while the sample is spinning at other than the magic angle.[21]

ACKNOWLEDGEMENT

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