M96050219-T
DOE/PC/95227-1

ADVANCED SOLIDS NMR STUDIES OF COAL STRUCTURE AND CHEMISTRY

PROGRESS REPORT

including
the period September 1, 1995 to February 28, 1996

Kurt W. Zilm, PI
Department of Chemistry
Yale University
New Haven, CT 06511

Prepared for the Department of Energy
Agreement No. DE-FG22-95PC95227

Granting period: 9/1/95-8/31/98

Award: \$200,000/3 yrs., \$63,116 current year

Program Manager: Richard F. Sprecher

COR: Suzanne K. Polmar

MASTER

RECEIVED
USDOE/PETC
96 JUN -6 PM 2:33
ACQUISITION & ASSISTANCE DIV.

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe on privately-owned rights.

US/DOE Patent Clearance is not required prior to publication of this document.

ABSTRACT

This report covers the progress made on the title project for the project period. The study of coal chemical structure is a vital component of research efforts to develop better chemical utilization of coals, and for furthering our basic understanding of coal geochemistry. In this grant we are addressing several structural questions pertaining to coals with advances in state of the art solids NMR methods. Our goals are twofold. First, we are interested in developing new methods that will enable us to measure important structural parameters in whole coals not directly accessible by other techniques. In parallel with these efforts we will apply these NMR methods in a study of the chemical differences between gas-sourcing and oil-sourcing coals. The NMR methods work will specifically focus on determination of the number and types of methylene groups, determination of the number and types of methine groups, identification of carbons adjacent to nitrogen and sites with exchangeable protons, and methods to more finely characterize the distribution of hydrogen in coals. We will also develop NMR methods for probing coal macropore structure using hyperpolarized ^{129}Xe as a probe, and study the molecular dynamics of what appear to be mobile, CH_2 rich, long chain hydrocarbons. The motivation for investigating these specific structural features of coals arises from their relevance to the chemical reactivity of coals, and their suitability for possible correlations with the oil sourcing potential of some types of coals. The coals to be studied and contrasted include oil-prone coals from Australia and Indonesia, those comprising the Argonne Premium Coal Sample bank, and other relevant samples.

In this report period we have focused our work on 2 segments of the program. First, a new set of editing methods has been developed which provides a significant time savings over previous techniques. Secondly we have applied these methods to a model mixture of hydrocarbons chosen to mimic the functional group distribution in a mid-rank coal to study any sources of error in quantitation.

I) Progress on NMR methods Development

An improved spectral editing method for solids has been developed which obtains a complete set of edited spectra in less time than that required for our earlier technique. This time savings is afforded by a new pulse sequence which is used to acquire a CH plus CH₂ spectrum with very little CH₂ or non-protonated carbon contamination. By using this new sequence the CH only subspectrum is obtained more efficiently.

We have recently proposed spectral editing methods that rely upon the domination of CP dynamics at short times by the strong dipolar couplings between a ¹³C nucleus and its directly bonded protons, and the ratio of the heat capacities of the ¹³C and these directly attached protons. Methods of this type are less sensitive to molecular mobility than those which rely solely on the strength of the ¹³C-¹H dipolar interactions.

In our previous method four spectra are combined to obtain the C, CH, CH₂ and CH₃ subspectra. A sequence consisting of a short contact time cross polarization (SCP) followed by a short polarization inversion (PI) interval (SCPPI) is used to obtain the CH₂ only subspectrum. To acquire a CH only subspectrum several spectra are combined. Using an SCP sequence, a spectrum dominated by CH and CH₂ signals is obtained. Subtraction of the SCPPI spectrum results in a CH dominated spectrum. Unfortunately the intensity of the nonprotonated C and CH₃ signals in this difference spectrum is too large for this alone to be a useful means of producing CH only spectra. These undesired signals are however closely reproduced in a spectrum acquired using a SCP sequence which is followed by a depolarization interval (SCPD) which removes the CH and CH₂ resonances. A second subtraction can then be used to generate a good CH only spectrum, albeit at a penalty in signal-to-noise ratio. The advantages and disadvantages of this particular approach have been described previously.

This report describes the use of a sequence we call cross polarization dipolar dephasing recross polarization (CPDDRCP see Figure 1). This sequence is used to obtain a CH plus CH₂ only spectrum in which the C and CH₃ resonances are more completely suppressed. In principle this makes generation of the CH only subspectrum feasible with a single subtraction, and reduces the amount of time needed to collect a spectral editing data set. While the original editing protocol is still found to produce the most accurate editing data in terms of quantitation, the new method does produce results that are of comparable quality and is preferable if signal to noise is at a premium.

Methods

The sequence shown in Figure (1) has been devised with the aim of producing a CH plus CH₂ only spectrum. In the first step a SCP sequence is applied which polarizes the CH and CH₂ groups to a quasi-equilibrium state. A small amount of C and CH₃ polarization is also produced. At this point the ¹H magnetization has been largely unaffected; application of a $\pi/2$ pulse with a $\pi/2$ phase shift in the ¹H channel returns the ¹H magnetization to the z axis where it can be stored. The ¹³C magnetization is then permitted to evolve with no ¹H RF applied, causing the CH and CH₂ signals to dephase. Refocusing of the chemical shift evolution during this interval places the

small C and CH₃ ¹³C magnetizations back in phase where they can be spinlocked once more. This spinlocked state is then the starting point for a second SCP period. By proper adjustment of the relative phases, the C and CH₃ signals are now depolarized, whereas the CH and CH₂ which are starting with no net polarization are allowed to again reach their quasi-equilibrium intensities. The resulting spectrum will contain CH and CH₂ signals with intensities similar to those obtained in a SCP experiment. The principal difference is that the C and CH₃ error signals are now greatly reduced in intensity.

Similar to the earlier method, the editing protocol requires the experimenter to take spectra of a model compound using the editing pulse sequences (see Figure 2) to calibrate their particular instrument, and to empirically account for departures from the idealized spectral intensities predicted from the quasi-equilibrium theory. The first of these sequences (Figure 2a) is the normal long time CP or LCP sequence. A 90° pulse is first applied to the protons after which they are spinlocked. Thermal contact between the carbon and proton nuclei ensues as the carbon spin locking field is applied subject to the Hartmann-Hahn match condition. Simultaneous phase inversion is used during the CP period to broaden the matching width and decrease the sensitivity to RF amplitude fluctuations. The carbon nuclei then remain spinlocked until the FID is acquired during high power proton decoupling. Figure 2b represents the SCPPI or CH₂-only sequence. The sequence begins with a short CP period of 40 μs which significantly polarizes the CH and CH₂ groups only. In this quasi-equilibrium the CH groups have a relative intensity of about 1/2, and the CH₂ groups have approximately 2/3 of their full intensity. The subsequent short polarization inversion nulls the CH signals and any small -C- or CH₃ signals that were produced. The fourth editing pulse sequence, the LCPD or long CP depolarization sequence is displayed in Figure 2c. After a long CP period of 1.5 ms, the proton spinlock is turned off, allowing the proton magnetization to dephase. When the Hartmann-Hahn match condition is reinstated, the carbons are depolarized as the magnetization flows back to the protons. The timing of this depolarization period is arranged to principally effect the strongly coupled CH and CH₂ groups.

Examples of these calibration spectra are shown in Figure 3. In order to simplify the presentation of the data, the LCP and LCPD spectra are scaled by a factor of 1/2. Otherwise, the scale of each trace is the same. The SCP spectrum displays the division of the tightly coupled and weakly coupled groups on the basis of intensity differences. The SCPPI or CH₂-only spectrum has essentially zero intensity for each of the -C-, CH, and CH₃ groups. Depolarization cleanly removes the CH and CH₂ signals from the LCPD spectrum and does a reasonable job in the SCPD for which the CH signal turns out to be very slightly negative instead of the intended zero intensity. At the top of the figure, the CPDDRCP spectrum is displayed. For this spectrum the intensities of the -C- and CH₃ resonances are much less than in the SCP spectrum. By integration of these calibration spectra one generates the intensity matrix (see Figure 4) which determines the linear combinations used to produce the subspectra for a given carbon type.

Experimental

All experiments were performed on a homebuilt NMR spectrometer based on a Tecmag Libra data system and using an Oxford Instruments 2.35 T, 110 mm room-temperature bore superconducting solenoid. A homebuilt CPMAS probe incorporating a 7 mm MAS stator with a variable pitch RF coil from Doty Scientific was used. Samples were spun at the magic angle at 4.0 kHz. Proton decoupling was accomplished at 3.0 ppm with an 80 kHz or 92 kHz decoupling field. The Hartmann-Hahn match condition was set at $\gamma_I H_I^I = \gamma_S H_I^S = 55$ kHz by maximizing the adamantane signal as a function of ¹³C RF field strength. For this determination the adamantane

sample was spun at ca. 800 Hz in order to remove the possibility of accidentally finding a side-band match. It is important that the RF amplitudes be stable such that the Hartmann-Hahn match condition can be maintained within roughly 1 kHz.

Results and Discussion

Once the intensity matrix has been defined, the ethyl fumarate spectra are edited to verify that the matrix elements are correct. The result of this procedure is displayed in Figure 5. These editing experiments may now be applied to other samples in order to examine the generality of the method. Figures 6 and 7 show results from a sample of cholesteryl acetate using the new CPDDRCF editing method and the normal method. Although the spectra were acquired with different decoupler power and acquisition times, they clearly show that the two methods are comparable. The advantage of the CPDDRCF method lies in the time savings.

The set of edited spectra in Figure 7 was acquired in significantly less time than that of Figure 6. Since the CH-only subspectrum is composed of a sum of relatively low signal to noise spectra, it will generally have the worst signal to noise of the edited set. The gain in signal to noise of the new technique can be appreciated by considering the signal to noise of the CH-only subspectrum which can be written as follows:

$$\left(\frac{S}{N}\right)_{\text{CH-only}} = \frac{S_1^{(\text{CH})} + a_2 \frac{N_a^{(1)}}{N_a^{(2)}} S_2^{(\text{CH})} + a_3 \frac{N_a^{(1)}}{N_a^{(3)}} S_3^{(\text{CH})}}{\left(N_1'^2 + \left(a_2 \frac{N_a^{(1)}}{N_a^{(2)}} N_2' \right)^2 + \left(a_3 \frac{N_a^{(1)}}{N_a^{(3)}} N_3' \right)^2 \right)^{1/2}}$$

$$= \frac{S_1^{(\text{CH})}}{N_1} \left(\frac{1}{N_a^{(1)}} + \frac{a_2^2}{N_a^{(2)}} + \frac{a_3^2}{N_a^{(3)}} \right)^{-1/2} \quad \text{if } S_2^{(\text{CH})} = S_3^{(\text{CH})} = 0$$

where:

$S_i^{(j)}$ = intensity of the j^{th} resonance in the i^{th} spectrum

$s_i^{(j)}$ = intensity matrix element for the j^{th} resonance of the i^{th} experiment

$N_a^{(i)}$ = number of acquisitions for spectrum i

$N_i' = N_1 (N_a^{(i)})^{1/2}$ = noise in spectrum i

a_i = coefficients of linear expansion

This function of the numbers of acquisitions $N_a^{(i)}$ can be maximized subject to the constraint that the total experimental time (time = $\sum_i N_a^{(i)}$) is constant. One finds:

$$N_a^{(2)} = a_2 N_a^{(1)} \quad ; \quad N_a^{(3)} = a_3 N_a^{(1)}$$

This gives:

$$\begin{aligned} \left(\frac{S}{N}\right)_{CH\text{-only}}^{Optimum} &= \frac{s_1^{(CH)}}{N_1} \left(\frac{1}{N_a^{(1)}} + \frac{a_2^2}{a_2 N_a^{(1)}} + \frac{a_3^2}{a_3 N_a^{(1)}} \right)^{-1/2} \\ &= \frac{s_1^{(CH)}}{N_1} \sqrt{N_a^{(1)}} (1 + a_2 + a_3)^{-1/2} \end{aligned}$$

for the optimum signal to noise ratio.

The relative signal to noise advantage of the new method over the normal editing protocol can be calculated as the ratio of the optimized signal to noise for the CH only subspectrum in the two cases using the same experimental time. Substituting the experimental time (time = $\sum_i N_a^{(i)} = N_a^{(1)} (1 + a_2 + a_3)$) gives:

$$\begin{aligned} \left[\frac{\left(\frac{S}{N}\right)_{cpddrcp}^{Optimum}}{\left(\frac{S}{N}\right)_{normal}^{Optimum}} \right]_{CH\_only} &= \frac{s_1^{(CH),cpddrcp} (1 + a_2^{normal} + a_3^{normal})}{s_1^{(CH),normal} (1 + a_2^{cpddrcp} + a_3^{cpddrcp})} \\ &= \frac{0.42(1 + 2.88 + 2.00)}{0.57(1 + 2.38 + 0.12)} = 1.24 \end{aligned}$$

If quantitation is not critical, edited spectra may be obtained in substantially less time by using the LCP spectrum as the CH signal source. Figure 8 illustrates this technique by making the appropriate linear combination of data from a sample of cholesteryl acetate.

Conclusions

The CPDDRCP spectrum allows for the acquisition of a CH-only subspectrum of equal or better quality to that obtained with the original method in less time. Spectral editing can now be accomplished by several different but related methods, the best one being chosen for a particular application. The strength of the original method lies in its nearly quantitative ability to separate carbon resonances. The CPDDRCP method offers a time savings which can be attractive for dealing with low signal to noise systems. If quantitation is not important the LCP editing method can be used. This has the advantage of requiring even less time to implement. Further work on improving the spectral editing method is in progress. This work will focus on improvements in signal to noise and/or decreasing the experimental time without compromising the quantitative nature of the method. In addition to this, work is in progress with the aim of making the editing experiments less sensitive to timing errors and possibly RF amplitude errors.

II) Quantitative Study of a Model Coal Mixture

The quantitative response of the spectral editing of CPMAS ^{13}C spectra with depolarization and polarization inversion described above has been investigated. The technique was applied to a physical mixture of model organic compounds. The carbon composition of the organic mixture was chosen to be similar to a mid rank coal. Other parameters contributing to the selection of model compounds are the chemical shifts of the ^{13}C , oxygen content, and the minimum presence

of non-protonated aliphatic carbon. The intensities of the non-protonated ^{13}C , ^{13}CH , $^{13}\text{CH}_2$, and $^{13}\text{CH}_3$ groups determined from the subspectra are compared to the actual values of the model mixture. These experiments permit us to place confidence limits on the numbers derived from spectral editing analysis of a complex mixture of hydrocarbons.

Sample preparation

The selection of model compounds was based on ^{13}C chemical shifts and functionalities that are similar to the Illinois #6 coal from the Argonne Premium Coal Sample Program (APCSP). The percentage of the carbons with different proton multiplicities for the Illinois #6 coal are known from previous experiments, as well as ranges of the chemical shifts, and the data are shown in Table 1.

Table 1: Carbon composition and chemical shift range for Illinois #6 coal

Carbon type	%	Chemical shift range(ppm)
Ar -C-	47	100-170
Ar -CH-	24	100-140
Al -CH-	7.9	20-60
-CH ₂ -	11	0-60
-CH ₃ -	12.1	0-60

Compounds such as congressane and menthol have favorable carbon chemical shifts and compositions, but were excluded because their presence would collapse the final mixture into a liquid-like gel. In our experiments, eleven compounds were selected, which are shown in Figure 9. They were weighed out with an accuracy of 0.1 mg. Purity of the chemicals are 95% or better. The amounts and the carbon functionalities of the physical mixture are listed in Table 2.

Table 2: Amounts and % carbon functionalities for the model mixture

Cmpds*	ν^{**}	CH ₃	CH ₂	Al.CH	Ar. CH	C	Total	Oxygen
A	1.03	0	0	0	12	12	24	0
B	3.39	0	0	0	18	18	36	0
C	2.20	0	6	0	4	6	16	0
D	1.01	6	0	0	0	6	12	0
E	1.35	3	0	1	3	3	10	1
F	1.22	1	2	0	9	9	21	0
G	2.07	0	9	0	2	9	20	1
H	3.54	5	0	0	0	7	12	2
I	1.13	3	0	1	8	6	18	0
J	3.33	0	3	1	8	8	20	1
K	3.38	8	0	4	2	4	18	0
Total		59.3	43.84	19.35	141.96	196.14	460.58	13.83
%		13	9.6	4.3	30.6	42.5	100	3

* Compound name given in Figure 9, **Occurrence frequency

The percentages for each type of carbons for the final mixture are 13% for CH₃, 9.6% for CH₂, 4.3% for aliphatic CH, 30.6% for aromatic CH and 42.5% for aromatic nonprotonated C as seen from Table 2. These values are fairly similar to those from the Illinois #6 coal. In addition, there are no aliphatic non-protonated carbons in this mixture. The chemical shift requirement was difficult to fulfill as the coal has a broad range of chemical shifts that exceed those of the compounds considered.

NMR Experimental

Experiments were carried out in a homebuilt spectrometer coupled to a Tecmag system with a 2.35 Tesla wide-bore superconducting magnet from Oxford. A homebuilt CPMAS probe incorporating a 7 mm MAS stator with a variable pitch RF coil from Doty Scientific was used. The magic angle spinning speed was 4 kHz. The Hartmann-Hahn match condition was determined by optimizing signal intensity with adamantane and the magic angle was set with hexamethylbenzene. A decoupling power of 80 kHz and a CP matching power of 55 kHz were used in all experiments. A high decoupling power was used because with a lower decoupling power, some CH₂ signal were buried in the baseline.

The spectral editing experiments were first performed on monoethyl fumarate to calibrate the machine and verify the intensity matrix for editing. The same set of the editing experiments were then performed on the model organic mixture. The only differences are the recycle delay and the number of transients. The recycle delay was changed to 20 seconds and the number of transients was increased to enhance NMR sensitivity. The choice of a 20 second recycle delay time is a compromise. It was found that the proton T₁ relaxation times are very diverse among the compounds in the mixture, some being longer than 30 seconds. If a recycle delay of 150 seconds (5 x T₁) is chosen, it would take one month to complete the experiment if the same signal/noise ratio is desired. In the present method, there is some distortion due to the short recycle time, however, the distortion is relatively easy to correct.

Results and Discussion

The spectral editing intensity matrix was determined by the experiments on monoethyl fumarate and was consistent to the universal set of values for the technique we determined previously.

The four experimental spectra of the model organic mixture are displayed in Figure 10, while the individual subspectrum for each carbon resonance is displayed in Figure 11 along with the LCP spectrum. These subspectra were determined from a linear combination of LCPD, SCPPI, CPDDRCF spectra with coefficients from the intensity matrix. In Figure 12, LCP, synthetic and the difference spectra are compared. All spectra in the figures are plotted on the same scale.

In order to get quantitative information from the edited spectra, two other factors have to be taken into account. The first one is the effect of different CP rates for different carbon groups. The normalization factor for each individual carbon resonance was again determined based on the result of the LCP experiment on monoethyl fumarate. All carbon signals are normalized to the CH₃ polarization. The normalization factors are 1, 0.931, 0.96, 0.816 for CH₃, CH₂, CH and nonprotonated C respectively. The CH₃, CH₂, and CH carbons are fully polarized after a contact time of 1.5 ms. The slight loss of intensity for the CH₂ and CH carbons is probably a result of inefficient proton decoupling due to RF inhomogeneity. The nonprotonated C is polarized poorly because of a much slower CP rate.

The second one is the effect of T_1 relaxation time. The comparison between the LCP spectra with different recycle time showed that, with 20 seconds of recycle time, the methyl groups and the nonprotonated carbon at chemical shift of 140 ppm have full intensity, while others have 80% intensity. The spectrally determined carbon composition and the actual composition for the model mixture are listed and compared in Table 3.

Table 3: Carbon compositions, actual values vs. values from the spectral editing technique

Carbon type	Actual value	Experimental value
Ar -C-	0.425	0.436
Ar -CH-	0.306	0.294
Al -CH-	0.043	0.041
-CH ₂ -	0.096	0.082
-CH ₃ -	0.13	0.137

Conclusions

The spectral editing method has been shown to faithfully decompose the ^{13}C spectrum of a complex mixture into components based on proton multiplicity. The differences between a normal LCP spectrum and the synthetic spectrum generated by adding up the individual subspectra are quite small. On the basis of these experiments, and past experience with many model samples, we have a great deal of confidence in ability of the spectral editing protocol presented here to accurately pull apart a complicated ^{13}C CPMAS spectrum into methyl, methylene, methine and non-protonated carbon components.

In order to obtain quantitative intensities in the subspectra, operating conditions must be adopted that result in a quantitatively reliable CPMAS spectrum to begin with. Errors associated with heterogeneity in the proton T_1 or with inefficient CP transfer to non-protonated carbons have to be accounted for independently in quantitative work as indicated here. Such errors are not amplified by the editing protocol, as evidenced by the small differences observed in LCP and synthetic CPMAS spectra. The fact that the intensity errors produced by such effects do not adversely impact the ability of our editing protocol to separate a complex mixture spectrum into its multiplicity selected subspectra is one of its great strengths. The subspectral intensities for any particular sample mixture then are just as quantitative as the intensities of the corresponding standard CPMAS spectrum taken under the same experimental conditions. If more accurate intensities are desired the spectroscopist is able to make a separate assessment of the quantitative response of their sample without having to consider additional complications from the spectral editing method.

III) Future Work Plans

During the coming reporting period quantitative studies along the lines of those described above where T_1 effects are taken into account will be performed on the Argonne sample suite. A further development will involve computer fitting of the coal subspectra to facilitate making use of chemical shift resolution gained in the subspectra. Additional studies will begin using these methods to compare a series of gas-prone and oil-prone coals and kerogens.

Figure 1: The CPDDRCP sequence showing the optional rotor synchronization. This sequence may be used to acquire CH + CH₂ dominated spectra.

Figure 2: a) LCP sequence; b) SCPPI sequence; and c) LCPD sequence.

Figure 3: Calibration spectra of ethyl fumarate.

SPECTRUM	-C-	CH	CH ₂	CH ₃
LCP	1.00	1.00	1.00	1.00
SCP	0.09	0.57	0.69	0.24
SCPPI	0.01	0	-0.24	0
SCPD	0.08	-0.03	-0.01	0.12
LCPD	0.86	0	0	0.61
CPDDRCF	-0.01	0.42	0.57	0.07

Figure 4: Matrix of spectral intensities. Ratios of these intensity matrix elements define the coefficients used in the linear combination of spectra to produce the edited spectra.

Figure 5: CPDDRCP editing of ethyl fumarate.

difference

Figure 6: Normal editing of cholesteryl acetate.

difference

synthetic
cpmas

normal
cpmas

200 150 100 50 0
ppm

CH₃

CH₂

CH

C

200 150 100 50 0
ppm

Figure 7: CPDDRCP editing of cholesteryl acetate.

difference

synthetic
cpmas

normal
cpmas

200 150 100 50 0

ppm

CH₃

CH₂

CH

C

200 150 100 50 0

ppm

Figure 8: LCP editing of cholesteryl acetate.

A. Coronene

B. Decacyclene

C. Hexahydropyrene

D. Hexamethylbenzene

E. Isopropylmethylbenzene

F. Methylcholanthrene

G. Octahydrobenzopyrenone

H. Pentamethylbenzoic acid

I. Retene

J. Tetrahydrobenzopyrenol

K. Tetraisopropylbenzene

Figure 9 : Selected Organic Compounds

Figure 10

Figure 11

Difference

Synthetic

LCP

Figure 12