

CARBON-13 NMR STUDIES OF COALS BY CROSS POLARIZATION AND
MAGIC-ANGLE SPINNING

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INTRODUCTION

Knowledge of the chemical structures of the organic compounds in fossil fuels is essential for a fundamental understanding of these important materials and how to utilize them most effectively. For solid fossil fuels (e.g., oil shales and coals) this kind of chemical characterization has been difficult because many of the most powerful analytical techniques for organic structure determination, including conventional nuclear magnetic resonance (NMR) have required liquid samples. However, for coals and oil shales only small fractions of the organic constituents can be dissolved under conditions for which one can be confident that the structural integrity of the organic compounds is retained.

Until recently NMR spectra of solid samples have usually consisted of featureless, broad resonances with little or no useful information available regarding molecular structure. Recently, it has been demonstrated that useful ^{13}C NMR spectra can be obtained on solid samples by using some newly developed techniques.

Standard continuous wave or pulse Fourier transform NMR approaches on powdered or amorphous samples give very broad lines of generally low intensity. The breadth of ^{13}C resonances is due to the manifold of ^1H - ^{13}C dipole-dipole interactions and the chemical shift anisotropy resulting from random orientation of the molecules in the sample. The low signal-to-noise ratio found in such ^{13}C NMR spectra is at least partly due to the long ^{13}C spin-lattice relaxation times (T_1) characteristic of solids and the fact that repetitions of the experiment are thereby constrained to long time intervals. Pines, Gibby and Waugh^{1,2} have shown how the ^1H - ^{13}C dipole-dipole problem can be eliminated by a high-power ^1H decoupling method which also provides an enhancement in the ^{13}C NMR signal and effectively deals with the problem of long T_1 's. This approach has previously been applied to coal samples.^{3,4,5}

The remaining line broadening source one would like to remove, chemical shift anisotropy, can be eliminated by rapidly spinning the sample about an axis at an angle of 54° ^{6,7,8}, the "magic-angle," with respect to the axis of the static magnetic field. A combination of cross polarization and magic-angle spinning techniques has provided promising spectra for coals and oil shales.

While anticipated improvements in the ^{13}C techniques--e.g., using larger static magnetic fields--may provide more detailed structural information, valuable information on the aromatic/aliphatic character of coals is presently obtainable using CP-MAS techniques. This paper provides information at that level on some representative coals and coal-derived materials.

EXPERIMENTAL

The coals on which ^{13}C NMR measurements were made include a Texas lignite, three Wyoming subbituminous coals (two from Hanna, one Wyodak), an Illinois bituminous, two Indiana bituminous, two eastern bituminous coals and an anthracite. In addition, the following coal-derived materials were studied: metallurgical coke; a Hanna coal that had been subjected to reverse combustion; and a solvent refined coal derived from the Wyodak coal. Each sample was studied as a powder, about 1.4 cm^3 in each case.

The ^{13}C NMR measurements were based upon the single-contact cross polarization method.^{1,2} A 90° ^1H pulse is applied, followed by a 90° phase shift, after which ^1H rf power is maintained during the ^{13}C cross polarization and for ^1H decoupling during data acquisition. Radio frequency power at the ^{13}C resonance frequency is applied according to the Hartmann-Hahn condition during the contact period and then turned off during the period in which the ^{13}C resonance frequency of 15.1 MHz on a home-built spectrometer, using a 14 kgauss magnet, and a commercially available ^{13}C Fourier transform data system. The H_1 field for ^1H was 10 gauss and that for ^{13}C was 40 gauss. Magic-angle spinning rates of 1.9 to 2.4 kHz were achieved with a spinner of the Andrew type, using air pressure of 13 to 20 lb/in². All spectra obtained using magic-angle spinning resulted from data accumulated from 4000 scans.

RESULTS

Before truly quantitative results can be reported from ^{13}C NMR techniques of the type employed in this study, a great deal of calibration work will be required with standards, and the detailed dynamics of the cross polarization phenomenon will have to be characterized for each coal type. Such work is not yet completed, but was not considered a prerequisite for reporting the essence and qualitative significance of the present results. VanderHart and Retcofsky⁴ and Bartuska et al.⁵ have previously discussed the problems of obtaining quantitative analytical data from cross polarization experiments.

In order to choose a reasonable set of experimental parameters, which could be expected to give integrated intensities of at least semiquantitative significance, parameter variations were carried out in experiments on the Illinois bituminous sample. The contact (cross polarization) time, which must be chosen to conform with the dynamics of ^{13}C - ^1H cross polarization and ^1H T_1 constraints, was varied over the following values: 0.5 msec, 1.0 msec, 3.0 msec, and 5.0 msec. Using a repetition time of 4.0 sec, we measured the integrated signal intensity of the "aromatic" and "nonaromatic" carbon resonances and the apparent carbon fraction found in the aromatic region, f_a (aromaticity); these values were found to be 0.75 and 0.76 for 1 msec and 3 msec, and 0.72 and 0.68 for 5 msec and 0.5 msec, respectively, for the contact time. The best signal-to-noise ratio (S/N) was found for the 1 msec contact time; S/N deteriorated badly at 5 msec. Choosing the 1 msec contact period, we repeated the experiment with a repetition time of 8.0 sec, obtaining a 0.74 value for f_a . Settling on 1 msec and 4 sec contact and repetition times, respectively, all cross polarization results reported in this paper were obtained using these parameters.

In order to check that by using the above-mentioned experimental parameters reasonable f_a values would be obtained in cross polarization experiments, we made ^{13}C NMR measurements on the Illinois bituminous sample by using the pulse Fourier transform method, with magic-angle spinning and high-power ^1H decoupling, but without cross polarization. Intensity data of such experiments are still subject to uncertainties associated with nuclear Overhauser effects and differing relaxation times,¹⁵ but such uncertainties are entirely different from those associated with the cross polarization approach. When pulse repetition times of 30 and 99 sec were employed, f_a values of 0.71 and 0.77, respectively, were obtained. Hence, while

there is no guarantee that the same cross polarization parameter set (1.0 msec and 4.0 sec) will serve equally well for all of the coal samples, indications are that this set leads to no major intensity distortions for the Illinois bituminous sample, and is a reasonable set to employ in the present survey.

DISCUSSION

An example of the advantages of magic-angle spinning in conjunction with cross polarization and high-power decoupling is shown in Figure 1a and b for the Hanna subbituminous coal. Clearly, the main structural distinction that can be made is between aliphatic and aromatic carbons. The spinning case shows much better resolution because the chemical shift anisotropy, which is evident in the aromatic region of Fig. 1a, has been eliminated. Aromaticity values are determined by dividing the integrated intensity of the aromatic band by the integrated intensity of the complete spectrum.

A ^{13}C spectrum of the Hanna coal which had been subjected to reverse combustion at 500°C is shown in Fig. 1c. The spectra clearly show depletion of the aliphatic carbons, relative to the aromatic carbons. Similarly, the CP-MAS spectra of a Wyodak coal (Fig. 2a) and its solvent refined product (Fig. 2b) show that the solvent refining process increases the aromaticity of subbituminous coals. These examples suggest the use of CP-MAS techniques for studies of coal combustion and processing.

^{13}C NMR spectra of a series of coals of varying rank are shown in Fig. 3a-f. This simple montage of ^{13}C spectra shows quite graphically that the aromaticity of coals increases with increasing rank. The metallurgical coke is included because it had a measured f_a of 1.00. A matter of concern regarding quantitative measurements in CP-NMR of solids is whether all the carbon types in the sample are being polarized equally, particularly aromatic carbons in condensed systems. The fact that the f_a of the coke yielded a very reasonable value of 1.00 implies that all of the carbons in the coal are being observed. Recent work on oil shales also addresses this problem.^{12,13}

One fuel property that would be interesting to relate to structural features is the heating value. Figure 4 shows a plot of the heating values of the coals vs. the f_a values derived from the ^{13}C spectra. That a simple correlation is not found is not surprising, as a variety of variations occur within these samples. In progressing from a lignite to a bituminous coal to an anthracite, the percent organic carbon of the material increases, which tends to increase the heating value.

An increase in f_a , by itself, would tend to decrease the heating value, as can be seen from the following heats of combustion: benzene, 782.3 kcal/mole; cyclohexane, 937.8 kcal/mole; n-hexane, 989.8 kcal/mole; phenol, 732.2 kcal/mole; cyclohexanol, 890.7 kcal/mole. In addition, within a collection of coal samples there are substantial variations in the percent oxygen, nitrogen and sulfur--i.e., in the occurrence of oxygen-, nitrogen- or sulfur-containing organics. Oxygen-containing species tends to decrease the heating value of a coal, for a given amount of carbon, as seen from the following heats of combustion: benzene, 782.3 kcal/mole; phenol, 732.2 kcal/mole; cyclohexane, 937.8 kcal/mole; cyclohexanol, 890.7 kcal/mole; toluene, 934.3 kcal/mole; benzyl alcohol, 894.3 kcal/mole; benzoic acid, 771.2 kcal/mole.

In viewing variations of heating values of coals, if one wishes to eliminate the factor due to percent organic carbon in the coal, the heating value per pound of carbon (maf) is of interest. Figure 5 shows a plot of this heating value vs. f_a . Note that, if the organic constituents of coal were strictly hydrocarbons, such a plot would be expected to show a decrease in BTU/lbc as f_a increases, reflecting the heat of combustion pattern stated above. Instead, Figure 5 shows a nearly

constant value of about 1.75×10^4 BTU/lbC for coals with apparent aromatic fractions ranging from 0.70 to 0.75 and a fall off on both sides of that f_a range.

This pattern can be understood as follows: As stated above, if coal were composed of only hydrocarbons, the trend would be to lower BTU/lbC for higher f_a values. This trend is responsible for the fall off of the curve for the highest three f_a values. However, organic compounds containing oxygen, but equivalent numbers of carbon atoms have lower heats of combustion than analogous hydrocarbons. The coals with the lowest observed f_a values, which might have been expected have the highest BTU/lbC values, also have the highest total oxygen contents (maf), and their lower BTU/lbC values may be associated with these high oxygen contents. The coals with highest f_a values (0.81, 0.95, and 1.0) have very low oxygen contents, and there is a roughly decreasing progression of oxygen contents as f_a increases from 0.59 to 1.0. Hence, there are two competing influences on the BTU/lbC parameter, giving rise to the broad maximum at about 1.75×10^4 BTU/lbC.

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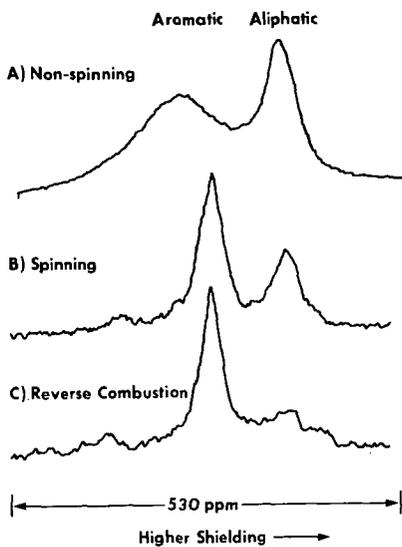


Figure 1. ^{13}C NMR Spectra of Hanna, Wyoming Coal

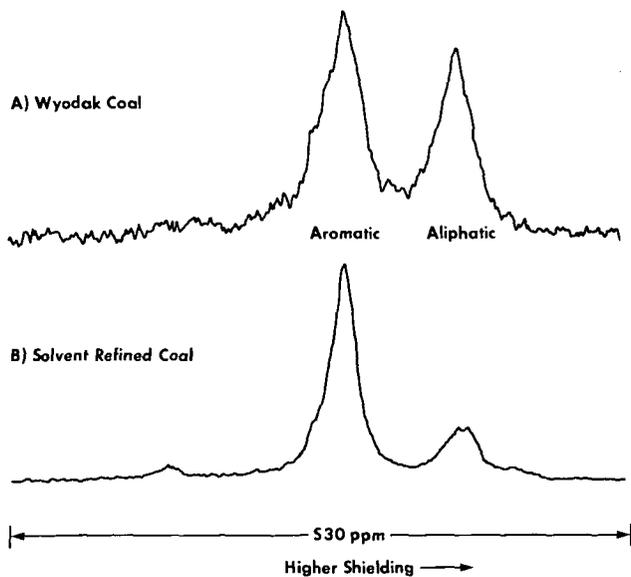


Figure 2. ^{13}C NMR Spectra of Wyodak Coal and SRC Product

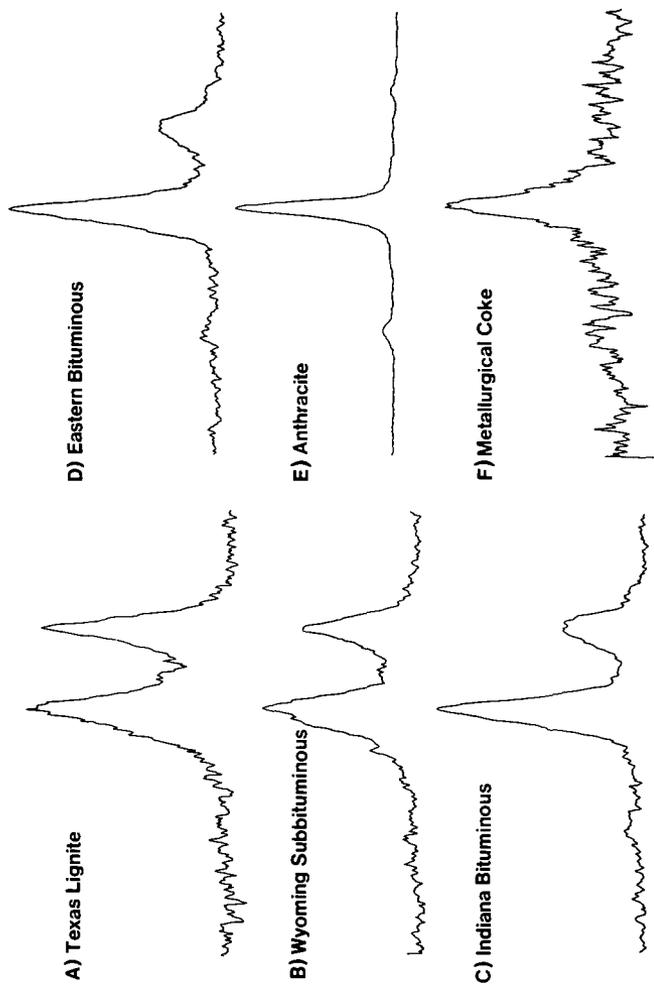


Figure 3. ^{13}C NMR Spectra of Coals of varying rank

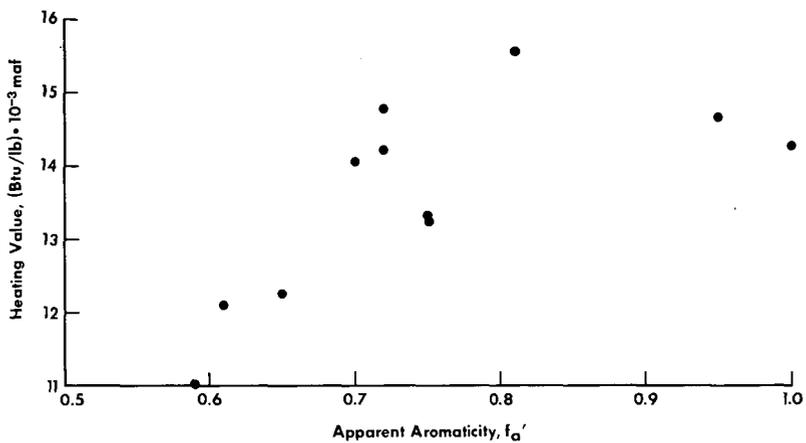


Figure 4. Plot of heating value versus aromaticity

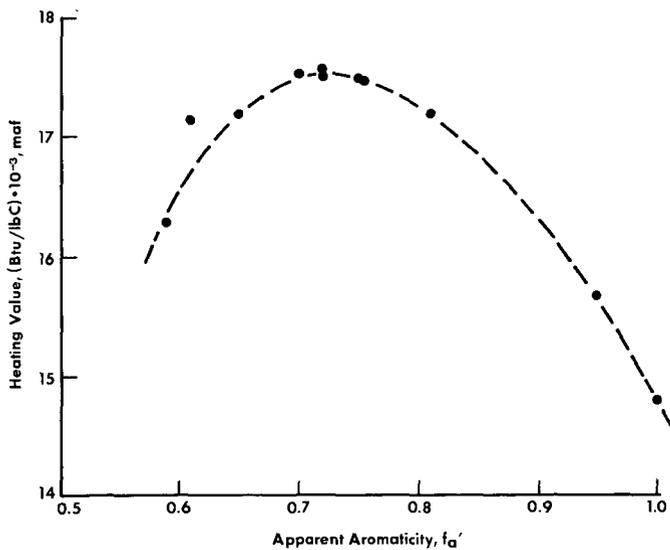


Figure 5. Plot of heating value/pound of carbon versus aromaticity