13C NMR STUDIES OF COAL AND OIL SHALES

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^{13}C NMR Studies of Coals and Oil Shales

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INTRODUCTION

The "standard" ^{13}C nmr techniques, including pulse Fourier transform (FT) approaches[1] have not been generally useful for solid samples because of (1) the excessive line broadening due to dipole-dipole interactions between ^{13}C and ^{1}H magnetic dipoles, (2) chemical shift anisotropies (different shielding values for the many different orientations of the molecules in an amorphous state with respect to the magnetic field direction), and (3) long ^{13}C spin-lattice relaxation times (T_1).[2] All of these problems are eliminated in liquids (or in the case of long T_1 values, at least greatly reduced) by the normal tumbling motions occurring randomly in the liquid state.

For an analytical technique in the field of fossil fuels, the constraint to liquid samples has been very restrictive. For many types of samples, e.g., oil shales and typical coals, only a small fraction of the organic substances can be extracted from a solid under mild conditions that would be expected to retain the primary structural integrity of the organic compounds.

The recently developed techniques used to narrow the lines of ^{13}C nmr signals in solids are high power ^{1}H decoupling[3] and magic-angle spinning.[4-7] The former involves irradiation of the proton manifold at the ^{1}H resonance frequency. It is analogous to the common "spin-decoupling" technique for eliminating splittings due to indirect spin-spin coupling in standard high-resolution nmr experiments; but it requires much higher radio frequency power, because direct dipolar $^{13}C,^{1}H$ interactions are much larger than indirect $^{13}C,^{1}H$ coupling constants.

The importance of magic-angle spinning is that rapid sample spinning at the magic angle eliminates the effects of chemical shift anisotropy, *i.e.*, averaging the resonance positions corresponding to the various orientations of a particular type of carbon atom in the solid sample to the isotropic limit that would be observed if the sample were in a nonviscous liquid state.[7,8] This is because the anisotropic part of the shielding tensor involves a trigonometric factor which vanishes at a value 54.7° (the magic angle) for the angle between a shielding tensor axis and the magnetic field axis.

The remaining source of line broadening expected of ^{13}C resonances in solid fuels is the dispersion of (isotropic) chemical shifts of a given class of carbon atoms over a range due to subtle structural differences associates with the complex structural variations in such samples. This dispersion of chemical shifts is <u>not</u> removed by the techniques discussed in this paper, and is ultimately a genuine source of structural information.

The third problem mentioned above, the long spin-lattice relaxation times in solids, is circumvented by the development by Waugh and coworkers of cross polarization methods, or Proton Enhanced Nuclear Induction Spectroscopy.[3] In cross polarization an enhanced ^{13}C magnetization is achieved at a rate much faster than the rate of reestablishment of an equilibrium ^{13}C magnetization <u>via</u> ^{13}C spin-lattice relaxation. This is achieved by the ^{1}H spin-lock procedure[3] and the establishment of Hartmann-Hahn conditions, $\gamma_C H_1^C = \gamma_H H_1^H$, where γ_C and γ_H are the magnetogyric ratios of ^{13}C and ^{1}H, respectively.

Although several variations of the general type of cross polarization experiment have been suggested, the form employed in this work is that originally described by Pines, Gibby and Waugh[3] for ^{13}C; it is shown schematically in Fig. 1. The key feature responsible for the success of the cross polarization experiment for ^{13}C in solid samples is the rapid transfer of magnetization from the proton spin set to the ^{13}C spin set under the Hartmann-Hahn condition. This transfer permits the establishment and repetitive reestablishment of the ^{13}C spin polarization needed for ^{13}C nmr detection, without waiting the long times (three to five ^{13}C T_1's) required for establishment of the polarization <u>via</u> normal ^{13}C spin-lattice relaxation processes. The experiment can be repeated after waiting for the protons to repolarize (three to five ^{1}H T_1's). This repolarization is generally a much more efficient process than ^{13}C repolarization by spin-lattice processes.

Using the cross-polarization/high-power ^{1}H decoupling technique, ^{13}C spectra of the type shown in Fig. 2 were obtained. A variety of factors preclude using spectra obtained in this way <u>directly</u> for the quantitative determination of the aliphatic carbon/aromatic carbon ratio.[4] These factors include chemical shift anisotropies and related peak overlaps, unequal cross-polarization efficiencies and the undetermined distribution of relevant proton relaxation times. This current limitation can be eliminated only by overcoming or characterizing these factors, a subject of continuing research in these laboratories. Nevertheless, we have observed a very interesting and useful correlation obtained directly from the raw spectra.

In the spectra of the type shown in Fig. 2, the region to the right (higher shielding) of the arbitrarily-drawn vertical dashed line can be identified largely with the resonances of aliphatic carbons, while the region to the left is associated mainly with aromatic carbons (perhaps some olefinic carbons and carbonyl carbons). If the area under the spectrum to the left of the line is referred to as A, the area to the right as B, and the total area (A+B) as C, then A/C is roughly the fraction of total organic carbon that is aromatic and B/C

is roughly the fraction which is aliphatic. Then, if P is the percent (by weight) organic carbon in the sample, measured independently (by total carbon minus carbonate and bicarbonate), the quantity AP/C is an indication of the percent aromatic carbon in the sample and BP/C is the percent aliphatic carbon. Figures 3 and 4 show the results of plotting these fractions against oil yield (gal/ton). For the twenty oil shales and kerogens examined in this study, the total organic carbon content (P) ranged from 11 to 81 percent (by weight) and the (apparent) fraction of aliphatic carbon (B) ranged from 0.37 to 0.85.

Fig. 3 indicates that there is little correlation between the amount of aromatic carbon in an oil shale and its oil yield. By contrast, Fig. 3 shows a high level of correlation between the amount of aliphatic carbon in an oil shale and the yield of oil obtained in retorting. These results support the thesis that it is the aliphatic part of the kerogen that is largely responsible for the oil retorted from oil shale. The results are also consistent with earlier evidence that higher H/C ratios in oil shales are associated with higher oil yields.[10] Furthermore, the results suggest that refined ^{13}C nmr measurements (faster and more accurate) may provide a convenient method for determining not only the structural characteristics of kerogen, but also the economic potential of individual shales.

Similar experiments on a wide range of coal samples are underway and will be described in the talk. The resolution of aromatic and aliphatic carbons can be improved from what is shown in Fig. 2 by magic-angle spinning. The consequences of this improvement are also discussed.

Acknowledgement

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Figure Captions

Figure 1. Timing sequence of ^{1}H and ^{13}C irradiation and ^{13}C observation in a typical cross polarization experiment.

Figure 2. Cross polarization spectra of three oil shales with different aliphatic C/aromatic C ratios. The arbitrary vertical line roughly separates the aliphatic from the aromatic regions of the spectra.

Figure 3. A plot of the apparent percent aromatic carbon (AP/C) of twenty oil shales and kerogens vs. the oil yields of the oil shales in gal/ton.

Figure 4. A plot of the apparent percent aliphatic carbon (BP/C) of twenty oil shales and kerogens vs. the oil yields of the oil shales in gal/ton.

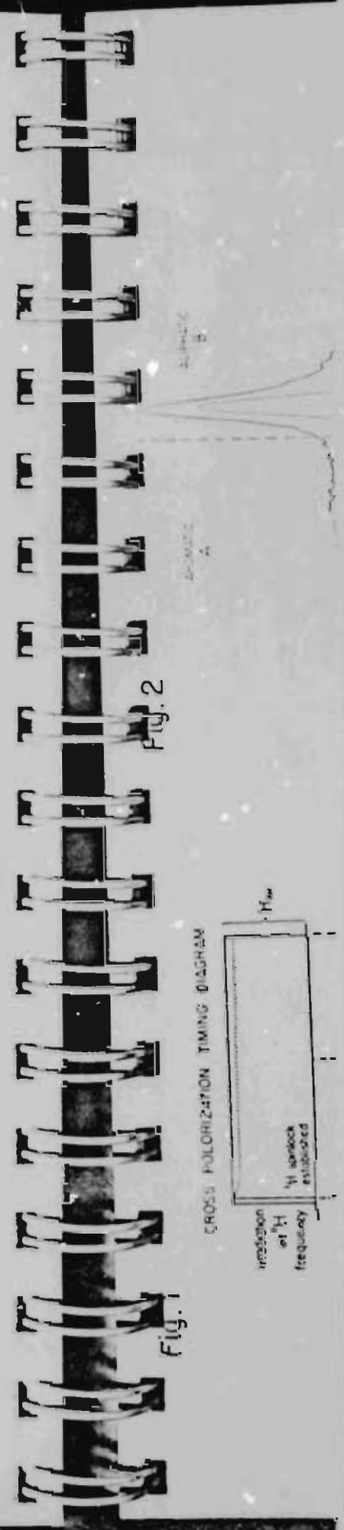


Fig. 1

Fig. 2

Fig. 1

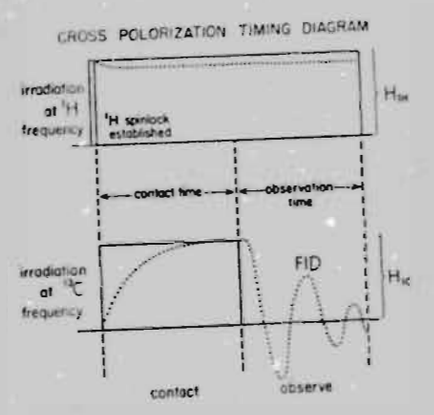


Fig. 2

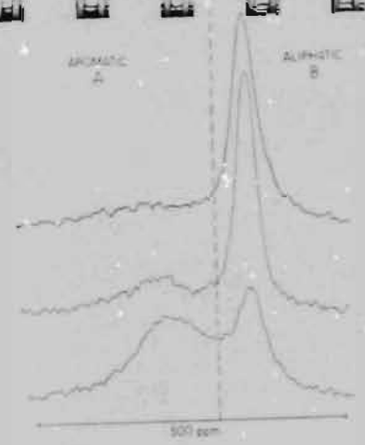


Fig. 3

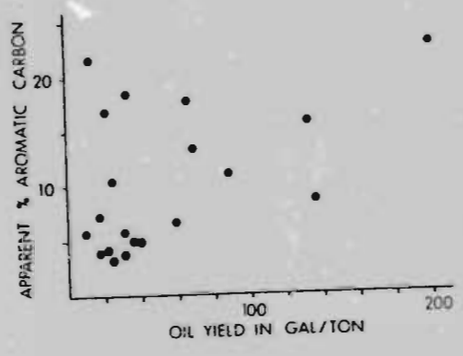
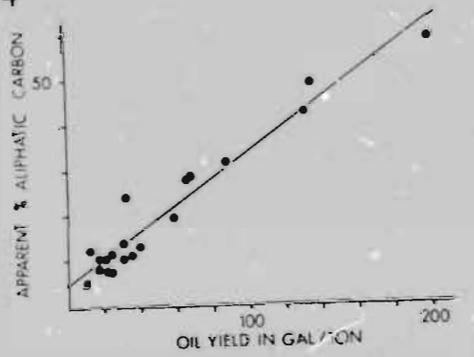


Fig. 4



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