

Organic Structure Studies of Fossil Fuels
by Nuclear Magnetic Resonance

Victor J. Bartuska and Gary E. Maciel
Department of Chemistry, Colorado State University
Fort Collins, Colorado 80523

and

Francis P. Miknis and Daniel A. Netzel
Laramie Energy Research Center, U.S. Department
of Energy, Laramie, Wyoming 82070

Nuclear magnetic resonance (nmr) is playing an increasingly important role in the characterization of the organic constituents of fossil fuels.¹⁻¹⁷ The nmr techniques that are currently being applied to fossil fuel characterizations utilize both the ¹H and ¹³C nuclides and can conveniently be divided into those that apply to liquid samples and those that apply to solids. For solids one has to contend with line-broadening influences of dipole-dipole interactions and chemical shift anisotropies (especially for carbon) and with long spin-lattice relaxation times; some recent advances have largely circumvented these problems for ¹³C.¹⁴⁻²⁰ For liquids, rapid isotropic molecular tumbling averages dipolar splittings to zero and the chemical shift tensor to its isotropic average, and gives rise to relatively efficient spin-lattice relaxation (permitting one to reduce the wait time between pulse repetitions).

For solid fossil fuels, a considerable amount of structural information can be obtained by modern ¹³C techniques.¹⁴⁻¹⁷ Proton experiments on solids determine the amplitude of the free induction decay (FID) following a 90° pulse; this amplitude is a measure of the organic proton content of the sample for oil shales and has been related empirically to the oil yield one can obtain by retorting (Figures 1 and 2).^{8,9}

For ¹³C studies on solids, rapid spinning of the intact or powdered sample about an axis making an angle of 54° 44', the "magic angle", relative to the field axis eliminates broadening due to chemical shift anisotropy.^{17,19,20} High-power ¹H decoupling eliminates broadening due to ¹³C-¹H dipole-dipole interactions.¹⁸ If the high-power ¹H decoupling and ¹³C resonance are carried out under conditions obeying the Hartmann-Hahn condition,¹⁸ then the problem of long ¹³C spin-lattice relaxation times can also largely be overcome. The net result of applying these techniques to homogeneous, pure organic solids is sharp-line spectra, reminiscent of spectra obtained on analogous liquid samples. For solid fossil fuels, however, the great complexity of mixtures of closely related chemical structures gives rise to resonance "bands", rather broad lines, encompassing the ¹³C resonances of a given structural type, e.g., aliphatic carbons. While greater structural detail may sometime be available, (especially from spectra obtained at high field strength), at present the greatest current capability of this approach is a clear distinction between the resonances of aromatic or olefinic carbons and the aliphatic carbon resonances. Typical spectra are shown in Figures 3 and 4.

For liquid samples, standard pulse Fourier transform methods¹⁻⁷ are applicable to both ¹³C and ¹H. Because of the great chemical complexity typical of samples, very complex spectra are usually obtained. Nevertheless, considerable information can usually be extracted regarding the occurrence of specific structural types.

By combining the various techniques described above, a great deal can be learned about a fossil fuel system and the processes involved in typical characterization procedures and, more importantly, in its conversion into a useable fuel source. We have applied the various nmr techniques described above to solid and liquid samples derived from oil shale of the Green River Formation. The purpose was to explore the potential applicability of nmr methods to answer such questions as: Do procedures for concentrating the kerogen in oil shale alter the distribution of organics in kerogen significantly? How similar are the kerogen, shale oil and bitumen derived from a specific oil shale? What, if any, types of organic structural features are present in the spent shale after retorting?

Using solid-sample techniques one can determine the total organic proton content and the aromatic/olefinic and aliphatic carbon contents of the raw shale, of the solid remaining after bitumens are extracted, of the solid kerogen concentrate obtained from the shale and of the residue from retorted shale. Using standard FT techniques for liquids, analogous information and considerably greater structural detail can be obtained on the bitumens extracted from the shale and on the shale oil retorted from the shale. Examples of relevant spectra are shown in Figures 5-8. In interpreting the intensities of the resonances of such carbon spectra, one has to pay close attention to intensity distortions associated with nuclear Overhauser effects and the dynamics of the cross polarization experiment.²⁰

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Figures

- Figure 1. Proton free induction decay (at 20 MHz) for oil shale before and after heating to remove free water (From Miknis et al, BuMines Rep. Invest. No., 7984 (1974).
- Figure 2. Correlation between proton free induction decay amplitude and average Fischer assay oil yields (From Miknis and Netzel, Magnetic Resonance in Colloid and Interface Science, H.A. Resing and C.G. Wade, Eds., ACS Symposium Series, 34, 182 (1976).
- Figure 3. ^{13}C nmr spectrum of Hanna (Wyoming) coal, with high-power ^1H decoupling, cross polarization and magic-angle spinning, obtained at 15.1 MHz. 530 ppm range. Higher shielding on the right.
- Figure 4. ^{13}C nmr spectrum of Australian oil shale, same conditions as for Figure 3.
- Figure 5. ^{13}C Fourier transform nmr spectrum of shale oil retorted from Colorado oil shale of Fig. 7. 530 ppm range. Higher shielding on the right.
- Figure 6. ^{13}C Fourier transform nmr spectrum of bitumen (in CDCl_3) extracted with benzene from Colorado oil shale of Fig. 7. Same conditions as for Fig. 5.
- Figure 7. ^{13}C nmr spectrum of raw Colorado oil shale. Same conditions as for Fig. 3.
- Figure 8. ^{13}C nmr spectrum of kerogen concentrate obtained from Colorado oil shale of Fig. 7. Same conditions as for Fig. 3.

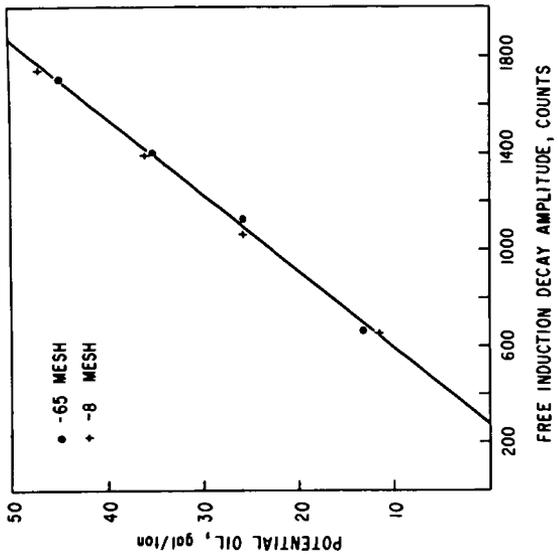


FIG. 2
CORRELATION BETWEEN FID
AMPLITUDE AND OIL YIELD

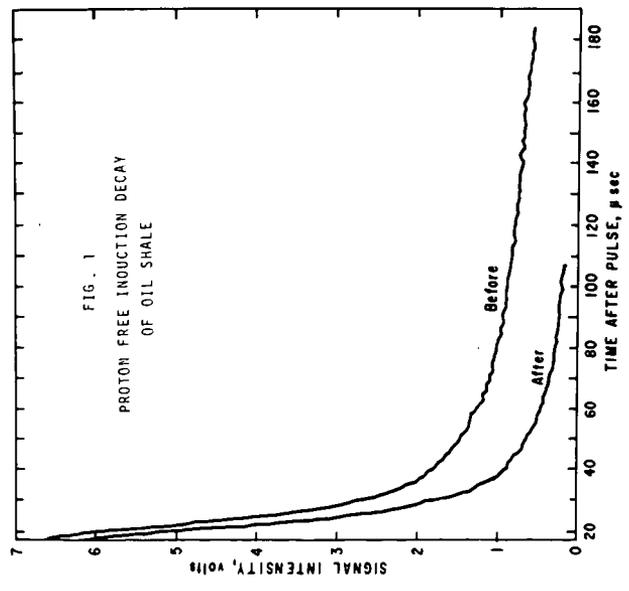


FIG. 3

^{13}C SPECTRUM OF
HANNA COAL

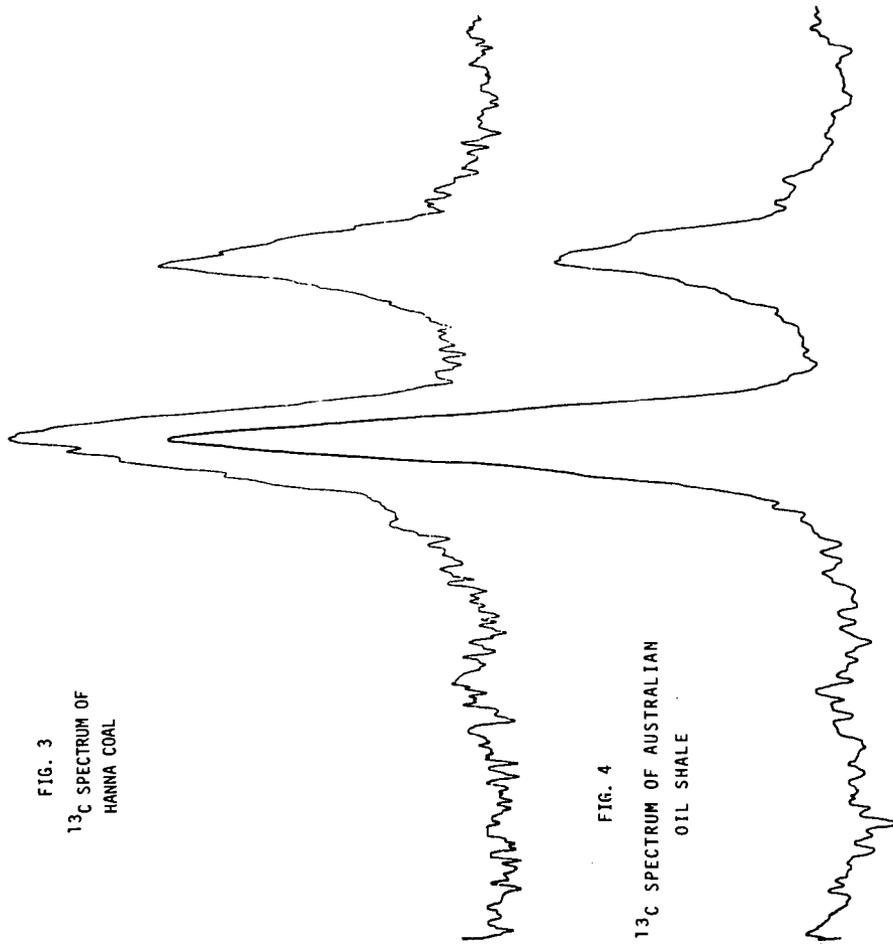


FIG. 4

^{13}C SPECTRUM OF AUSTRALIAN
OIL SHALE

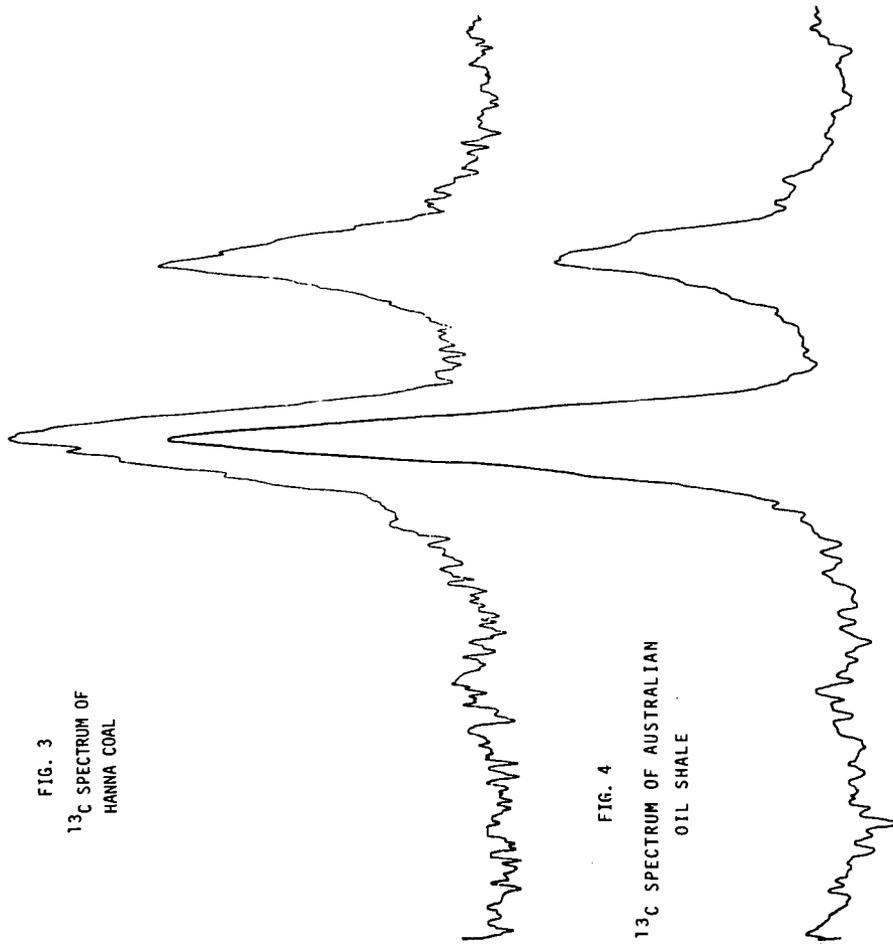


FIG. 5
 ^{13}C FT SPECTRUM OF SHALE OIL

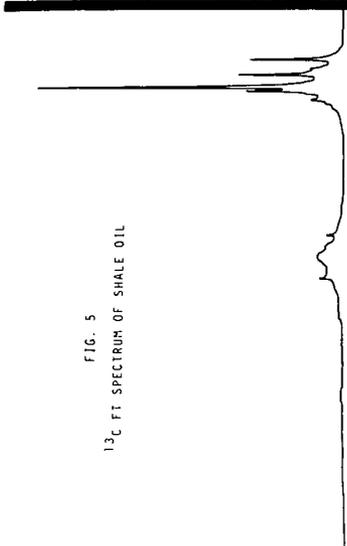


FIG. 7
 ^{13}C SPECTRUM OF RAW OIL SHALE

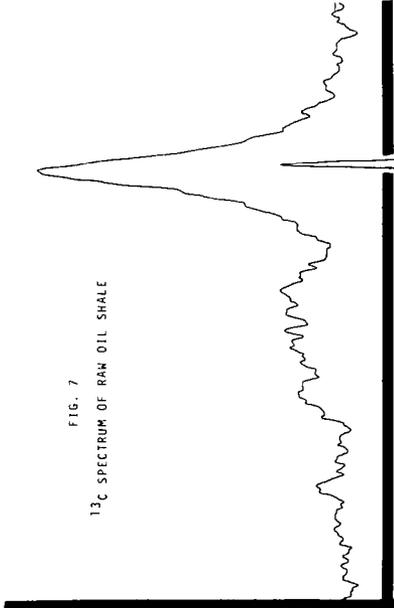


FIG. 6
 ^{13}C FT SPECTRUM OF
OIL SHALE BITUMEN

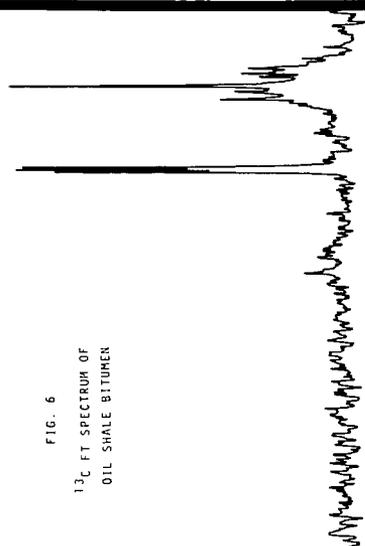


FIG. 8
 ^{13}C SPECTRUM OF KERGEN CONCENTRATE
FROM OIL SHALE

