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A SOLID-STATE NMR STUDY OF CONDENSATION/RETROGRADE REACTIONS DURING COAL LIQUEFACTION

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BACKGROUND

The objective of this work is to perform an NMR study of the aromaticity in coals, coal derived products and/or model compounds generated by pyrolysis and thermal solubilization of coal in the presence of a hydrogen donor solvent. Cross Polarization with Magic-Angle Spinning (CP/MAS) will be used to measure the carbon aromaticity, and Combined Rotation and Multiple Pulse Spectroscopy (CRAMPS) NMR techniques will be used to measure the hydrogen aromaticity. From these NMR measurements the aromatic hydrogen-to-carbon ratio will be obtained and used to study condensation/retrograde reactions during coal liquefaction.

The study consists of four tasks: 1) develop NMR methods to determine aromatic carbon by CP/MAS and aromatic hydrogen by CRAMPS for low hydrogen containing organic solids such as coals, and coal residues; 2) characterize the feasibility of applying the NMR methods for quantitative measurements in coals; 3) analyze selected samples of coals and coal-derived products to demonstrate applicability of the NMR methods to study coal liquefaction, and 4) report the results to the Department of Energy.

ACCOMPLISHMENTS

The development of the CP/MAS and CRAMPS methods for coals is being done at the Colorado State University in Fort Collins, Colorado. During the quarter, work continued on the development of CP/MAS ^{13}C NMR techniques for quantitative carbon aromaticity measurements in coals using a large-volume sample spinner, and Delrin as a "built in" intensity standard for ^{13}C spin counting.

Large Sample ^{13}C NMR Spectroscopy of Coal

The newly developed large-sample (2.5 cm^3) magic-angle spinning (MAS) system (spinning speed $\leq$ 4.5 kHz) has been employed in single-pulse (SP) and cross-polarization (CP) MAS experiments on three premium coals from the premium coal bank of the Argonne National Laboratory. The dramatically enhanced signal-to-noise characteristics achieved with this MAS system, roughly 4-6 relative to what is achieved with "conventional" MAS devices, permit us to a) carry out reliable relaxation measurements with good precision; b) to carry out extensive SP experiments, thereby avoiding the quantitation uncertainties associated with CP strategies; c) to obtain reliable and reproducible intensities of low-intensity peaks, e.g., minor peaks or shoulders in the spectra and even in dipolar-dephasing spectra; and d) to carry out quantitative spin counting experiments in both the SP-MAS and CP-MAS modes. The "built-in" Delrin reference signal of the spinner is used, as described previously, as a quantitative intensity reference. The relaxation measurements carried out include: CP-based T_{1H}; CP-based T_{1C}; SP-based T_{1C}; T_{1H} and T_{CH} via variable contact-time experiments; $T_{1\rho}$ via CP, using a variable ^1H spin-lock period; and detailed dipolar dephasing measurements. Using these results, spin counting in the CP-MAS approach is being evaluated by a new strategy developed recently at Colorado State University by R. A. Wind.

Samples are now being acquired from the DOE to test the application of the ^{13}C large-volume sample spinner on samples generated during coal liquefaction experiments. Some of these results should be available for reporting next quarter.

^{1}H CRAMPS Studies

Quantitation of the CRAMPS technique has not received much attention because of the previous difficulties in simply obtaining a CRAMPS spectrum. The CRAMPS technique is now being perfected to the extent that its quantitative reliability can be addressed (1). In principle, the CRAMPS technique should be quantitative because the signal intensity is directly proportional to the number of protons (hydrogens) in the sample. Because the CRAMPS experiment is entirely different from the CP/MAS experiments, concerns such as those described above for CP/MAS are not relevant for CRAMPS. The relevant areas of concern regarding quantitation in CRAMPS are mainly instrumental artifacts, spectral deconvolution, and finding a suitable internal standard for spin counting (1). Because the CRAMPS technique is so new, the jury is still out regarding its application and usefulness in coal science. However, work conducted during this study will be useful for assessing its validity.

With regard to peak overlap, significant improvements have been made in resolution of CRAMPS spectra using deuterated pyridine to swell the coal (2). The ^{1}H CRAMPS spectrum of an original coal and a coal saturated with pyridine-d_5 is shown in Figure 1. The improvement in resolution is clearly evident. The source of the increased resolution in the pyridine is not fully understood at this time (2). The hydrogen aromaticities obtained by deconvolution of the spectra are both about 0.47.

Quantitation of ^{1}H CRAMPS spectra is limited by the overlap of the aliphatic and aromatic resonances. The use of pyridine-d_5 should help alleviate some of the problem. However, a suitable intensity standard must be found before total quantitation is realized. Such a standard should (1) be chemically inert, so that is can be mixed with other powdered materials; (2) not be hygroscopic, which would compromise weighings and possibly violate criterion 1; (3) not have such a large number of equivalent hydrogens with a narrow resonance that a dynamic range problem is encountered; and (4) have chemical shifts outside the normal range (0-11 ppm for most samples) and T_1s of less than about 4 s. Experiments are under way to find a suitable reference material possessing these characteristics.

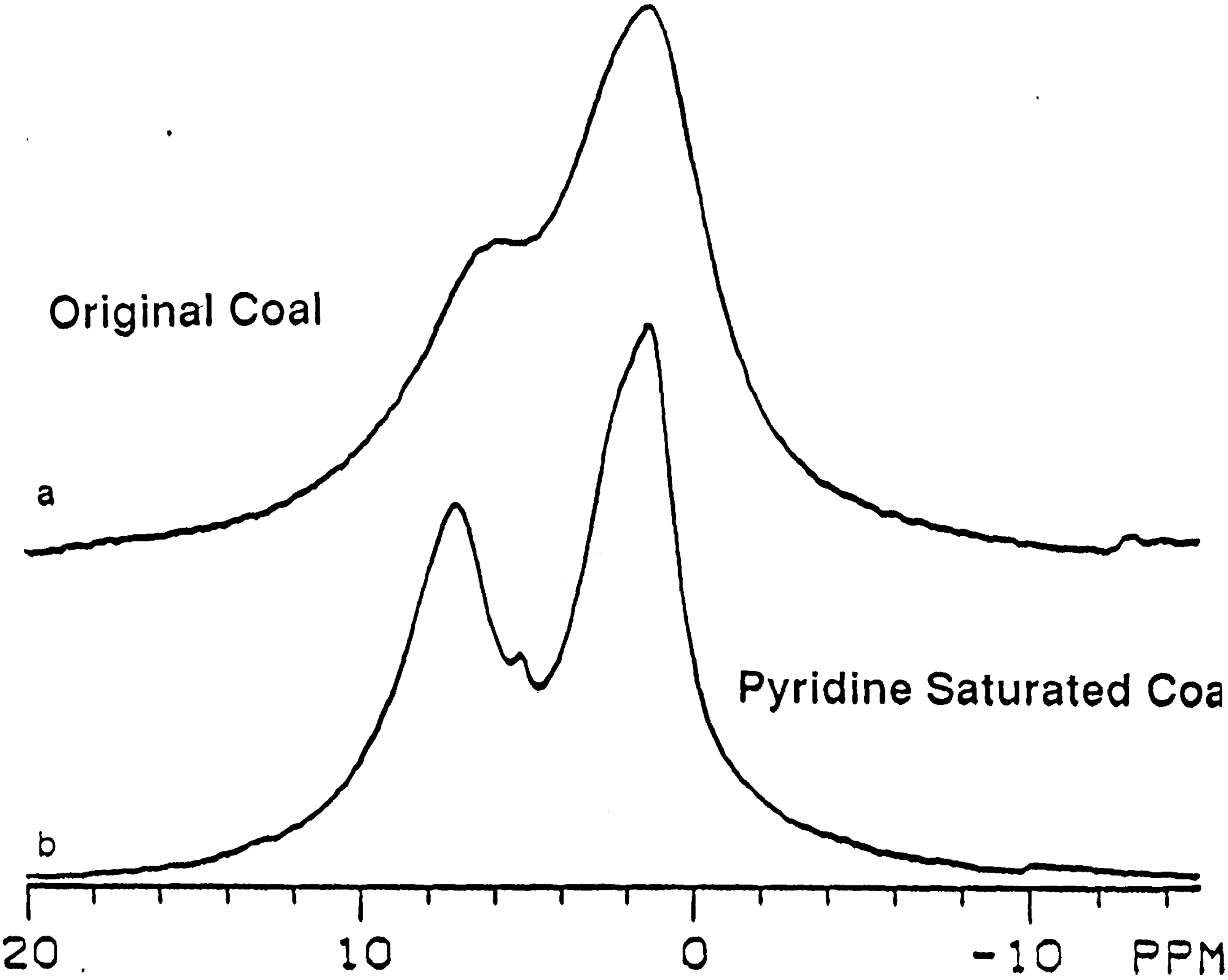

Figure 1. ^{1}H CRAMPS spectra of coal: (a) original coal; (b) coal saturated with pyridine-d_5

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