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Title: SPIN-MAPPING OF COAL STRUCTURES WITH ESE AND ENDOR

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ABSTRACT

Advanced electron paramagnetic resonance (EPR) techniques — ENDOR, ESE, and VHF-EPR — are used to probe the molecular structure and surface properties of coals. With additional support from DOE through the Illinois Clean Coal Institute (ICCI), we have been able to use novel, very high frequency electron paramagnetic resonance (VHF EPR) spectroscopy techniques and instrumentation (the only cw W-band spectrometer in existence) developed earlier by these authors, to conduct further qualitative and quantitative studies of heteroatomic organic molecules in coal with particular emphasis on sulfur. Previous W-band (96 GHz) work is being extended to studies of new model compounds as well as coal and desulfurized coal samples. Typically, the model compounds under investigation and their analogues are found in coals as stable free radicals which give rise to an EPR signal.

The work this quarter focused on the W-band EPR of Illinois Basin Coal (IBC) samples 101 through 109, and several very high organic sulfur coals. The variation observed between the VHF-EPR spectra of different types of coal is enough to justify calling the method a fingerprint technique. When integrated EPR signals believed to be from radical thiophenic forms of sulfur are taken as a rough measure of these forms of sulfur, the thiophene-type organic sulfur appears roughly to parallel the total organic sulfur content, as expected. Careful studies of preparation techniques show that while X-band spectra are only slightly affected by evacuation, the W-band spectra of several coals show irreversible modification in the VHF-EPR spectra. W-band spectra of some coals show distinct dependence of lineshape on microwave power, with some spectral components saturating prior to others. It may be possible to exploit these variations to pick out subtly different thiophenic species, or distinguish different environments. Work is in progress to better investigate these effects.

More radicals were prepared from organic sulfur compounds in various glasses, at catalytic surfaces, and in solution; 2,3-benzodiphenylene (DBF) oxide has been added to the growing number of new compounds, which are themselves often commercially derived from coal extracts. DBF radical has been prepared both on a catalytic surface, and in a BAG matrix. Its W-band spectra show quite different features than the thiophenic compounds studied so far.

In this reporting period, we were operating under a no-cost extension of this DOE grant; most of the grant funds have been expended, and the major part of this work for the quarter was supported by DOE through the ICCI contract. Therefore, the work is reported in more detail through that agency. The report which follows summarizes selected information from the ICCI report.

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REPORT

This work addresses the need for innovative approaches to characterize the organic sulfur in coals by means of advanced Electron Paramagnetic Resonance (EPR) methods, including ENDOR, pulsed EPR, and very-high-frequency electron paramagnetic resonance (VHF-EPR) spectroscopy operating at W-band microwave frequencies (96 GHz). VHF-EPR spectra taken using this unique instrument show unique sensitivity to heteroatoms in coal, the technique can be successfully applied to the problem of **non-destructive determination of organic oxygen and sulfur aromatic species in coal**. Data from Illinois coals and separated macerals indicate that **it is possible to distinguish aromatic from aliphatic sulfur, and may be useful in assessing the extent of conjugation in aromatic portions of the coal**. It should be emphasized that the only other technique for obtaining this type of information is the XANES/EXAFS techniques developed by Gorbaty, Hoffmann, and others. Though these techniques are somewhat more advanced in terms of their development, no single technique should be relied upon entirely, and without other methods of corroboration. An additional advantage of VHF-EPR is that it has a potential for the routine analysis of aromatic heteroatoms rivaling that of other analytical techniques.

Previously, we have shown EPR spectra of whole coals taken at different microwave frequencies: 9, 35, and 96 GHz. At 96 GHz, a new feature characteristic of sulfur is resolved.

In the lower frequency spectra, thiophenic sulfur and furanic oxygen atoms shift the EPR resonance line, but the shift is too small to be readily resolved. In order to resolve the sulfur and oxygen peaks, higher field strengths and frequencies must be used. The resonance occurring at lower field strength is due to heteroatoms such as sulfur and oxygen. In coal, this signal is largely the result of organic sulfur. The goal of our current work is to develop a non-destructive spectroscopic technique to resolve qualitatively and quantitatively the molecular forms of organic sulfur in coal that are responsible for these spectra. To that end, a number of coals, inertinites, chars, and model thiophenic compounds continue to be studied using the W-band spectrometer under a variety of conditions.

Because the information about the amount and chemical forms of organic sulfur in coal contained in VHF EPR spectra is new, it is very important that we develop correct interpretations of these data. To accomplish this task we have continued in this quarter to pursue the chemistry of synthetic thiophenic systems which mimic the properties of aromatic organic sulfur in coal. Previously reported methods of preparation utilizing boric acid glass matrix isolation of the compounds followed by UV irradiation have been perfected, and we are currently developing other methods to prepare smaller sulfur-containing compounds (thiophene, benzothiophene). Later, mass spectrometry will be used as a final check of all model compound preparations. The goal of this phase of the work is the elucidation of relationships between molecular structure and VHF EPR spectra that will allow us to make more accurate and insightful interpretations of the data from coal. The latest model compound to be generated is 2,3-benzodiphenylene oxide, or dibenzo-naphtho-furan (DBT). Its W-band spectrum is shown

elsewhere[1] along with several other representative model compounds.

W-band spectra of all the Illinois Basin Coal Sample Program (IBCSP) coals were acquired in this second quarter. Samples IBC101 through IBC109 were received directly from the IBCSP, with the exception of IBC107, which we were informed was not available due to a supply shortage. Very briefly, their description is as follows:

IBC101: High organic sulfur (3.08%) conventionally washed Herrin (IL No.6) coal.

IBC102: High pyritic, low organic sulfur (0.98%), Colchester (IL No. 2) coal.

IBC103: Low sulfur, 1:1 pyritic to organic sulfur ratio, 80% Springfield (IL No. 5) and 20% Herrin (IL No. 6) washed blend.

IBC104: High ash, high sulfur Herrin (IL No. 6).

IBC105: Near pristine channel sample.

IBC106: Low sulfur, 1:1 pyritic to organic sulfur ratio, Springfield (IL No.5).

IBC108: Very low pyrite and ash, micronized; physically cleaned (froth flotation) blend, 80% Springfield (IL No. 5) and 20% Herrin (IL No. 6).

IBC109: Low sulfur, high chlorine, cleaned and processed.

In addition to these coals, others were studied, including two extremely high sulfur coals: Răsu Lignite #1 (~13% total organic sulfur (TOS)) [2], and Spanish Mequinenza Lignite (~11% TOS) [3] were obtained. Care was taken to prevent any exposure to air, although the IBCSP does not provide coals that are "premium" in the way the term is used to characterize Argonne's Premium Coal Sample Program (APCSP).

In all, ten coals were studied this quarter, under both nitrogen and evacuated conditions, and at different microwave powers. Dramatic changes in spectral features appeared for several whole coals after evacuation — especially IBC105 and IBC106, though all samples showed some changes. The effects are dependent on how long the sample is evacuated, and even the length of time from sealing of the evacuated tube appears to be important, since the material being removed apparently continues to diffuse out of the coal. Spectra continue to change for two days and in some cases, even up to 1 week after the sample is sealed. These changes may be due to volatile matter, water, or oxygen adsorbed to the coal. Up to now, the changes have been irreversible, and the possibility that this is the result of structural or chemical changes in the coal itself cannot be ruled out. Other workers in dewatering coal using vacuum pre-processing have

[1] Quarterly Report by R.B. Clarkson, R.L. Belford, *et al.* to the Illinois Clean Coal Institute, Carterville, IL, March 1, 1992.

[2] This sample was provided by H.L. Retcofsky, Pittsburgh Energy Technology Center U.S.D.O.E.

[3] Provided by Kurt S. Rothenberger, Pittsburgh Energy Technology Center, U.S.D.O.E.

made similar suggestions [4]. For IBC108, a froth-flotation-washed coal supplied wet with a moisture content of 45%, no W-band spectra could be obtained since water adsorbs too much of the incident microwave power. But removal of water alone probably could not account for the large differences between evacuated and non-evacuated coal samples, especially as several of the higher-moisture coals, IBC101 and IBC102 with about 14.5% moisture showed less spectral effect than a lower-moisture sample.

We found that the coal samples undergo saturation very readily, probably due to the high spin concentration. Some coals show more dramatic effects, especially where several components are present which saturate at different powers. This can affect microwave spectra in several ways, but primarily saturation broadens spectral lines, and intermixes the adsorption and dispersion signals. When this happens, spectra typically begin to show dependency on the Zeeman modulation frequency, typically 100 KHz. In the past, the microwave power has been kept low to avoid these effects, but it may be possible to use just this phenomenon to differentiate between different structural environments using for example, factor analysis of the adsorption, or adsorption and dispersion spectra.

Experiments are underway to explore further the nature of these spectral changes on evacuation. This will include repeating the Argon Premium coals under vacuum. Followup plans are described in the following outline:

- 1) Vacuum studies
 - a) Repeat Argon coals under vacuum
 - b) Test the reversibility of evacuation effects on coal
 - c) Collection of gas for GC and mass spec. analysis
- 2) Improvement of quantitative measurement
- 3) Resolution of different sulfur species
 - a) Simulations
 - b) Use of second derivative spectra to better study spectral features
 - c) Use of differing saturation effects of various lines to separate out distinct organic species.
- 4) Model compounds
 - a) Begin mass spectroscopy of both whole coals and model compounds
 - b) Based on (a) above, extend W-band spectra to all compounds of sufficient purity.
 - c) Prepare model compounds made from chars of sucrose and sulfur.

[4] Karl S. Vorres, Roger Kolman, and Timothy Griswold, Preprints, Fuel Chem. Div., Am. Chem. Soc. 33(2) 333-342, (1988).

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