

NMR IMAGING: A 'CHEMICAL' MICROSCOPE FOR COAL ANALYSIS

D. C. French, S. L. Dieckman†, N. Gopalsami†, and R. E. Botto
Chemistry Division and †Materials and Components Technology Division
Argonne National Laboratory
9700 So. Cass Avenue
Argonne, IL 60439

Keywords: NMR, Imaging, Coal

ABSTRACT

This paper presents a new three-dimensional (3-D) nuclear magnetic resonance (NMR) imaging technique for spatially mapping proton distributions in whole coals and solvent-swollen coal samples. The technique is based on a 3-D back-projection protocol for data acquisition, and a reconstruction technique based on 3-D Radon transform inversion. In principle, the 3-D methodology provides higher spatial resolution of solid materials than is possible with conventional slice-selection protocols. The applicability of 3-D NMR imaging has been demonstrated by mapping the maceral phases in Utah Blind Canyon (APCS #6) coal and the distribution of mobile phases in Utah coal swollen with deuterated and protic pyridine.

INTRODUCTION

Coals are comprised of microscopically discernible regions (termed macerals) corresponding to different plant materials that have been geologically altered over time.¹ These discrete regions are known to exhibit widely different chemical behavior, thereby complicating coal processing technologies for the production of usable, high quality fuels and chemicals.

NMR imaging is sensitive to local chemical environments in complex molecular solids. Moreover, the technique has the unique capability of spatially mapping a sample's chemical or physical properties independently. Two-dimensional NMR imaging has proven to be a promising tool for the characterization of macerals in a dried specimen of Utah Blind Canyon coal.² However, a major difficulty in obtaining adequate spatial resolution in the third dimension rests with the intrinsic NMR properties, i.e., broad line widths, that are characteristic of many solids.

In this paper, we describe a 3-D NMR method that is based on a back-projection protocol in combination with image reconstruction techniques based on 3-D Radon transform inversion. Similar techniques have been described previously for imaging of liquid samples.^{3,4} The method incorporates the experimental flexibility to overcome the difficulties which are presented by broad-line materials.

EXPERIMENTAL METHODS

The NMR imaging system used in this study consisted of a Bruker CXP-100 NMR spectrometer fitted with a home-built imaging accessory which is described in detail elsewhere.⁵ The accessory, designed specifically for examining solid materials, consists of a versatile home-built IBM-PC based pulse programmer, three (X,Y,Z) Techron audio range 1-kW gradient amplifiers, a RF shaping unit, and a home-built, singly-tuned imaging probe capable of operating at 1-kW RF levels. The probe also contains forced-air-cooled gradient coils capable of operating with duty cycles in excess of 20% while producing a higher linear magnetic field gradient of 58 G/cm over a spherical space of 30 mm in diameter.

In a conventional 2-D NMR back-projection tomographic experiment, one applies a linear magnetic field gradient in a plane at numerous projection angles. For each angle, the Fourier transform of the data represents a planar integral of the proton density normal to the gradient vector. Similarly, in the 3-D back-projection experiment, by varying the gradient vector in order to sample the entire 3-D space, one obtains a 3-D Radon transform of the proton density. Let $Rf(P)$ be the Radon transform of the object function $f(M)$, where P and M are discrete points in the Radon and object space, respectively (Fig. 1).

$$Rf(P) = \int_{(OP,OM)=0} f(M) dM \quad (1)$$

The inversion of this transform can be obtained by double differentiation and back projection. Marr et al.⁶ have shown that the fastest way to invert the Radon transform is to use two sets of back projections, one along the meridian planes and the other along planes of constant latitude. The inversion can then be written as (Fig. 2):

$$f(M) = \frac{1}{4\pi} \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=\pi} \frac{\partial^2 Rf}{\partial \rho^2} (\rho(M, \theta, \phi), \theta, \phi) \sin \theta d\theta d\phi \quad (2)$$

where ρ , θ , ϕ are the classical parameters of spherical coordinates, and $\rho(M, \theta, \phi) = OM \cdot n$, where O is the origin and n is the unit vector in the direction (θ, ϕ) . The reconstruction algorithm of the 3-D Radon transform inversion was implemented as proposed by Grangeat and coworkers.⁷

Three-dimensional NMR imaging data were acquired on specimens using 128 complex data points, and a total of 3600 projections (30 θ angles over $\pi/2$ radians \times 120 ϕ angles over 2π radians). A gradient strength of 25 G/cm and a sweep width of 200 kHz were used. A total of 64 averages were acquired by using an approximate 90° pulse and a recycle delay time of 0.25 s. A spectroscopic resolution of 80, \times 80, \times 80, μm^3 was achieved. A total of 9 hours was required for data acquisition using these parameters.

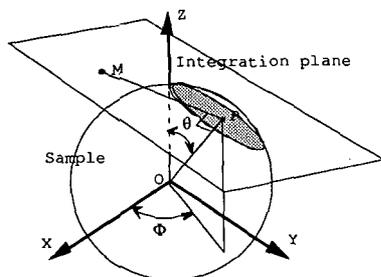


Fig. 1. Definition of 3-D Radon transform. Value of 3-D Radon transform in P is the integral of points M in plane defined by OPMP.

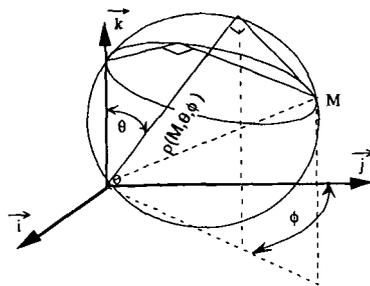


Fig. 2. Decomposition of integral over a sphere in two series of back-projections.

RESULTS AND DISCUSSION

In an earlier study, we had demonstrated the use of multi-pulse proton decoupling and back-projection reconstruction imaging methods to spatially resolve macroscopic resinite and vitrinite regions within a dried sample of Utah Blind Canyon coal.² Image contrast between the maceral phases was achieved on the basis of differences in proton density or spin-lattice relaxation (T_1). In the present study, we focus on the effects of solvent penetration to the swelling behavior of Utah coal.

The proton NMR spectrum of a specimen of Utah Blind Canyon coal swollen with "100%" deuterated pyridine is shown in Fig. 3. The spectrum displays three distinct proton resonances: there is a broad resonance (ca. 27 kHz) that corresponds to rigid protons in the sample, and there are two relatively narrow resonances (see expanded region at upper right) that correspond to aromatic and aliphatic protons in mobile environments. Line simulation subspectra were calculated from the experimental data by using a Pascal line simulation program on the Aspect 3000 computer as shown in Fig. 3. Analysis of the broad and narrow components indicates that approximately 14% of the protons are in the mobile phase. The fraction aromaticity (f_a^{H1}) of protons in this mobile phase is calculated from line simulation as 0.45, compared with a value of 0.24 obtained from proton CRAMPS analysis of the dried coal. Because residual protons of the deuterated pyridine are expected to contribute less than 0.1% of the total proton signal, one can conclude that pyridine mobilizes highly aromatic regions within Utah coal preferentially.

A 3-D surface-rendered NMR image of the Utah coal specimen swollen with deuterated pyridine is shown in Fig. 4. The image was recorded with a short recycle-delay time in order to suppress signal from the broad "solid" component having a longer T_1 . Thus, the image displays the proton distribution of mobile phases within the coal specimen preferentially. Surface rendering is performed by applying a user-adjusted threshold intensity to define a minimum intensity that is used to calculate the contiguous surface. The particular threshold employed was chosen to give the most accurate representation of the sample topology while suppressing low signal-to-noise structures near the sample surface. The image displayed is a good representation of the topology of the coal specimen; however,

it should be realized that surface features seen in the image represent areas with more or less density of mobile protons. For example, the feature seen at the front left of the object (indicated by arrow) is a crack in the specimen resulting from swelling with pyridine. Other features on the surface may be due to regions where there is a higher density of solid phase.

An 80-micron thin section (slice) of the 3-D NMR reconstructed image taken as a horizontal plane near the center of the specimen is shown in Fig. 5. Areas of bright intensity represent highly mobile regions within the specimen. Low intensity regions indicate solid phases or voids within the coal. The crack is clearly visible at the lower right portion of the image (indicated by arrow).

SUMMARY

We have demonstrated the feasibility of performing microtomographic NMR imaging on solid materials in three spatial dimensions. Methods were developed which combined 3-D back-projection protocol with image reconstruction using a Radon transform inversion technique. Using this methodology, we were able to spatially map maceral phases within a solid Utah coal specimen and monitor the distribution of mobile phases created upon swelling the specimen with pyridine.

ACKNOWLEDGMENTS

This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under contract number W-31-109-ENG-38, and by the U.S. Department of Energy, Assistant Secretary for Conservation and Renewable Energy, Office of Transportation Systems, as part of the Ceramic Technology for Advanced Heat Engines Project of the Advanced Materials Development Program, contract number ACK-85234.

REFERENCES

1. *Chemistry and Characterization of Coal Macerals*; Winans, R.E. and Crelling, J.C., Eds.; ACS Symposium Series 252, American Chemical Society: Washington, D.C., 1984.
2. Dieckman, S.L.; Gopalsami, N.; Botto, R.E. *Energy and Fuels* 1990, 4, 417.
3. Lauterbur, P.C.; Lai, C.-M. *IEEE Trans.* 1980, 27, 1227.
4. Lai, C.-M.; Lauterbur, P.C. *J. Phys. E.* 1980, 13, 747.
5. Gopalsami, N.; Foster, G.A.; Dieckman, S.L.; Ellingson, W.A.; Botto, R.E. *Development of NMR Imaging Probes for Advanced Ceramics*, Rev. Prog. in QNDE, Thompson, D.O. and Climenti, D.E., Eds.; Plenum Press, 1990.
6. Marr, R.B.; Chen, C.; Lauterbur, P.C. In *Aspects of Computerized Tomography*; Herman, G.T. and Natterer, F., Eds.; Springer-Verlag, 1980.
7. Grangeat, P.; Hatchadourian, G.; Le Masson, P.; Sire, P. *Logiciel Radon, Notice Descriptive Des Algorithmes Et Des Programmes*; Version 2.1 du 13-04-1990, LETI/DSYS/SETI/90-180 PS, Grenoble, 1990.

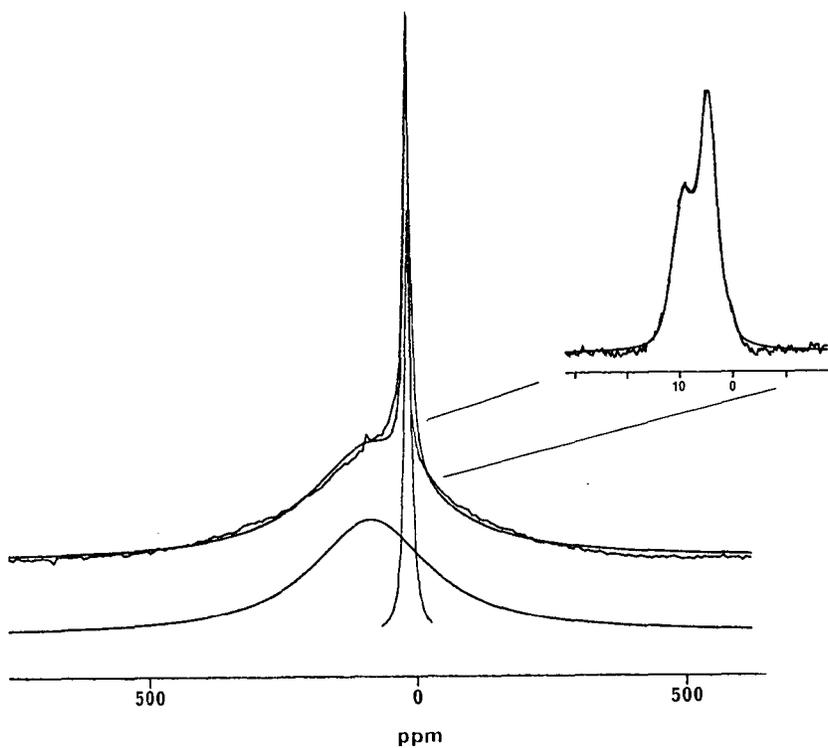


Fig. 3. Proton NMR spectrum of Utah Blind Canyon (APCS #6) coal specimen swollen with "100%" deuterated pyridine. Expanded plot at upper right displays narrow resonances with baseline correction applied.

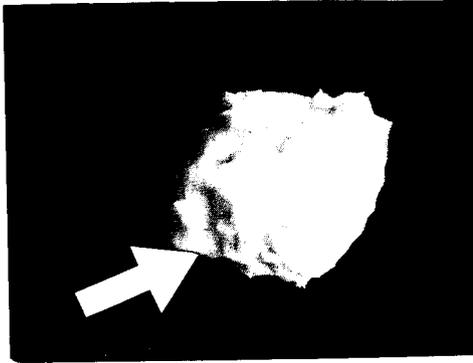


Fig. 4. Surface reconstructed 3-D NMR image of Utah Blind Canyon (APCS #6) coal specimen swollen with deuterated pyridine.

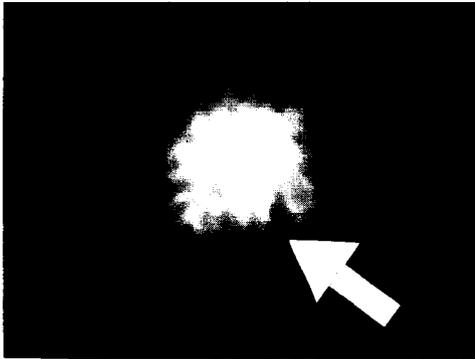


Fig. 5. Internal 2-D thin section of 3-D NMR reconstructed image of Utah coal specimen as shown in Fig. 4.