

# **<sup>1</sup>H PULSED SOLID-STATE NMR T<sub>2</sub> RELAXATION STUDIES OF MACROMOLECULAR STRUCTURES OF ARGONNE PREMIUM COALS**

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## **Abstract**

NMR studies of free induction decay (FID) have been made for as received and dried samples of North Dakota, Illinois #6 and Pittsburgh #8 coals.

Modifications of the NMR measurement and data treatment lead to an unambiguous separation of the FID signal into three components: two gaussians and one lorentzian. The two gaussians can be related to the macromolecular structures of coal, and their relaxation behaviors are comparable with model polymer systems. The lorentzian is almost entirely due to absorbed water, and the water content determined for the coals as received agrees very well with those reported using other methods.

High vacuum dried coal samples are also studied, and the results are compared with those of as-received coals. The drying is very effective, evidenced by almost complete loss of the lorentzian component. Interestingly, neither  $T_2$  nor  $I_2(0)$  is changed after drying, indicating that the drying process does not have a damaging effect on coal structures.

## **Introduction**

The determination of moisture in coals, the investigation of effective ways for coal drying, and the evaluation of the effect of the drying process on coal structures are both of fundamental importance in coal science and of commercial value in industry applications.

Several experimental methods have been developed in the analysis of moisture in coals, e.g., ASTM (1) and <sup>18</sup>O isotope dilution (2). NMR relaxation measurement has been used for a long time in water quantification in coals (3). A recent work by Wroblewski et al. (4) using <sup>31</sup>P NMR relaxation technique not only provided a new method for coal moisture quantification, but also presented an excellent review and comparison among different techniques and results in the literature on coal moisture determination.

Coal drying is often the first step in coal experiments and coal treatment both in laboratory and industry scale. However, contrary to the studies of wet coals, much less work has been done for dried coals. Although both wet and dried coals were

studied using solid-state NMR a long time ago (5), much of the attention lately have been given to the kinetics of the drying process (6). In other words, there is a need of a systematic evaluation of the effectiveness of various drying methods, and a investigation of the impact of the drying processes on coal structures.

Recently, we have conduct a series of experiments on as-received, dried (in different ways), and solvent swelled Argonne Premium coals using pulsed solid-state NMR techniques (7). Here, we present part of these results, i.e.,  $^1\text{H}$  NMR  $T_2$  relaxation measurement of as-received and high vacuum dried Illinois #6, Pittsburgh #8 and North Dakota coals. The main purpose of this paper is to demonstrate:

- (1) a new method for coal moisture quantification,
- (2) a establishment of the relationship between NMR relaxation behaviors and coal structures, and
- (3) an evaluation of the effectiveness of drying, and its impact on coal structures.

### Experimental

The as-received samples were prepared by directly transferring well-shaken 100 mesh Argonne premium coals from the original ampules to a 5 mm NMR tube under nitrogen atmosphere. The dried coal samples are prepared using high vacuum pumping at about  $1 \times 10^4$  torr for 48 hours. The NMR tube was sealed under a vacuum of  $1 \times 10^2$  torr while the sample was frozen with liquid nitrogen. The sealed tube is about same length as that of the NMR probe coil (2 cm), and about two-thirds of it is filled with the sample.

The relaxation measurements were carried out on a Bruker MSL-360 spectrometer operated at 360 MHz. A two-pulse (the output of the RF pulse is about 1kW)  $90_x - \tau - 90_y$  solid-echo sequence was used in order to get the entire FID. The signal is recorded by a Bruker BC-131 transient digitizer with a sampling speed of  $0.2 \mu\text{s}$ . The data was stored in an Aspect 3000 computer and treated with the Lotus-123 data spreadsheet. The parameters used in the measurement, e.g., pulse width D1, pulse spacing  $\tau$ , repetition time D0, and number of scans NS were systematically optimized, and the typical values used in the data collection are  $1.0 \mu\text{s}$ ,  $4.0 \mu\text{s}$ , 6s and 512 for D1,  $\tau$ , D0 and NS respectively.

Effort was made to shim the NMR magnet to reduce the inhomogeneity as much as possible. With liquid cyclohexane, the line width measured is less than 100 Hz.

A Kel-f probe base was made to reduce the background proton signal to about 0.3% relative to the intensity of dried coals (the original Bruker probe base gives a background proton signal of about 4% due to absorbed water).

## Results and Discussion

The coal structure is complex. The protons measured by  $^1\text{H}$  NMR can be of different structural origins. In terms of the free induction decay, these 'different' protons can relax to equilibrium by different mechanisms and at different rates. Thus, a proper deconvolution of the FID into different components is crucial, and also valuable, in understanding coal structures. Following, a brief discussion of the fitting routine used in the present experiment is given.

In this work, a step-by-step least-linear-square analysis of the natural logarithm of the FID intensity was used to deconvolute the FID signal. For both as-received and dried coals, the FID signal can be fitted best by minimum of two gaussian and one lorenzian functions:

$$I = I_{g1}(0) \text{EXP}[-(t/T_{2g1})^2/2] + I_{g2}(0) \text{EXP}[-(t/T_{2g2})^2/2] + I_l(0) \text{EXP}(-t/T_{2l}) \quad [1]$$

where  $T_2$  is the transverse relaxation time and  $I(0)$  is the intensity extrapolating to  $t=0$  for any one of the components. The subscriptions  $g$  and  $l$  abbreviate gaussian and lorenzian respectively.

It was found previously (8) that, by using a nonlinear-least-square fitting method, the FID signal can be fitted by either two gaussians and one lorenzian or two lorenzians and one gaussian (those authors chose the later). However, we find that our fitting procedure provides an unambiguous deconvolution of the FID signal into two gaussians and one lorenzian, as demonstrated in Figure 1 for as-received Illinois #6.

In Figure 1(A), the long decaying component is clearly a lorenzian function. After subtracting the lorenzian component, the natural logarithm of the rest of the signal is plotted in Figure 1(B) as a function of  $t$  (lorenzian) and in Figure 1(C) as a function of  $t^2$  (gaussian). The lorenzian fitting in Figure 1(B) for the second component would lead to an erroneous extrapolation to  $t=0$ , while the gaussian fitting in Figure 1(C) not only gives a reasonable value to  $I_{g2}(0)$ , but also leads to an almost-perfect gaussian fitting for the last component in Figure 1(D).

All the measured relaxation parameters defined in Equation 1 are listed in Table 1 for both as-received and dried coals. By inserting the values of Table 1 into Equation 1, it can be easily verified that the three components are indeed well separated in each of their time regions. Generally, the accuracy in determination of the relaxation time  $T_2$  is greater than that of  $I(0)$  since the former is derived from the slope of the plots as showed in Figure 1, while the later is obtained from the extrapolation to  $t=0$  where fluctuation at the beginning of the decay could cause more uncertainty. For the dried coals, uncertainty in both  $T_{2l}$  and  $I_l(0)$  can be even higher since water concentration in dried coals is so low. Nevertheless, the accuracy in present experiment is good enough for the following discussions.

From Table 1, it can be seen clearly that water has a profound effect on the relaxation dynamics of coals, mainly the lorenzian component. A slow lorenzian decay is usually due to protons with high isotropic rotational mobility. The fact that the lorenzian component for the coals as received is almost completely gone after drying leads to a speculation that this lorenzian component is entirely due to the contribution from physically absorbed water protons. This speculation is strengthened by the fact that the weight percentage of water in coals  $W\%$ , derived from  $I_t(0)$  in the present experiment, compares very well with those obtained using other established methods for coal moisture determination. The comparison is made in Table 2, where the literature values of  $W\%$  are listed and compared with ours derived from  $I_t(0)$  using the following equation:

$$W\% = \frac{I_t(0) \times 18/2}{I_t(0) \times 18/2 + [100 - I_t(0)] / H_{\text{coal}}} \quad [2]$$

where  $H_{\text{coal}}$  is the weight percentage of proton in dried coal obtained from elemental analysis (1). Thus, the  $^1\text{H}$  NMR relaxation measurement not only serves for understanding coal structures, but also provides a new method for quantitative determination of moisture in coals.

It is known that strongly coupled rigid-lattice structures usually give a FID signal of gaussian shape (9). The coal structure, which is represented by the two gaussian components, seems indeed a tight one. As shown in Table 1, neither wetting nor drying has a significant effect on the structure, which evidenced by the fact that almost same values of  $T_{2g}$  and  $I_t(0)$  are obtained for both as-received and dried coals.

The shorter time gaussian component is dominant, accounting for more than 90% of the FID signal, and its  $T_2$  values are nearly same for all of the three coals. It has been proposed that the coal structure consists mainly of a three-dimensional cross-linked polymer network (10). The present experimental observations are consistent with this picture. Further support for this model comes from the fact that similar NMR experiments on a cross-linked polystyrene in this laboratory (7) gives just one gaussian component with a  $T_2$  of 9.7  $\mu\text{s}$  which is very close to the  $T_{2g1}$  values for the first gaussian component of the coals.

The second gaussian component also presents part of the coal structure not only because the decay has a gaussian form, but also because the relative intensity of this component,  $I_{22}(0)$ , is independent of the water present in the coals. The clear correlation between  $T_{2g1}$  and  $T_{2g2}$  (a ratio about 1/2) indicates that certain kind of relationship exists between the two types of coal structures. It has been suggested (11) that the restricted rotation of methyl groups and hydrocarbon chains in the macromolecular framework of coals is likely responsible for this component of higher mobility. Further experiments on model polymers might lead to a more definite structural identification.

### Conclusions

A step-by-step least-linear-square fitting in the present work leads to an unambiguous deconvolution of the FID signal into two gaussian and one lorentzian components. The lorentzian arises from the protons of physically absorbed water in coals, and the quantitative measurement of the lorentzian component provides a new way for the moisture determination in coals.

More than 90% of the coal structure behaves as a rigid-lattice. The relaxation time measured for coals is very similar to that of cross-linked model polymer. Less than 10% of the coal structures shows higher mobility, and a possible source for this intermediate component may be the hindered rotation of methyl groups or hydrocarbon chains of the coal macromolecular structure.

The drying by high vacuum pumping is almost complete, and no significant structural change in coal was observed during the drying process.

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### References

1. Vorres, K. S. "User's Handbook for the Argonne Premium Coal Sample Program", U.S. Department of Energy, October 1, 1989. See also: Vorres, K. S. *Energy and Fuel* 1990, 4, 420.
2. Finseth, D. *Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.* 1987, 32, 260.
3. Lynch, L. J. and Webster, D. S. *Fuel* 1979, 58, 429.
4. Wroblewski, A. E.; Reinartz, K.; Verkade J. G. *Energy and Fuel* 1991, 5, 786.
5. Gerstein, B. C.; Chow, C.; Pembleton, R. G.; Wilson, R. C. J. *Phys. Chem.* 1977, 81, 565.
6. For example, Vorres, K. S. and Kolman, R. *Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.* 1988, 33, 7.
7. Yang, X; Garcia, A; Larsen, J. W.; Silbernagel, B. G., unpublished results.
8. Gerstein, B. C., unpublished results.
9. For example, see Abragam, A. "The Principles of Nuclear Magnetism", Clarendon Press: Oxford, 1961.
10. Larsen, J. W.; in "New Trends in Coal Science", Yürüm, Y. Ed., Kluwer Academic Publisher: New York, 1988, 73-84.
11. Kamieński, B; Pruski, M; Gerstein, B. C.; Given, P. H. *Energy and Fuel* 1987, 1, 45.

**Table 1:** Summary of the  $^1\text{H}$  NMR relaxation measurements

Coals		Gaussian 1		Gaussian 2		Lorenzian	
		$T_{2g1}^{\#}$	$I_{g1}(0)$	$T_{2g2}$	$I_{g2}(0)$	$T_{2l}$	$I_l(0)$
Pittsburgh #8	as*	10.1	90	19.6	5	23.3	5
	dried	10.1	95	20.6	5	25	1
Illinois #6	as	9.9	76	18.8	5	155	19
	dried	10.0	95	20.9	5	27	1
North Dakota	as	9.5	35	16.5	9	258	56
	dried	9.6	91	19.8	7	25	2

<sup>#</sup> The unit for  $T_2$  is  $10^{-6}$  sec.

\* as = as received.

**Table 2:** Moisture in coals (W%) determined with various methods

Coals	$H_{\text{coal}}$	$^{31}\text{P}$ NMR	Moisture W%		
	(Dry%) Ref(1)		ASTM Ref(1)	$^{18}\text{O}$ dilt. Ref(2)	$^1\text{H}$ NMR This work
Pittsburgh #8	4.83	2.85	1.65	2.5	2.2
Illinois #6	4.23	9.35	7.94	9.6	8.2
North Dakota	4.36	31.05	32.24	34.4	33

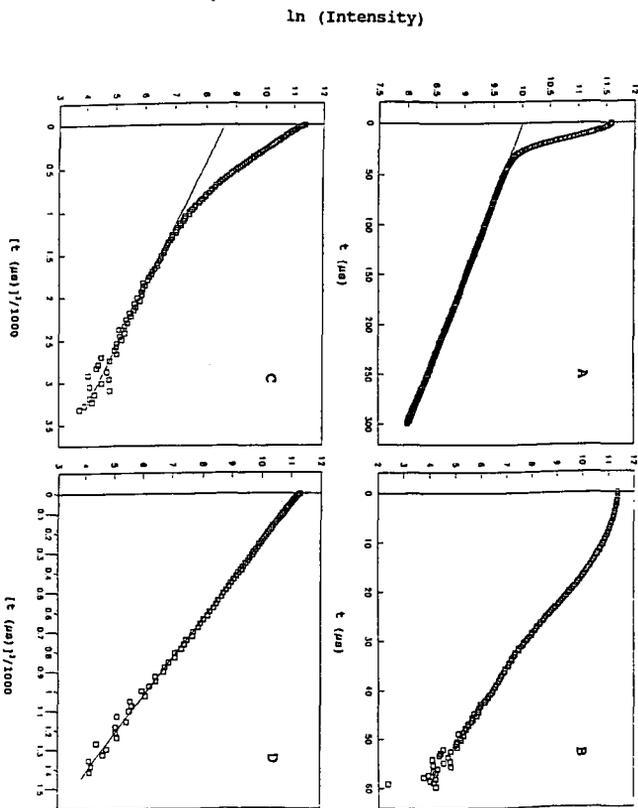


Figure 1: The natural logarithm of the FID intensity of as-received Illinois #6 as a function of relaxation time  $t$  and  $t^2$ . D is the experimental data point and the solid line is the least-square fitting. (A) the original FID, (B) after subtracting the lorentzian component from (A), (C) same as (B) except plotted as function of  $t^2$ , and (D) after subtracting the intermediate gaussian component from (C).