

## Spontaneous Luminescence of Coal During Dehydration

Rita K. Hessley and Lelia M. Coyne\*

Department of Chemistry, Western Kentucky University, Bowling Green, KY 42101 and  
\*NASA-Ames Research Center, Moffett Field, CA 94035

### Introduction

Triboluminescence (TL) is the emission of light which occurs when a solid is subjected to some form of "stress." Although the phenomenon was named for the Greek root for the verb "to rub"(1), it is now known that mechanical action other than grinding, scrapping or rubbing will initiate triboluminescence. It has been observed that static electrification, exposure to light, the motion of a fluid (most notably mercury) over the surface, thermal shock and the release of adsorbed or adsorbed gases can provide sufficient energy to induce TL in a solid (2). Furthermore, although light emission has been associated largely with organic crystalline materials, recent research has shown that some rock minerals also display triboluminescent properties (3,4).

It has been reported that TL is frequently observed to occur in materials which also give rise to a photoluminescence (PL) spectrum, but PL is not a necessary characteristic for TL behavior (2). There is an extensive body of literature on the subject of TL, but to date neither the exact origin(s) nor the mechanism(s) of TL have been delineated precisely. Investigators have most commonly studied the role of crystal fractures, plastic and elastic deformations, particle size, the presence or alteration of crystal defects, and/or the presence of impurities for their potential relationship to TL (6).

Coyne et al. were the first to report that dehydration of some clay minerals results in triboluminescence (4). That work also revealed that in addition to a burst of photons, a continued release of measurable energy was recorded for periods of time as long as several days (4,5).

Coyne's work prompted us to investigate TL properties in coal in spite of its non-crystalline structure. Coal is frequently underlain with clay beds and clay minerals are the most common inorganic components in coal. Because coal is a complex and a notoriously variable substrate, it was desirable to test its luminescent properties under the simplest of conditions. Coyne's work has shown that dehydration causes sufficient "stress" upon the clay structure to stimulate TL, and is a process that can easily be achieved using a common desiccant (4). Since the porous coal structure makes it possible for liquids to be imbibed into the pores as well as to adhere to the surface of the macromolecule, it was decided to monitor TL from coal when water was removed from coal previously suspended in water in a manner analogous to that described by Coyne (4). The primary focus of this study, then, was to determine whether TL could be observed in coal when moisture was removed from it, and whether any photon emission observed could be related to the mineral matter content of the coal. As far as is known, this report marks the first discovery that coal, a complex but clearly an amorphous solid, does exhibit pronounced triboluminescence when an aqueous slurry is subjected to dehydration. In addition to studying the effects of mineral matter content on coal TL, this report includes data on the effect of particle size on coal triboluminescence.

### EXPERIMENTAL

#### Preparation of Aqueous Coal Slurries

Two coals have been used throughout this study. Both are Western Kentucky hvB coals obtained from the Western Kentucky University Center for Coal Science. A summary of the analysis of both coals is given in Table I. It should be noted that these two coals were selected because of the wide divergence in the ash content which is represented.

In the initial series of trials to determine TL, -60 mesh coal was mixed (20% by weight) with water and micronized in a Union Process Model 1-S stirred ball attritor mill for 2 hours. For determinations of the effect of particle size on TL, 120 g of -60 mesh coal #85098 (high ash) and 480 g water were placed in the attritor mill. The micronization process was timed, and at pre-determined intervals the rabble arm was stopped long enough to withdraw approximately 5 mL of the coal-water slurry. Table II summarizes the particle size reduction with milling time for such a slurry. Particle size determinations were made using a Spectrex SP-410 particle size analyzer.

Table II

Particle Size Reduction with Short-term Milling of Coal #86024\*

Milling time, min.	% +325 mesh	% -325 mesh
0	12.3	39.0
.5	13.0	58.8
1	17.9	69.2
2	11.0	86.7
4	2.6	97.1

\* Coal #86024 is a hvBb coal similar to the #82089 used in this work (7).

#### Measurement of Triboluminescence

Triboluminescence of the coal was measured as a function of desiccation with time. Photon output was monitored using a Beckman LS-100SC liquid scintillation counter operating in the total photon mode with a 50 - 1,000 window on the discriminator, and full gain. Data was registered as counts per minute and was printed on a paper tape at pre-set intervals. Typically, data was collected at 0.5 min intervals for 2 minutes and at 1 min intervals thereafter for periods as long as 700 min. The coal slurry was applied as a uniform coating about 2.5 cm high around the center of the inside of a standard glass liquid scintillation vial. Blue ("indicating") CaSO<sub>4</sub> was poured into the vial to a depth of about 1 cm before applying the coal slurry. The amount of sample applied to the vial was determined directly by weighing. The total sample weight ranged from 60 - 200 mg, or from 12 - 40 mg coal. The vial containing the sample and desiccant was capped and wiped with a damp tissue before being placed in the counting well. The determination of background activity and the photon emission of the coal slurry in the absence of the desiccant was determined by omitting the coal, the desiccant, or both, from the vial before monitoring the photon emission.

#### RESULTS AND DISCUSSION

Figure 1 shows a portion of the photon output for the #82089 low ash coal which had been micronized for 2 hours (mean particle size about 5 microns) and was then dehydrated with CaSO<sub>4</sub> in a closed scintillation vial. Figure 2 shows two additional trials for the same coal using different sample sizes. It is apparent from the recorded counts per minute that triboluminescence does occur in this coal upon dehydration. These graphs show that the intensity of the maximum luminescence is not as sensitive to the size of the sample as the time of drying before on-set of the emission is. For the 87 mg and the 101 mg samples a small emission occurs at 22 and 37.5 min, respectively, followed by a larger and a more gradually decaying

emission maximum at 60 and 69.5 min, respectively. For the 164 mg sample, only one emission peak was observed and it did not occur until an elapsed drying time of 105.5 min. The background, which is not shown on the graphs, was 7,200 +/- 200 cpm throughout the period monitored.

The significance of the apparent delay in the appearance of the emission is not certain at this time. The time plotted on the graphs has not been corrected for the time which elapsed from the preparation of the sample to initiation of counting. However, this did not vary from sample to sample by more than 2 - 3 minutes and clearly does not account for the differences observed for these samples. With increased sample size there is, of course, more total water present. The moisture content at peak emission could not be determined for these samples. An alternative sample configuration, in which the desiccant is held in the center of the vial in a tube punctured with holes, will be tested. It is believed that such a configuration may dry the coal more uniformly and will permit the desiccant to be removed and weighed at any time. It will then be possible also to monitor the change in weight of the desiccant and of the sample, permitting a correlation to be made between the moisture content and photon emission.

The decrease in the intensity of light released was expected to decrease as the film thickness was increased because of increased self-absorption or increased scattering. The data shows that this does occur.

Figure 3 shows a similar pattern of decreased intensity and a longer time before the onset of the photon emission with increasing sample size for the \*85098 high ash coal. When the same sample size (87 mg) was used for both coals, the intensity of the first emission peak is substantially larger in the high ash sample, while the intensity of the second emission peak is nearly the same for both coals. Coyne reported that multiple peaks were frequently observed in TL measurements on kaolinites, but appeared to be only artifacts from non-uniform sample application or variation in particle size distribution (4). There is no justification at this time for discounting the smaller emission peak observed for these coals, however. Because of the heterogeneous nature of coal, the possibility does exist that TL related to organic constituents, or adsorbed gases, as well as to inorganic components is being observed, or that TL related to more than one of the mineral constituents is giving rise to a second emission signal. Additional data are needed to rule out any of these possibilities and to draw a definite correlation between the first emission peak and the ash content of the coal.

Table III summarizes the data from samples obtained by withdrawing aliquots from the attritor mill at timed intervals.

Table III

Effect of Milling on Duration & Intensity of Luminescence of High Ash Coal

Milling time, min.	Sample Wt., mg	Area under peak	Duration of peak, min. (time to max.)	CPM at max.
8	99	82	63 (31)	22,490
16	99	81	32 (42)	20,110
32	80	68	39 (30)	24,180
64	80	43	28 (18)	25,400
128	125	17	22 (20)	13,420

There does not appear to be any direct correlation between the total milling time and either the time of onset of the light emission or the intensity of the light released at the peak maxima. It is apparent, however, that the overall duration of the emission is related to some property of the coal affected by the milling time. Our original hypothesis was that the dehydration was initiating TL by permitting

some "relaxation" in the coal structure, perhaps pore shrinkage, and that TL would be maximized at some critical particle size. Table II shows that after 4 minutes milling time virtually all of the coal has been reduced to -325 mesh (less than 5 microns). Thus, particle size alone can not be giving rise to the photon emission pattern recorded for these samples. The most unexpected observation about the effect of milling on coal is the alteration of its apparent density with extended milling. It was reported that after 4 minutes milling more than 50% of the coal sinks in a 1.3 specific gravity media (7). The discussion and the explanation for these observations is the subject of another study being carried out at Western Kentucky University. For this investigation, it is clear that the observed TL behavior is not related to the internal pore structure, which is rapidly compressed and almost completely destroyed by milling longer than 15 minutes (7).

#### CONCLUSIONS

To date this study has shown that coal exhibits triboluminescent behavior when an aqueous slurry is subjected to dehydration. The luminescence data is complex. Both the high ash and the low ash coal exhibited a delayed burst of photons. In some cases only one emission maximum was observed which continued to decay monotonically for several hours. The time and the intensity of the emission were related to the sample size, and may be attributed to the total moisture content. In other cases, two distinct emission events were observed. Both peaks were affected by the sample size. Although it has been reported that extended milling effectively destroys the pore structure, triboluminescence is not eliminated when the coal is micronized. This suggests that the observed TL is a surface phenomenon rather than one related to alteration of the pore structure. No clear correlation can be made regarding the effect of ash content on triboluminescence in coal. Work in progress will address both the effect of ash content and the effect of variations in moisture content on TL behavior in more detail. The determination of the wavelength(s) of photons emitted will also be attempted.

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Table 1

Characterization of Coals

I.D. *	82089	85098
Seam/ County	Butler Co.	KY #11/Muhlenburg Co.
<u>Proximate</u>		
Moisture **	5.8	4.31
Ash	3.17	18.96
Volatile matter	45.25	34.72
Fixed carbon	51.57	46.30
<u>Ultimate</u>		
Carbon	79.09	63.22
Hydrogen	5.73	4.35
Nitrogen	1.6	1.28
Sulfur	1.08	5.96
Oxygen(diff.)	9.3	6.19
Apparent rank ***	hvB-B	hvB-A
<u>Major Inorganics</u>		
SiO <sub>2</sub>	--	19.93
CaO	--	2.76
Fe <sub>2</sub> O <sub>3</sub>	--	32.42
MgO	--	1.51
K <sub>2</sub> O	--	1.13
P <sub>2</sub> O <sub>5</sub>	--	7.8
Al <sub>2</sub> O <sub>3</sub>	--	(33-est.)

\* Accession, WKU Center for Coal Science

\*\* Moisture as-determined; other values reported on dry basis

\*\*\* Using as-determined moisture

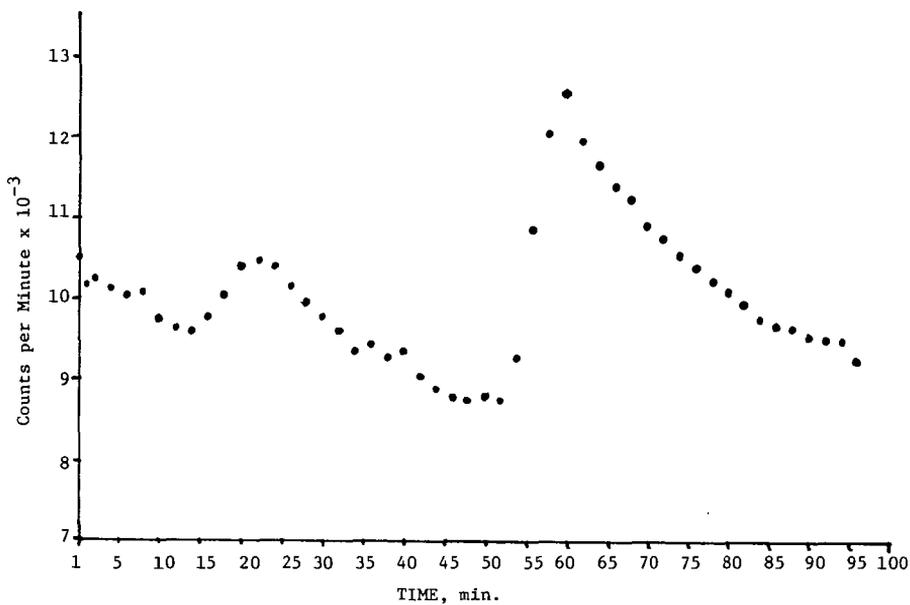


Figure 1. Luminescence on Dehydration for 87 mg Low Ash Coal 20%(w/w) in H<sub>2</sub>O

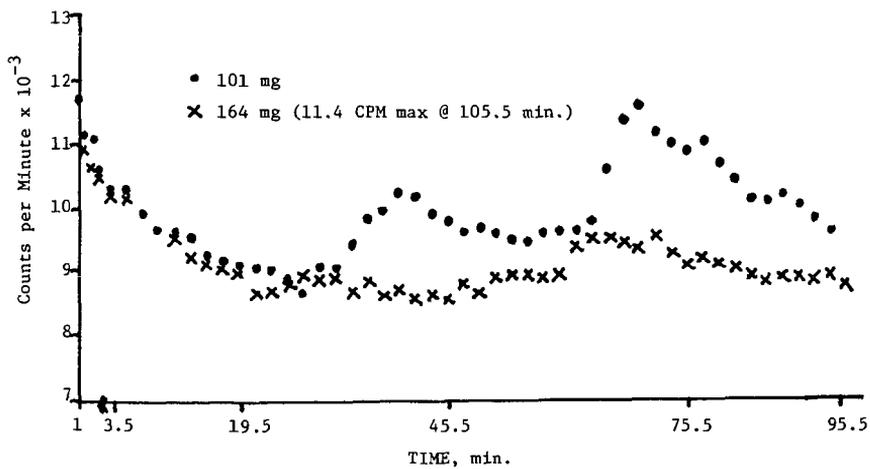


Figure 2. Effect of Sample Size on Luminescence of Low Ash Coal, 20% in H<sub>2</sub>O

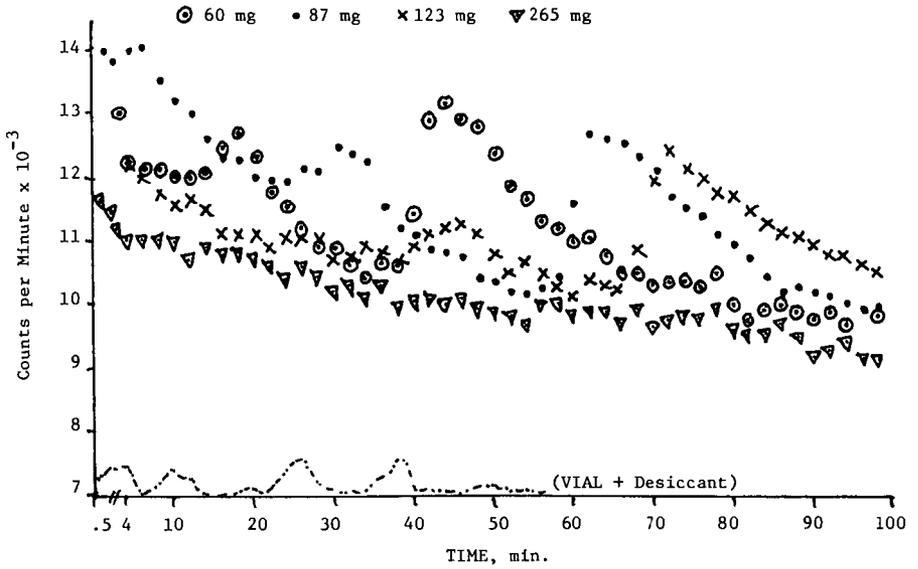


Figure 3. Effect of Sample Size on Luminescence of High Ash Coal, 20% in H<sub>2</sub>O

## CHARACTERIZATION OF A RESINITE MACERAL FRACTION

David M. Bodily and Vance Kopp

Department of Fuels Engineering, University of Utah  
Salt Lake City, Utah 84124

### INTRODUCTION

Resinite in coals is attributed to plant resins and essential oils in leaves which are converted during coalification to spherical or oval shaped bodies and occasionally lenses or thin bands of fluorescing material (1). Chemically, the resins consist of terpenoid structures (2). Resinite is often found in Tertiary brown coals and is even found in Carboniferous bituminous coals (1). Reflectance, refractive index, fluorescence wavelength and other optical properties vary with origin of the resins and the degree of maturation. The observation of resinates in cell fillings indicates that at some point in the coalification process, the resinite is relatively fluid. In the Lower Cretaceous period, conifers were a source of resins for incorporation into coal. In the Upper Cretaceous period, angiosperms which are richer in waxes began to appear and coals of this period would contain relatively more wax and less resinite.

In a study of the swelling of coal macerals in organic solvents, a resinite maceral fraction was separated from Hiawatha, Utah coal. Hiawatha coal is from the Wasatch Plateau field, and dates from the Cretaceous period. Coals of the Wasatch Plateau are relatively rich in resinite. As part of the study of maceral swelling, the properties of the resinite fraction were measured.

### EXPERIMENTAL

Maceral fractions were prepared by density gradient centrifugation according to the method of Dyrkacz and Horwitz (3). The coal was ground in a ball mill and then in a fluid energy mill until the size was reduced to less than 10 microns. The sample was demineralized with HCl and HF and introduced into the density gradient prepared from aqueous CsCl. After centrifugation, the gradient was displaced by a heavy fluid and fractions of different density were collected in a fraction collector. A sample obtained by commercial flotation of larger resinite particles was also used in this study.

Solubilities were measured in organic solvents in Soxhlet extractors at the boiling point of the solvent. Swelling of the whole coal samples was measured by the method of Green et al. (4). Coal was centrifuged, solvent added and allowed to come to equilibrium and the sample was again centrifuged. The increase in the height of the column of coal was used as a measure of swelling.

### RESULTS AND DISCUSSION

Properties of Hiawatha coal and the resinite fraction separated from Hiawatha coal are listed in table 1. The coal is a high volatile bituminous B coal. Resin particles are visible in the raw coal lumps. Petrographic analysis indicates that resinite comprises 11 percent of the coal. The density distribution of the Hiawatha coal is shown in figure 1. The resinite fraction does not show as a distinct peak, although the material with a density less than  $1.10 \text{ g/cm}^3$  represents about 11% of the total sample and has the appearance and properties of

resinite. The density distribution of a resinite sample obtained by flotation is also shown in figure 1. The sample shows a narrow density distribution of 1.01 to 1.05 g/cm<sup>3</sup> and an average density of about 1.04 g/cm<sup>3</sup>. This differs significantly from the vitrinite density of about 1.28 g/cm<sup>3</sup> for Hiawatha coal and exinite densities of 1.16 g/cm<sup>3</sup> for bituminite and 1.19 g/cm<sup>3</sup> for sporinite measured in other coals.

Hiawatha coal shows the typical swelling behavior of bituminous coals. Maximum swelling was observed in pyridine and a bimodal curve was obtained when swelling was plotted versus solubility parameter. The second maximum in THF at a solubility parameter of about 19 MPa<sup>1/2</sup> is attributed to solvation of the macromolecular structure of the coal with an increase in hydrodynamic volume while the swelling in pyridine is associated with cleavage of hydrogen bonds which serve as crosslinks and limit coal swelling (5). The resinite fraction shows a high solubility in solvents with solubility parameters in the range 15 to 20 MPa<sup>1/2</sup>. The solubility is shown in figure 2. Solubility is high in non-polar and moderately polar solvents, but is very low in pyridine or methanol. Although the resinite comprises 11% of the whole coal sample, solubility of the coal in the non-polar solvents is less than 11%.

Murchison (6) studied a group of hand-picked resinite samples. Samples from bituminous coals showed carbon contents of the range observed for the Hiawatha resinite, but hydrogen contents were significantly less, 7-9% compared to 12%. The hydrogen to carbon ratios were 1.04 to 1.35 compared to 1.72 for the Hiawatha resinite. Oxygen contents were about double that observed in the Hiawatha resinite. Infrared spectra of the resinite fraction shows strong absorption due to aliphatic C-H species in the range 2800-3000 cm<sup>-1</sup>. Sharp bands are observed at 1370 and 1450 cm<sup>-1</sup>, attributed to aliphatic structures. Only slight absorption is observed from the O-H group at 3300 cm<sup>-1</sup>. A broad absorption occurs at 1600 cm<sup>-1</sup> and more intense absorption at 1700 - 1750 cm<sup>-1</sup>. Broad absorption also occurs at 1000-1200 cm<sup>-1</sup>. The spectra is in agreement with the high hydrogen content which indicates an aliphatic structure.

Thermal gravimetric analysis shows weight loss starting at 275C and a maximum rate of weight loss at 440C. The weight loss to 700°C was 86%, less than the observed volatile matter content. Pyrolysis of the whole coal samples shows loss of the fluorescing resinite after heating to the range 400 to 450C in nitrogen (7). Heating in hydrogen decreases the temperature at which the resinite fluorescence disappears.

## CONCLUSIONS

Relatively pure resinite fractions can be recovered from coal using the density gradient centrifugation technique. The resinite separated from Hiawatha, Utah coal is highly aliphatic. The chemical structure of this resinite appears to be different from those of amber and resinates from bituminous coals and lignites separated and studied by Murchison (6), although some of the differences may be attributed to purity of the samples. The unique properties of the resinite account for its use as a chemical.

## ACKNOWLEDGMENTS

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Table 1. Properties of Hiawatha Coal and Resinite Maceral Fraction

	<u>Hiawatha Coal</u>	<u>Resinite Fraction</u>
Carbon, maf %	77.6	83.7
Hydrogen, maf %	6.4	12.0
Nitrogen, maf %	1.4	0.4
Sulfur, maf %	1.2	
Oxygen, % (difference)	13.4	3.9
H/C, atomic ratio	0.99	1.72
Moisture, %	1.6	0.3
Ash, %	19.4	0.5
Volatile Matter, %	36.5	93.9
Heating Value, Btu/lb	13,917	18,095
Vitrinite Reflectance, %	0.48	
Petrographic Analysis		
Vitrinite, %	75.7	
Semifusinite, %	4.0	
Fusinite, %	0.7	
Macrinite, %	6.2	
Sporinite, %	0.6	
Resinite, %	11.0	
Cutinite, %	1.8	

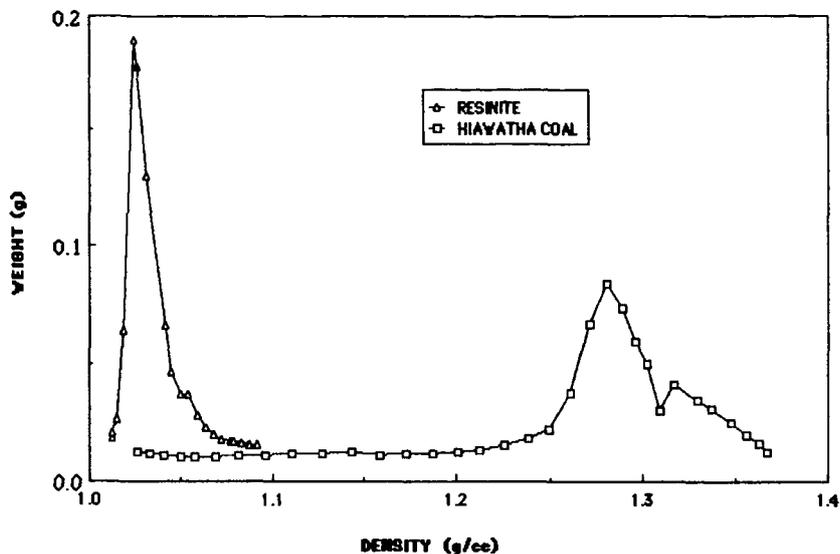


Figure 1. Hiawatha Coal and Resinite Maceral Density

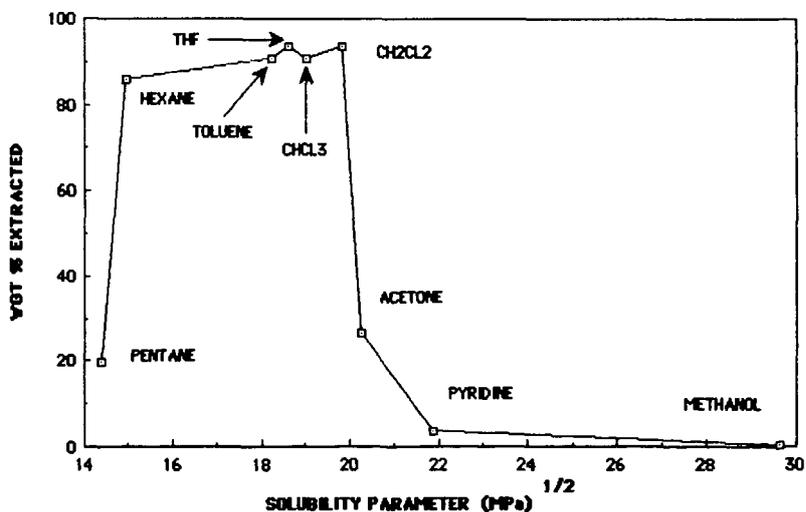


Figure 2. Solubility as a function of Solubility Parameter

## OXIDATIONS OF COALS AT AMBIENT TEMPERATURES

Frank R. Mayo

SRI International, Menlo Park, California 94025

### INTRODUCTION

This paper extends the work of Liotta, Brons, and Isaacs (1) on the weathering of coal. They crushed freshly-mined Illinois No. 6 Coal (Monterrey Mine) to a maximum size of 6.4 mm, spread it over the ground, and allowed it to weather with daily mixing. Samples were removed periodically and Soxhlet-extracted with tetrahydrofuran. The amount extracted (dmmf basis) decreased from 21.3% at zero time to 14.5% at 56 days and then did not change further. During the exposure, the dmmf carbon content of the coal decreased from 69.3 to 66.9% and its oxygen content increased from 9.0 to 11.3%. No new carbonyl groups were found by FTIR and the phenol and carboxyl contents did not change. The authors propose that free alkyl radicals react with nearby hydroperoxide groups to give ether crosslinks and hydroxyl radicals. However, the alkyl radicals should react much faster with oxygen than with coal. This paper describes some related experiments done to obtain material balances and better control of conditions.

### EXPERIMENTAL

In my work samples of about 5 g of coal were exposed in Pyrex-covered Petrie dishes (area 61 cm<sup>2</sup>) either in a dark cabinet at 23°C or to ambient temperatures on the roof of the laboratory. For a density of 1.35 g/cm<sup>3</sup>, the average thickness of the coal layers was ~0.6 mm. The samples on the roof were also covered by a Pyrex beaker for rain protection and were agitated about twice a week. Each sample suffered a loss from a wind gust during agitation. To measure changes in carbon and oxygen contents, I then had to assume that there was no change in mineral matter during exposure. One coal was 100-200 Tyler mesh Illinois No. 6, Herrin Mine, PSOC 1098; the other was ~200 mesh from the Wyodak Mine at Cambell, Wyoming. In general, the analyses reported are on coal samples dried over anhydrous calcium sulfate at about 2000 Pa (15 torr) and room temperature, but the oxidations were done at ambient humidities.

The remaining oxidized coals are similar to the initial coals. The probe chosen was the solubilities of the coals in pyridine (1 day extraction at 100°C) and benzylamine (1 week extraction at 100°C) as in another paper.(2) Most of the solvents from the soluble and insoluble coal fractions were removed at reduced pressure. The residues were then neutralized with aqueous HCl, washed three times each with 3 M HCl and 3 M NH<sub>3</sub> and dried as indicated previously. The washings removed about half of the mineral matter but caused no significant change in the organic material.(2)

### RESULTS

Analyses of the aged and unaged coals are in Table 1 with oxygen and sulfur together determined by difference (1.55% organic S in Illinois 6, 0.45% in Wyodak). Weight changes are shown in Figure 1. The figure shows that there was little change during the cool and cloudy season but that change was relatively fast during clear, warm weather.

Table 2 shows the weight changes normalized to 100 g of initial coal and also shows the carbon contents of the coals. In 311 days in the dark at 23°C, Illinois No. 6 coal lost about 0.14% of its original weight and 0.90% of its original carbon. Wyodak lost 1.5% of its weight and 5.2% of its carbon. However, in 282 days to sunlight, the Illinois

coal lost 17% of its weight and 23% of its original carbon. The corresponding numbers for Wyodak coal are 26% of its weight, 15% of its carbon. In the light experiments, the calculations assume that there was no change in mineral matter during exposure. Neither sample changed much in total O + S content. These results show that both moderately dried coals, and especially the Illinois coal, are fairly stable to ambient air in the dark at room temperature but that both are unstable in sunlight.

Because coal temperatures in sunlight sometimes reached 60°C (annual average about 15°), an effort was made to estimate the effect of solar heating on the light oxidations. The temperature of a thin film of coal in sunlight under Pyrex was measured on a warm (not hot) day in May. The maximum temperature reached was 58.3°C and the temperature exceeded 50°C for about 5 hours. The maximum temperature in the shade was 29°C and the temperature exceeded 25° for 6 hours. To determine the effect of heat alone on oxidation, about 2 g of each coal was also exposed to air with weekly air changes in Pyrex flasks in a brown glass bottle in a thermostat at 60°C. Figure 1 and Tables 1 and 2 show that continuous heating in the dark at 60° caused weight losses that were much smaller than those in sunlight with temperatures above 50° for only 4-6 hours on most days. Thus, the weight losses in sunlight are due mostly to light, not higher temperatures.

Table 2 also lists the solubilities of the initial coals and their oxidation products in pyridine and benzylamine, after correction for excess nitrogen.(2) Some of these corrected carbon contents are too high for reasons unknown. Our previous work(2) shows that pyridine partly dissolves coals at 100° without chemical reaction and that benzylamine dissolves additional coal to the extent that it cleaves ester and ether groups. Thus, the changes in solubility on aging are a measure of chain scission and crosslinking in the surviving coal. In comparison with the unaged coals, the changes are small to moderate. The solubility differences between the unaged coals and those aged in the dark are small and insignificant; little oxidation occurred. However, in comparison with the unaged coals, the light-aged coals give lower recoveries of carbon on extraction, probably because of greater losses of volatile or water-soluble products. The second number in some carbon recoveries counts this missing carbon as soluble carbon.

#### DISCUSSION

A simple and reasonable explanation of my light results is that my oxidations caused successive oxidation, photolysis, and evaporation of outside layers of coal particles. Penetration of light into the coal particles is apparently severely limited and there was little change in the unexposed coal until it became exposed. I cannot explain the cessation of change after 56 days in the oxidation of Liotta et al.(1) Their large particles and sample sizes and limited penetration of light suggest that much of their oxidation was a thermal dark reaction.

My results with oxidations of dried coals at ambient humidities may seem inconsistent with the well-known spontaneous heating and combustion of coal in storage.(3,4) I suggest some possible explanations: mild drying decreased the oxidizability of my coal; Liotta has suggested that water causes oxidation of pyrite to iron sulfates, which may catalyze oxidation. Both a much faster spontaneous oxidation than mine and limited heat loss appear to be necessary to account for spontaneous combustion in storage. It follows that moderate drying of coal and protection from rain might eliminate combustion in storage.

#### ACKNOWLEDGEMENT

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Keywords: coal, oxidation, photooxidation, pyridine, benzylamine

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Table 1

## ANALYSES OF COAL PRODUCTS

Coal <sup>a</sup>	%C	%H	%N	%(S+O)	%M	H/C
Illinois No. 6						
Unaged	67.0	4.59	1.22	7.9	19.3	0.817
PS	80.2	6.10	1.98		11.7 <sup>b</sup>	
PI	68.6	4.53	1.89		25.0	
BS	79.0	5.72	2.58		12.7	
BI	65.5	4.52	2.21		27.8	
Aged in dark	66.5	4.54	1.18	8.5	19.4	0.814
PS	79.1	6.00	2.46		12.4	
PI	67.4	4.52	1.86		26.2	
BS	75.2	5.63	3.93		15.3	
BI	67.6	4.61	2.10		25.7	
Aged at 60°	66.2	4.12	1.18	9.1	19.4	0.742
Aged in light	62.2	4.08	0.94	9.5	23.3	0.782
PS	76.8	5.93	1.66		15.6	
PI	65.7	4.31	2.06		28.0	
BS	80.6	6.04	3.85		9.5	
BI	66.0	4.46	2.75		26.8	
Wyodak						
Unaged	65.1	4.70	0.92	20.5	8.8	0.860
PS	77.2	7.77	2.18		12.8	
PI	63.9	4.43	2.88		28.8	
BS	75.4	6.44	3.61		14.5	
BI	69.9	5.14	3.65		21.3	
Aged in dark	62.6	4.53	0.83	23.1	8.9	0.862
PS	76.8	8.87	0.78		13.6	
PI	64.8	4.56	2.50		28.1	
BS	77.1	6.42	4.20		12.3	
BI	70.5	5.14	3.79		20.6	
Aged at 60°	64.2	4.22	0.80	21.8	9.0	0.783
Aged in light	60.7	4.07	0.89	24.4	9.9	0.860
PS	74.6	9.18	1.08		15.2	
NH <sub>3</sub> -S	59.6	6.35	4.97		29.1	
PI	60.8	4.15	3.13		31.9	
BS	76.4	6.13	4.92		12.5	
BI	67.9	4.85	4.10		23.2	

<sup>a</sup>P=pyridine; B=benzylamine; S=soluble; I=insoluble

<sup>b</sup>Numbers in this column are S + O + M by difference from C + H + N.

Table 2

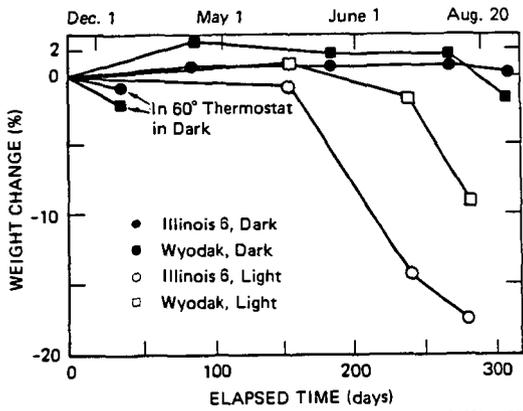
Extractions of Illinois No. 6 and Wyodak Coals at 100°C  
Normalized to 100 g coal; corrected for excess nitrogen

Illinois Coal									
g coal, g C, %	<u>311 days in dark at 23°</u>			<u>Unaged</u>			<u>282 days in sunlight</u>		
		99.9	66.4	99.1 <sup>a</sup>	100	67.0	100 <sup>a</sup>	82.7	51.4
Extracted 24 hours with pyridine									
PS	12.0	9.5	14.3	11.7	9.4	14.0	6.5	5.0	8.0
PI	90.6	60.8	91.4	91.5	62.4	93.2	91.4	59.3	95.3
Extracted 1 week with Benzylamine									
BS	33.1	24.5	36.2-37.0 <sup>b</sup>	35.3	28.0	41.8	29.1	23.6	38-40 <sup>b</sup>
BI	62.8	41.8	62.6	61.4	39.5	59.0	58.4	37.4	60.2
Wyodak coal									
g coal, g C, %	98.5	61.7	94.8 <sup>a</sup>	100	65.1	100 <sup>a</sup>	90.7	55.1	84.6 <sup>a</sup>
Extracted 24 hours with pyridine									
PS	4.6	3.5	5.6-15.9 <sup>b</sup>	5.84	4.51	6.9-19.2 <sup>b</sup>	6.8	4.4	7.1-25 <sup>b</sup>
PI	82.8	52.6	84.1	84.4	52.6	80.8	77.0	45.0	74.2
NH <sub>3</sub> -S <sup>c</sup>	0.81	0.48	0.78				4.6	2.8	6.2
Extracted 1 week with Benzylamine									
BS	19.9	15.2	24.2-33.9 <sup>b</sup>	17.2	12.8	19.7-28.4 <sup>b</sup>	28.6	21.4	35.3-45.3 <sup>b</sup>
BI	61.2	41.4	66.1	69.3	46.6	71.6	52.0	33.2	54.7
Aged 35 days in dark at 60°									
Illinois	99.6	66.0	98.5						
Wyodak	97.8	62.8	96.5						

<sup>a</sup>The three numbers in each group are, respectively, the recovery of coal in grams, recovery of carbon in grams, and the % recovery of carbon, on the basis of original carbon for lines marked a but on the weights or C contents of the a lines for other lines.

<sup>b</sup>Last number of pair counts missing carbon as soluble material.

<sup>c</sup>Soluble in 3M aqueous NH<sub>3</sub>; calculated on basis that excess N comes from NH<sub>2</sub>. This product is included in the PS fractions above; dark products calculated from analysis for light products.



JA-320522-45B

FIGURE 1 WEIGHT CHANGES OF COALS IN THE DARK AT 23°C AND IN OUTSIDE EXPOSURE AT 0 - 60°C

Dates refer only to light experiments.

## USE OF SEM WITH WAVELENGTH-DISPERSIVE SPECTROMETRY FOR ORGANIC OXYGEN IN COAL

G. A. Norton, K. A. Younkin, W. E. Straszheim, and R. Markuszewski

Ames Laboratory, Iowa State University, Ames, Iowa 50011

### ABSTRACT

Scanning electron microscopy (SEM) and wavelength-dispersive spectrometry (WDS) were used to determine organic oxygen in four geographically diverse coals and in amber. Subsequent to the previously reported feasibility study, analytical modifications and refinements in sample handling and preparation were made. In addition, the precision of the SEM-WDS analyses was examined. SEM-WDS results were comparable to values obtained by neutron activation and by the indirect ASTM procedure for one coal, while significant discrepancies were observed for the other coals and the amber. Preliminary results suggest that the discrepancies may be caused by the electron beam, which possibly volatilizes oxygen-containing compounds in some of the samples analyzed by this SEM technique. Results also indicated that additional work is required to reduce matrix correction factors.

### INTRODUCTION

Organic oxygen in coal is an important measure of coal quality, and thus it is determined as an integral part of routine coal analyses. A variety of techniques, including oxidative, reductive, and radiochemical methods, have been employed for directly determining the oxygen content of coal. The oxidative procedures, which generally use gaseous oxygen as the oxidizing medium (1), are cumbersome and incorporate potentially large relative analytical errors. In general these methods are not widely used.

In the reductive methods, coal is pyrolyzed, and oxygen in the pyrolysis products is then reduced with hydrogen or carbon. When hydrogen is used, oxygen in the pyrolysis products is catalytically converted to water, which is then taken as a measure of the oxygen content of the coal (1). Disadvantages of this method include relatively complex apparatus and possible catalyst poisoning by sulfur and chlorine in the coal. Methods employing carbon as a reducing agent, such as the classic Unterzaucher method (2), are relatively common. These methods generally involve reducing oxygen in the coal pyrolysis products to CO, which is then oxidized and determined as CO<sub>2</sub>. Although satisfactory results can be obtained by such pyrolysis methods, they are usually slow and tedious.

Fast-neutron activation analysis (FNAA), which has been used relatively recently for oxygen in coal (3,4), is based on irradiating the coal with 14-MeV neutrons and measuring the radiation of the <sup>16</sup>N produced from the oxygen. However, this technique requires a suitable nuclear reactor and specialized equipment for radiochemical analysis.

A general drawback to the above methods is that all or part of the inorganic oxygen is included in the determination. Therefore, corrections for the inorganic oxygen must be made, or else the coals must be demineralized prior to analysis.

Because of difficulties and/or errors associated with these techniques, ASTM Method 3176, the Standard Method for Ultimate Analysis of Coal and Coke (5), specifies that the organic oxygen content be determined by difference from the ultimate analysis, using the equation:

$$\%O_{org} = 100 - (\%C + \%H + \%N + \%S + \%ash) \quad 1)$$

This indirect determination, however, is also plagued by potential analytical errors. In addition to cumulative errors associated with the other five constituents in the ultimate analysis, the nature of the mineral matter is significantly changed during ashing. Furthermore, the ASTM procedure is designed for unaltered coals and may not be applicable to chemically treated coals. Clearly, the need remains for a fast, simple, direct, versatile, and accurate method for determining the organic oxygen content of coal.

Electron beam microanalytical techniques provide possible alternatives for determining directly the organic oxygen content of coal. Such techniques have been used previously for the direct determination of organic sulfur in coal (6-8). In one of those studies, the organic oxygen content of various coal macerals was also determined (8).

In previous work at Ames Laboratory, the feasibility was explored of using scanning electron microscopy (SEM) with wavelength- and energy-dispersive spectrometry (WDS and EDS, respectively) for the direct determination of organic oxygen in coal (9). X-ray analysis techniques were emphasized, while sample preparation and handling were not carefully monitored or controlled. Because of encouraging results with the SEM technique, additional exploratory work was performed in this study.

## EXPERIMENTAL

### Samples

The four coals in this study were Illinois No. 6 (Captain Mine, Percy, Illinois), Pittsburgh No. 8 (Grafton Mine, Churchville, West Virginia), Dietz No. 1 and 2 (Decker Mine, Decker, Montana, and Charming Creek (Charming Creek Mine, Buller Coalfield, New Zealand). These coals were ground to -200 mesh, dried at 100-110°C for two hours under vacuum and stored under argon in a freezer. Sample pellets were prepared by mixing the coal with ultra-high molecular weight polyethylene powder, pouring the mixture into a hot press, and heating to 140°C for about five minutes under 4200 psi pressure in a nearly air-tight chamber. The pellets were ground with silicon carbide sandpaper and lapping oil and polished with a diamond paste and oil. The pellets were then cleaned in a mixture of hexanes (Skelly-B), coated with approximately 50A of carbon, and stored under nitrogen at 5°C prior to analysis.

In addition to the coals, a sample of amber from an unspecified source from the Baltic Sea region in Poland was analyzed. It was thought that the amber could serve as a model compound for certain coal macerals, particularly resinite. This sample was ground to -60 mesh and was then prepared for analysis in the same manner as the coals.

### Conventional Analyses

Ultimate analyses were performed with a Perkin-Elmer Model 240 CHN Analyzer and a Fisher Model 470 Total Sulfur Analyzer. Ash was determined by conventional ASTM procedures and the organic oxygen was then calculated by difference as shown in Eq. 1. Data for total oxygen in coal were obtained by FNAAs at the University of California at Irvine. These analyses were for different sample splits than the ones used for the ASTM and SEM analyses and were performed on "as-received" rather than on dried coals. After correcting the total oxygen values to a dry basis per ASTM standard D-3176 (5), which includes the correction to account for oxygen in moisture, the organic oxygen was estimated by assuming 50% of the mineral matter to be oxygen (10). The FNAAs and

ASTM organic oxygen values were converted to a mineral matter-free basis by using a modified Parr formula (11) to estimate the mineral matter content of each coal.

#### Thermogravimetric Analyses (TGA)

TGA was performed on the coals and the amber with a DuPont Model 1090 thermogravimetric analyzer. The samples were heated from room temperature to about 800°C at a rate of 10°C per minute under a nitrogen atmosphere.

#### SEM-WDS Analyses

A JEOL (Japan Electron Optics Laboratory) Model JSM-U3 scanning electron microscope was used in conjunction with a Microspec WDX-2A spectrometry system to quantify oxygen in the samples. Energy-dispersive spectrometry (EDS) was performed with a KEVEX Si(Li) detector and a Tracor Northern Model TN-2000 energy-dispersive x-ray analyzer. Since the low energy oxygen x-rays are absorbed by the beryllium window in our EDS detector, oxygen had to be measured by WDS.

For the coals, x-rays were collected in the spot mode using typical analysis conditions of 15 kV accelerating voltage, 30 nA beam current, and a 25° x-ray take-off angle. For the amber, a 20 x 20 μm square raster was used with an accelerating voltage of 10 kV. Samples were first screened visually at 5000x in the SEM to avoid mineral inclusions. EDS was then used to monitor the particles for Al, Si, Ca, and Fe. Since oxygen was determined by WDS only when significant levels of these elements were absent, the oxygen had to be associated with the organic matrix. Two points within each of 12 particles were analyzed for each coal. This sampling approach, used previously to determine organic sulfur in coal, was found to give statistically acceptable results (7). Due to analytical difficulties, only one point for each of 7 particles was analyzed for the amber.

Because organic sulfur and small amounts of Al, Si, Ca, and Fe were sometimes present in the analyzed particles, EDS was used to collect spectra for a set of standards containing these elements prior to analyzing the coal. Quartz (SiO<sub>2</sub>) was used for Si, aluminum metal for Al, apatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH) for Ca, and pyrite (FeS<sub>2</sub>) for the Fe and S. Quartz was also used for the oxygen standard since a suitable organic oxygen standard for the SEM technique has not yet been found. Although boric acid, citric acid, urea, and acetanilide were tested as possible organic oxygen standards, they could not withstand the high beam currents. Other materials could be investigated for use as organic oxygen standards.

After collecting the spectra from the sixth and twelfth coal particles, additional spectra from a standard were collected to monitor the beam current. Each coal was analyzed twice by the SEM technique. For the second SEM-WDS analysis, the same pellet was used, but a new surface was exposed and analyzed. Sample pellets of amber were only analyzed once.

For each coal, the wavelength of the maximum oxygen intensity was measured for 10 sampled points. The values were averaged, and organic oxygen was determined by collecting oxygen intensities at the average wavelength for a given coal. For the amber, the average wavelength from 6 sampled points was used.

Energy-dispersive spectra and oxygen x-rays obtained by WDS were each collected for 30 seconds. The total oxygen intensity was transferred to the EDS unit for data reduction. The Tracor Northern program "Super ML", a multiple least-squares fitting program, was used to reference the sample spectra against the standards. The organic oxygen concentrations were calculated from the observed oxygen intensities using the Tracor Northern "ZAF" correction program to correct for the

atomic number, absorption, and fluorescence effects in the coal matrix.

The theoretical detection limit for oxygen for the equipment used in this study was determined using Ziebold's equation (12):

$$C_{d.l.} \geq 3.29a / (n\tau P \cdot P/B)^{0.5} \quad 2)$$

where  $C_{d.l.}$  is the minimum detectable limit, " $\tau$ " is the time of each measurement, " $n$ " is the number of repetitions of each measurement, " $P$ " is the pure element counting rate, " $P/B$ " is the peak to background ratio of the pure element, and " $a$ " relates composition and intensity of the element of interest by:

$$a = c (1 - k) / (1 - c)k \quad 3)$$

where " $c$ " is the concentration and " $k$ " is the measured intensity ratio. For typical operating conditions,  $C_{d.l.}$  was about 1%, which is well below the oxygen concentration in the samples used for this study.

## RESULTS AND DISCUSSION

The organic oxygen values from the ASTM ultimate analyses, shown in Table 1, were converted to a mineral matter-free basis and incorporated into Table 2 for comparison of the ASTM results with the FNAA and SEM results. The error limits of the SEM analyses shown in Figure 2 were calculated directly from the analytical statistics and represent 95% confidence limits (i.e.,  $\pm 2\sigma$ ). The error limits for the ASTM values were calculated by summing the reproducibility limits for the C, H, N, S, and ash analyses. For the FNAA values, error limits were calculated from counting statistics and represent 95% confidence limits. As can be seen in Table 2, the SEM-WDS organic oxygen values were comparable to those obtained by the ASTM and FNAA techniques for the Pittsburgh coal, while significant discrepancies were generally noted for the remaining coals and the amber. Although the SEM oxygen value for the amber was fairly close to the ASTM value, SEM analysis of this sample was unsatisfactory due to poor contrast between the amber and mounting material as well as other analytical problems. Reproducibility was best for the Dietz coal and was worst for the Illinois coal. The low, yet consistent SEM-WDS values for the Dietz coal suggest a systematic error in the SEM-WDS procedure.

The discrepancies between the SEM values and those obtained by the FNAA and ASTM procedures may reflect errors in the SEM technique it-

Table 1. ASTM Analyses of Samples Used in This SEM-WDS Study for Organic Oxygen<sup>a</sup>

	Charming Creek Coal	Dietz Coal	Illinois Coal	Pittsburgh Coal	Baltic Amber
Moisture	0.71	2.47	1.24	1.07	0.85
C	78.48	70.07	65.39	76.01	79.89
H <sup>b</sup>	5.12	4.41	4.11	4.86	10.69
S <sub>tot</sub>	5.63	0.48	4.56	3.20	0.46
N	1.31	0.91	1.11	1.15	0.98
Ash	1.23	5.25	13.97	6.93	0.19
O (By Diff.)	8.23	18.87	10.85	7.83	7.79

<sup>a</sup>Values are in % and, except for moisture, are reported on a dry basis.

<sup>b</sup>Corrected for hydrogen in the moisture.

Table 2. Organic Oxygen Values Determined by ASTM, FNAF, and SEM-WDS<sup>a</sup>

Sample	ASTM	FNAF	SEM-WDS	
			Analysis 1	Analysis 2
Charming Creek Coal	8.35±0.72	not detd.	4.97±0.62	5.99±0.90
Dietz Coal	20.06±0.72	19.85±0.16	8.43±1.10	8.67±1.58
Illinois Coal	13.04±1.02	10.51±0.24	8.38±1.00	11.94±1.54
Pittsburgh Coal	8.56±1.02	8.21±0.12	9.71±0.56	8.34±0.62
Baltic Amber	7.89±0.67	not detd.	5.9±1.2	not detd.

<sup>a</sup>Values are in % on a dry, mineral matter-free basis.

self. These errors may involve differences in oxygen peak shape and/or location, volatilization of oxygen-containing species during analysis, or potential errors in the matrix correction routine.

Peak shape and location can possibly be affected by the distribution of oxygen functional groups in the coal, since differences in bonding energy will change slightly the energy of the emitted x-rays, particularly for light elements. If these effects are significant for the samples analyzed in this study, then determining the oxygen at a single wavelength for a given sample could introduce significant errors into the determination. Integration of peak areas may be required for accurate analyses. Oxygen peak shapes and locations for the coals and quartz are shown in Figure 1. An oxygen curve was not obtained for the amber. Although additional work is required for confirmation, the peak shapes appear to be significantly different between samples. Also, it can be seen that variations of only 0.050A in the peak location could result in variations in the measured intensity by as much as 20%.

To study the possibility of sample volatilization, oxygen counts were collected for successive five-second intervals under different operating conditions for the Dietz and Illinois coals. Twelve measurements were collected on each of several particles for both coals, with a one-second break in between each interval. When relatively high energy fluxes were used, oxygen counts for both coals decreased by 18-36% over a 72-second period. However, the Illinois coal was able to withstand a higher beam current without experiencing a decrease in the oxygen count. Results of thermogravimetric analyses, shown in Figure 2, indicate that the Dietz coal is more volatile than the other coals. Thus, it is probably more susceptible to loss of oxygen during SEM analysis. In view of this, the Dietz coal was reanalyzed using milder operating conditions. Under the modified analytical conditions, the oxygen content was about 15%, as opposed to the values of 8-9% reported in Table 2. This adds additional support to the sample volatilization hypothesis. No similar experiments were performed on the amber.

The "ZAF" matrix correction routine is a third possible source of error. Using typical operating conditions, absorption factors for oxygen in coal were between 7 and 9, which are of particular concern since the oxygen standard (SiO<sub>2</sub>) is not similar to the coal matrix. The absorption corrections can be minimized by altering operational parameters. Also, in lieu of a different oxygen standard, using other correction routines could minimize errors associated with the matrix corrections.

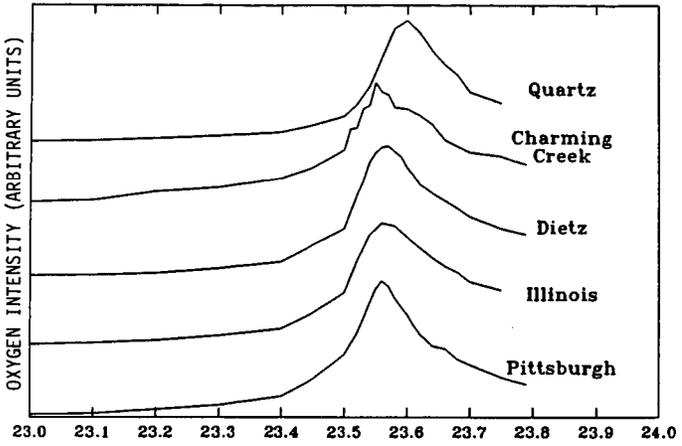


FIGURE 1. Oxygen peak shapes for quartz and coals used in this study.

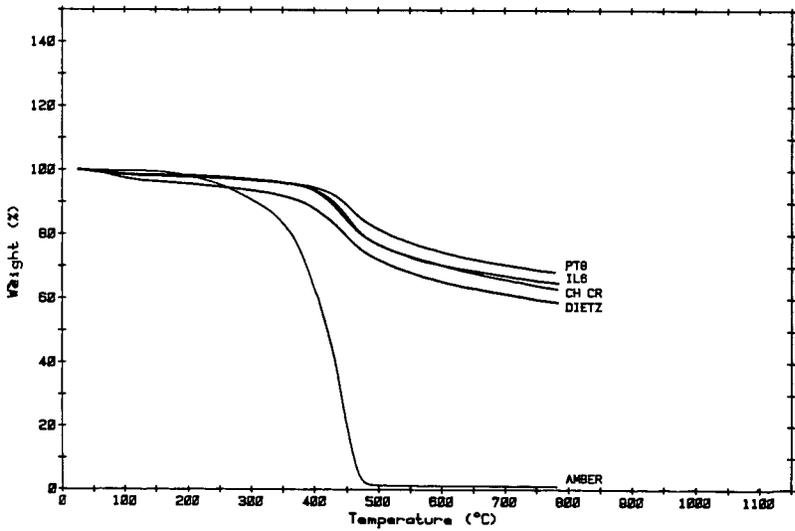


FIGURE 2. TGA analyses of coals and amber.

## CONCLUSIONS

Although some encouraging results were obtained with the SEM-WDS technique, additional work is required to optimize analytical conditions to perform quantitative oxygen determinations. Maintaining sample integrity will need to be considered when selecting optimum x-ray acquisition parameters. Additional work is also required to further ascertain analytical precision and to further establish statistical parameters. The validity of the sampling approach, which has been shown to be acceptable for determining organic sulfur in coal, should be evaluated further to test its applicability to organic oxygen determinations. The theoretical detection limit of about 1% for oxygen is low enough for the technique to be applicable to a wide variety of coal and coal products. Difficulties with analysis of the amber indicate that alternate sample mounting techniques should be available for analyzing different sample types.

## ACKNOWLEDGEMENTS

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## The Solvent Swelling Behavior of $\text{AlCl}_3$ -Treated Coal Molecules

T. K. Green, G. T. Ransdell, and J. S. Flynn

Department of Chemistry, Western Kentucky University, Bowling Green, KY 42101

### INTRODUCTION

Coals are known to be largely insoluble in most common solvents at their boiling points. A good solvent such as pyridine dissolves at best only 10-30 weight percent of the solid. However, the insoluble portion of coals is known to swell up to two to three times its own volume in good solvents, and this lends support to the idea that the insoluble portion is best viewed as a three-dimensionally crosslinked macromolecular solid (1). A minor amount of smaller molecules are thought to be trapped within this three-dimensional network and can be released by good swelling solvents such as pyridine. This paper is concerned with the relationship of the three-dimensionally crosslinked macromolecules that constitute the insoluble portion of coals and the smaller, potentially-extractable molecules.

The relationship between the macromolecular portion of coal and the smaller molecules has been of considerable interest to coal chemists for some time. A fundamental question concerning this relationship is whether the smaller molecules represent much the same stuff as the crosslinked macromolecules. This question has been addressed by Given in a recent review (2). Van Krevelen, in his proposed model of the coalification process, regarded the smaller molecules as the unreacted fragments of a condensation polymerization reaction (3). The insoluble macromolecular network was regarded as the product of this condensation polymerization. Thus the soluble, smaller molecules and the insoluble macromolecules were regarded by van Krevelen as much the same stuff. Given has rejected this view as not in accord with the facts (2). The details of his arguments are not presented here. Larsen and co-workers, in a study of the molecular weight distributions of pyridine extracts, have shown that coalification is not a simple condensation polymerization as proposed earlier by van Krevelen (4).

In spite of the evidence arguing against van Krevelen's view of the coalification process, we were intrigued by the possibility of modeling the insoluble macromolecules in coal by somehow "polymerizing" or crosslinking the soluble, smaller molecules into an insoluble network. If this could be accomplished, the various properties of the two materials (e.g. swelling behavior) could be directly compared. A study of this nature might lend insight into the relationship between the macromolecular network and the smaller molecules in coals.

### APPROACH

Winans and co-workers have shown that lignin can be transformed into an insoluble material resembling low rank coals in the presence of montmorillonite at  $150^\circ\text{C}$  (5). In addition, aluminum bromide ( $\text{AlBr}_3$ ) was shown to transform lignin to a coal-like material in a very short time (24 hr at  $120^\circ\text{C}$ ). This fascinating result suggested to us that Lewis acids might promote crosslinking reactions between soluble coal molecules, leading to an insoluble three-dimensionally crosslinked material capable of swelling in organic solvents. Thus we chose to treat soluble coal molecules with  $\text{AlCl}_3$  to see if an insoluble material might be produced.

The choice of  $\text{AlCl}_3$  as a reactant imposed a significant constraint on our experimental approach. Most coals are largely insoluble in solvents that would be compatible with Lewis acids. For example, hydrocarbon solvents such as toluene will not strongly coordinate with Lewis acids in Friedel-Crafts alkylation reactions (6), but these solvents dissolve only a small fraction of most coals. On the other hand, pyridine and other donor solvents are effective extraction solvents for coals, but strongly coordinate to Lewis acids, rendering them ineffective as alkylation

catalysts (6). Thus pyridine would be a poor choice as a reaction solvent in the presence of  $\text{AlCl}_3$ .

An alternative approach is to make the coal more soluble in solvents compatible with Lewis acids. One way of doing this is by O-methylation of the hydroxyl groups in coal. Liotta has shown that the extractability of an Illinois No. 6 coal in chloroform ( $\text{CHCl}_3$ ) is increased from 3.2% to 21.7% upon O-methylation (7). The reaction is thought to render the coal free of its secondary structure by disrupting coal-coal hydrogen bonds. The primary covalent framework of the coal is left intact. The  $\text{CHCl}_3$ -soluble fraction of the O-methylated Illinois No. 6 coal was found by us to be completely soluble in  $\alpha$ -dichlorobenzene, a nonreactive solvent compatible with Lewis acids. Thus  $\alpha$ -dichlorobenzene was chosen as the reaction solvent for the treatment of the coal extract with  $\text{AlCl}_3$ .

#### EXPERIMENTAL

##### O-methylation

O-methylation of the Illinois No. 6 coal was carried out according to Liotta's method (7). Elemental analyses of both the native and O-methylated coals are given in Table 1.

Table 1  
Elemental Analyses of Illinois No. 6 Coal<sup>a</sup>

	C	H	N	S	O <sup>b</sup>	MM <sup>c</sup>
Illinois No. 6	78.3	5.4	1.3	4.5	10.5	13.3
O-methylated	76.5	6.0	1.7	2.9	12.8	9.6

<sup>a</sup> dmmf basis

<sup>b</sup> by difference

<sup>c</sup> mineral matter, calculated according to MM=1.08 Ash +.55S

The Soxhlet extractability of the O-methylated Illinois No. 6 coal in chloroform was found to be 19.3%, (dmmf), in good agreement with Liotta's findings (7).

##### Treatment of $\text{CHCl}_3$ extract with $\text{AlCl}_3$

5 mL of nitromethane was placed in a 100 mL round bottom flask. Approximately 2 g of anhydrous  $\text{AlCl}_3$  was dissolved in the nitromethane. 30 mL of  $\alpha$ -dichlorobenzene and 1.75 g of coal extract were then added. The flask was flushed with  $\text{N}_2$ , stoppered and allowed to stir at room temperature for three days.

A separate reaction identical to the above reaction was conducted, except that no nitromethane was added to the flask.

After three days, the contents of the flask was suction filtered. The residue was washed with  $\alpha$ -dichlorobenzene, acetone, and then water. The residue was then placed in a thimble and Soxhlet extracted overnight with water, which was sufficient to give a negative silver nitrate test for chloride ion. The residue was then dried under vacuum at 105°C overnight.

##### Swelling Procedure

The residue from the  $\text{AlCl}_3$ -treated coal extract was swollen in series of solvents using an established procedure (8).

## RESULTS

The yield of *m*-dichlorobenzene insoluble material was 30% (based on the starting weight of extract) when nitromethane was used as a co-solvent. In contrast, the yield of insoluble material was only 5% when nitromethane was omitted from the reaction.

The insoluble material obtained from the  $\text{AlCl}_3$ -treatment was swollen in series of solvents according to an established technique<sup>3</sup>(8). The volumetric swelling ratio, *Q*, is a measure of the volume of solvent absorbed by a unit volume of coal, and is defined as

$$Q = \frac{\text{Volume of Swollen Coal}}{\text{Volume of Unswollen Coal}} \quad 1)$$

When *Q* is 1.0, the coal has absorbed no solvent. The results of these measurements are presented in Table 2. The *Q* values for the native, *O*-methylated, and  $\text{CHCl}_3$ -extracted *O*-methylated Illinois No. 6 coals are also presented.

The hydrogen to carbon ratios of the coals and the insoluble material from the  $\text{AlCl}_3$  treatment are also shown in Table 2.

Table 2  
Solvent Swelling Ratios (*Q*) and H/C ratios for Illinois No. 6 Coals  
and  $\text{AlCl}_3$ -treated Coal Extract<sup>a</sup>

Coal	H/C	Q				
		Cyclohexane	Ether	Benzene	THF <sup>b</sup>	Pyridine
Illinois No. 6	0.83	1.0	1.2	1.1	1.9	2.6
<i>O</i> -methylated	0.94	1.1	1.4	1.7	1.9	2.2
<i>O</i> -methylated, $\text{CHCl}_3$ -insoluble	0.89	1.1	1.5	1.8	1.9	2.5
<i>O</i> -methylated, $\text{CHCl}_3$ -soluble	1.1	N/A	N/A	N/A	N/A	N/A
$\text{AlCl}_3$ - <i>NO</i> <sub>2</sub> - <i>Me</i> -treated, $\text{CHCl}_3$ -extract <sup>c</sup>	0.90	1.1	1.4	1.8	1.9	2.3
$\text{AlCl}_3$ -treated, $\text{CHCl}_3$ -extract <sup>c</sup>	--	--	--	1.5	1.7	--

<sup>a</sup> Extract was obtained from  $\text{CHCl}_3$ -extraction of *O*-methylated coal.

<sup>b</sup> Tetrahydrofuran.

<sup>c</sup> Insoluble fraction only.

## DISCUSSION

The yield of insoluble material from the  $\text{AlCl}_3$ -treatment of the  $\text{CHCl}_3$ -extract was found to increase from 5 to 30% when nitromethane was added as co-solvent.

Nitromethane is known to be an effective solvent for  $AlCl_3$  (9), and the  $AlCl_3$ -nitromethane complex that forms is known to be catalytically active in alkylation reactions (10). In contrast,  $AlCl_3$  is only slightly soluble in *o*-dichlorobenzene at room temperature. We can speculate that the role of nitromethane as a co-solvent is to provide a homogeneous solution of  $AlCl_3$ , which somehow promotes condensation of the soluble coal molecules. Polish workers have found nitromethane to be an effective solvent for alkylation of coals with alkyl chlorides in the presence of  $AlCl_3$  (11).

The swelling ratios of the coals and the insoluble material produced from the extract are presented in Table 2. The O-methylated coal is observed to swell substantially more in benzene than the native Illinois No. 6 coal. This effect has been previously described (12), and is attributed to the disruption of the hydrogen bond crosslinks in the native coal upon O-methylation. The O-methylated coal has a lower effective crosslink density than the native coal and swells more in good nonpolar solvents such as benzene. Pyridine, a good hydrogen bond acceptor, disrupts most of the hydrogen bond crosslinks and therefore swells both coals to nearly the same extent. The chloroform extraction is observed to have little effect on the swelling behavior of the O-methylated coals.

Remarkably, the swelling behavior of the insoluble material produced from  $AlCl_3$ -treatment of the extract is virtually identical to that of the O-methylated Illinois No. 6 coals. The H/C ratio of this material also closely matches that of the  $CHCl_3$ -insoluble, O-methylated coal. It is substantially lower than that found for the  $CHCl_3$ -extract from which it was produced. This latter result is expected if a more highly-crosslinked material is being produced from the  $CHCl_3$ -extract.

It is clear from these results that the insoluble material produced from the  $AlCl_3$ -treatment of the coal extract has as apparent crosslink density identical to that of the  $CHCl_3$ -insoluble, O-methylated Illinois No. 6 coal. The underlying reason(s) for this result is not known, but we do not believe the result is fortuitous. It clearly suggests a close structural relationship between the insoluble macromolecules and the  $CHCl_3$ -extractable molecules of the Illinois No. 6 coal. It also suggests the possibility that the macromolecules are derived from the smaller molecules in coal, although we have no independent evidence to support this claim. Finally, the insoluble material produced from the coal extract is presumably insoluble because covalent bonds hold the molecules together. If so, a knowledge of the reactions leading to the formation of this material should provide a better understanding of the nature of the covalent crosslinks in coals.

#### ACKNOWLEDGEMENT

We wish to thank the Exxon Education Foundation for the support of this work.

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## HYDROGEN BONDING AND COAL STRUCTURE

P. C. Painter, J. Nowak, M. Sobkowiak and J. Youtcheff

Polymer Science Program  
Penn State University  
University Park, PA 16802

### Introduction

There is now a wealth of literature that discusses coal structure in terms of the concepts of polymer science (1-7). Coal is considered to be a macromolecular network with a degree of cross-linking and a sol/gel ratio (soluble extract/insoluble network) that varies with rank. Although we consider the central premise of this approach intuitively pleasing, we believe there are a number of major problems with the applications of specific theories, notably those that involve the assumption of Gaussian chains and the use of the Flory-Huggins equation to calculate molecular weights from mechanical and swelling measurements. In addition, during the last ten years there has been a revolution in polymer theory based predominantly on the work of the French schools and summarized in de Gennes book (8). In many areas this supplements rather than replaces the classic approach of Flory (9), but recent work on swollen polymer gels by Candau and co-workers (10,11) clearly demonstrates that measurements on the swelling of coal have to be considered in a totally different fashion.

In this communication we will attempt to critically assess these factors. In particular, we will point out the key role played by hydrogen bonding in coal structure and how the presence of such strong, directional interactions does not permit the use of Flory-Huggins solution theory. We will then discuss aspects of various new theoretical approaches that hold promise for describing the structure of coal.

### Hydrogen bonding and the macromolecular structure of coal

At the last ACS meeting we discussed various aspects of hydrogen bonding in coal and presented FTIR results that demonstrated that the predominant species present involved various chains and/or cyclic complexes of phenolic OH groups, typical examples of which are illustrated in figures 1 and 2. There are certainly some hydroxyl/ether and hydroxyl/pyridine-type base hydrogen bonds as well, but in most coals these do not seem to be the principle species present. We will not reproduce the experimental evidence, as this will be presented in a special issue of Fuel (12). As far as the arguments we wish to make here are concerned, the precise nature of the hydrogen bonded complexes are not important. Just the fact that hydrogen bonds are present in significant concentrations has a profound influence on the behavior of a polymer material and what theoretical tools can be successfully applied to a description of structure.

The molecular weight or chain length between cross-link points ( $M_c$ ) is a key parameter in describing polymer networks. Theoretical descriptions of

these materials are of necessity based on a number of simplifying assumptions. The most critical of these are that the chain statistics are Gaussian, all the chain ends are joined to the network, entanglements can be neglected and deformations are affine (the displacements of the cross link points are linear in strain). In testing the predictions of theory it has proved necessary to put together (with some very clever polymer chemistry) networks with precisely defined structures. Monodisperse chains are synthesized and linked through their ends in solution. This minimizes entanglements and provides a prior knowledge of the quantity of interest,  $M_c$ . Even so, the effect of "dangling ends", those chains with only one end joined to the network, can be important (10,11). Clearly, in coal the situation is far worse. The chain segments between cross link points are probably too short and too stiff to be anywhere near Gaussian and it would be extraordinary if dangling ends were not present. If this were not bad enough, some measurements have been made on solvent swollen samples. Here, even if the chains were long and flexible enough to be considered Gaussian, the distance between cross links no longer scales as  $N^{0.5}$  (where  $N$  is the number of "repeat units"). Instead, excluded volume effects become important and  $M_c$  scales as  $N^{0.6}$  (8,10). Of course, there have been various modifications of rubber elasticity theory to account for some of these factors, but the virtue of simplicity is lost and the equations incorporate additional parameters that have to be fitted to the data.

Although these problems are considerable, and have been clearly recognized by a number of workers that have attempted to apply rubber elasticity theory to coal, if all that we required was a very rough "ballpark" estimate of  $M_c$ , it might be possible to live with these limitations. There are two additional factors that have to be considered, however, and they are so crucial that they make estimates of molecular weight presented in the literature essentially meaningless. The second of these will be considered in a separate section. The first is the use of Flory-Huggins theory to describe polymer solvent interactions. This theory provides beautiful insight into the major factors that affect solubility, but in terms of predictive calculations it has two major defects, well-recognized in the polymer literature, but largely ignored when this equation is applied to coal. The first problem involves free volume effects. These have been accounted for, most notably in the equations of state approach (13) and we presume that a modified or approximate treatment could be applied to coal. This is not the principle concern at this stage of our research program, however. We are much more interested in the second "defect" of Flory Huggins theory when applied to coal, the use of the  $\chi$  interaction parameter.

Flory-Huggins theory is basically an extension of regular solution theory. Two terms are considered, a combinatorial entropy expression and a van Laar type exchange interaction term that has the form  $\phi_1 \phi_2 \chi$ , where  $\chi$  is the exchange energy and  $\phi_1 \phi_2$  are the volume fractions of solvent and polymer in the mixture. The product  $\phi_1 \phi_2$  represents the probability of contact between polymer segments and solvent molecules and implicitly assumes random mixing. The  $\chi$  term for hydrocarbons is derived by assuming weak London dispersion forces and in the original formulation is always positive (actually  $> 0$ ). Hydrogen bonding cannot be accounted for in this scheme. Secondary forces that are strong, specific and directional will result in a number of 1:2 contacts that exceeds that due to random mixing by an amount that will depend upon the energy of the interaction. Furthermore, the formation of hydrogen bonds results in a change of entropy as well as enthalpy (that is, an additional

entropy term to that describing combinatorial mixing). As Prigogine (14) has pointed out, there is no satisfactory theory of strong interactions, principally because the rotational partition function is not independent of the translational partition function. It is possible to use an equilibrium scheme to describe these systems, however, and we have recently adapted treatments used to describe the behavior of alcohols in hydrocarbon solvents. This is described in detail elsewhere (15), but the key point as far as this discussion is concerned is that the Flory-Huggins equation is modified by the addition of a term  $\Delta G_H$ , which describes the change in the free energy due to the change in the pattern of hydrogen bonding when a material that self associated (eg. coal, through OH groups) is mixed with a species that competes with these hydrogen bonds. The equations are obtained in a conceptually simple fashion, but the algebra necessary to describe and explain the result is too lengthy to reproduce in this short preprint. The key point is that we obtain an expression for  $\Delta G_H^M$  that consists of parameters that are experimentally determinable (most significantly, the fraction of OH groups that are not hydrogen bonded, measured by FTIR). We will discuss the application of this approach more completely in a future publication. The central point we are making is that hydrogen bonds do not permit the use of conventional solution theory and a new approach is required.

Before proceeding to a discussion of the second factor that obviates the use of traditional polymer theory for determining coal molecular weights, it is important to consider one or two additional factors associated with hydrogen bonding in coal. First, in many studies the degree of swelling of coal samples is plotted as a function of solvent solubility parameter values. Two maxima were observed in one recent study (17) and these were separately assigned to the solvation of the macromolecular network by a solvent with a solubility parameter similar to the coal, while the second was assigned to the breaking of hydrogen bonds. This interpretation is just plain wrong. Solubility parameters are related to the Flory X parameter and are simply a different formulation of a van Laar type interaction term. Plotting data for hydrogen bonding materials as a function of such parameters is meaningless for the reasons given above. A double maximum was observed because THF and pyridine both contain hydrogen bond "acceptor" groups (atoms with a lone pair of electrons) and so will both hydrogen bond to coal phenolic OH groups. However, they have very different "solubility parameters" and so are separated in this dimension by non-hydrogen bonding solvents. The double maxima are simply an artifact of this condition. If, instead, we could plot swelling against the strength of competing hydrogen bond formation (coal/solvent vs coal self-association), then a much more credible plot would be obtained. Szeliga and Marzec (17) produced one such plot using the donor number-acceptor number approach of Gutmann (18). The physical meaning of these numbers is obscure, however. In order to illustrate our point we therefore plot swelling measurements reported in the literature against the strength of the hydrogen bonds formed between the solvents in question and phenolic OH groups, which can conveniently be measured by shifts in OH stretching modes (12). There is a straightforward correlation and no double maxima (see Figure 3).

Finally, the presence of hydrogen bonds has an extremely important but largely ignored effect on the determination of the molecular weight of soluble coal derived liquids. These will hydrogen bond to form multi-molecular complexes. The size of these aggregates will depend upon the hydrogen bonding capacity of the solvent. Because this is an equilibrium process, however, it

is easy to show that there will always be aggregates present (15), even in extremely dilute solutions of hydrogen bonding solvents. Discounting other problems associated with molecular weight measurements, this alone brings into question the reliability of most published values.

### Desinterspersion

The final "problem" in using the concepts of polymer science that we wish to discuss is a phenomenon called desinterspersion by Candau et al. (10,11). This concept arose from observations made in neutron scattering studies of model polymer networks. LITTLE or NO CHAIN EXTENSION WAS OBSERVED IN SWOLLEN POLYMER NETWORKS, relative to the unswollen state. Following Flory (13), it was then noted that this effect is not topologically forbidden. A distinction can be made between topological neighbors (crosslink points connected by the same chain in the network) and spatial neighbors, connected by longer network pathlengths, as illustrated schematically in Figure 4. Desinterspersion is then an accordionlike unfolding of to give the type of swollen structure shown in Figure 5. A considerable degree of "untangling" can occur before chains change conformation or end-to-end distance.

It is more than likely that coal, with its relatively short, stiff chains, swells at least in part in such a fashion. Theoretical descriptions of swelling have to change to account for this. One promising approach is the analogy to polymer semidilute solutions suggested by De Gennes (8). Much work remains before this can sensibly be applied to coal, however.

### Conclusions

Our conclusions, stated baldly, sound rather harsh. Previous applications of polymer theory to coal are unsound and quantitatively without meaning because hydrogen bonding and desinterspersion have been largely neglected. However, these statements have to be placed in the context that it is only recently that these factors have been considered by polymer theoreticians. It is our view that the scientists who pioneered the study of coal as a macromolecular network made a major conceptual advance. The work presented here is not a criticism of this fundamental premise, but a refinement based on recent advances.

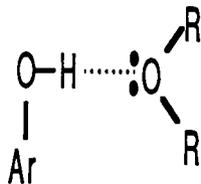
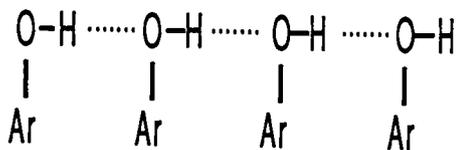
### Acknowledgement

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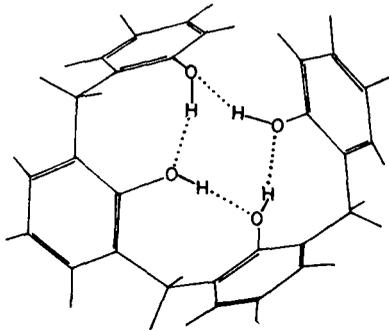
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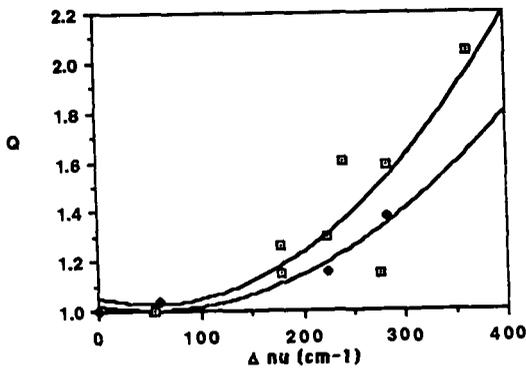
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**Figure 1** Schematic representation of (top) chains of hydrogen bonds formed between phenolic OH groups and (bottom) phenolic OH-ether hydrogen bonds.



**Figure 2** Cyclic tetranuclear complex formed between four phenolic OH groups.



**Figure3** Degree of swelling of coal (data from References 16 and 17) plotted against the infrared frequency shifts of the phenolic OH group when dissolved in the same solvents.

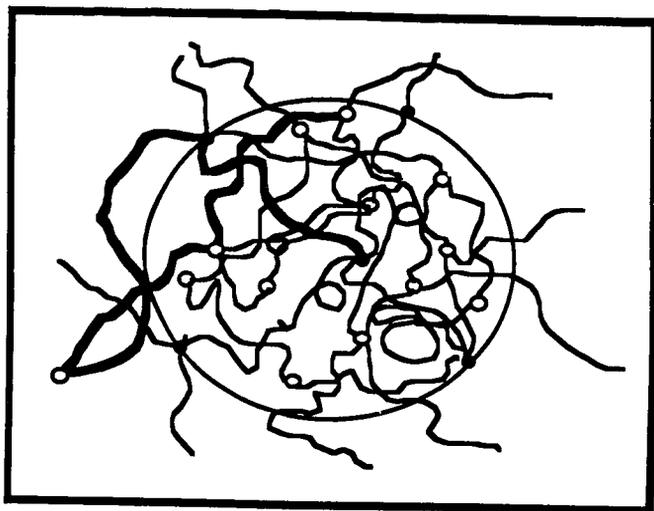


Figure 4 Schematic representation of a polymer network. The heavy lines illustrate the spatial separation between topological neighbors (after Candau et al., References 10,11).

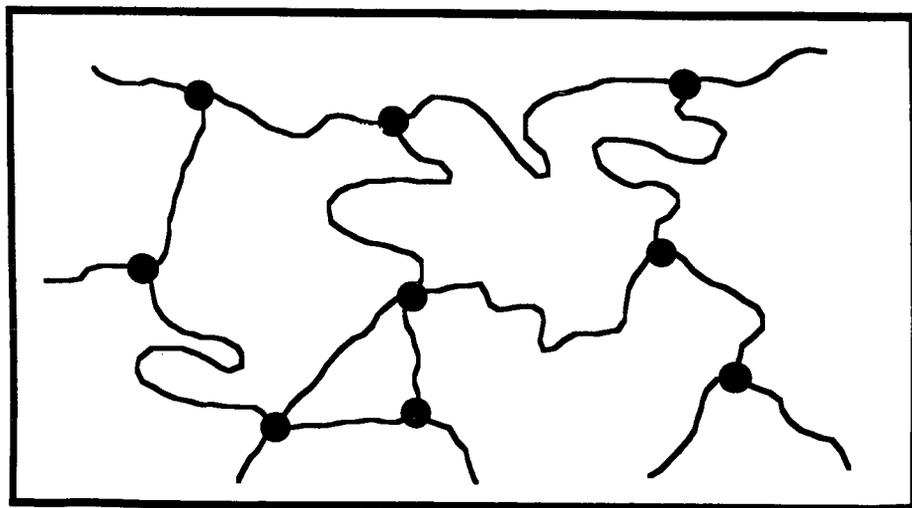


Figure 5 Schematic representation of the swollen network with "desinterspersions" of the cross link points.

## Studies on the Reaction of Coal with Ethoxycarbonylcarbene

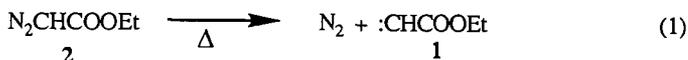
Martin Pomerantz and Peter Rooney

Department of Chemistry  
The University of Texas at Arlington  
Arlington, Texas 76019-0065

### Introduction

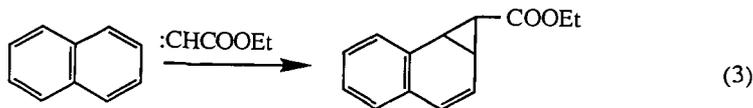
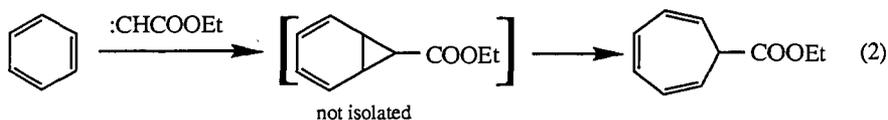
Studies of the molecular structure of coal have relied heavily on the chemical reactions of the coal and on the structure of the products produced. Many of these reactions involve high temperatures and fairly severe conditions, and, as a result, it is frequently difficult to relate the reaction products to coal structure because of molecular rearrangements and unanticipated reactions. For this reason people have sought mild reactions which would depolymerize the coal and provide tractable, identifiable products. Among these are oxidations using trifluoroperoxyacetic acid (1),  $\text{Na}_2\text{Cr}_2\text{O}_7$  (2),  $\text{Ag}_2\text{O}$  (3),  $\text{HNO}_3$  (4) and  $\text{H}_2\text{O}_2$  (5), and alkylation (6). Most other attempts at depolymerization involve high temperatures and much more severe conditions (7).

In this report we examine the reactions of coal with ethoxycarbonylcarbene (1) formed by the mild thermal decomposition of ethyl diazoacetate (2; eqn. 1). There are a few reports in the literature of



studies involving reaction of coal with diazo compounds or carbenes. All but one have involved the use of diazomethane to analyze for  $-\text{COOH}$  and phenolic  $\text{OH}$  groups (8,9) and these studies have shown that it is a rather poor analytical method. One recent study (9) reports on the reaction of labeled  $^{14}\text{CH}_2\text{N}_2$  and  $^{14}\text{CCl}_2$  with coal and coal-derived materials. The conclusions, based strictly on the uptake of reagent both before and after exposure to air, were that air exposed fractions exhibited more ketonic and carboxyl groups at the expense of phenolic hydroxyl, benzylic methylenes and other oxidizable moieties.

The reactions of carbenes, particularly ethoxycarbonyl carbene (1), with a very large variety of organic compounds is quite well known (10). They will add to aromatic molecules to form 3-membered and 7-membered rings, they will insert into C-H bonds, will react with some heteroatoms and will undergo various free radical reactions. Equations 2 and 3 illustrate the first of these reactions by showing the reaction of the carbene 1 with benzene and naphthalene respectively.



In this paper we report on the reactions of 1 (prepared by mild thermal decomposition of 2) with an Illinois No. 6 HVCB bituminous coal (PSOC-1351) and studies of the products involving thermal

analyses (TGA, DTA), diffuse reflectance FT-IR spectroscopy (DRIFT), and some preliminary GC analyses.

## Results and Discussion

A sample of Illinois No. 6 HVCB bituminous coal obtained from the Pennsylvania State University Coal Research Section (PSOC-1351) was crushed to <100 mesh under argon, dried at 120-125°C, and then treated with ethyl diazoacetate (**2**) in pentane. The mixture was stirred overnight at room temperature, under N<sub>2</sub>, the pentane was removed in vacuum and the coal/**2** mixture was slowly heated to 100°C until nitrogen evolution ceased. The temperature was then raised to 120°C for an additional 30 minutes to insure complete decomposition of **2**. After weighing, a portion of the samples was extracted (Soxhlet) for 24 hours with toluene/methanol (9:1), and the extract was concentrated by distillation.

The above procedure was run using 1, 2 and 3 grams of **2** to 1 g of coal and, in addition, a control experiment, using the coal but omitting **2**, was run. (The runs were called Coal 1, 2, 3 and 0 respectively.) Further, a control experiment without the coal (monitored by <sup>1</sup>H NMR spectroscopy) showed that **2** was stable to the overnight stirring procedure. Table 1 shows the results. It should be noted that the decomposition of **2** apparently begins below 80°C and N<sub>2</sub> evolution is fairly vigorous at 80°. This suggests that, since ethyl diazoacetate normally requires higher temperatures for decomposition (10), the reaction is being catalyzed, presumably by the mineral matter in the coal. It is also well known that catalyzed decomposition of **2** gives rise to carbene products (10).

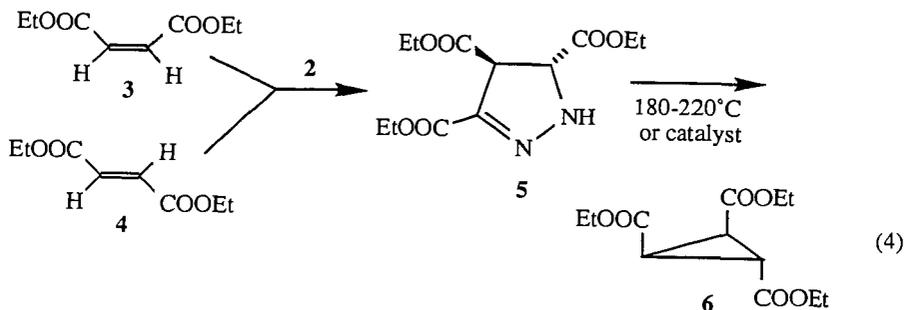
Table 1. Results of the Reaction of N<sub>2</sub>CHCOOEt (**2**) with Illinois No. 6 Coal

	Coal 0	Coal 1	Coal 2	Coal 3
<b>2</b> (g)	0	1.016	2.028	3.000
coal (g)	1.004	1.002	1.010	1.015
Amt. recovered (g) <sup>a</sup>	1.015	1.563	2.264	2.654
% yield <sup>b</sup>	101	88	89	81
% extracted	31	45	63	71

a) Weight after heating and loss of N<sub>2</sub>.

b) Calculated based on weight of coal and carbene **1**.

In order to be sure that the major reactions were of the carbene, **1**, with the coal, we independently prepared the known products formed when **2** decomposes by itself and when **2** reacts with the dimers of **1**. The dimers, namely, diethyl maleate (**3**) and diethyl fumarate (**4**) are known to give the pyrazoline, **5**, on reaction with **2**, and this, in turn, thermally (above 180°C) or catalytically is known to decompose to cyclopropane, **6** (equation 4) (10-12). Capillary gas chromatographic analysis of the concentrated extracts showed small amounts of **3-6** in coal 1 (about 8 area percent total of the non-solvent peaks eluting from the column), a little more of these in coal 2 (ca. 10%) and a bit more in coal 3 (ca. 13%). Also, since **5** does not produce **6** below 180°C except by catalysis with metal ions (12), we must conclude that the reaction **5** → **6** was catalyzed in the coal. It was thus clear that the major reaction of the species **1** and **2** was with the coal.



In addition to the peaks corresponding to 3-6 there were, of course, many other peaks in the GC of the extracts. The number of peaks in coal 3 was about the same as in coal 2 while in coal 1 the number was smaller and was smallest in coal 0. Work is in progress to try to identify these peaks, or at least the major ones.

Table 2 shows the results of thermogravimetric analyses (TGA) giving weight loss between 200° and 600°C for the coal samples before extraction. It should be noted that carbene treatment increased the amount of material which is volatile below 600°C by a factor of 2 to 3, a rather significant increase. Also, the major effect is shown on going from coal 0 to coal 1 and 2 while a smaller effect is shown on going from coal 2 to 3. The derivative plots (DTA) show the maximum rate of weight loss for coal 0 (2.0%/min) at 470°C, for coal 1 (6.2%/min) at 260°C, and for coal 2 (9.1%/min) at about 260°C. Coal 3 is essentially the same as coal 2. It is thus clear that in addition to increasing the amount of material which can be volatilized below 600°C, carbene treatment also lowers very substantially the temperature of maximum decomposition. Also, since the TGA curves change substantially in the carbene treated coals compared with the control, coal 0, the diazo compound (2) and hence the carbenes must be getting into the interior pores of the coal and giving rise to reaction. Thus we are not looking simply at a surface reaction.

Table 2. Results of Thermogravimetric Analysis

	Coal 0	Coal 1	Coal 2	Coal 3
% weight loss <sup>a,b</sup>	21 ± 1.0	45 ± 1.5	57 ± 2.1	63 ± 1.9

a) % weight loss between 200° and 600°C.

b) Average of 5 separate runs each.

Finally, diffuse reflectance FT-IR (DRIFT) spectra were obtained for the various samples. There were several differences observable upon carbene treatment. First, and most trivial, is that an ester carbonyl appeared at 1736 cm<sup>-1</sup> in all samples. More significantly, a small peak at about 3050 cm<sup>-1</sup>, which is presumably due to aromatic C-H (13,14), disappeared with increasing amount of 2. A new

aliphatic CH peak appeared at 2962  $\text{cm}^{-1}$  while a substantial aromatic peak at 1610 (13,14) in coal 0 got much smaller in coal 1 and disappeared in coals 2 and 3. A peak at 856  $\text{cm}^{-1}$  appeared with carbene treatment and a smaller one at 771  $\text{cm}^{-1}$  also grew in. One or both of these could be due to alkene C-H out of plane deformations which occur in this region (13).

One area that also merits notice is the 400-550  $\text{cm}^{-1}$  region. According to Solomon (15) and references cited in this publication, this region is due to metal-sulfur and metal-oxygen bonds in the minerals of the coal. In the present study the 546  $\text{cm}^{-1}$  peak progressively disappeared in going from coal 0 to coal 3 and the 475  $\text{cm}^{-1}$  peak also got smaller. This is consistent with the suggestion that the diazo compound decomposition was catalyzed and the reaction of the minerals with the ethyl diazoacetate (2) caused these absorptions to vanish.

## Summary

Ethoxycarbonylcarbene (1) produced by the mild thermal decomposition of ethyl diazoacetate (2) has been reacted with Illinois No. 6 coal. Thermal analysis has shown that the treated coal is considerably more volatile than untreated coal and that the temperature of maximum volatility is significantly reduced. Infrared studies have shown that, in addition to the appearance of ester carbonyl absorption in the treated samples, there were also peaks attributable to aromatic rings and to mineral matter which diminish and peaks attributable to alkenes which also appeared. This is consistent with the known reactions of ethyl diazoacetate and ethoxycarbonylcarbene (10).

## Experimental Section

**General.** Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Capillary GC was on a Varian model 3700 gas chromatograph using a 0.315 mm x 30 M DB-5+ column with injector temperature at 250°C, FID detector at 300°C, and temperature programmed at 10°C/min from an initial temperature of 60°C (held for 5 min) to a final temperature of 270°C. Diffuse reflectance FT-IR was carried out on a Biorad-Digilab FTS-40 instrument equipped with a TGS detector and a Barnes Analytical-Spectra Tech diffuse reflectance accessory. The samples were 2 mg of coal and 100 mg of KBr. Thermal analyses were done on a DuPont system including a model 1090 thermal analyzer, 951 thermogravimetric analyzer and 1091 microprocessor.  $^1\text{H}$  NMR spectra were obtained on a Varian T-60 60 MHz spectrometer.

**Materials.** Illinois No. 6 HVCB bituminous coal was obtained from the Pennsylvania State University Coal Research Section (PSOC-1351), and was reported to have the following elemental analysis: (wt. %-dry) C = 67.33%; H = 4.11%; N = 1.17%; organic S = 2.93%; O = 10.74%; and mineral matter 13.72%. The proximate analysis: ash = 11.49%; volatile matter = 40.34% and fixed carbon 48.17%. Pentane was stirred with several portions of  $\text{H}_2\text{SO}_4$  until there was no color produced, with 0.5 N  $\text{KMnO}_4$  in 3 M  $\text{H}_2\text{SO}_4$  for 12 hr., washed with  $\text{H}_2\text{O}$  and then aqueous  $\text{NaHCO}_3$  and dried with  $\text{MgSO}_4$ . It was distilled through a 12 in. Heli-pak column and the fraction boiling 35-36°C was collected and stored over 4Å molecular sieves. Ethyl diazoacetate was prepared from ethyl glycinate hydrochloride and distilled, b.p. 24-26°C/1.5 torr (16). Methanol was distilled through a 12 in. Heli-pak column and the fraction b.p. 64.0-64.5°C was collected and stored over 4Å molecular sieves. Toluene was distilled through a 12 in. Heli-pak column and the fraction b.p. 110-110.5°C was collected and stored over 4Å molecular sieves.

**Reaction of Coal with Ethyl Diazoacetate.** The Illinois No. 6 coal was crushed under argon to pass through a 100 mesh screen and dried at 120-125°C for 3 hr. under  $\text{N}_2$ . After cooling for 30 min., 1 g portions of coal were put into 100 mL round-bottomed flasks into which was put 10 mL of pentane and the ethyl diazoacetate (none for coal 0 and 1, 2 and 3 g for coal 1, 2, and 3 respectively). The mixture was stirred under  $\text{N}_2$  overnight and the pentane was removed in vacuum over ca. 30-40 min. The flasks were heated slowly to 100°C until the  $\text{N}_2$  evolution ceased (20-30 min.; monitored with a bubbler) and then the temperature was raised to 120°C for an additional 30 min. After they were weighed the samples were stored under  $\text{N}_2$ . Approximately 0.4 g of these samples were extracted with

9:1 toluene:methanol in a Soxhlet extractor for 24 hr. and the extract was concentrated to about 1.5 mL by distillation through a 12 in. Vigreux column.

TGA analyses were done on 10-20 mg samples in an Ar or N<sub>2</sub> atmosphere. The temperature was programmed from 85°C to 1050°C at a rate of 20°C/minute. In general 5 runs were done on each sample.

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