

Macromolecular Structure of Coals. IV. Equilibrium Swelling Studies of Coal Networks Subjected to Various Treatments

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Synopsis

The macromolecular network structure of the organic phase of bituminous coals was investigated with equilibrium swelling experiments at 35° and 60°C. It was determined that an oxygen-methylation technique led to cleavage of hydrogen bonds and significant increase of swelling. Pyridine preextraction led to significant differences in swelling due to partial incorporation in the network structure.

INTRODUCTION

There exists considerable evidence in the literature which suggests that the organic phase of coal is a highly crosslinked macromolecular network. This analysis is supported by the fact that the organic phase of coal can swell in thermodynamically compatible solvents to twice its original volume without complete dissolution.¹⁻⁸

Coal consists of an organic phase which is the highly crosslinked macromolecular network and a gel phase which is trapped in the network due to size considerations and physical bonding. To study the highly crosslinked macromolecular network, one must initially remove the gel phase or the extractable portion.⁹

The prevailing view of the chemical structure of coal is one of a system of aromatic/hydroaromatic/heterocyclic condensed ring clusters, crosslinked by methylenic, ethylenic, sulfidic, and/or etheric bridges.^{1,10-12} Several models have been developed to depict the aromatic and crosslinked structure of coal.

To aid in the study of the highly crosslinked coal network, Lucht and Peppas^{1,3} proposed a simplified description of the organic phase of coal which contains tetrafunctional and multifunctional crosslinks, unreacted functionalities, chain ends, entanglements, chain loops, and effective network chains. Physical crosslinks occur because the system is highly entangled. The chains have limited mobility and therefore are unlikely to disentangle. Chemical crosslinks result from chemical reactions and are stable under a variety of conditions.

In previous studies in this series of papers,^{1,13,14} we discussed the equilibrium swelling behavior of various coal structures in a variety of solvents

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including pyridine, cyclohexane, methanol, ethanol, and propanol. Based on these studies, it was concluded that coal is a macromolecular network. A simplified macromolecular model was presented and the molecular weight between crosslinks, \bar{M}_c , was analyzed.^{2,13}

In all previous studies the coal samples had been analyzed either "as received" or upon extraction in pyridine. It was, however, desirable to perform swelling studies on a series of coal samples pretreated in various ways in order to elucidate the coal structure during or after depolymerization. For this reason, we used several depolymerization techniques including that of Hooker et al.¹⁵

EXPERIMENTAL

Sample Preparation

The coal samples, which had been ground to an average particle size of 20–30 mesh (600–850 μm) and packed under nitrogen into stainless steel cans, were furnished by the coal bank group of Pennsylvania State University (PSU). The identification numbers used are those assigned by PSU. The PSU coal samples were sieved to 20–30 (600–850 μm) and 80–100 mesh (150–180 μm) with ASTM-approved stainless steel sieves at room temperature under nitrogen for 1 min or less to avoid formation of fines.

Extraction separates the coal matrix from material which is free or loosely held in the interstices.⁹ In a typical extraction, a coal sample of 20–30 mesh particle size and approximately 3.0 g was weighed to ± 0.0001 g, placed in a cellulose Whatman extraction thimble of medium porosity, and the thimble placed in a Soxhlet extraction apparatus. All extractions were carried out under nitrogen using pyridine (Aldrich, Fisher, or Mallinkrodt, reagent grade) at its atmospheric boiling point of 115.5°C. Recycling typically occurred about four times an hour. The extract solution was replaced every 1–4 days with fresh pyridine until the extract solution appeared to be pure pyridine. This procedure required extraction periods of 1–8 weeks. Acetone was then used as the extraction solvent as its atmospheric boiling point of 56.2°C for 24 h to sweep out pyridine. At completion of this process, the extracted residue was dried to constant weight under vacuum at ca. 60°C and ca. 0.93 MPa (700 torr) under flowing nitrogen. The residue was weighed and stored under nitrogen.

Sample Pretreatments

Atmospheric Oxidation. Atmospheric oxidation was performed to investigate its effects on the crosslinked macromolecular structure of coal and the dynamics of the sorption of pyridine. The 20–30 mesh coal samples were maintained at a temperature range of 61–63°C with air flowing over it for 1 week.

Liotta Oxygen Methylation. Coal owes some of its crosslinked nature to the presence of hydrogen bonds between phenolic and carboxylic groups. A complete characterization of the macromolecular structure of coal obviously includes the percentage of crosslinking arising from hydrogen bonds. The Liotta O-methylation¹⁶ was developed specifically to first swell the coal

sample, thereby opening up reaction sites, and then to neutralize the phenolic and carboxylic functionalities by replacing their hydrogens with a methyl group.

A 5-g sample of coal particles of 80–100 mesh (150–180 μm) was suspended in tetrahydrofuran (THF) in a 500-mL three-neck roundbottom flask at room temperature under nitrogen. Ten cm^3 of a 40 wt % aqueous solution of tetrabutylammonium hydroxide (TBAH, Aldrich) was added, with agitation, to the suspension until a neutral pH was reached. This served to remove all acidic protons in the coal. Then another 0.2 g eq of TBAH were added and the mixture was stirred for 2 h. Iodomethane as the alkylating agent was added in twofold excess, or approximately 3 cm^3 , and stirring was continued overnight. The volatile materials were removed by vacuum distillation in the rotating evaporator at 50–70°C. Then, the TBAH was removed by washing with water several times. The methylated coal was dried under vacuum of ca. 667 Pa at 120°C for 24 h to constant weight. Infrared spectroscopy (IR) of the methylated coal in KBr pellets was used to verify the methylation of the sample.

Equilibrium Swelling

Equilibrium swelling studies provided the final values of the equilibrium volume fraction of coal in a solvent-swelled system, at a specified swelling temperature. Data were collected via gravimetric sorption studies. Samples were dried at 60–80°C under flowing nitrogen at slightly greater than atmospheric pressure for at least 24 h to remove free surface water. They were then transferred to a nitrogen-purged glove box. Preweighed samples were exposed to an environment saturated with the vapor of the swelling agent. Samples were weighed periodically to determine whether or not equilibrium had been established.

In a typical swelling experiment, coal samples of 1–2 g were placed in Coors crucibles, weighed to ± 0.005 g and sealed in dessicators. Each dessicator contained the liquid swelling agent in sufficient quantity to provide an excess of solvent vapor for swelling. For the duration of the swelling experiments, constant temperature was maintained with either a water bath or a convection oven. The time required for swelling equilibrium to be achieved was between 5 and 12 weeks. At the end of the swelling period, the samples were removed and reweighed.

RESULTS AND DISCUSSION

Extraction with Pyridine

Exhaustive pyridine extractions were performed on 3 g samples of 20–30 mesh, of 11 untreated coals. In addition, a 1-g PSOC-207 coal sample of 60–100 mesh, with 79.82% C (dmmf), which had been subjected to the O-methylation technique, was exhaustively pyridine-extracted. The percentage of extractables is shown in Table I for all coals tested. It must be noted that the quantity of extractable materials is probably low because pyridine tends to be trapped or irreversibly adsorbed into the structure of coal. For example, Table II shows the increase in the nitrogen content of sample PSOC-207 (determined by Galbraith Laboratories, Knoxville, TN)

TABLE I
Composition of Pyridine Extractables in Coal Samples

Coal sample PSOC code no.	Unextracted coal content (%, dmmf)	Carbon content (%C, mmf)
418	69.94	20.2
414	72.99	38.2
211	77.08	15.9
266	77.58	18.3
207	79.82	5.3
402	82.48	30.2
341	86.01	19.8
1029	88.12	4.7
647	91.54	1.6
384	94.17	0.0
207La ^a	79.82	68.6

^aLa = Liotta¹⁶ O-methylated coal.

TABLE II
Chemical Analysis of Coal PSOC-207 after Various Pretreatments^a

Coal sample PSOC code no.	% C	% H	% O	% N	% H ₂ O	% CH ₃ O—	%SO ₄
207La	60.43	7.80	6.95	—	0.20	2.73	—
207Raw	73.00	5.43	13.40	1.63	0.21	0.058	1.37
207Ox	69.96	5.18	14.48	—	0.25	—	—
207Ex	72.06	5.05	13.85	4.48	0.24	—	—

^aPretreatments of the samples: (1) La: Liotta-O-methylated; (2) Raw: no pretreatments; (3) Ox: atmospheric oxidation; (4) Ex: Soxhlet-extracted with pyridine.

from $1.63 \pm 0.005\%$ N to $4.48 \pm 0.013\%$ N, both on a whole coal basis, due to irreversible adsorption of pyridine during the extraction process. This change in the nitrogen content indicates that irreversibly adsorbed pyridine is approximately 16.0 wt % of the extracted PSOC-207 coal sample. These results lead to similar conclusions as the studies of Mallya and Stock¹⁷ and Larsen et al.¹⁸

Up to a carbon content of about 90% (dmmf), there is no apparent correlation between the percent of coal extractables and coal rank. As the carbon content increases above 90% C (dmmf), the percent of coal which was extracted drops to zero.

The percentage of the coal sample PSOC-207 which was extracted increased dramatically from 5.3 to 68.6% (both based on mmf weight of coal) when this type of coal was subjected to methylation of its phenolic and carboxylic groups prior to the extraction procedure.

Methylation of Hydroxyl and Carboxyl Groups

A 5-g sample of PSOC-207 with 79.82% C (dmmf) was O-methylated. Chemical analyses (performed by Galbraith Laboratories, Knoxville, TN) and

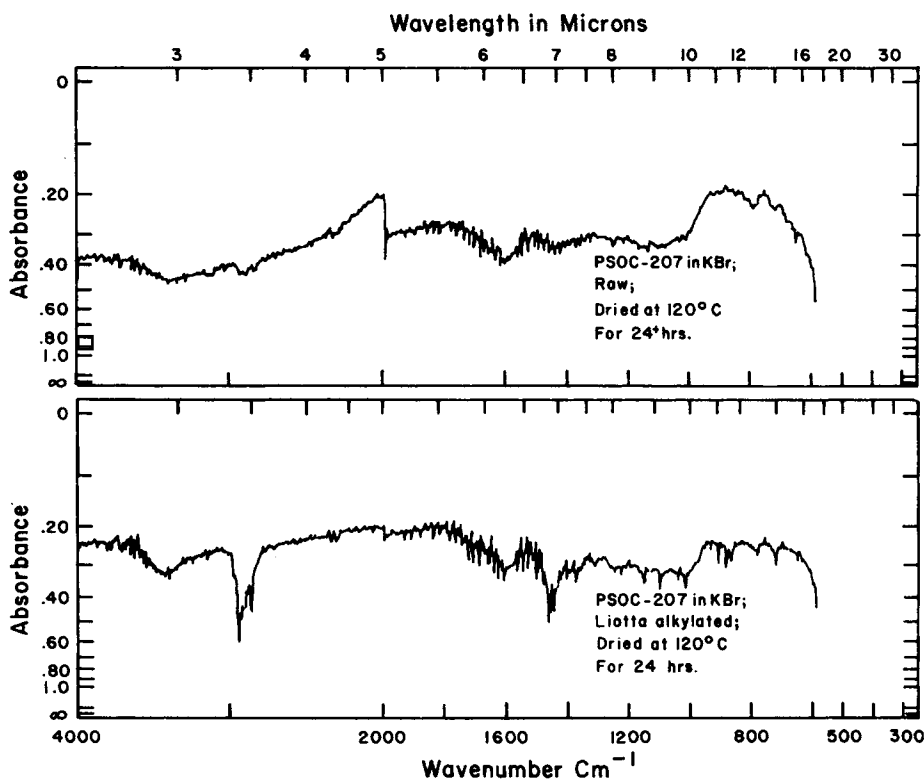


Fig. 1. Infrared spectra of untreated (a) and O-methylated (b) PSOC-207 coal samples.

IR scans of PSOC-207 were used to verify that methylation had taken place. The IR scans are shown in Figure 1. Table III identifies the frequencies associated with chemical entities in coal.

The spectrum of the untreated sample of PSOC-207 shows strong evidence of intermolecular hydrogen bonding in the strongly absorbing and unresolved band from 3100 to 3600 cm^{-1} . Between 3400 and 3500 cm^{-1} , primary amines also absorb, but weakly. As PSOC-207 contains 1.63% nitrogen, compared with its oxygen content of 13.4%, intermolecularly bonded $-\text{OH}$ is believed responsible for this band. After O-methylation, the band from 3100 to 3066 cm^{-1} is much less broad and shows lower absorption, indicating that the intermolecular hydrogen bonds were removed to a great extent. The remaining band, centered at 3400 cm^{-1} , could be assigned to primary amines or physically bound water not removed in the drying process.

Other changes which occur in the IR spectrum after O-methylation of PSOC-207 are the appearance of the strong methyl or methylene absorption bands which range from 2800 to 3000 cm^{-1} and from 1420 to 1480 cm^{-1} . These indicate that methyl groups were incorporated¹⁹ into the structure of PSOC-207.

Evidence that oxygen methylation occurred is also provided by the increase of the content of methoxyl groups after the methylation procedure from 0.058 ± 0.00006 to $2.73 \pm 0.008\%$. Since the combined quantity of organic hydroxyl and carboxylic acid groups averages²⁰ ca. 3% (daf) in a bituminous

TABLE III
 Absorption Bands in the Infrared Spectra of Coal

Band position		Assignment
cm ⁻¹	μm	
3300	3.0	—OH (stretching), —NH (stretching)
3030	3.3	Aromatic C—H (stretching)
2940	3.4	Aliphatic C—H (stretching)
2925	3.42	—CH ₃ (stretching), —CH ₂ (stretching)
2860	3.5	Aliphatic C—H (stretching)
1700	5.9	C=O (stretching)
1600	6.25	Aromatic C=C (stretching), C=O ··· HO—
1500	6.65	Aromatic C=C (stretching)
1450	6.9	Aromatic C=C (stretching); —CH ₃ (asymmetric deformation) —CH ₂ (scissor deformation)
1380	7.25	—CH ₃ (symmetric deformation); cyclic —CH ₂
1300–1000	7.7–10.0	Phenolic and alcoholic C—O (stretching) C _{ar} —O—C _{ar} (stretching); C _{al} —O—C _{al} (stretching) C _{ar} —O—C _{al} (stretching)
900–700	11.1–14.3	Aromatic bands

coal of 80% C (daf), we concluded that a large fraction of the —OH groups in the O-methylated sample of PSOC-207 was reacted.

Atmospheric Oxidation

A 1-g sample of PSOC-207 was oxidized at $60.0 \pm 5.0^\circ\text{C}$ under a flow of air for 1 week. The oxygen content of PSOC-207 increased from $13.4 \pm 0.04\%$ to $14.48 \pm 0.04\%$ on a whole coal basis after atmospheric oxidation, as shown in Table II and Figure 2. The sulfate content is used as an indication of the degree of oxidation of a coal sample, since the majority of sulfur in coals occurs as sulfides. Sulfate content greater than 0.5% is an indication of atmospheric oxidation.²¹ As the percent of sulfate in the untreated sample of

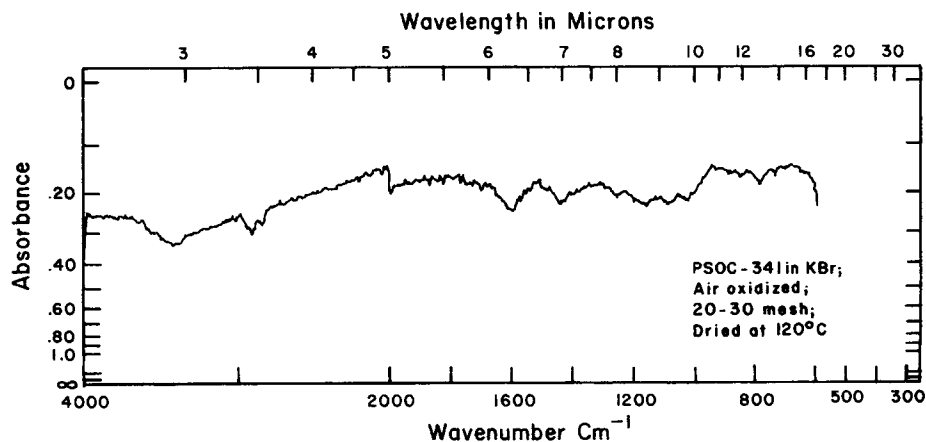


Fig. 2. Infrared spectrum of an air-oxidized PSOC-207 coal sample

PSOC-207 was 1.37% (whole coal), this coal was oxidized prior to its treatment with air.

Equilibrium Swelling Studies

Equilibrium swelling studies provided the final values of the equilibrium volume fraction of coal in a solvent-swelled system, v_2 , at a specified swelling temperature. The degree of swelling, $Q = 1/v_2$, is an indicator of both solvent/coal thermodynamic interactions and of the physiochemical structures of coal. Results can be used to quantify favorable thermodynamic interactions with a solvent for liquefaction purposes.^{4, 22, 23}

Experimental data were obtained which show the effects of various pretreatments on the solvent vapor swelling of coals. Equilibrium swelling of these samples was performed at $60 \pm 0.5^\circ\text{C}$ for 51 days, and these data are shown in Figure 3. The shape of the curve in Figure 3 is similar to that of unextracted coals swelled by pyridine,¹³ although the magnitude of the degree of swelling in the pyridine extracted coals over the carbon content range of 69.94–82.48% C (dmmf) is somewhat lower than for the unextracted coals, ranging from $Q = 2.2$ – 2.5 for the pyridine-extracted coal samples as compared to $Q = 2.5$ – 2.8 for the untreated coal samples.

Table IV compares the data from the equilibrium swelling with pyridine at $35.0 \pm 1.0^\circ\text{C}$ for 32 days and at $60.0 \pm 1.0^\circ\text{C}$ for 16 days of PSOC-207 samples which: (i) had not been pretreated; (ii) had been previously extracted with pyridine; (iii) had been oxidized with air at 60 – 80°C ; and (iv) had been oxygen-methylated via the Liotta technique. It must be noted that the oxygen-methylation used here leaves a residue of R_4N^+ in the coal which may affect the swelling behavior.²⁴ The swelling behavior of oxidized coal has been discussed by Larsen et al.²⁵ as well.

The values of the degree of swelling are virtually identical at $Q = 1.85$ at 35°C and $Q = 2.90$ at 60°C for coal samples of 20–30 and 80–100 mesh, which had not been pretested, and for the sample which had been previously

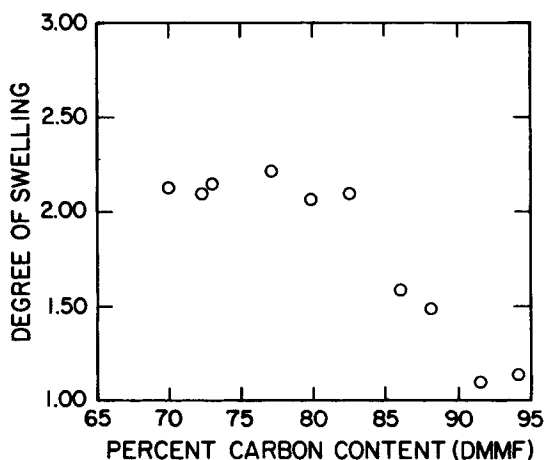


Fig. 3. Equilibrium pyridine degree of swelling of 20–30 mesh, pyridine-extracted coal particles at 60°C , as a function of carbon content in coal (% dmmf).

TABLE IV
Equilibrium Pyridine Degree of Swelling of PSOC-207 Coal Samples (with 79.82% C, dmmf)

Sample conditions	Degree of swelling at 35°C	Degree of swelling at 60°C
O-methylated, 60-100 mesh	2.05	2.95
Pyridine-extracted, 20-30 mesh	1.75	2.28
Untreated, 80-100 mesh	1.85	2.92
Oxidized, 20-30 mesh	1.84	2.90
Untreated, 20-30 mesh	1.85	2.89

oxidized. The sample of PSOC-207 which had been O-methylated showed more swelling, $Q = 2.05$ at 35°C, than the other samples. At 35°C, the pyridine extracted sample of PSOC-207 swelled only slightly less, $Q = 1.75$, than the other samples, while at 60°C, the degree of swelling was only $Q = 2.28$ for the pyridine-extracted sample compared to $Q = 2.9$ for the other samples.

These results indicate that the O-methylation technique leaves the hydrogen bonds in coal and leads to a less crosslinked system.

CONCLUSIONS

In summary, air oxidation does not seem to affect significantly the cross-linked structure of the organic phase of bituminous coals, at least as indicated by pyridine equilibrium swelling experiments at 35°C. However, O-methylation using the Liotta technique¹⁶ clears macromolecular chains leading to a significantly less crosslinked network.

This work was supported by Grant No. DE-FG22-78ET13379 from the Department of Energy. Technical assistance by Gavin W. Sinclair is acknowledged.

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Received August 30, 1986

Accepted November 18, 1986