

The Macromolecular Structure of Coal- Its Relationship to Diffusion and Reaction Processes in Coals

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INTRODUCTION

Recently, a considerable amount of attention has been directed at understanding how the macromolecular structure of coal influences its reaction behavior. The fact that coal must have a macromolecular structure has been recognized for some time, and has been embodied in many of the "classic" models of coal structure (e.g. refs. 1-5). The recognition that coals will behave accordingly naturally accompanied the development of these models. Van Krevelen² and Kreulen⁶ recognized the colloidal nature of coals and used this to explain many important features of their behavior. Wolfs et al.⁷ demonstrated that that certain polymeric substances were good analogs for coal, with respect to pyrolysis behavior. This work remains the cornerstone for many of the sophisticated models of coal pyrolysis behavior today. The development of models of fluidity has long been based on "depolymerization" as a key step (e.g. ref.8). And of course extraction of soluble material from coal has been understood for many years as the segregation of small soluble components from an insoluble matrix which can also be broken down to some extent by thermal decomposition.⁹

What has changed in recent years is mainly the level of understanding of the macromolecular structure of coal, and the number of tools (mostly borrowed from the polymer field) used to study that structure. The review by Green et al.¹⁰ has summarized much of the historical development of the coal macromolecular concept, as it exists today, and discusses many of the tools that have been applied in studying the problem.

The present paper is concerned mainly with some rather specific aspects of the problem of characterization of the macromolecular structure of coals, and their relationship to key reaction processes and physical properties. The main characterization technique used throughout this work is solvent swelling¹¹, as has been used extensively in recent years to characterize the extent of crosslinking in coals¹²⁻¹⁶. This classic technique was originally developed for examination of extents of crosslinking in polymers. The simplest relationship that embodies the essence of the technique is the Flory-Rehner equation, a relationship between the molecular weight between crosslinks in a polymer (M) and the extent to which the polymer is volumetrically swollen by a particular solvent (Q):

$$M = - \left[\frac{\rho_c M_s}{\rho_s} \right] \left[\frac{(1/Q)^{1/3}}{\ln [1-(1/Q)] + (1/Q) + \chi(1/Q)^2} \right]$$

where ρ_c is the density of the original coal, ρ_s is the density of the solvent, M_s is the molecular weight of the solvent and χ is the solvent-network interaction parameter. The measurement of χ is difficult, as is its estimation for specifically interacting solvents such as pyridine. Values range between 0.3 and 0.6 for typical pairs of solvents and coals. It has been suggested that the Flory-Rehner equation does not hold particularly well for coals, which are highly crosslinked rigid networks^{12,13}. Its use here is only illustrative, and more sophisticated approaches have been developed^{17,18}; unfortunately these other approaches require more information about the structure of the coal- namely, the molecular weight of repeat units within the coal structure. Since such information is not readily available at present, this will tend to restrict somewhat the use of these more sophisticated approaches. For the purposes of modeling transport and reaction processes in coals, detailed information about the structure will not always be necessary, and progress can be made without having the exact form of the structure-swelling relationship available. It is in this light that the

present results are presented.

The present paper considers two entirely different aspects of the relationship between macromolecular structure and reactivity and transport in coals. The first aspect concerns the reactions of crosslinking in coals during thermal treatment. This topic has been previously explored using the solvent swelling methodology^{15,16}. Here the work is extended to consider how the colloidal structure of coal is affected by moisture removal, and by further heating. The second aspect concerns the diffusive transport of solvent species in coals, and the activation energies for such processes.

EXPERIMENTAL

The analyses of the coals examined in this study are provided in Table 1. Except where otherwise noted, the coals were ground and sieved to the size range 53-88 μ m. Special care was given to the lignites to avoid any more drying than necessary while processing. The first four samples in Table 1 were judged to have dried to only a limited extent since mining, and all were crushed in-house from large lumps. To prevent drying, these four samples were stored at 100% relative humidity conditions, at room temperature, by suspending the samples above a large reservoir of clean water, in a sealed container. It is of course difficult in practice to maintain truly 100% relative humidity conditions in such a manner, particularly if the chamber must be occasionally opened for sample removal. There was consequently a small difference in measured moisture contents between bed-moist samples (which are effectively immersed storage samples) and those used in this study. The difficulty in characterizing the initial moisture contents of immersed samples was what prompted us to use this slightly different storage method. Related sample storage and characterization information concerning these lignites can be found elsewhere¹⁹.

Thermal treatments of the samples were always performed under inert gas (high purity helium or nitrogen), to avoid any possible role of oxidation in the results. The thermal treatments were performed in either standard tube furnaces, in which the samples were normally heated at low heating rates (a few tens to hundreds of degrees per minute) or in a wire mesh type of apparatus, in which small amounts of sample are contained in the folds of a stainless steel wire grid that is heated at rates of order 1000K/sec.

Solvent swelling measurements were performed largely as described in other studies²⁰. In the present case, however, the measurements were performed in small tubes of a few millimeters inner diameter and less than 5 cm in length. This technique permitted such measurements to be made with modest quantities of sample, provided that the sample and solvent is frequently stirred during the first phases of the swelling process. This technique gives reproducibility comparable to that for the standard technique with large tubes. A major reason for the difference between the standard solvent swelling techniques and those employed here stems from a concern about measuring accurately rates of swelling. In the second part of this paper, results will be given for activation energies of diffusion processes in coals, which were determined from timed swelling experiments. In the cases in which rate data were of interest, the swelling experiments were performed in thermostatted baths. The small diameter of the tubes and the frequent mixing of the contents with a small stirrer assured good heat transfer between the environment and the sample. In order to determine the height of the column of coal at any particular time (and thus the volumetric swelling ratio), the samples were "quenched" by immersion in an ice bath, and were quickly centrifuged in a high speed centrifuge, with cooling. The centrifugation takes only about ten minutes, during which time, because they are cooled, the samples swell negligibly.

RESULTS AND DISCUSSION

THE CROSSLINKING BEHAVIOR OF COALS DURING DRYING AND PYROLYSIS

Some aspects of this problem have been discussed previously, both in connection with the drying behavior of lignites¹⁹ and the pyrolysis behavior of various ranks of coal^{15,16}. This work has been extended in order to understand more fully how the macromolecular structure is altered during these processes.

At the outset, it is important to note that all ranks of coal have a colloidal structure, that will shrink and swell in response to imbibation of a solvent. The most common "solvent" is water, in that it is naturally present in all ranks of coal at the time of mining. The shrinkage and swelling behavior of lignites and brown coals in response to moisture loss and gain, respectively, has been quantitatively studied^{19,21}. In these earlier studies, it was noted that the extent of shrinkage was closely related to the amount of moisture lost from the lignite-- to a crude approximation, the extent of shrinkage was calculable assuming the the water lost from the coal had a specific volume of 1 cc/g. This is why measurements of BET surface area (or any of the other usual measurements of porosity) often reveal so little micro- and transitional porosity in lignites-- the porosity essentially collapses as the samples are being dried for examination by the usual porosity determination methods.

More recently, we have extended the examination of drying phenomena to include a much wider range of ranks. Figure 1 shows the volumetric shrinkage of coals ranging from lignite up to bituminous in rank, and surprisingly, a very good linear correlation exists between the volumetric shrinkage and moisture content throughout the entire range. The actual correlation is:

$$\% \text{Shrinkage} = 0.94(\% \text{Moisture Loss}) - 0.6$$

Thus it is apparent that colloidal swelling behavior is observed with water as a "solvent" even in ranks up to bituminous. This means that this entire range of ranks is subject to the same qualitative kinds of uncertainty in porosity characterizations as are lignites. To be sure, the effects are not nearly as large in bituminous coals, but there is no question that porosity does collapse upon drying.

It has been shown that the shrinkage that accompanies drying of lignites is to some extent irreversible. Typically, only about 80% of the shrinkage is recoverable¹⁹. The question is, what determines the extent of irreversibility of shrinkage? There are apparently some processes that occur, presumably on a molecular level, that prevent full reswelling of the coal, once it is rewet. This raises a general question of how coals crosslink during thermal treatments of any kind. We have explored some aspects of this problem by performing solvent swelling measurements on thermally treated coals. The results on one set which was heated slowly in a tube furnace is shown in Table 2. Several features may be noted in Table 2. First, coals that are still wet generally do not swell to as great an extent in pyridine as do coals that are dried at ordinary conditions. This is easily understood in terms of the network having already swollen to a significant extent in water. The fact that pyridine is able to swell it as much as it does is evidence of its stronger interaction with the lignites, relative to water with the lignites. Tetrahydrofuran (THF), on the other hand, is only a marginally better solvent for these lignites than water itself, as indicated by the modest swelling of wet coals in this solvent. There appears to be no constant ratio of swelling in pyridine to swelling in THF, nor is there a constant ratio of swelling in THF compared to that in water; this makes the point that even in fairly similar coals of identical rank, such as in this set of North Dakota lignites, the individual interactions of solvent and coal are rather important in determining swelling behavior.

The swelling ratio of a wet coal in pyridine is related to the swelling ratios of room temperature dried coals in pyridine. If the pyridine swelling ratio of a wet sample is multiplied by the ratio of (water) wet to dry volume of the lignite, the actual swelling ratio of the dry sample in pyridine may be estimated, i.e. there is no evidence of co-operative swelling effects involving pyridine and water.

The samples that are heated directly to 373K from a wet state obviously crosslink to a much lesser degree than do the samples that were first dried, and then heated. This is evidence that there are crosslinking processes that must occur at temperatures at least as low as 373K, and in the absence of oxygen from the atmosphere. Further, the processes are apparently strongly promoted by the absence of moisture during heating. The carboxyl contents of the lignites have been measured directly by barium exchange after reaction under these conditions, and in no case was a reduction greater than 10% seen in increasing the drying temperature from 373K to 473K. Together, this information suggests that the decarboxylation reactions that have been postulated to determine crosslinking in high temperature processes¹⁵ (and which has received support from modeling work²²), may be supplemented by another process that is promoted by the absence of water during the initial phases of the heating process. For comparison, high heating rate pyrolysis

behavior is shown in Figure 2. The illustrated behavior is fairly typical of all of the lignites, whether dried or undried, except as noted below. The experiment in this case consisted of heating a wet lignite at a rate of roughly 1000K/sec to a peak temperature, shown as the abscissa value, and then immediately cooling at a rate of about 300K/sec. It can be seen that the extent of crosslinking remains much lower at much higher temperatures in these rapid heating experiments. There is, however, still a slight tendency to crosslink at temperatures below about 625K. Above about 650K, all the lignites show a tendency to depolymerize, shown as an increase in solvent swelling tendency, and coinciding with the onset of the tar formation process. A similar observation has recently been independently reported²³. The swelling ratio decreases rapidly beyond about 700K, as the crosslinking reactions occur rapidly in this temperature range. It was in this temperature range that the decarboxylation reactions were thought to dominate. The directly determined decrease in carboxyl content did, in the one case studied, exactly equal the amount of CO₂ formed in the temperature range up to 900K. The mechanism of the decarboxylation, and more importantly, how it participates in the crosslinking process remains unknown. Again, the absence or presence of water had no effect on these higher temperature mechanisms, except in one sample. This may not be surprising in view of the fact that the water should have evaporated by the time these high temperatures are attained. However, earlier pyrolysis results for the Beulah lignite did show an effect of predrying even at high heating rates¹⁵.

In addition to the effects of thermal treatment noted above, 373K drying was also noted to considerably decrease the rate of diffusion into coals, compared to the rate of diffusion into room temperature air-dried samples. The rate of swelling of even a low moisture bituminous coal, such as Powhatan was decreased by a factor of two by 373K drying (i.e. standard ASTM conditions). The ultimate swelling ratio was however unaffected by the drying. This suggests that physical crosslinking of some kind is promoted by the drying procedure, but may be reversed if the solvent is strong enough. This reversible crosslinking is also noted in the lignite samples, and is distinct from the irreversible crosslinking that occurs above 373K, or in some cases, even at 373K.

ACTIVATION ENERGIES FOR DIFFUSION

The above discussion of the effects of crosslinking has pointed up how crosslinking may affect the diffusion process in coals. As part of an effort to characterize better the diffusion of solvents and large molecules through the bulk of the coal (as opposed to through pores), we have made measurements of diffusion rates of various solvents by tracking solvent swelling as a function of time. The process of diffusion in the bulk of a crosslinked macromolecular material is generally an activated process, meaning that the diffusion coefficient varies according to: $D=D_0\exp(-E/RT)$. Very good recent studies of the diffusion process, under conditions similar to those of interest here have shown the process to actually be of the "Case II" type; i.e. relaxation controlled^{14,18}. There is not space here to go into the details of the process.

The process of diffusion has been studied at temperatures from 298K up to 318K, with pyridine, tetrahydrofuran and water as diffusants. Various ranks of coal, and heat treated coals have been examined. Selected results are given in Table 3. Several features are important to note. First, there is a large difference in activation energies between the different ranks of coal, and between different solvents. Heat treatment seems to have the expected effect - not only does the diffusion become slower at all temperatures, but the activation energy increases, presumably as the structure becomes more rigid, and the vibrational conformations necessary to allow for solvent molecules to pass become ever less probable. The value of activation energy is felt to depend more upon the size of the penetrant species, and less upon the specific interactions of the coal and the solvent molecule. Note that the activation energy for THF is considerably lower than that for pyridine, however the rate of swelling in pyridine is more than an order of magnitude higher than in THF at room temperature, and the extent of swelling is also much higher in pyridine.

CONCLUSIONS

This paper has, in a very brief manner, touched upon two different aspects of how the macromolecular structure of coal relates to important physical and chemical phenomena. The studies continue as of this writing, on both of the above topics. The utility of straightforward techniques of characterization of macromolecular structures, such as solvent swelling, cannot be underestimated as important contributors to the more complete understanding of complex processes and phenomena in coals.

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Table 1-Coals Studied

sSAMPLE	C	H	N	S	ASH	O	Moisture
Beulah lignite ^a	65.6	3.6	1.1	0.8	11.0	17.9	26.0
Freedom lignite ^a	63.5	3.8	0.9	1.4	6.1	24.3	27.9
Glenn Harold lignite ^a	61.1	4.4	0.8	0.4	7.4	25.9	28.9
Gascoyne lignite ^a	60.9	4.2	0.6	1.4	8.2	24.7	30.7
Beulah lignite ^b	65.9	4.4	1.0	0.8	9.7	18.2	32.2
Texas lignite (PSOC1036) ^c	61.5	4.7	1.4	1.3	12.5	18.5	31.8
Belle Ayr Subbit.	69.3	4.4	1.0	0.5	10.3	14.5	30.3
Big Brown Subbit.(PSOC785) ^c	62.8	4.6	1.1	1.1	12.6	17.8	27.8
Montana Subbit.(PSOC837) ^c	57.8	4.3	0.8	0.7	11.9	24.6	17.0
Pittsburgh No.8 (HVBIt.) ^b	74.2	4.1	1.4	2.3	13.2	4.8	1.7
Bruceton HVBit. ^d	80.4	5.3	1.6	1.0	4.6	6.7	1.7
Powhatan HVBit.	72.3	5.1	1.5	3.6	9.7	7.8	1.1

*All results on a dry weight percent basis, except moisture which is ASTM value on an as-received, bed moist basis.

*Oxygen by difference.

a- Grand Forks Energy Research Center lignite sample bank.

b- Argonne National Laboratory Premium Coal Samples.

c- Pennsylvania State University Coal Sample Bank.

d- U.S. Bureau of Mines Standard Sample.

Table 2- Effect of Drying and Thermal Treatments on Solvent Swelling of Lignites

Condition	Beulah	Freedom	Gascoyne	Glenn Harold
Wet	1.48/1.08	1.62/1.00	1.33/1.07	1.60/1.18
0% R.H.,300K,24hrs	2.20/-	2.01/-	1.90/-	2.10/-
0%R.H.,300K, 30days	2.22/1.28	2.06/1.33	2.10/1.32	2.14/1.32
Wet, dried at 373K,1hr	2.34/-	2.50/-	2.05/-	2.47/-
Dry, then 373K,1hr	2.0/1.34	1.70/1.35	1.68/1.38	1.81/1.33
" , then 473K, 1hr	1.43/1.25	1.66/1.28	1.54/1.29	1.75/1.22
" , then 573K, 1 hr	1.22/1.16	1.45/1.15	1.50/1.06	1.50/1.15
" , then 573K, 2 hr	1.14/1.10	1.30/1.12	1.42/1.06	1.45/1.13

*All values are volumetric swelling ratios, given as:

(pyridine volumetric swelling ratio/tetrahydrofuran volumetric swelling ratio).

*0% R.H. refers to drying over concentrated sulfuric acid, a 0% relative humidity environment. Samples marked "dry" were initially dried in this manner at room temperature, prior to thermal treatment.

Table 3- Activation Energies for Diffusion in Coals

<u>Coal</u>	<u>Treatment</u>	<u>Activation Energy (kcal/mol)</u>
Beulah (Argonne Sample)	Air dried, 1day	18.0
" "	Air dried, 3days	17.9
" "	Vacuum dried, 298K	19.4
" "	Vacuum dried, 373K	21.5
Montana Subbit.	Air dried	18.1
Pitts. No. 8	Vacuum dried, 373K	12.6
Bruceton HVBit.	Vacuum dried, 373K	13.
Bruceton HVBit.	Vacuum dried, 373K	8.8 (THF)

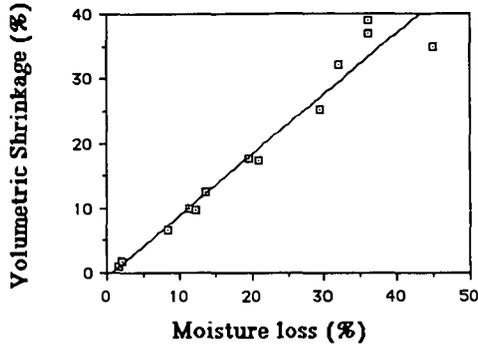


Figure 1. Volumetric Shrinkage of coals during room temperature drying.

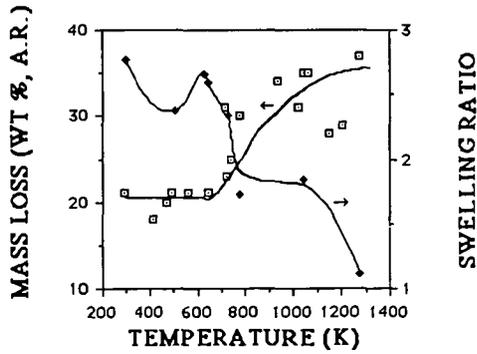


Figure 2. Mass loss and pyridine solvent swelling behavior of "wet" Freedom lignite, rapidly pyrolyzed under non-isothermal conditions to indicated peak temperatures.