SOLVENT SWELLING AS A MEASURE OF THE BREAKDOWN OF THE MACROMOLECULAR STRUCTURE OF COAL

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Introduction

The characterization of coal's macromolecular structure by the use of solvent swelling techniques has been the subject of renewed interest in recent years (see, for example, a review of the topic[1]). The systematic examination of the swellability of coals in various solvents has its roots in the work of Dryden[2,3], although the first attempts at quantitative analysis of coals macromolecular network structure by this method were made some time later[4]. It is only relatively recently that the technique has begun to find widespread application in the study of processing of coals[5-11].

Generally, solvent swelling is used as an index of the extent of crosslinking of the coal's structure; the more highly crosslinked the structure, the less swellable it is in a good solvent. Solvent swellability of quenched char residues has normally been used to obtain information regarding the conditions that favor so-called "retrograde reactions", which take the thermally degrading coal particle on a path to a char or coke product. This is marked by the loss of swellability in the char (i.e. the retrograde reactions crosslink the structure). The swelling data cannot normally be used to obtain quantitative information concerning the network structure of the chars for the same reason that such information cannot be obtained on coals themselves-- there is a lack of a proven, quantitatively reliable model of coal swelling. This is particularly the case when the swelling data are obtained using strong, specifically interacting solvents (e.g. pyridine). Nevertheless, the change in swellability of the char has been viewed as a valuable qualitative indication of crosslinking.

This presentation explores the application of the solvent swelling technique, using specifically reacting solvents, to the problem of tracking changes in pyrolysis char residues. It does so in the context of a number of new conclusions concerning the nature of the swelling process in specifically interacting solvents. It also explores the use of these techniques in a number of new ways.

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Experimental

The general experimental approach involved examining changes in the macromolecular structure of various coals induced by pyrolysis of the coals in an inert gas environment. The effects of different pyrolysis conditions on the macromolecular structure was revealed by solvent swelling of the quenched chars. The pyrolyses were always performed in helium or nitrogen, so as to preclude oxygen contact while the samples were hot. The reactor system has been described in detail elsewhere[5,6]. No attempt was made in this case to prevent oxygen contact with the samples once they were cooled, but the time of exposure of any sample to air, after it was cooled, was generally only as long as necessary for preparation of the sample, as outlined below.

The solvent swelling procedures employed in this study have been described in detail elsewhere[12]. The technique involves a minor adaptation of earlier established methods for studying swelling by immersion in liquid solvents[13,14]. It involves the measurement of the change of height of a column of coal held in a constant diameter glass tube, after addition of liquid solvent to the tube. In our case, the tubes are 3 mm inner diameter and 5 cm in length. The measurements could thus be made on modest amounts of sample (50 to 100 mg). The height of the column of dry coal is determined after centrifugation for 3 min at 7500 rpm in a 30 cm horizontal rotor. Solvent was then added, with vigorous stirring for at least the first one half hour of contact. The height of the column of coal was then remeasured at several times, following centrifugation each time, to establish that equilibrium had been achieved. Normally at room temperature, using good solvents, equilibrium could be achieved within a day or two. The volumetric swelling ratio (Q) is merely the ratio of the height of the swollen column of coal to the height of the dry column of coal. Again, it is generally true that all else being equal, the more highly crosslinked a sample, the lower value of Q it would give.

The elemental analyses of the coals studied in this work are provided in Table 1. Since the method of preparation of samples (particularly how they are dried) has a significant effect on the subsequent swelling behavior of the samples, preparation procedures will be discussed below, together with results. Generally, the coals were sieved prior to use. For most pyrolysis experiments, particles in the size range from 45-100 μm were utilized.

Results and Discussion

Effect of Drying Conditions on Swelling Behavior

It is often difficult to compare solvent swelling values obtained under nominally identical conditions in two different laboratories. This is a consequence of the very significant effect that drying conditions may have upon the swelling behavior. As is well known, coal has a colloidal gel structure that collapses upon removal of moisture. The collapse is significant in the case of lignites and brown coals[15,16], but is quite easily discernible in coals up to high volatile bituminous in rank[17]. The collapse is greater with increasing severity of drying conditions, and is in part irreversible even if drying is carried out at room temperature[16].

An illustration of the problem that this might cause in terms of comparison of

solvent swelling results between laboratories is given in Table 2. The results are all for North Dakota lignites. If coals are dried under such mild conditions that they retain significant moisture, they will give low values of the swelling ratio in a good solvent (e.g. pyridine) because their structure is initially somewhat swollen by water. It can be seen from the first three rows of Table 2 that increasing the time of drying at 298K increases the swelling ratio in pyridine. This probably does not reflect any decrease in crosslink density, but merely the difference in the base value against which swollen coal volume is compared. Drying an initially wet sample at 373 K results in a higher swelling ratio in all but one case (results given in the fourth row). The weight loss in the 373K drying process (carried out in inert gas) is generally only 1 to 2% greater than that obtained by drying at room temperature at zero relative humidity for 30 days. Thus we do not believe that the generally significant differences in swelling ratios reflected between the third and fourth rows reflects the effect of merely removing this small additional volume of moisture (if this were all that happened, the coal would shrink by only 1 to 2% in "dry" volume, and the swelling ratios would not be significantly affected). We believe that drying at elevated temperatures in addition allows some reorganization of the dried coal structure into a more compact form, which then can exhibit an even larger extent of swelling upon exposure to solvent. This is not, however, the only effect that elevated temperature drying may have.

The significant effect that the drying history may have on swelling behavior is seen in comparing the fourth and fifth rows of Table 2. Predrying the samples at room temperature before 373K heating, reduces swellability relative to preparation either by extended room, temperature drying, or direct heating to 373K, in all cases. The last three rows of the table illustrate the continuation of the trend towards lower swellability as the severity of drying conditions is increased by raising temperature. This trend likely illustrates the increase in crosslinking as the temperature of drying is increased. This will be further discussed below.

These observations show the difficulty that will be inherent in any attempts at quantitatively applying the solvent swelling method in an effort to determine the macromolecular structure of "raw" coals. Great thought will have to be given to the preparation of samples, particularly in the case of low rank coals.

The Effect of Pyrolysis Conditions on Solvent Swelling

It has been earlier firmly established that the decrease in swellability of low rank coals during the early stages of pyrolysis correlates well with the evolution of CO_2 as a product of pyrolysis[5,8,10,11], though preliminary results from this laboratory cast doubt upon the conclusion that the correlation between decrease in swellability and carboxyl group loss is linear. This loss of swellability has been interpreted as indicating an increase in crosslinking in the structure of the coal, and this in turn is thought to explain the inability of lower rank coals (lignites and subbituminous coals) to soften during pyrolysis under "ordinary" low and moderate heating rate conditions. Recently, it has been suggested that the process of crosslinking (swellability loss) also correlates with evolution of the water product of pyrolysis[18], in support of an earlier similar conclusion[8].

The general pyrolysis behaviors of low rank coals and high rank coals are illustrated in Fig. 1. The figure illustrates how the observable weight loss correlates with changes in the swellability of the char residue. The heating rate for pyrolysis was about 8 K/min, and the

samples were allowed to cool immediately upon reaching the indicated maximum temperature. Solvent swelling measurements were performed only on cooled chars. The coals were not completely dried prior to pyrolysis, so the weight losses at low temperatures may be viewed as indicative of the moisture content of the samples at the beginning of pyrolysis (some drying, during sieving, occurred in both the low rank coals). These data are in qualitative agreement with results from Solomon et al.[9]. What is important to note from this figure is that periods of apparently rapid crosslinking do not necessarily coincide with periods of rapid mass loss. Crosslinking apparently occurs quite readily at temperatures as low as 423K (150°C).

These data support the conclusion of the previous section, that swellability is lost even at temperatures normally regarded as only causing drying. We have observed by direct measurements changes in the carboxyl group contents of the four lignites shown in Table 2 (using barium cation exchange[19]). The loss of carboxyl content between 373K and 473K is between 5 and 15% of the total. The implication of these results is that if lignites are to be processed to give high yields of low molecular weight products, even very mild preheating might be detrimental.

In contrast to the behavior of the low rank coals, the macromolecular structure of the high volatile bituminous coal apparently changes very little until temperatures in excess of 700K are achieved. This is, however, not entirely accurate. The choice of pyridine as solvent means that most of the internal hydrogen bonding or ordinary acid-base interactions in the coal should be disrupted and that these should not act as virtual crosslinks. The extent to which pyridine is effective at disrupting other non-covalent crosslinks (due to aromatic-aromatic interactions of as yet unknown nature) remains somewhat unclear. Use of a less effective electron donor solvent, such as tetrahydrofuran (THF), would be expected to induce less swelling, because it will not be able to disrupt even the well known donor-acceptor interactions[20,21]. The data of Fig. 2 show that the use of the weaker solvent is quite revealing, in this case.

Whereas in higher rank bituminous coals the swelling of the chars in THF follow the trends shown by swelling measurements in pyridine, in the Pittsburgh No. 8 sample a distinctly different event is revealed by THF than is observable in pyridine. In the neighborhood of 550K, the THF swellability increases abruptly, while the pyridine swellability is constant. Bearing in mind that the measurements are performed on quenched chars, the change revealed by the THF must be an irreversible change in structure, which does not coincide with any particular weight loss events, and to which the pyridine is insensitive. Presumably the event is not observable in pyridine because the swelling in pyridine itself induces the change. This conclusion is supported by the observations by Cody et al.[22] that suggest that pyridine causes irreversible changes in the structure of the Pittsburgh No.8 sample, during the first cycle of swelling. It is also consistent with the observation of Hsieh and Duda[23] that weak solvents may swell coal structure without fully relaxing it.

In the present case, the abrupt change in THF swellability at 550K must reflect an irreversible thermal relaxation of the coal's structure, possibly associated with a phase transition of some kind. The most likely possibility appears to be a glass transition. Lucht et al.[24] have studied glass transitions in coals of similar rank and determined that the it occurs at roughly 600K, at a very similar heating rate of 10K/min., in the absence of solvents. In a rubbery state above the glass transition temperature, the structure of the coal can elastically deform in response to any residual stresses remaining as a result of coalification under geological pressure. Brenner has suggested that the glass transition temperature of pyridine swollen coals is most likely below room temperature[25], and therefore rubbery behavior and full

relaxation of the structure can be expected even at room temperature.

It is noteworthy that the Upper Freeport coal shows an increase in swellability in both pyridine and THF at around the same temperature range of 550 - 600K (see Fig. 2). This coal shows high fluidity and softening in a comparable range of temperatures as the Pittsburgh No. 8 coal[26]. It appears that the softening of both the coals (reported to occur at around 640K, for a heating rate of 3K/min) cannot be governed by whatever processes are initially responsible for the increased swellability. (If the softening phenomenon were governed by an activated process, then increasing the heating rate to a comparable 8K/min would induce fluidity at an even higher temperature). The mass loss from the Upper Freeport coal at 600K, under these heating conditions, is 1%, showing that only moisture loss has occurred, when the large increase in swellability occurs. Thus the conclusion is that as in the case of the Pittsburgh No. 8 coal, the increase in swellability in the Upper Freeport coal probably reflects a glass transition, that allows the structure to relax. Pyridine is not as good a solvent for the Upper Freeport coal as it is for the Pittsburgh No. 8 coal, and is unable to penetrate the structure without thermal relaxation of that structure.

The similarity of the softening temperatures of the Pittsburgh No. 8 and Upper Freeport coals, and the absence of any accompanying decrease in crosslinking in the relevant temperature range lends strong support to the view that the initial softening event, in these coals, is mainly a physical phenomenon[27,28]. This is not thought to be true in the case of the highest rank coal of Fig. 2, the Pocahontas low volatile bituminous.

Figure 3 shows the weight loss and swelling behavior of the Pocahontas coal at two different heating rates, 8K/min and 1800K/min. All phenomena are offset by a bit more than 200K, from the low to the high heating rate case. There is a unique relationship between swelling and mass loss, irrespective of heating rate, as noted in Fig. 4. This coal also softens at a considerably higher temperature (about 730K[26]) than the lower rank bituminous coals of Fig.2. All indications are that in this case, the change in swellability with temperature is an activated process, that depends upon actual pyrolytic bond breakage processes. The higher softening temperature for this coal is expected to be a consequence of the need to initiate true bond breakage as a prerequisite to softening. Fig. 5 shows the relationship between the swelling ratio in pyridine and the temperature range of fluidity in this coal.

Summary

The implications of the above results are that several quite different processes can be responsible for major changes in the nature of the macromolecular structure of coal during pyrolysis. In low rank coals, the process of crosslinking begins almost immediately with the drying of the coal. The changes are very significant, even if they involve very small amounts of pyrolytic mass loss. In higher rank (bituminous) coals, the drying process is not thought to be significant (unless it involves oxidation[9]). There may be a thermally induced glass transition phenomenon (at around 600K) before true softening occurs. This may not be accompanied by significant mass loss, but might be of great importance in terms of increased penetrability of the coal structure. Diffusion phenomena are generally faster in coals that have been partially relaxed by a good solvent, e.g. water[17], and the same would be expected to hold for thermal relaxation.

Initial softening during pyrolysis in most high and medium volatile bituminous coals appears, from other studies, to be a mainly physical phenomenon, and this seems to be

supported by the observations made here. Softening does not appear to coincide with any particular crosslink breakage events. In a low volatile bituminous coal, however, there is evidence that the softening process is indeed tied to bond breakage. This could help to explain why rank appears to play some role in the modeling of pyrolysis phenomena[26].

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Table 1-Coals Studied

SAMPLE	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
Pittsburgh No.8 (HVBit.)[b]	75.5	4.8	1.5	2.2	9.3	6.7	1.7
Upper Freeport (MVBit.)[b]	74.2	4.1	1.4	2.3	13.2	4.8	1.1
Pocahontas (LVBit.)b	86.7	4.2.	1.3	0.7	4.8	2.3	0.7

•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.

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

Condition	Beulah	Freedom	Gascoyne	Glenn Harold
Wet	1.48	1.62	1.33	1.60
0% R.H.,298K,24hrs	2.20	2.01	1.90	2.10
0%R.H.,298K, 30days	2.22	2.06	2.10	2.14
Wet, dried at 373K,1hr	2.34	2.50	2.05	2.47
Dry,then 373K,1hr	2.00	1.70	1.68	1.81
", then 473K, 1hr	1.43	1.66	1.54	1.75
", then 573K, 1 hr	1.22	1.45	1.50	1.50
", then 573K, 2 hr	1.14	1.30	1.42	1.45

•"Dry" refers to samples stored at 0% relative humidity for 30 days , before heating.

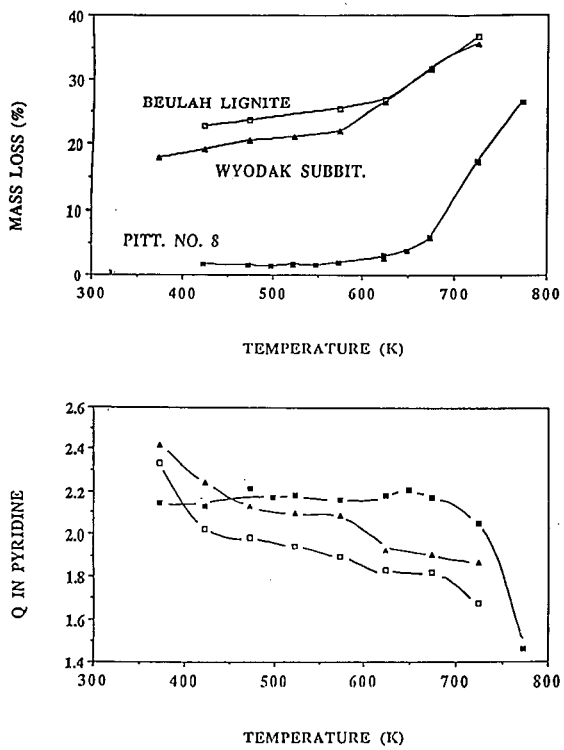

Figure 1. Mass loss and changes in pyridine swelling ratio upon pyrolysis at 8K/min.

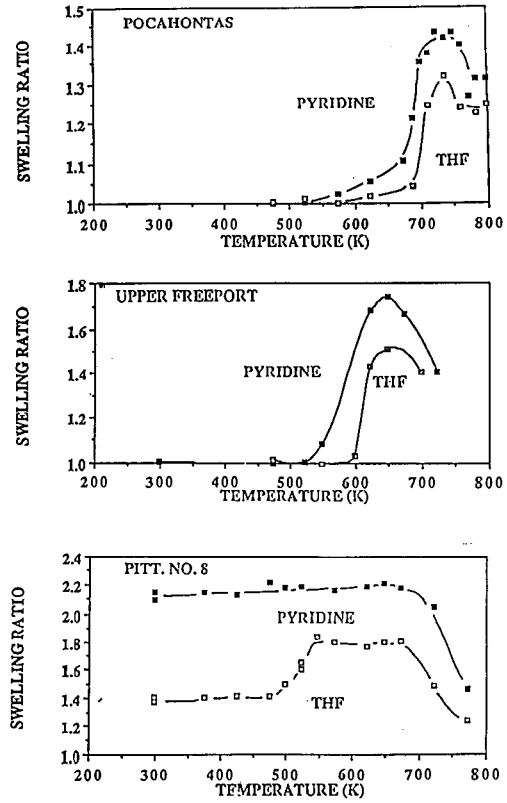

Figure 2. Swelling ratio changes with pyrolysis temperature for pyridine and tetrahydrofuran.

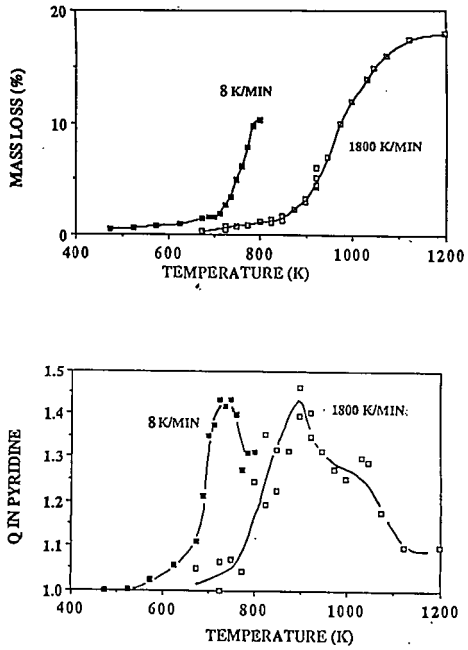

Figure 3. Mass loss and changes in pyridine swelling ratio of Pocahontas coal at two heating rates.

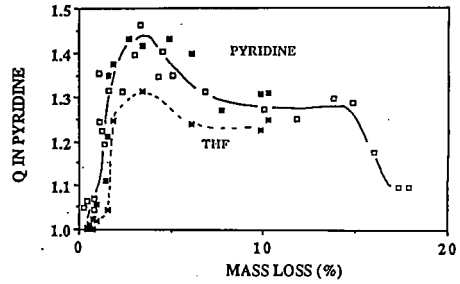

Figure 4. Variation of pyridine swelling ratio with mass loss for Pocahontas coal. Solid points-8K/min, open points 1800K/min. THF swelling ratio for 8K/min only.

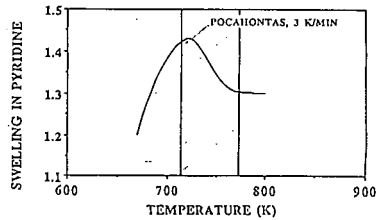

Figure 5. Calculated variation in swelling ratio at 3K/min, and the limits of temperature over which the coal is in a softened state (shaded area).