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Physical transitions in Pittsburgh No. 8 coal as observed by differential scanning calorimetry and solvent swelling

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Table I. Major Identified Peaks in Figure 3

no.	MW	identified compd
1	106	<i>p</i> -xylene
2	106	<i>o</i> -xylene
3	120	C ₃ -benzene
4	120	C ₃ -benzene
5	94	phenol
6	108	<i>o</i> -cresol
7	108	<i>m</i> - + <i>p</i> -cresol
8	122	dimethylphenol
9	122	ethylphenol
10	128	naphthalene
11	136	C ₃ -phenol
12	110	catechol
13	124	methylcatechol
14	142	methylnaphthalene
15	124	methylcatechol

from methyl carbons (0-25 ppm) increases. Integration of the ¹³C NMR spectra shown in Figure 2 gave aromaticity (*f_a*) values of 0.66 (A in Figure 2), 0.67 (B), 0.68 (C), 0.75 (D), 0.77 (E), and 0.78 (F).

Figure 3 shows some of the Py-GC-MS chromatograms, the major peaks in which are identified in Table I. Phenol, alkylphenols, alkylbenzenes, and catechols as well as alkanes and alkenes are formed from flash pyrolysis of the THF-extracted raw coal. Relative to this sample, there is apparent change in Py-GC-MS profile of the residue from TPL at 300 °C. The appearance of a major peak for naphthalene and disappearance of catechol differentiate the latter from the former. This is especially interesting, since the NMR spectra of these two samples and the corresponding yields of THF-soluble (7-9%) are similar to each other. From these results, it is clear that the reaction at 300 °C did cause structural change. The naphthalene peak in Figure 3B is due mainly to the use of tetralin solvent, because the naphthalene peak was found to be very small with other solvent or without solvent. Since the residue has been extracted by THF for over 24 h and dried in vacuum at 100 °C for 6 h, the naphthalene/tetralin remaining in the residue must be either chemically bound to other species or physically entrapped in solvent-inaccessible micropores. Also, it appeared that Py-GC-MS can detect some subtle differences in coal structure which are not easily detectable by NMR. Combination of the NMR and Py-GC-MS data suggests that the original coal contains significant quantities of catechol-like structures, which disappear in the liquefaction residues above 300 °C, and carboxyl groups, which almost disappear after 350 °C, and also phenolic structures which diminish in concentration with increasing temperature. These results point to the progressive loss of oxygen functional groups and aliphatic species from the macromolecular network of the subbituminous coal during its depolymerization in tetralin under TPL conditions. The higher conversions in TPL runs suggest that the removal of carboxylic and catechol groups from the coal during the programmed heat-up (≤350 °C) in tetralin may have contributed to minimizing the retrogressive cross-linking at higher temperatures.

Low-rank coals are characterized by low aromaticities and high oxygen functionalities. Probably the retrogressive reactions occurring during liquefaction of low-rank coals under conventional high-severity conditions are, at least in part, associated with the reactions of their oxygen functional groups, such as cross-linking caused by decarboxylation¹⁰⁻¹² and the condensation of polyhydroxy

structures.¹³ It seems possible from comparative examination of the coal conversion data that the TPL conditions may facilitate the reduction of cross-linking reactions of the thermally sensitive groups such as oxygen-functional groups at low temperatures in the H donor.

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Physical Transitions in Pittsburgh No. 8 Coal As Observed by Differential Scanning Calorimetry and Solvent Swelling

Sir: There has been much speculation concerning the existence of a glass transition in coal, based upon the observations obtained from various physical techniques,¹⁻³ including differential scanning calorimetry (DSC).⁴⁻⁸ In an earlier study,³ we noted that Pittsburgh No. 8 coal exhibits a unique tetrahydrofuran (THF) swelling behavior with pretreatment temperature. The THF swellability increases abruptly when the coal is preheated (in inert gas) to around 200-270 °C. This irreversible change in the coal's structure did not coincide with any significant weight loss, nor was there a change in the covalent bonding structure, as indicated by a constant swellability in pyridine. We report here more detailed evidence on the nature of the transition. Two analytical techniques are employed: DSC and solvent swelling.

Aliquots of Pittsburgh No. 8 coal (-20 mesh) from the Argonne National Laboratory Premium Coal Sample Program were used as received. A DuPont 2910 DSC system was employed and the sample cell was operated under a nitrogen flow rate of 90 mL/min in order to keep the cell free of oxygen during measurements. Samples (ca.

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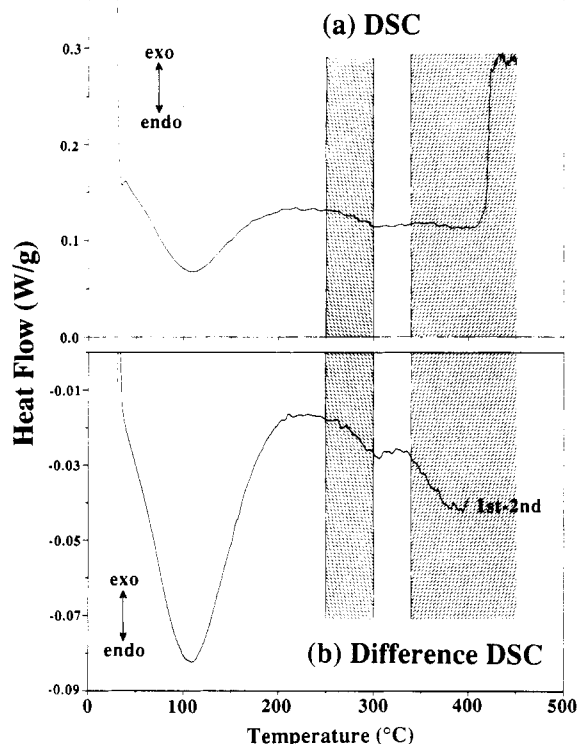


Figure 1. DSC and difference DSC thermograms for Pittsburgh No. 8 coal, obtained at 8 °C/min.

25 mg) were initially isothermal for 5 min at 30 °C and then heated at 8 °C/min to 400 °C. Detailed procedures for solvent swelling have been described elsewhere.^{9,10} Samples (22–28 mg) for the solvent swelling experiments were prepared in the DSC at a heating rate of 8 °C/min.

Figure 1 shows the DSC thermogram obtained from Pittsburgh No. 8 coal sample as well as a difference DSC thermogram, discussed below. In Figure 1a, the endothermic peak around 100 °C is due to water evaporation whereas the sharp rise in DSC response in the exothermic direction around 420 °C is caused by the mass loss accompanying pyrolytic decomposition. Around 250–300 °C, evidence of a physical transition is observed. This transition is difficult to discern on the original DSC spectrum (Figure 1a) except as a subtle increase in apparent heat capacity, as is typical for glass transition. The subtraction of a first scan thermogram from a second scan thermogram on the same sample (as a reference) allows very subtle irreversible changes to be examined (see Figure 1b). If no irreversible changes were involved, the subtracted spectrum would be flat, at a value of zero. In Pittsburgh No. 8 coal, the (first–second) difference thermogram shows significant irreversible changes in 250–300 °C range. There is also a larger irreversible heat effect in the temperature range above 340 °C.

The heat effect observed above 340 °C cannot be clearly interpreted, since even if there were a physical transition, it merges with the onset of pyrolytic breakdown of the coal structure. The curve of mass loss with pretreatment temperature (Figure 2c) shows a significant increase in slope at 350 °C and the curve of pyridine swellability with pretreatment temperature (Figure 2b) shows a slight increase at 350 °C. Pyridine is a strong solvent and can be expected to disrupt most, if not all, noncovalent interactions in the network structure. The fact that pyridine

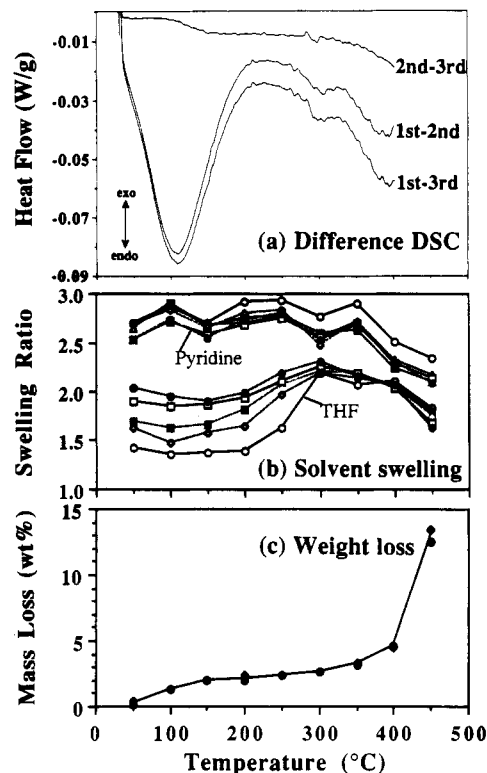


Figure 2. Difference DSC thermograms as well as profiles of solvent swelling ratio and weight loss obtained at 8 °C/min for Pittsburgh No. 8 high-volatile bituminous coal (–20 mesh). The results shown in (b) were obtained on samples used to generate the data in (c) that were quenched at the indicated temperature and subsequently subjected to solvent swelling analysis (swelling time: ○, 5 h; ◇, 1 day; ■, 2 days; △, 4 days; □, 5 days; ●, 6 days).

swellability increases suggests removal of covalent crosslinks. In addition, it was observed that above 340 °C the coal begins to show the first signs of softening and agglomeration. The small increase in mass loss upon softening at around 350 °C could initially involve evaporative escape of small “guest” molecules, physically trapped until softening (loosening) of the structure, and known to be released prior to the main pyrolysis events.^{11,12} This transition does, however, unquestionably merge into a truly pyrolytic regime above 400 °C.

The lower temperature transition (250–300 °C) involves a physical relaxation process. The network structure of the as-received coal is not in a relaxed equilibrium state. Passing through the thermally induced transition helps achieving a thermodynamically preferred state. The absence of a glass transition peak at the same range of temperatures in the second heating cycle shows that it is not a true glass transition. Thus earlier DSC examinations of the glass transition phenomena must be viewed in this light; if no second heating examination of the transition was performed, the observed transition may well be a relaxation rather than a true glass transition.

The interpretation of the lower temperature transition revealed by DSC is aided greatly by a knowledge of the solvent swelling behavior of the coal as a function of temperature. First the focus is turned to 5-h swelling data (see Figure 2b). It is noted that there is an irreversible increase in THF swellability achieved in heating the coal to the

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range of temperatures 200–300 °C with the most dramatic effect seen at 250–300 °C. This is not accompanied by any significant weight loss. Nor is this change accompanied by any increase in pyridine swellability (in fact there is, if anything, a decrease in pyridine swellability). Thus, there is little evidence to support covalent bond breakage in this temperature regime. The weaker THF is not as effective as pyridine in removing all noncovalent crosslinks, as is evident, in that it does not swell the coal as much (note the molecular sizes are quite similar for pyridine and THF, so it is not a steric effect that is responsible). For Pittsburgh No. 8 coal, heating the coal to the range of temperatures 200–300 °C thus apparently results in an irreversible removal of some noncovalent cross-links, but not much change in covalent cross-links. With the pyridine-dissociable, THF-nondissociable cross-links thermally disrupted (irreversibly), the two solvents approach each other more closely in swelling behavior.

The above effect is presumably related to the observation made by Larsen and co-workers¹³ that the first cycle of a swelling in a good solvent such as pyridine normally involves an irreversible expansion of the network structure, due to structural relaxation. Our results are also consistent with the results of Sakurovs,¹⁴ which showed pyridine to be as effective as heating with respect to creating "mobility" (at least in bituminous coals up to 86% C content).

The temporal behavior of swelling in the two solvents also clearly indicates that a transition of some kind has taken place in the 200–300 °C pretreatment temperature range. The pyridine readily swells the coal to near equilibrium values in 5 h. We have reported that the activation energies for swelling and the temporal swelling behavior both indicate that relaxation processes generally control the time for swelling at room temperature.⁹ The fact that the pyridine swelling ratio decreases with time is felt to be an artifact, due to extraction of the coal by the swelling solvent; the solvent is quite heavily extract-laden when it

is periodically removed and replaced with fresh solvents.

The THF swelling behavior, below the 200–300 °C transition, is quite sluggish in comparison to the pyridine swelling behavior. The relative increase in rate of swelling in THF after 300 °C preheating coincides with the transition seen in the DSC.

The thermally induced relaxation during the first cycle of heating is thus taken to reflect a physical transition of the raw coal. One can imagine that the thermally induced transition might involve the disruption of aromatic-stacking interactions formed under geological pressure. Alternatively, it could be hydrogen-bonding interactions that are involved.⁷ Since there is no comparable pressure applied when the sample is cooled in a DSC, the same interactions would not be restored.

Finally, we could not confirm the result reported on other coals by Yürüm et al.⁶ that such physical transition temperatures are independent of heating rate. We observed a significant shift with heating rate in the transition temperature, in our work with the Pittsburgh No. 8 coal. The transitions were centered around 281, 292, 302, and 310 °C at 8, 30, 60, and 80 °C/min, respectively. The transition temperature at each heating rate is constant regardless of sample amount (3–30 mg), sample size (–20, 100 mesh), or the sealing condition of aluminum pans containing samples. Thus, we are confident that our results are not subject to artifacts due to heat- or mass-transfer limitations.

Further work is under way with a wide variety of coals under a variety of different heating conditions and different solvents. These results will be reported shortly.

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