

New Applications of Differential Scanning Calorimetry and Solvent Swelling for Studies of Coal Structure

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Introduction

There have been several reports of structural changes in coal at low temperature (<400°C) indicated by increased mobility of the coal [1] or by crosslinking (associated with the evolution of water and carbon dioxide [2,3]). Since no significant weight loss is normally observed in this low temperature range except moisture and small amount of CO₂, glass transition and/or physical melting have been suspected as responsible for the increased mobility observed in bituminous coals. Some bituminous coals, e.g., Pittsburgh No. 8 coal, are known to contain a considerable amount of thermally extractable mobile phase at temperatures below 400°C [4,5] and thus the role of physical structural changes in releasing this material cannot be ruled out. Recent results on pretreatment of coal for liquefaction by steam, solvent swelling, and preheating have proved that elevated temperatures below those needed for thermal decomposition help enhance the efficacy of the pretreatments, perhaps by promoting greater accessibility of the structure in coal.

Many analytical tools, e.g., GC, MS, TG/FTIR, TG/MS, which focus on gas phase volatiles, are useful for studies involving thermally induced changes in some functional groups of coal whereas FTIR, NMR, Gieseler Plastometry, Dilatometry, and TMA (Thermomechanical Analysis) focus on the study of the char residue with the first two again directed mainly at obtaining functional group information and the last three at obtaining physical structural data. Differential Scanning Calorimetry (DSC) has been used less for the latter purpose, but as will be seen, can be a suitable tool for studying the structural changes involved at low temperatures.

DSC has earlier been used for measurements of the heats of pyrolysis and hydropyrolysis [6-10], as well as for the determination of glass transition temperatures of coal [11,12]. Because of its sensitive nature, DSC is an ideal tool for investigating the thermal changes associated with softening as well as glass transition and thus for identifying the temperatures of significant structural changes. Therefore, DSC has been heavily applied in polymer science and many commercial devices are available. The application of DSC to coal has been hampered by problems caused by weight loss that accompanies most heat effects and also by tar condensation in the DSC cell. Although hermetic sealing of the coal sample is possible, the pressure build-up inside the cell can easily exceed the maximum allowable pressure of the normal sealed capsules (usually 10 atm). This is apparent, considering that at 200°C the vapor pressure of water is already 15.3 atm. Thus it is difficult to measure well-defined heat effects, partly for this reason. Moreover, water evolution can continue up to 300°C, depending on heating rate and sample, and thus overshadow the heat effects due to structural changes below 300°C.

In this paper, we applied DSC in a way such that minute heat effects could be identified by subtracting consecutive DSC scans. Several groups have already applied this type of methodology in helping identify problems with heat capacity measurement [13,14], but did not draw any conclusions concerning the role of structural changes in heat effects. In combination with solvent swelling, which has been also extensively used for characterizing the density of crosslinking in the macromolecular structure of coal, DSC appears to be a powerful tool for evaluating the extent of

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thermally induced structural changes.

Experimental

Aliquots of several coal samples, obtained from the Argonne National Laboratory - Premium Coal Sample Program, were analyzed by DSC and solvent swelling techniques. These samples included Pittsburgh No. 8 (-20 mesh), Illinois No. 6 (-20 mesh), Blind Canyon (-20 mesh), Upper Freeport (-100 mesh), and Pocahontas No. 3 (-20 mesh) coals. They were used as-received. Detailed petrographic, chemical, and physical analysis data on these coals can be found elsewhere [15].

Differential Scanning Calorimetry

A DuPont 2910 DSC system with a liquid nitrogen cooling accessory (LNCA-II) was employed in this study. The sample cell was operated under a nitrogen flow rate of 90 ml/min in order to keep the cell free of oxygen during measurement. Aluminum sample pans were generally used in an unsealed mode. This was done by just pushing down the top sample pan cover gently onto the bottom pan containing the coal. Samples were heated from 30°C at 8 °C/min or 30 °C/min. Typically 22-28 mg of sample was used in an experiment. Cooling of the cell between consecutive heating scans normally involved air convection, but several runs were cooled at a controlled rate of 20 °C/min with liquid nitrogen as a cooling medium.

Solvent Swelling

The details of this technique were described earlier [16]. In short, coal samples were placed in constant diameter tubes (3 mm i.d., ca. 5 cm high) and centrifuged at 7500 rpm for 3 min in a roughly 30 cm horizontal rotor (SAVANT HSC-10K high speed centrifuge), after which the initial height of the sample was measured by a caliper. The choice of 7500 rpm was rather arbitrary and selected only to be as high as could be comfortably tolerated by the equipment. Solvent was then added and stirred until a visual check showed the total submergence of coal in solvent. The stirring was repeated frequently (normally 3 times) during the first 30 min following solvent addition. At the desired measurement times, the sample tubes were centrifuged again (7500 rpm for 3 min), the swollen coal height measured, and the solvent replaced with the clean solvent. This assured that the concentration of extractable was not so high as to interfere with the measurement.

Samples (22-28 mg) for solvent swelling were prepared in the DSC at a heating rate of 8 °C/min under a nitrogen flowrate of 90 ml/min. After reaching the desired temperature, each sample was cooled immediately by contacting the bottom of the sample pan with ice or cold water.

Swelling solvents employed (tetrahydrofuran(THF), pyridine) were all reagent grade and were used without any further purification.

Results and Discussion

DSC is a very sensitive technique for determining the difference in heat flow between a sample and a reference material, both heated (or cooled) at a controlled rate. The main purpose in employing DSC here was to determine whether DSC can be used more effectively than it has been, as a tool for examining structural changes in coal, particularly those that occur before pyrolysis. One of the phenomena we were concerned with was the so-called glass transition. The glass transition temperature, T_g , is defined as the temperature at which amorphous polymers transform in structure from the glassy state to liquid/rubbery state. In coal, this transformation has been suggested to appear just before thermal degradation begins [11,12]. Due to the heterogeneity and complexity of constituents involved in coal, a clear-cut determination of T_g in coal has been difficult, as might be

expected.

Figures 1-3 show blank background-subtracted DSC thermograms for three high volatile bituminous coals, i.e., Pittsburgh No. 8, Illinois No. 6, and Blind Canyon coals. Samples were predried inside the DSC up to 150°C just before the first run in Figures 1(a)-3(a). The drying occurred at the same experimental conditions as the following DSC runs. Intermediate oxygen exposure was avoided. Figures 1 through 3 also show difference DSC thermograms for three consecutive scans of the same sample. The general trend for three consecutive scans of a sample in Figures 1(a)-3(a) is that the earlier scans show a slightly more endothermic response above 250°C than do later scans. The sharp initial peaks at ca. 40°C on initial heating do not represent any physically significant heat effects. The general downward direction of the thermograms upon heating represent the effect of heat capacity of coal. The subtraction of a first or second thermogram from a second or third one (as a reference) allows very subtle irreversible changes to be examined. If no irreversible changes were involved, the subtracted spectra would be flat, at a value of zero. In Pittsburgh No. 8 coal, the (1st-3rd) difference thermogram shows significant change in 200-300°C range, while the (2nd-3rd) shows much less change. The reasons for this are discussed below.

Illinois No. 6 and Blind Canyon coals also demonstrate the same behaviors, described above. The peak around 110-120°C in the third scan of Illinois No. 6 coal was due to inadvertent water vapor readsorption from ambient air, which occurred while cooling the sample for the 3rd run in the DSC. This water readsorption peak (up to 150-200°C) helps define the temperature range at which moisture would have influenced the DSC thermogram. The distinct downward peak around 190°C in Blind Canyon coal (Figure 3) was also found to be related to incomplete drying; drying was performed inside the DSC cell at a heating rate of 8 °C/min up to 150°C, which was apparently not sufficient to completely drive off all moisture.

The observations in Figure 1 appear to confirm an earlier suggestion [17] that Pittsburgh No. 8 coal has an irreversible heat effect associated with glass transition around 275°C, while Illinois No. 6 and Blind Canyon coals have a T_g value higher than Pittsburgh No. 8 coal. The transition in Illinois No. 6 coal appears to be centered at around 300°C and that in Blind Canyon coal at 275-300°C. The irreversible heat effect was endothermic (downward in the figures) which is an indication of structural relaxation in the first scan. It must be noted that the transition is irreversible, otherwise it would not be visible in the subtractive technique. We earlier saw an irreversible change in THF swellability at this temperature [17]. This in no way suggests that the glass transition itself is irreversible, but rather that the relaxations that occur with glass transition, are irreversible (vide infra). All three coals exhibited initial agglomeration behavior from ca. 340°C, as observed visually from the coal sample after cooling. Thus the softening of coals, leading to gross agglomeration, has not yet commenced at the observed temperature range of the structural transition that we hypothesize to be a glass transition.

Another noteworthy fact observed in Figures 1(a)-3(a) is the reproducibility of small peaks in the thermograms starting from around 150°C, indicating that more or less reversible transitions occur along with the irreversible processes (reversible because the peaks always reappear). These thermograms were reproducible in several independent runs. There may be a wealth of information in the small reproducible peaks, which probably reflect different melting processes.

It is well known that higher heating rates will increase the "intensity" of heat flow at any temperature while decreasing the sensitivity. This is obvious considering that at higher heating rates, thermograms of kinetic events will be broadened in terms of temperature scale although the shape will be comparable in time scale regardless of heating rates. In other words, if peaks are overlapped in a narrow temperature range, slower heating rate run will enhance the separation of peaks. When peaks exhibit low intensity, higher heating rate runs will sharpen them and make them more obvious. The effect of heating rate on DSC thermograms is illustrated in Figures 4, 5 and considerably

simplified thermograms, compared to Figures 1 and 2, can be noted.

Samples for Figures 4 and 5 were not dried and the initial endothermic peaks observed at 60-240°C range were caused by water desorption. In Pittsburgh No. 8 coal, the irreversible transition in the 270-310°C range is more apparent than that observed at lower heating rate of 8 °C/min (Figure 1) and the temperature region of transition is increased by ca. 15°C at high heating rate of 30 °C/min, suggesting that the irreversible transition is an activated process. This would be expected for a glass transition. In Illinois No. 6 coal containing 7.97% moisture, the initial water endothermic peak is the dominant feature of the thermogram as could be expected from the high moisture content of this coal. Subtle changes in the subsequent runs for Illinois No. 6 coal are still visible in the difference DSC thermograms, as shown in Figure 5(b) for which temperature range 250-350°C was chosen for clarity. The downward (endothermic) trend above 300°C is most distinct in the (1st-2nd) and (1st-3rd) runs whereas the (2nd-3rd) run exhibits a smaller transition. Again, this shows the irreversible change occurs mainly during first heating.

The interpretation of the transitions revealed by in the DSC is aided greatly by a knowledge of the solvent swelling behavior of the coal as a function of temperature. Figure 6 shows a comparison of pyridine and THF swelling behavior of the Pittsburgh No. 8 coal obtained on the samples after DSC analysis (a single scan only). It is noted that there is an irreversible increase in THF swellability achieved in heating the coal to the range of temperatures 200-300°C. This is not accompanied by any significant weight loss. Nor is this change accompanied by any increase in pyridine swellability (in fact, a small decrease is seen, if anything). Pyridine is a stronger solvent, and can be expected to disrupt all noncovalent interactions in the coal. Pyridine reveals the extent to which the covalent network structure has been altered (or not altered) in the range of temperature cited above, since it is believed to be the most effective solvent for disrupting non-covalent interactions in the coal. The weaker THF is not as effective 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). For Pittsburgh No. 8 coal, heating the coal to the range of temperatures 200-300°C apparently results in an irreversible removal of noncovalent crosslinks, but not much change in covalent crosslinks. This observation was reported previously by us [17]. This presumably occurs because the coal structure undergoes a glass to rubber transition in this temperature range, and once the structure is more flexible, it can relax to a new equilibrium configuration which is more easily swelled by THF. This effect is presumably related to the observation made by Larsen and coworkers [18] 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. This transition is not evident in post-heating pyridine swelling of coals because the solvent alone is already effective at relaxing the structure without the need for heating. This is consistent with the results of Sakurovs [19], 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 thermally induced relaxation during the first cycle of heating is thus taken to refer the T_g of the raw coal. The fact that repeated DSC scans reveal the transition to be stronger in the first scan than in any subsequent scans confirms the irreversible nature of the process that accompanies the glass transition. Again, a glass transition itself should, of course, not be irreversible. It is the release of stored strain energy that is irreversible. One can imagine that the thermally induced transition involves the disruption of aromatic stacking interactions formed under geological pressure. Since there is no comparable pressure applied when the sample is cooled in a DSC, the same interactions will not be restored; the thermodynamics has been changed.

Interestingly, Figure 6 shows that more time is required to reach THF swelling equilibrium for heat treatment temperatures below 300°C. This indicates that the accessibility of the coal is also irreversibly altered (increased) by heat treatment above this temperature (the structure swells more

readily to final equilibrium value above 300°C). Pyridine swelling ratio slightly decreased with time presumably by weight loss due to extraction of the coal by pyridine.

Figure 7 shows changes of the swelling ratio in THF against pyrolysis temperature for Illinois No. 6 coal along with the weight loss profile (the determination of the pyridine swelling profile against pyrolysis temperature for Illinois No. 6 coal is under way). In contrast to Pittsburgh No. 8 coal, Illinois No. 6 coal exhibits a drastically different THF swelling behavior with heat treatment temperature. Higher swelling ratio was obtained in the low temperature region (<300°C). The fact that Illinois No. 6 coal can swell significantly in THF without any heat treatment reflects a much different starting structure than that of Pittsburgh No. 8 coal. This clearly demonstrates the importance of coal composition in swelling. The swelling evidence to support the DSC interpretation is thus not as clear in Illinois No. 6 coal. The relatively small increase in swellability above 250°C is all that accompanies the transition identified by DSC. The swelling dynamics also suggest a small change at 250°C. Note that the highest swelling ratio is observed in 5 hours, and the ratio decreases with time. This is again presumably associated with a sudden increase in extractability at this temperature, and the swelling decreases as mass is removed. Presumably the increase in both swellability and extractability implies greater accessibility of the structure. From 350°C, pyrolytic crosslinking is clearly dominant as illustrated in the drop of THF swelling ratio and the increase in weight loss. Several pyridine swelling studies on bituminous coals [20] noted that pyridine swelling ratio starts to fall when the pyrolytic bond breakage commences. It should be noted from Figure 7 that the weight loss in the 150-300°C range was 10.3-10.9 wt%, which is clearly higher than the moisture content 7.97 wt% of this coal. This shows either that something other than moisture is being lost, or that an arbitrary drying procedure, such as the ASTM procedure, does not give the correct picture regarding possible moisture loss. This is also suggested by Figure 5(a), which shows "drying" well above 150°C.

Figures 8 and 9 illustrate the correlation between DSC thermograms obtained at 30 °C/min and solvent swelling profiles in two other coals. For Upper Freeport medium volatile bituminous coal, the main endothermic relaxation process starts from ca. 310°C (Figure 8(a)) while THF swelling ratio starts to shoot up around the same temperature (Figure 8(b)). Note that samples for swelling ratio experiments were in this case prepared in a wire-mesh pyrolyzer at 8 °C/min under nitrogen environment [17]. On the other hand, in Pocahontas No. 3 low volatile bituminous coal, the DSC difference thermogram exhibits a rather wider endothermic profile from ca. 230°C, which coincides with dramatic changes in pyridine and THF swelling profiles.

In the case of both the Upper Freeport and Pocahontas coals, swellability increases are difficult to separate from the onset of pyrolytic bond cleavage processes, as evidenced by rapid mass loss. The data certainly suggest that significant increases in swellability precede the period of rapid mass loss, which actually always seems to coincide with swellability decrease. It is difficult to unambiguously say that the data in hand argue for a physical transition prior to the commencement of bond cleavage processes. More work is planned to address this question. In any case, the solvent swelling data do correlate reasonably with the DSC data in terms of predicting increased structural mobility.

In summary, DSC confirms what was suspected from THF solvent swelling in the high volatile bituminous coals - that there is a glass transition in the range of temperature from about 230 to 300°C. This is lower than earlier reported values [11], but it is understandable that some variation might be due to sample differences, heating rates, and the difficulty of interpreting simple DSC scans without additional confirming data such as solvent swelling.

Conclusions

- DSC and solvent swelling techniques were applied to evaluate structural changes at low

temperature (<350°C) before any major pyrolytic bond breakage occurs. The results reveal the existence of reversible structural changes together with an irreversible transition, centered around 200-300°C in three high volatile bituminous coals.

- DSC thermograms appear to correlate with THF swelling ratio profiles, with regard to the information they convey on structural relaxation.

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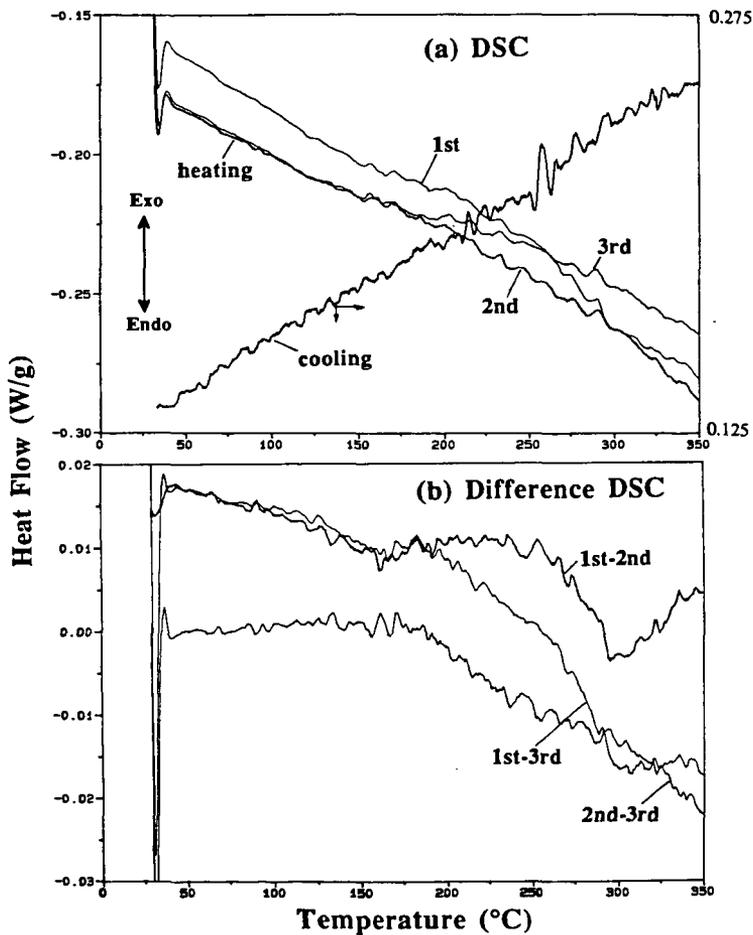


Figure 1. DSC and difference DSC thermograms for Pittsburgh No. 8 coal. After drying coal at 150°C in the DSC, DSC runs were repeated three times at 8 °C/min for the same sample. Difference thermograms in (b) were obtained by subtracting two thermograms in (a).

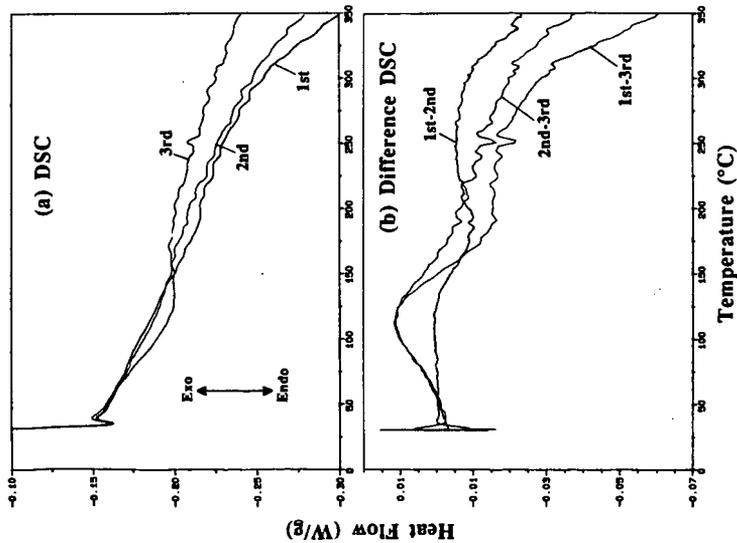


Figure 2. DSC and difference DSC thermograms for Illinois No. 6 coal. After drying coal at 150°C in the DSC, DSC runs were repeated three times at 8 °C/min for the same sample. Difference thermograms in (b) were obtained by subtracting two thermograms in (a).

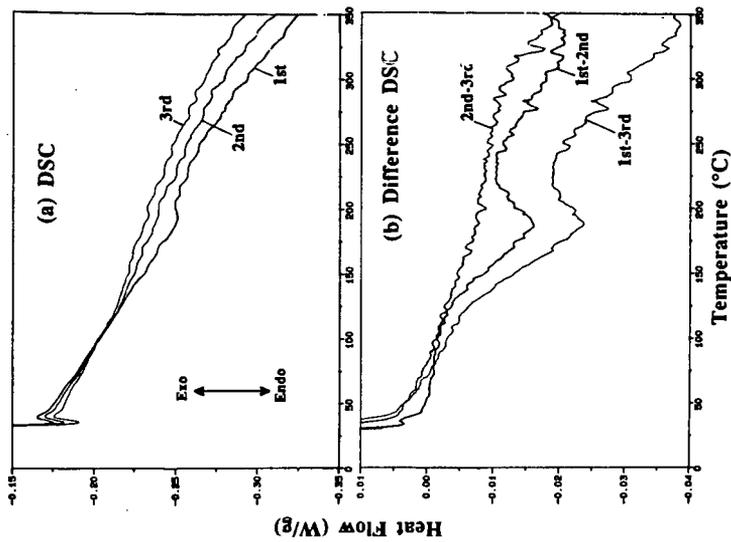


Figure 3. DSC and difference DSC thermograms for Blind Canyon coal. After drying coal at 150°C in the DSC, DSC runs were repeated three times at 8 °C/min for the same sample. Difference thermograms in (b) were obtained by subtracting two thermograms in (a).

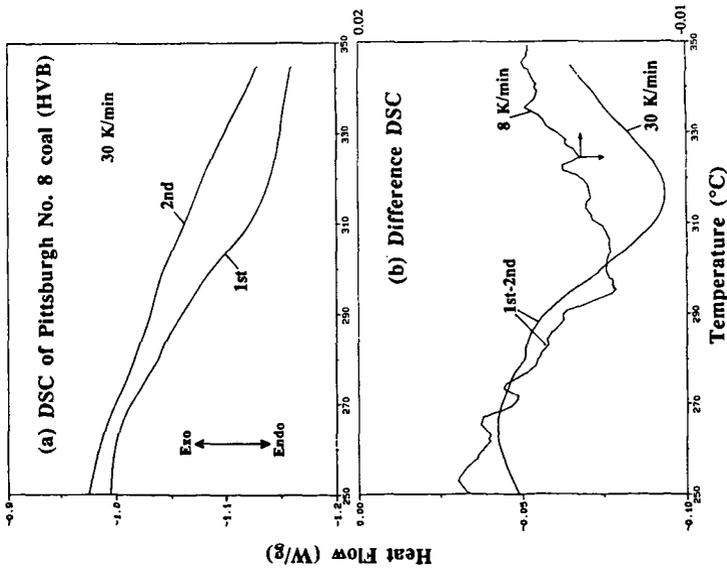


Figure 4. DSC and difference DSC thermograms for undried Pittsburgh No. 8 coal obtained at 8 °C/min and 30 °C/min.

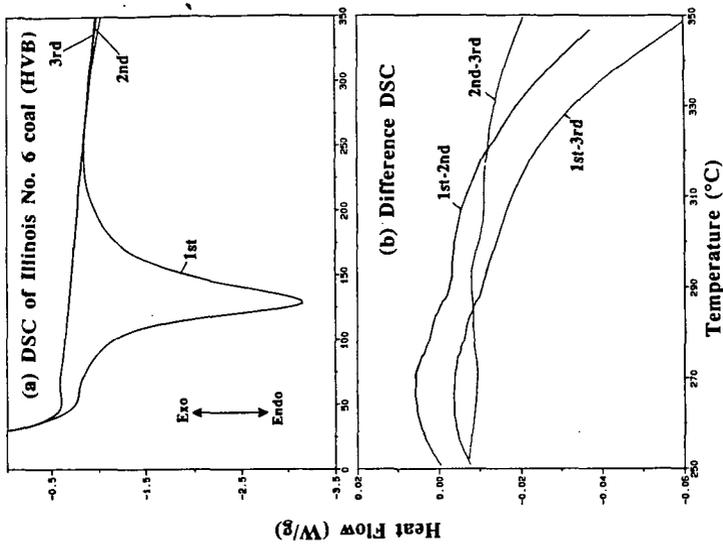


Figure 5. DSC and difference DSC thermograms for undried Illinois No. 6 coal obtained at 30 °C/min.

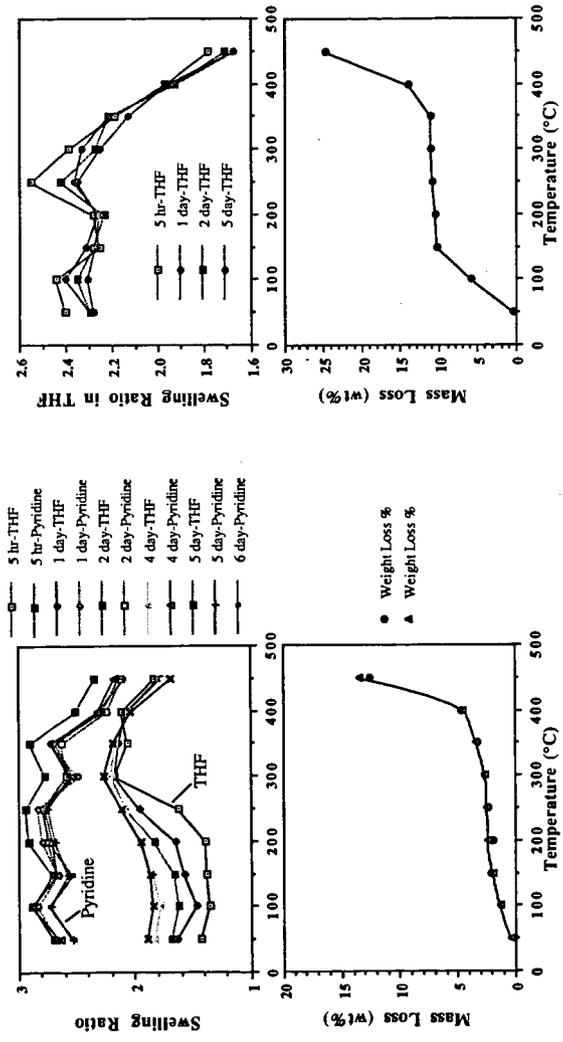


Figure 6. Changes of swelling ratio in tetrahydrofuran and pyridine as well as weight loss profile against pyrolysis temperature for Pittsburgh No. 8 coal (<20 mesh). Undried samples were placed in the DSC cell and heated at 8 °C/min under 90 ml/min nitrogen flow up to the specified temperature.

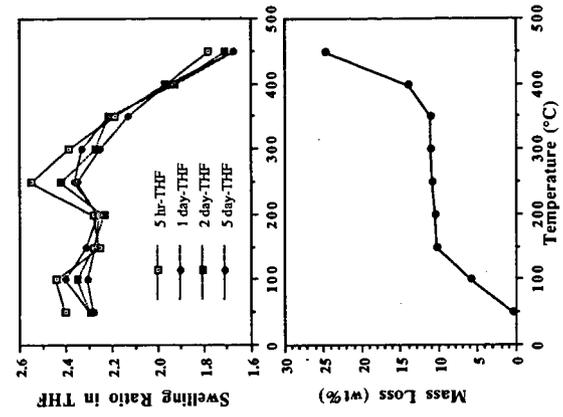


Figure 7. Changes of swelling ratio in tetrahydrofuran as well as weight loss profile against pyrolysis temperature for Illinois No. 6 coal (<20 mesh). Undried samples were placed in the DSC cell and heated at 8 °C/min under 90 ml/min nitrogen flow up to the specified temperature.

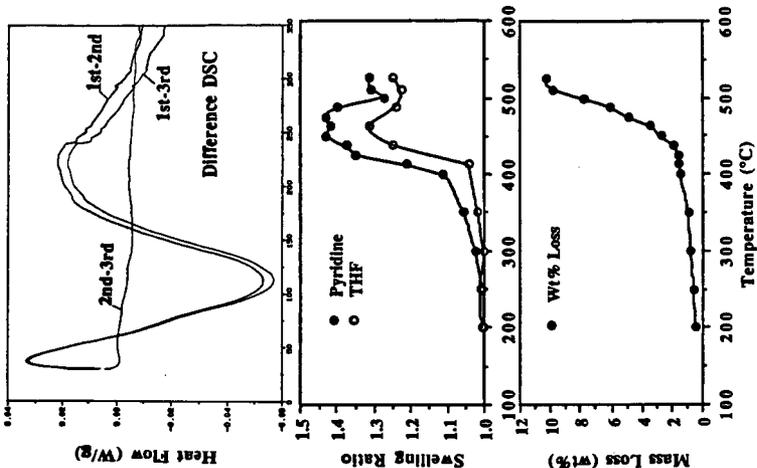


Figure 8. DSC difference thermograms as well as profiles of swelling ratio and weight loss for Upper Freeport medium volatile bituminous coal (:100 mesh). Note that DSC was performed at 30 °C/min whereas samples for swelling were obtained from the wire-mesh reactor at 8 °C/min.

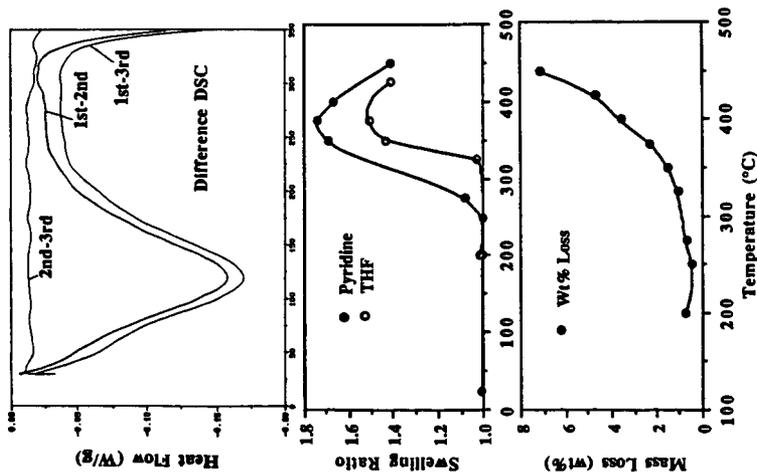


Figure 9. DSC difference thermograms as well as profiles of swelling ratio and weight loss for Pocahontas low volatile bituminous coal (:20 mesh). Note that DSC was performed at 30 °C/min whereas samples for swelling were obtained from the wire-mesh reactor at 8 °C/min.