# Prepyrolysis Structural Relaxation of Coal Studied by Differential Scanning Calorimetry and Solvent Swelling

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## SUMMARY

Differential Scanning Calorimetry (DSC) and solvent swelling technique have been applied for identifying physical transition temperatures in the macromolecular structure of coals. The transition processes seem to be associated with physical relaxation of the coal structure and are irreversible processes. In Pittsburgh No. 8 high volatile bituminous (hvb) coal, one physical transition was noted at 250–300℃ (at 8℃/min) without any significant accompanying weight loss. Coals of higher rank than high volatile bituminous, i.e., Upper Freeport medium volatile bituminous (mvb) and Pocahontas No.3 low volatile bituminous (lvb) coals, exhibit structural relaxation just before the major thermal decomposition process and a sharp increase in solvent swellability accompanies this relaxation. In the case of both the Pittsburgh No.8 and the Upper Freeport coal, structural relaxations at around 360℃ seem to coincide with release of "guest molecules."

## CONTENTS

There is increasing interest in the chemistry of coal pretreatment (or preconversion) processes that can be employed for increasing the yield of certain liquid products from (or reducing the required severity in) liquefaction processes. Moreover, it is believed nowadays that much of the important chemistry occurs very early in the liquefaction process, possibly even in a "preheating section" of a process. It is this realization that so much attention has been recently focused on "preconversion reactions." These preconversion pretreatments of coal involve heating in steam, mildly hydrogenating, solvent swelling, or temperature programming through the preheating phase. Common to all of these different strategies is an attempt to influence the chemistry of the coal in such a way that the liquefaction process will occur at lower severity, by modifying its structure through lower temperature preprocessing. The temperature that defines the lower and higher temperature regimes may be crudely taken as 350℃, since above this temperature pyrolytic processes begin to strongly manifest themselves.

Regardless of the specific nature of a coal liquefaction process, the principal goal is always to convert a material with basically insoluble crosslinked macromolecular nature into soluble molecules of low enough molecular weight such that they are either liquids themselves, or at least soluble in appropriate solvents at low temperatures. As a practical matter, heat is generally selected

as the agent for affecting bond cleavage in proposed commercial processes. This choice has the disadvantage that heat is not a selective agent, and it causes an enormous number of chemical pathways to occur simultaneously — some of these are desirable while others such as gas formation or "retrograde" reactions (to coke as a product) are highly undesirable.

In this regard, this paper is aimed to examine the macromolecular structural changes induced by heat and solvent, occurring below the temperature range of the major pyrolytic decomposition reactions. We applied DSC in such a way that small heat effects could be identified by subtracting consecutive DSC scans. In combination with solvent swelling, which has been extensively used for characterizing the density of crosslinking in the macromolecular structure of coal, DSC appears to be an effective tool for evaluating the extent of thermally induced structural changes.

## RESULTS AND DISCUSSION

Fig. 1 shows DSC responses of two high volatile bituminous coals (lower panel) and two higher rank coals (upper panel), under a nitrogen atmosphere and at a heating rate of 8℃/min. The most noticeable difference between the upper and lower panels is that Upper Freeport mvb and Pocahontas No.3 lvb coals in the upper panel exhibit distinctly endothermic peaks around 350℃ and 430℃, respectively. These peaks are similar to the "hysteresis" peak normally occurring just after the glass transition temperature in stressed polymers. The hysteresis peak is mainly caused by stress relief of the structure by heat, quite often observed in amorphous polymers such as epoxies, polycarbonate, polystyrene. These peaks are not ordinary melting endotherms because these samples do not give an analogous "fusion" peak upon cooling (not shown here).

The endothermic peaks at around 100℃ are caused by water evaporation. The sharp rises toward the exothermic direction at around 420–430℃ for Pittsburgh No.8 and Upper Freeport coals are due to a sudden expansion of sample volume, with the development of plasticity. A typical DSC thermogram for high volatile bituminous coals can be seen for Illinois No.6 coal, in which the water evaporation process (endothermic) is followed by a more or less stright DSC response curve corresponding to the heat capacity of coal, and then is followed by thermal degradation process where a peak occurs in the exothermic direction, in part due to weight loss.

The observations in Fig. 1 appear to confirm an earlier suggestion [1] that Pittsburgh No.8 hvb coal has an unusual irreversible heat effect associated with what is thought to be a physical transition around 275℃. This will be more readily apparent in Fig. 2.

While the DSC thermograms for Upper Freeport and Pocahontas No.3 coals in Fig. 1 exhibit distinct endothermic transition peaks, subtle effects in the DSC thermograms for Illinos No.6 and Pittsburgh No.8 coals can be better scutinized by subtracting consecutive DSC thermograms. The second—scanned

thermogram serves as a reference for the first thermogram of the same sample. A particular example illustrating the advantage of employing this subtraction method can be seen for the Pittsburgh No.8 coal, when comparing the lower panel of Fig. 1 and the upper panel of Fig. 2, in that the change in heat capacity around 275°C is more obvious in the difference DSC thermograms. It must be noted that the transition – most likely a physical transition – observed around 275°C is irreversible, otherwise it would not be visible in the subtractive technique. The irreversible heat effect was in an endothermic direction (downward in the figures) which is an indication of structural relaxation in the first scan.

The interpretation of the transitions revealed in the DSC is aided greatly by a knowledge of the solvent swelling behavior of the coal as a function of temperature. Fig. 2 shows a comparison of pyridine and tetrahydrofuran (THF) swelling behavior of the Pittsburgh No.8 coal obtained on the samples after DSC analysis (after only a single scan). 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. 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 pyridine 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 as pyridine does.

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 was hypothesized to occur because the coal structure undergoes a relaxation in this temperature range, and the structure achieves a new equilibrium configuration which is more easily swelled by THF. This relaxation 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 result of Sakurovs et al. [2], which showed pyridine to be as effective as heating with respect to creating "mobility" (at least in bituminous coals up to 86% C daf content).

Fig. 2 also 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).

For Upper Freeport mvb coal (see Fig. 3), the main endothermic relaxation process starts from ca. 310°C while the THF swelling ratio starts to increase around the same temperature. The apparently exothermic process caused by

thermal degradation follows the end of the endothermic peak at around 400℃. Similarly, in Pocahontas No.3 lvb coal (see Fig. 3), the DSC difference thermogram exhibits a rather sharp endothermic profile from ca. 390℃, which coincides with the onset of dramatic changes in pyridine and THF swelling profiles. Again, the endothermic peak is immediately followed by the exothermic peak due to pyrolytic bond breakage. In the temperature range above 350℃ of the Upper Freeport coal, pyridine swelling ratio decreases with temperatue as well as with time while THF swelling ratio stays same, since pyridine extracts materials and THF doesn't. This decreasing trend in pyridine swelling ratios is corresponding to the increase in weight loss, illustrating the breakage of covalent bonds.

In both the Upper Freeport and Pocahontas No.3 coals, the results in Fig. 3 reveal that significant increases in swellability precede the period of rapid pyrolytic mass loss, which actually always seems to coincide with swellability decrease. Note the low extents of mass loss up to 450℃; when fully pyrolyzed, the Upper Freeport coal typically exhibits mass losses of 25.2 wt% and the Pocahontas No.3 coal, 20.6 Wt% [3]. Swelling ratios for these two coals are virtually 1.0 at temperatures below 250℃ and starts to increase dramatically at temperatures corresponding to the structural relaxation process, as revealed in the difference DSC results. The swelling ratios increase sharply whenever there is a DSC peak or shift to the endothermic direction, as also observed in the Pittsburgh No. 8 coal. More detailed explanation has been reported elsewhere [4,5].

## CONCLUSIONS

• There are thermally induced (prepyrolysis) structural relaxations in coals that make them more easily penetrable, swellable and extractable in solvents.
• Reported "glass transitions" in the neighborhood of 270−380℃ are not true glass transitions. They are irreversible physical relaxations.
• DSC thermograms appear to correlate with THF swelling ratio profiles, with regard to the information they convey on structural relaxation.
• Heat can disrupt the macromolecualr structure of coal more effectively than can pyridine at >87%C.

## REFERENCES

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3. Solomon, P.R. et al. *Energy & Fuels* 1990, *4*, 319.
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**(a) Difference DSC** — 2nd-3rd, 1st-2nd, 1st-3rd

**(b) Solvent swelling** — Pyridine, THF

**(c) Weight loss**

Heat Flow (W/g)

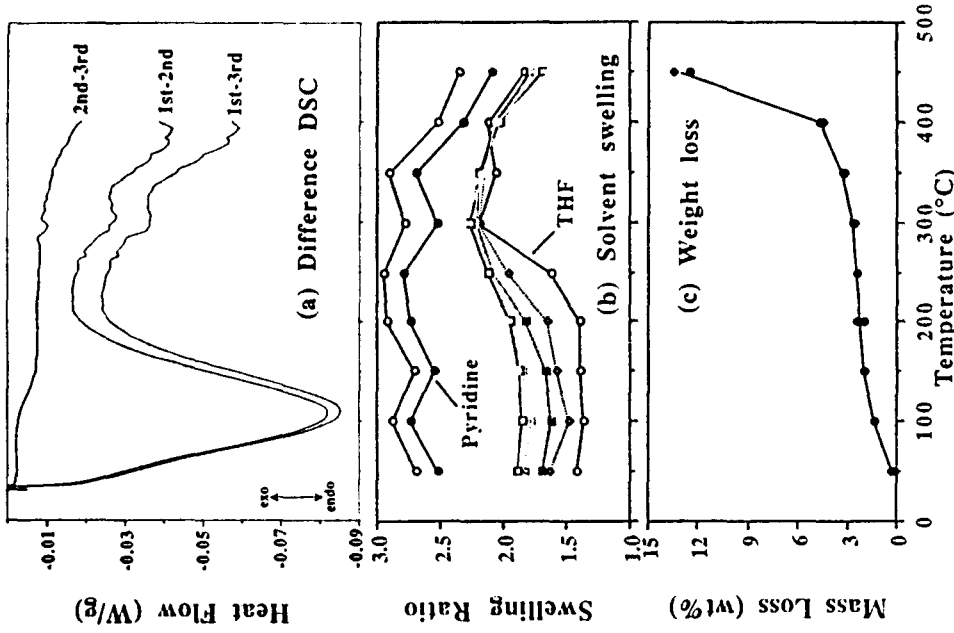Swelling Ratio

Mass Loss (wt%)

Temperature (°C)

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 (−20 mesh) coal (swelling time: ○, 5 h; ◇, 1 day; ■, 2 days; △, 4 days; □, 5 days; ●, 6 days).
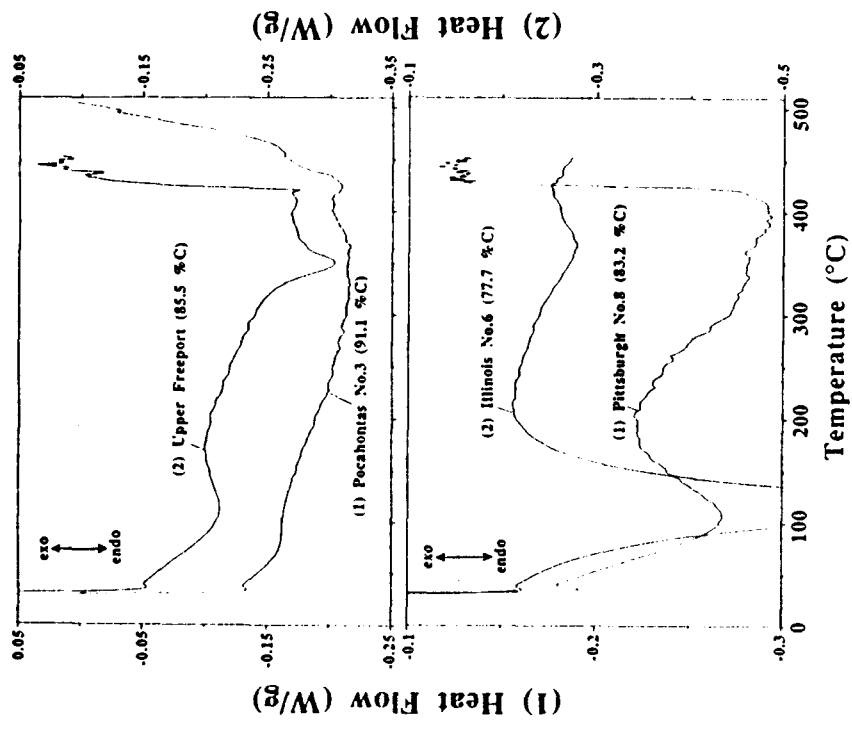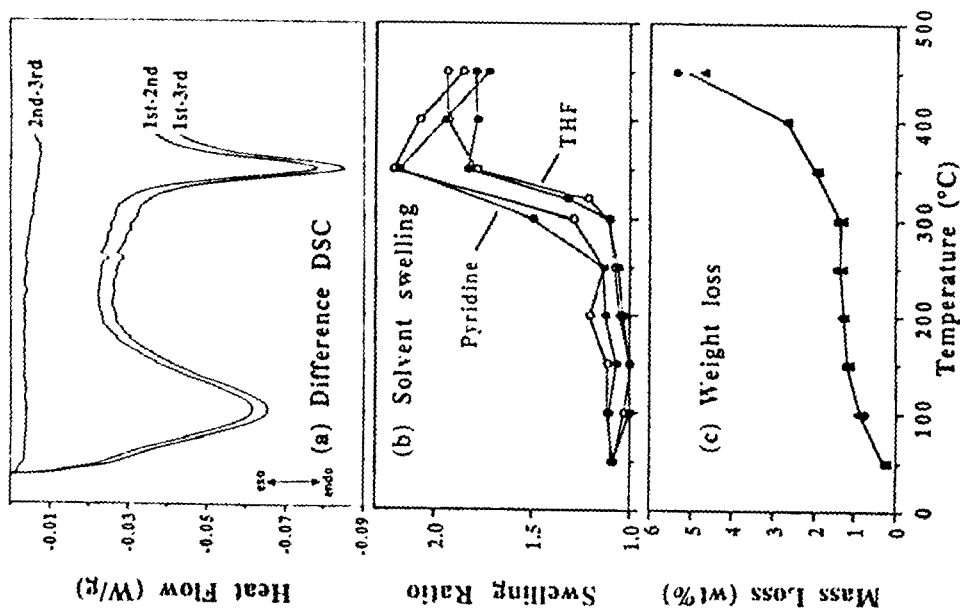


(2) Heat Flow (W/g)

(1) Heat Flow (W/g)

(2) Upper Freeport (85.5 %C)

(1) Pocahontas No.3 (91.1 %C)

(2) Illinois No.6 (77.7 %C)

(1) Pittsburgh No.8 (83.2 %C)

Temperature (°C)

Figure 1. Comparison of DSC thermograms obtained at 8°C/min for different rank bituminous coals.
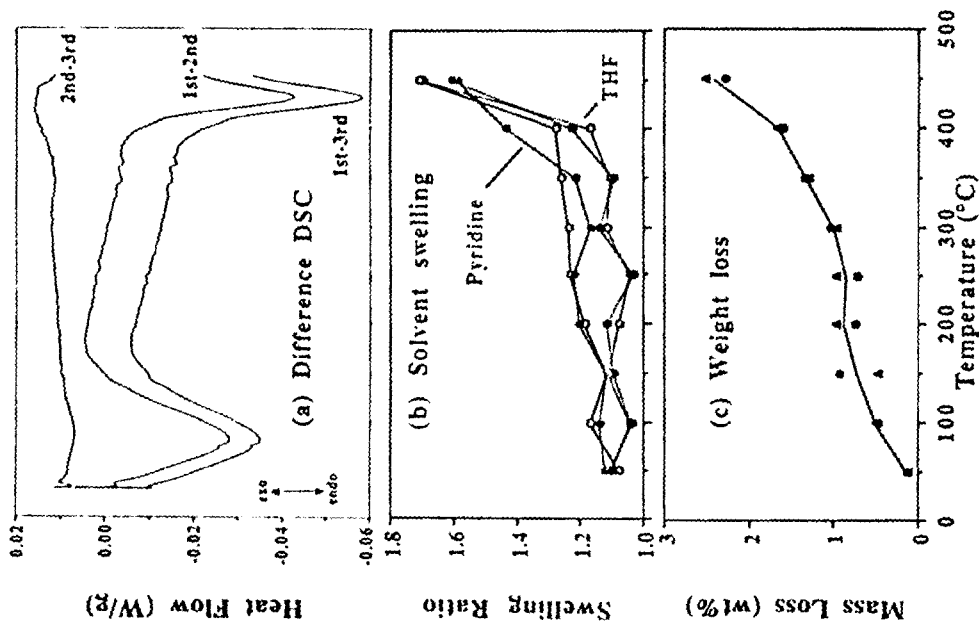
Figure 3. Difference DSC thermograms as well as profiles of swelling ratio and weight loss for Upper Freeport (-100 mesh) and Pocahontas No.3 (-20 mesh) coals. DSC was performed at 8°C/min under N₂ atmosphere.