PROBING COAL STRUCTURE WITH INVERSE GAS AND LIQUID CHROMATOGRAPHY.*

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Introduction

The objective of this study is to examine variations in coal structure using two inverse chromatography approaches. Inverse gas chromatography, a technique widely used for studying polymers, is being used to study phase transitions in coals upon heating. In contrast to classical GC, inverse chromatography probes the stationary phase, a coal, by determining the retention time of known compounds. This transposition of known and unknown in the GC experiment gives rise to the term "inverse chromatography". Inverse liquid chromatography, a new technique, is being used to examine coal surfaces. This approach is analogous to the GC method except that solvents are used. The coal samples will be chosen to examine variations with rank and to investigate structural changes in ground coals, both in air and in the absence of air, as a function of time. These approaches show promise for providing chemical information on subtle variations in coal structure. The initial experiments are described in this paper.

Inverse GC (1-3) has been applied to polymers to measure the glass transition temperature (4), the degree of crystallinity (5), melting point (6), thermodynamics of solution (4,7), and chemical composition (8,9). The first use of the term "inverse chromatography" is attributed to Davis and Peterson (8), who applied the technique to the determination of the degree of oxidation of asphalt. In later work, the experiments were extended to include measurement of thermodynamic properties of the asphalt.

Some other methods used to study the physical structure of coal and coal surfaces include measurements of heats of adsorption of organics on coal surfaces by GC, to probe the nature of solute-coal surface interactions (10); swelling indices, for the qualitative determination of the extent of cross-linking (11); initial swelling rates, to investigate the steric requirements of swelling (12); and microscopic observation of solvent diffusion through coal thin-sections (13).

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Experimental

Inverse gas chromatography: The coal used in the inverse GC experiments was an Illinois No. 2 hvC bituminous coal (analysis, dmmf basis: C 73.4%, H 5.3%, N 1.1%, S 1.6%, 18.1% (by diff.)), ground to -100 mesh and soxhlet extracted with an azeotropic mixture of benzene and ethanol, and dried under vacuum at 110°C. The coal was thoroughly mixed with non-porous glass beads (-40 to -60 mesh) to give coal/glass bead mixtures in the range of 2.5 to 30 w/w %. Stainless steel columns (1/4" od x 1 m) were packed with ca. 10 g of the coal/glass bead mixture.

The entire experiment was controlled by a DEC LSI 11/73 computer. The GC (Carla Erba, Model 4160), equipped with a single FID, was modified such that the oven temperature could be computer-controlled to within 1°C. The injector, a gas sampling valve, was housed in a thermostated box at 110°C. Carrier gas flow was provided by two controllers, one with a 0 - 5 mL/min element (low flow) and the second with a 0 - 60 mL/min element (high flow). The high flow controller was connected to the injector through a computer-controlled solenoid.

The probe sample, 5% methane in argon, is injected onto the column and its retention time at the specific temperature is determined. The column temperature is then increased and the FID signal determined. If the signal exceeds the baseline by more than four percent, the solenoid to the high flow controller is opened to give a carrier gas flow rate of approximately 20 mL/min. This extra flow is intended to purge the column of thermally released materials more rapidly, thus decreasing the time required for the experiment. Once the FID signal has returned to within four percent of the baseline signal, the probe sample is again injected and the process is repeated. The experiment was carried out at 3°C increments from 50°C to 450°C. A control experiment run with only glass beads in the GC column gives a slope of zero in a log t_{ret} - 1/T plot, when corrected for carrier gas viscosity.

Inverse liquid chromatography: The LC system consisted of a pump (Waters Model M-6000-A) equipped with a 10 μL sample loop, a differential refractometer detector (Waters), and a UV absorbance detector set at 254 nm (Schoeffel Model 770). Data were collected on a DEC LSI 11/23 interfaced through an A/D convertor. The mobile phase was high purity methanol (Burdick and Jackson), with a flow rate of 1.0 mL/min.

The stationary phase was prepared from an Upper Freeport medium volatile bituminous coal (analysis, dmmf basis: C 89.0%, H 5.2%, N 1.6%, ash 13.1%, S_{tot} 2.4%). The coal was ground to -100 mesh and extracted overnight with refluxing methanol. A 1 cm id x 10 cm stainless steel column was then slurry- packed with the coal at a flow rate of 2.0 mL/min. The column was jacketed and the column temperature maintained by a circulating bath. The void volume of the system was determined to be 3.4 mL by measurement of the retention volume of ethanol or of methanol-d_4.

Results and Discussion

Retention data from the inverse GC experiment are shown in Figure 1. There are three retention mechanisms likely to affect the inverse GC experiment. These mechanisms are molecular sieving, surface adsorption, and solution of the probe in the stationary phase. The observed retention behavior will be due to the combination of effects operating under the given conditions. The specific retention volume, V_g, is given by the sum of the retention terms:

$$V_g = K_d V_L + K_o A_L + K_s W_L \qquad 1)$$

where K_d, K_o, and K_s are the partition coefficients for gas-pore, gas-solid, and gas-liquid partition, respectively; V_L is the accessible pore volume; A_L is the accessible surface area; and W_L is the accessible mass of the stationary phase. It is largely the phase and physical state of the stationary phase which determines the retention mechanism. The retention volume may be related, through the partition coefficient, to the free energy or enthalpy of adsorption, and a plot of log t_{ret} vs. 1/T gives a slope proportional to ΔH_a. Changes in the thermodynamics of retention result in discontinuities or changes in the slope of the plot.

Three such changes in slope are shown enlarged in Figure 1. One, occurring at about 110°C, can be attributed to dehydration of the coal. An increase in retention is observed, which may be due to an increase in either the amount of accessible surface (A_L) or the volume of accessible pores (V_L). At temperatures below the glass transition temperature, gas-liquid partitioning will not play a major part in the retention of the probe molecule. The reproducible transition seen at 140°C may be due to the loss of tightly bound water and loss of other volatile species.

Other changes in the state of the coal are observed at ca. 350°C and 400°C. Similar transitions have been observed by other workers, with a variety of methods. For example, differential scanning calorimetry studies by Mahajan et al. (14) showed two endotherms in the 300-400°C range, which appear at increasing temperature with increasing coal rank (in the range hvA - hvC). Patrick, Reynolds, and Shaw (15) observed a transition to total anisotropic content at 370-420°C in optical anisotropy experiments on vitrains with C < 89%. In addition, several workers (16) have reported that, after heat treatment, both the amount of pyridine-soluble material and the average molecular weight of the material reach a maximum in the 300-350°C range.

It is also interesting to note the large change in slope of the log t_{ret} - 1/T plot at temperatures above 300°C. This is indicative of major changes in coal structure above this temperature.

Data from the inverse LC experiments are shown in Figure 2. As in the inverse GC experiment, retention behavior may be expressed by the sum of several retention terms, including those for liquid-liquid, liquid-solid, and size exclusion chromatography. In liquid chromatography, the capacity factor, k', is given by

$$k' = \frac{KV_s}{V_M} = \frac{t_r - t_m}{t_m} \qquad 2)$$

where K is the equilibrium constant of the retention mechanism, V_s is the effective surface area, volume, or pore volume of the stationary phase, and V_M is the mobile phase hold-up, or the void volume of the system. The capacity factor may be determined from the retention time of the solute (t_r) and the retention time of an unretained solute (t_m) or solvent front. The capacity factor may be related, through the equilibrium constant of the retention mechanism, to the thermodynamics of retention (17). A semi-log plot of k' vs. 1/T gives a slope proportional to the enthalpy of transfer between the stationary and mobile phases. Nonlinearities would be symptomatic of changes in the nature of coal-solute-solvent interactions. A van't Hoff plot for the retention of phenanthrene is shown in the lower part of Figure 2. Relatively good linearity is observed over the range 25-80°C.

A semi-log plot of k' vs. carbon number for the series of aromatic solutes benzene, naphthalene, phenanthrene, and triphenylene is shown in the upper part of Figure 2. This type of plot is useful for the comparison of the retention powers of different stationary phases. Data for the medium volatile bituminous coal indicate that this material is similar to some reversed-phase HPLC packing materials, particularly the porous carbon packings (18-20). One might expect pi-pi interactions between the coal surface and aromatic solutes to predominate in determining retention, so that the capacity factor increases with increasing solute surface area.

The initial results presented here demonstrate that these methods will provide reproducible results which can be interpreted. Coals from the Argonne Premium Coal Sample Program will be investigated using both approaches. We plan to examine possible changes of the physical structure of coals upon storage both in the oxygen and absence of oxygen.

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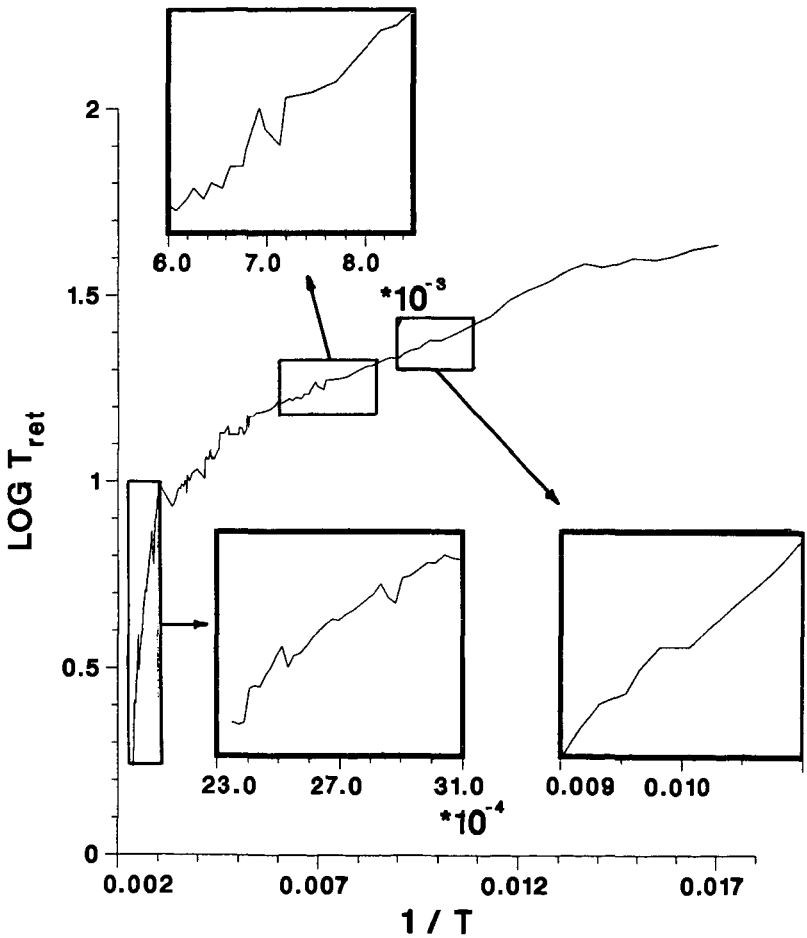

Figure 1. Inverse GC of Illinois No. 2 hvC bituminous coal. Top insert: 145°C region, lower left; 350-400°C region, lower right: 110°C region.

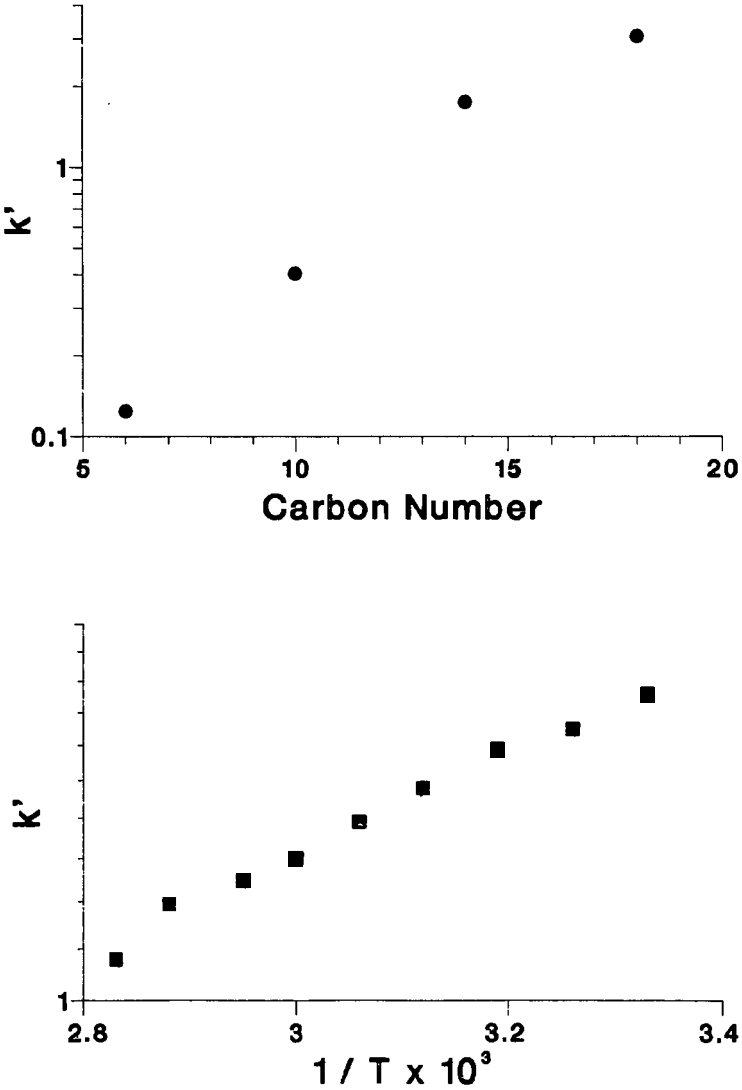

Figure 2. Inverse LC of Upper Freeport medium volatile bituminous coal. Top: retention data for benzene, napthalene, phenanthrene, and triphenylene. Bottom: retention data for phenathrene from 27.5-80°C.