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TRANSPORT OF PENETRANTS IN THE MACROMOLECULAR STRUCTURE OF COALS. VIII. TRANSPORT MECHANISM AS A FUNCTION OF TEMPERATURE

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ABSTRACT

Pyridine transport in 600–850-μm coal microparticles, pre-extracted with pyridine and redried, was studied as a function of time and temperature from 35 to 300 °C. Simultaneous thermogravimetric studies were run to determine the net weight loss due to thermal degradation. The true pyridine uptake in coals at high temperatures was thus established.

INTRODUCTION

In previous publications of this series [1–4] we examined the mechanism of penetrant transport in coal particles and thin sections at low temperatures, usually below 100 °C. We analyzed the mechanism(s) of pyridine transport using the theory of Fickian and non-Fickian transport in glassy macromolecular structures, and we offered molecular explanations about the relative importance of molecular diffusional and relaxational processes in the macromolecular coal network structure [2].

Similar studies at temperatures higher than 100 °C are more difficult to analyze because of the simultaneous degradation of the coal network. However, some recent experimental data presented here offer new insight into the solvent mass transfer characteristics in coals at high temperatures.

EXPERIMENTAL

Sample preparation

The coal samples (average size, 600–850 μm; packed under nitrogen) were supplied by the Pennsylvania State University Coal Bank (PSU). Table 1

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TABLE 1

Analysis of PSU coal samples

PSOC code No.	Rank	Carbon content (%, dmmf)	Oxygen content (%, dmmf)	Mineral matter (%, dry)
791	lignite	72.25	20.17	20.77
312	high volatile bituminous C	78.38	14.16	7.08
853	high volatile bituminous C	80.12	12.68	3.74
989	medium volatile bituminous C	88.19	3.79	5.08

includes pertinent information provided by PSU. The samples were sieved under nitrogen to the desired mesh sizes, and they were sealed and stored under nitrogen until use.

The 20–30 mesh coal samples were prepared for study by exhaustive Soxhlet extraction with pyridine. All extractions were carried out under nitrogen using pyridine at its atmospheric boiling point of 115.5 ° C. Acetone was then used as the extraction solvent at 56.2° C for 24 h under nitrogen to drive out the remaining pyridine. The samples were then dried, sealed and stored under nitrogen until needed for experimentation.

Dynamic and equilibrium swelling studies

These studies were performed in a thermogravimetric analyzer (Perkin-Elmer model TGA-2) and the associated sorption system. Approximately 5 mg of the preextracted coal sample was placed in a platinum pan which was suspended from a lever arm balance. The system was then placed in a microfurnace with a nitrogen atmosphere. After 1 h pyridine was allowed to bubble through the system and over the coal sample. Changes in weight due to sorption were recorded. The sorption experiments were carried out at constant temperatures of 35, 50, 100, 150, 200, 250 and 300 ° C.

Thermal degradation studies

These studies were carried out again in a thermogravimetric analyzer. Approximately 5 mg of the preextracted sample was placed in a platinum pan which was suspended from the lever arm balance. The system was then placed in a microfurnace which was purged with nitrogen. After 1 h the system was heated at a scanning rate of 10 ° C min^{-1} starting at 35 ° C and going up to 400 ° C. The weight loss due to the temperature increase was recorded.

RESULTS AND DISCUSSION

To study the effect of temperature on the dynamic swelling of coal by pyridine vapor, swelling studies were carried out at moderate and high temperatures. First, samples of 600–850-μm particles of PSOC 312 with 78.38% C (dmmf) were subjected to pyridine vapor at an activity of 0.002. Figures 1 and 2 show the pyridine uptake as a function of time for swelling temperatures of 35, 50, 100, 150, 200 and 300 °C. Experimental error for these studies was on the order of 0.5%.

The penetrant uptake as a function of time for the swelling studies at 35 and 50 °C showed similar swelling characteristics. However, as the temperature of the swelling experiments was increased to 100 °C and higher, the data showed a marked decrease in penetrant uptake. In fact, at the highest temperatures the samples showed a weight loss as a function of time.

To correct for the weight loss due to the degradation of coal at those temperatures, results from thermogravimetry were used to account for the degradation.

The first series of studies was performed to determine the effect of constant temperature over an extended time period on the degradation of the coal samples. These studies were carried out to determine if degradation occurred during the swelling process and how this affected the transport mechanism. Figure 3 gives typical results from these experiments. At 300 °C,

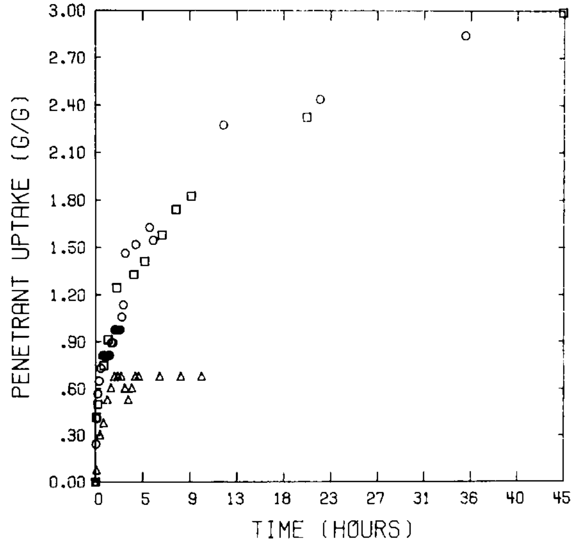

Fig. 1. Pyridine (activity of 0.002) uptake per gram of coal as a function of time for 600–850-μm particles of pyridine-preextracted PSOC 312 coal with 78.38% C (dmmf) at 35 °C (○), 50 °C (□) and 100 °C (△).

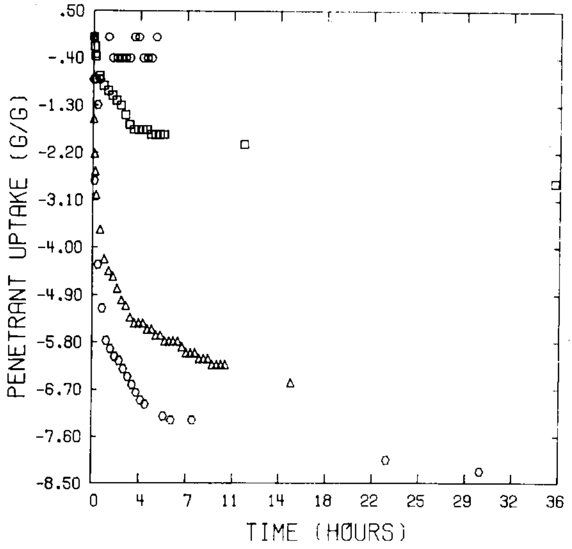

Fig. 2. Pyridine (activity of 0.002) uptake per gram of coal as a function of time for 600–850-μm particles of pyridine-preextracted PSOC 312 coal with 78.38% C (dmmf) at 150°C (○), 200°C (□), 250°C (△) and 300°C (○).

coal PSOC 853 with 80.12% C (dmmf) lost 11.5% of its weight after 200 h. However, of the 11.5% lost, 9.8% can be accounted for as loss of moisture from the coal and the rest is probably due to the loss of short-chain hydrocarbons. At higher temperatures, the degradation became more prominent.

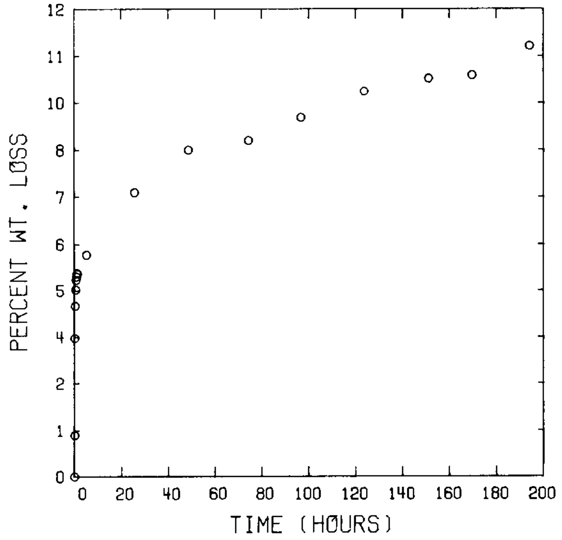

Fig. 3. Percent weight loss as a function of time under nitrogen purge for 600–850-μm particles of PSOC 853 with 80.12% C (dmmf) at a constant temperature of 300°C.

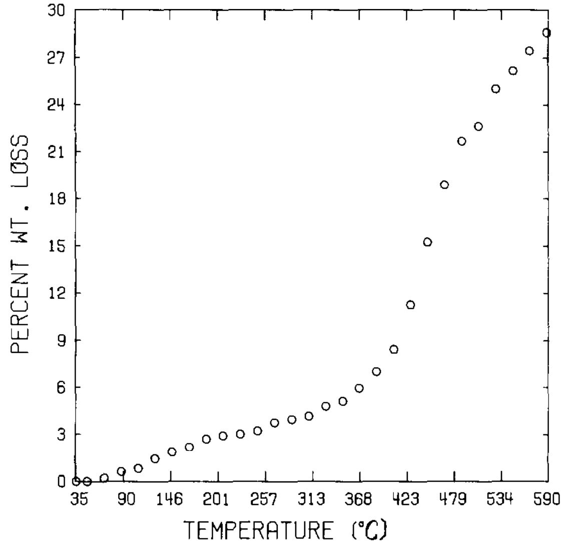

Fig. 4. Percent weight loss as a function of temperature under nitrogen purge for 600–850-μm particles of PSOC 853 with 80.12% (dmmf).

Similar studies for PSOC 312 with 78.38% C (dmmf) and PSOC 418 with 69.94% C (dmmf) gave weight losses of 3.5 and 12.7%, respectively, after 200 h at 116 °C (the temperature at which the pyridine extraction process occurs). The moisture content (10.7% for PSOC 312 and 29.9% for PSOC 418) can account for the weight loss at this temperature.

The studies indicated that degradation during the extraction process and the swelling process for temperatures below 100 °C was limited. However, for swelling studies performed at higher temperatures degradation became more important and must be accounted for in the analysis of the transport data.

A second series of experiments was performed to study the degradation of coal as a result of increasing temperature. Figure 4 shows typical results from these studies for PSOC 853 with 80.12% C (dmmf) starting at 35 °C and scanning at 10 °C min^{-1}. The graph shows that below the coal glass transition temperature of approximately 350 °C the weight loss can be accounted for as loss of moisture in the coal and above 350 °C there is not only transition to the rubbery state but also major degradation. Similar results were obtained for the other coal samples studied.

The pyridine transport data corrected for the degradation (weight loss) are presented in Fig. 5. It is obvious that penetrant uptake decreased as the temperature of swelling increased above 100 °C. Even after correcting for network degradation at these higher temperatures, uptake was still found to decrease. Similar results were also obtained for the coal model polymers

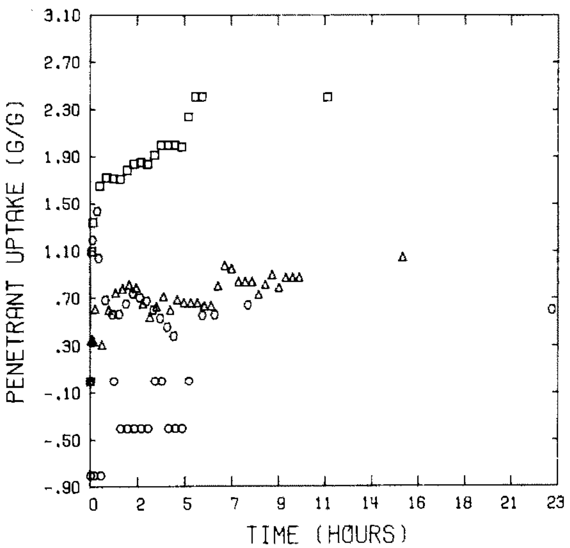

Fig. 5. Pyridine uptake as a function of time corrected for coal weight loss due to degradation. Studies with 600–850-μm particles of pyridine-preextracted PSOC 312 coal with 78.38% C (dmmf) at 150 °C (○), 200 °C (□), 250 °C (△) and 300 °C (○).

studied earlier [3]. For these samples, the penetrant uptake decreased above 50 °C.

There are crosslinked polymer networks which exhibit a similar decrease in penetrant uptake at higher temperatures than coal [5]. In poly(ethylene oxide) systems, for example, the increase in temperature was found to induce crystallinity thereby reducing the free energy of mixing and decreasing the penetrant uptake. However, the complex nature of the coal network would not allow the induction of ordered structure even at the higher temperatures. Therefore, there must be another mechanism which reduces the free energy of mixing as the temperature increases which ultimately leads to a decrease in the degree of swelling.

In conclusion, penetrant transport studies can be conducted at high temperatures using a thermogravimetric analyzer and a sorption system. The results indicate that pyridine transport is slowed down at high temperatures in the range of coal ranks studied.

ACKNOWLEDGMENT

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