

## THE GAS-PHASE DERIVATIZATION OF COAL

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### Introduction

Most of the spectroscopies employed to study reactive functionalities on the surface of coal suffer because a high percentage of adsorption from bulk or subsurface functional groups are included. For example, photoacoustic infrared Fourier transform (PAIFT) spectroscopy, while one of the most surface selective of the infrared spectroscopies, still has a thermal diffusion length of approximately 20 micrometers for a coal particle of 150 micrometers radius under typical experimental conditions.<sup>1</sup> Spectroscopic techniques are also limited in their ability to provide accurate quantification due to difficulties in estimating adsorption coefficients and the need to employ such techniques as curve deconvolution.

An alternative approach is to employ a probe molecule that will interact with reactive functional groups on the surface of coal and to quantify the degree of interaction. Although this approach is in its infancy, some success has been demonstrated for flow microcalorimetry using acidic and basic probes.<sup>2,3,4</sup> A logical extension to this approach would be to employ probe molecules that react with specific surface functionalities to form products that can be accurately quantified without the use of surface spectroscopies. Information on total surface functionality content should also provide complementary information to surface functionality densities obtained from spectroscopies such as X-ray photoelectron spectroscopy.<sup>5,6</sup> It was the purpose of this investigation to test the feasibility of this approach using the gas-solid phase silylation of hydroxyl groups on coal with hexamethyldisilazane (HMDS) in nitrogen.

The kinetics of the chemisorption of HMDS vapors into 100-mesh Illinois No. 6 coal particles were followed by periodic removal from the reactor of portions of the coal. The coal was subsequently analyzed for its trimethylsilyl ether content. The kinetics were evaluated using a mathematical model applied by Berens and Hopfenberg to describe the sorption of vinyl chloride monomer, acetone, and methanol vapors into powder samples of polyvinyl chloride.<sup>7</sup> For experiments in which "glassy" polymers were continuously exposed to relatively large concentrations of sorbate, a striking two-phase sorption process was observed by News<sup>8</sup> and by Long and Richman.<sup>9</sup> The two stages were separated in time and consisted of an initial, rapid Fickian diffusion process that was followed by a much slower relaxation process. Berens and Hopfenberg interpreted the diffusion process as involving migration of penetrant molecules into preexisting void space, and the relaxation process as related to swelling, resulting from large-scale segmental motions of the polymer.<sup>7</sup>

These preliminary investigations attempted to exploit the two-stage sorption kinetics to define reaction parameters that would result in a high level of surface selectivity while minimizing relaxation and swelling of the bulk of the coal's macromolecular structure. The effects of particle size were evaluated by Enscoe et al.<sup>10</sup> who demonstrated that under proper conditions of temperature and penetrant activity, n-hexane sorption into about 200 micrometer diameter polystyrene spheres was dominated by a relaxation mechanism whereas sorption into submicron polystyrene spheres was predominantly by way of Fickian diffusion. As suggested by Vrentas et al.,<sup>11</sup> the relaxation process is independent of the particle size of the polymer but the Fickian diffusion time frame varies with the square of the particle size. Two-stage behavior, therefore, can be approached by increasing the diffusion rate through increased reagent activity and by reducing the diffusive path length by decreasing the particle size. Ideally, the Fickian diffusion coefficient should be at least an order of magnitude greater than the first-order relaxation rate constant for the predominant relaxation mode.

A corollary consideration in designing experiments to elicit two-stage behavior would be to reduce the relaxation rate by selecting penetrants with a low solubility in the polymer. Ritgar and Peppas<sup>12</sup> modeled the sorption of pyridine vapors by thin films of bituminous coals using the Berens and Hopfenberg equation and found that the process could be modeled using a single first-order relaxation term. The relaxation rate constant remained nearly the same over a range of coal carbon content and sample thickness, indicating the process to be mechanistically characteristic of the penetrant. The relatively rapid relaxation of coal by pyridine vapor would presumably make it difficult to construct experimental conditions where two-phase behavior would be observed. Two-phase behavior was observed by Hsieh and Duda for the sorption of toluene vapor by pyridine extracted bituminous coal powders.<sup>13</sup> The removal of the "mobile phase" in coal by pyridine extraction decreased penetrant uptake. Hsieh and Duda also observed an initial rapid adsorption onto the surface of the coal particles.<sup>13</sup> These observations of two-stage behavior suggest an approach to obtaining surface selectivity. HMDS was selected as a suitable vapor phase chemisorption probe, in part, because of a low solubility in bituminous coals.

The Berens and Hopfenberg model is a linear combination of a Fickian diffusion component and of one or more first-order relaxation components.

$$M_t = M_\infty \left\{ 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 k_r t) \right\} + \sum_i M_{s,i} \left[ 1 - \exp(-k_{s,i} t) \right]$$

Where:  $M_t$  is the total sorption due to Fickian diffusion,  
 $M_{x,i}$  is the total sorption due to the  $i$ th relaxation mode,  
 $M_t$  is the total sorption at time  $t$ ,  
 $k$ , is the Fickian rate constant, and  
 $k_{x,i}$  is the first-order rate constant for the  $i$ th relaxation mode.

The relaxation components in this model are driven by the release of stresses within the polymeric macromolecule through penetrant-induced swelling. The relaxation processes are, unlike Fickian diffusion, unrelated to particle size.

### Experimental

The gas-solid phase silylation reactions were carried out in a 250-mL, three-necked, round-bottom, nitrogen-flushed flask. For kinetic studies, coal samples were periodically removed from the reactor through an "entrance port" fitting. The fitting directly above the coal sample was used for reagent addition. This fitting supported a Mininert valve above the reactor and a 1 mL, "evaporation" beaker which could be heated by being lowered against the bottom interior of the reaction flask. A glass capillary tube connected the Mininert valve to the evaporation beaker. The capillary tube could be raised or lowered through an O-ring fitting. The bottom of the flask was placed into a heating mantle and the temperature was monitored using a thermocouple. All fittings were Teflon with Viton O-ring seals to avoid the use of sealants that might contaminate the surface of the coal particles.

The coal sample (0.8 g of Argonne premium Illinois No. 6 coal) was spread out on the bottom of the flask and the flask flushed with nitrogen. The reaction was initiated by addition of 500 microliters of HMDS, which was rapidly volatilized. Saturation with HMDS was maintained throughout the experiment. Approximately 70-mg coal samples were removed at various time intervals for analysis. Their trimethylsilyl ether content was determined after 3 hours of vacuum drying to remove physically adhering reagent. The trimethylsilyl ether content was determined using a fluoride cleavage-G.C. headspace procedure. Gas-solid-phase silylations were carried out at coal temperatures of 123, 163, 178, and 196 degrees C. Ten mL of a solution of 65% THF, 25% concentrated HF, and 10% water (by volume) were used to cleave the trimethylsilyl ethers in a 30-mL Teflon test tube fitted with a Mininert cap, valve, and septum assembly. The reaction was carried out at room temperature. In the reaction, hydrofluoric acid cleaves the trimethylsilyl ethers, converting them into trimethylfluorosilane, which is largely soluble in the reaction solution. The coal-hydroxyl groups are regenerated in the process. One-half milliliter of headspace was sampled and analyzed for trimethylfluorosilane on a Poropak P column maintained isothermally at 185°C. The trimethylfluorosilane peak area was calibrated against a standard curve generated by fluoride cleavage of various amounts of the TMS ether of 1-naphthol (Figure 1). As shown in Figure 1, deviations from Henry's law (linearity) begin at 20 microliters of standard. Sample weights were adjusted to utilize the linear range of the standard curve. The TMS ether of 1-naphthol was obtained by refluxing 1-naphthol in a 1:1:2.5 mixture of HMDS:TMCS:Pyridine, and distilling the crude product at 90 -91°C under 1 mm of nitrogen.

## Results and Discussion

The Berens and Hopfenberg model was modified slightly by the addition of a separate term,  $M_1$ , to describe a rapid, initial chemisorption occurring within the first few minutes and presumably resulting from the unimpeded contact of reagent vapors with the surface of larger pores. The computer-assisted curve fitting process for obtaining equation parameters was essentially the same as that described by Berens and Hopfenberg.<sup>7</sup> A computer program was used to minimize the summed-squares deviations between measured values and the corresponding values generated from the equation by adjusting the constants.

A comparison between the equation and measurements obtained at 178°C is shown in Figure 2 together with curves representing contributions from individual terms of the equation. Two-stage behavior was clearly evident for curves generated over the reaction temperature range of 123° to 196°C. Appropriate, early termination of the reaction would result in the initial and diffusion terms constituting an average of 89% of the total chemisorption. The time required to reach diffusion equilibrium was less at 196°C, 3 hours to reach 93% of maximum, than at lower temperatures where 6 hours were required to reach 93% of maximum. The total contributions at infinity for the two relaxation terms,  $M_{r_1}$  and  $M_{r_2}$ , for the Fickian diffusion term,  $M_f$ , and for the summation of terms,  $M_{total}$ , are given as a function of reaction temperature in Figure 3. The Fickian diffusion term plateaued at 178°C as did the principle relaxation mode,  $r_2$ . The minor relaxation mode,  $r_1$ , does not plateau over the temperature range.

While specific polymeric motions cannot be identified with  $r_1$  or  $r_2$  relaxations, a case can be made for a linkage between the diffusion term and  $r_2$  relaxation (Figure 2.) Pore deformation and a corresponding expansion of the nascent void space might result from chemical modification of the pore surface, the disruption of intrapore hydrogen bonding, or from steric interactions as the pores are filled. Gethner<sup>8</sup> utilized light scattering to probe changes in the larger pores of an Illinois No. 6 coal when immersed in each of 7 different liquids and concluded that such pores were not rigid but easily deformed. Void-structure alterations were clearly evident and resulted in an increase of the total void-volume contributing to the light scattering. Information on sorbate-induced polymeric rearrangements or conformational transformations associated with the relaxation of coal cannot be obtained directly from phenomenological measurements of sorbate uptake. Coal relaxation linked to solvent or vapor sorption is, however, invariably correlated to coal swelling. In the chemisorption of HMDS into Illinois No. 6 coal, a single relaxation term accounts for the majority of reagent uptake and is assumed to reflect the gradual 'opening' of the macromolecular coal networks. For gas-phase, surface-limited applications, however, the silylation is terminated before appreciable polymeric relaxation and corresponding penetration of the coal matrix has occurred. This should presumably reduce opportunities for matrix entrapment of reagent.

The kinetic studies were used to define 'standard' conditions for surface-limited derivatizations of 178°C and a 6 hour reaction time. Ten replicate determinations under these conditions gave a total surface hydroxyl content of 0.76 hydroxyl groups / 100 carbon atoms with a standard deviation of 0.02 hydroxyl groups / 100 carbon atoms. This compares with a total hydroxyl content for Illinois No. 6 premium coal of 4.7 hydroxyl groups / 100 carbon atoms determined from liquid phase silylation reactions. This technique could be very

useful in following changes in coal surface chemistry when the surface is subjected to modification.

While the concept of coal surface is defined through the choice of experimental conditions and probe, an approach based upon limiting relaxation of the coal structure is reasonable. In contrast to spectroscopies, molecular probes should access the surface of pore systems where much of the liquid-solid and gas-solid interfacial chemistry of coal processing technologies occur. The gas-solid phase derivatization approach to coal surface analysis should result in an improved ability to quantify surface functionality content and to obtain a greater level of chemical selectivity through functionality specific reactions.

#### References

1. T. Zerlita *Applied Spectroscopy* 1986, 40, 214.
2. F.M. Fowkes, K.L. Jones, L. Guozhen, and T.B. Lloyd *Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.* 1987, 32(1), 216.
3. D.W. Fuerstenau, G.C. Yang, and S. Chander *Prepr. Pap. - Am. Soc., Div. Fuel Chem.* 1987, 32(1), 209.
4. D. Brooks, A. Finch, P.J. Gardner, and R. Harington *Fuel* 1986, 65, 1750.
5. D.L. Perry and A. Grint *Fuel* 1983, 62, 1024.
6. D.T. Clark and R. Wilson *Fuel* 1983, 62, 1034.
7. A.R. Berens and H.B. Hopfenberg *Polymer*, 1978, 19, 489.
8. A.C. Newns *Trans. Faraday Soc.* 1956, 52, 1533. (Ref. 9(12))
9. F.A. Long and D. Richman *J. Am. Chem. Soc.* 1960, 82, 513. (Ref. 7(14))  
10.D.J. Ensore, H.B. Hopfenberg, and V.T. Stannett *Polymer* 1977, 18, 793. (Ref. 7(8))
11. J.S. Vrentas, C.M. Jarzebski, and J.L. Duda *AIChE J.* 1975, 21, 894. (Ref. 7(7))
12. P.L. Ritger and N.A. Peppas *Fuel* 1987, 66, 1379.
13. S.T. Hsieh and J.L. Duda *Fuel* 1987, 66, 170.
14. J.S. Gethner *Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.* 1987, 32(1), 239.
15. H. Marsh *Carbon* 1987, 25(1), 49.

FIGURE 1

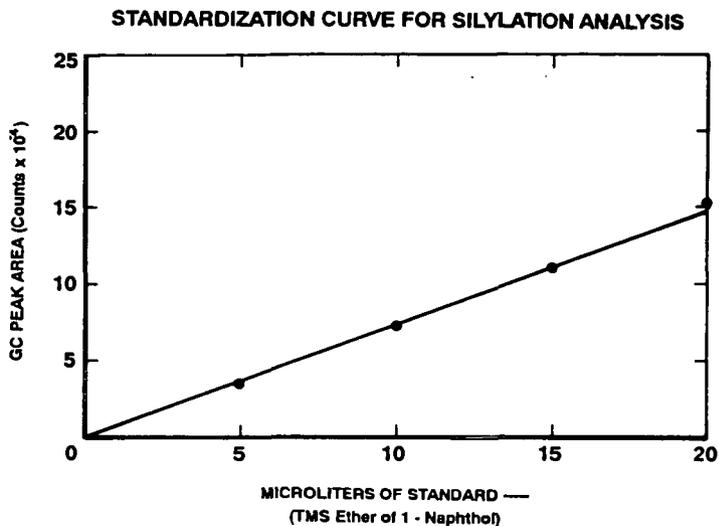


FIGURE 2

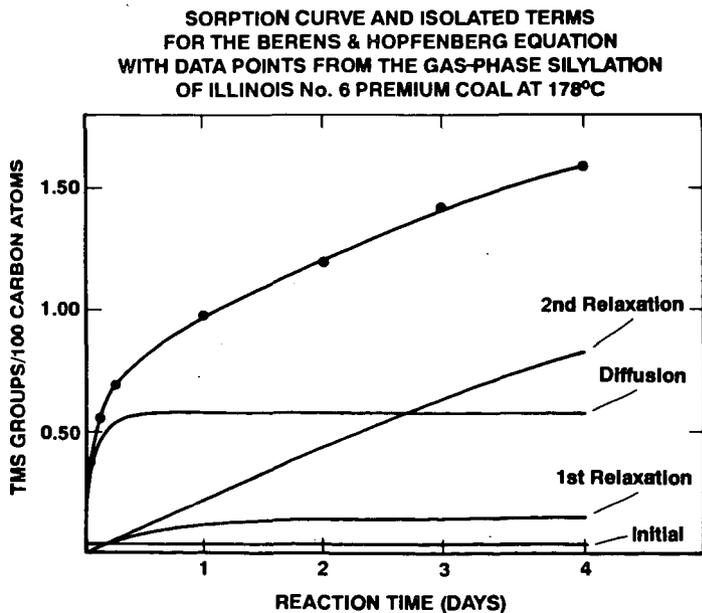


FIGURE 3

TEMPERATURE PROFILE OF TERMS  
FROM THE BERENS & HOPFENBERG EQUATION  
AT INFINITY FOR THE GAS-PHASE SILYLATION  
OF ILLINOIS No. 6 PREMIUM COAL

