

The Effect of Moisture on the Diffusion of Organic Molecules in Coal

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INTRODUCTION

Diffusional limitations are of importance in a large number of coal utilization processes. Common examples may be seen in many different kinds of processes; in donor solvent liquefaction, the coal must be broken down finely enough so that donor solvent transport into the coal does not become a limiting step (this is generally true at the usual process conditions); in coal devolatilization, during a pyrolysis or combustion process, the rate of escape of tars from coal particles is often limited by diffusional mass transfer in the particles; in natural weathering of coal, diffusional processes limit the rate of oxidation. The potential list of examples is much longer, and it may be quickly concluded that from a technological point of view, knowledge of diffusion rates in coals is generally quite useful. Relatively little such information exists in the literature because the historical method of handling questions of diffusional limitations has involved the empirical approach of grinding particles progressively finer, until no effects of further comminution were seen in the chemistry of interest. As the understanding of the chemical mechanisms involved in coal processing has improved, it now makes sense to improve on the understanding of the transport phenomena as well, and to move away from the empirical approaches to handling questions concerning mass transfer.

The present paper is concerned with diffusional transport occurring in both 1. micropores, and 2. the bulk solid. The distinction between processes in these two nominally distinct places in the coal is unimportant, because the distinction between "micropores" and "gaps between molecules" in a bulk solid is not always clear. The well-known problem of measuring surface areas of coals with N_2 and CO_2 is an example. There are certain portions of the coal porosity that are inaccessible to N_2 that are quite accessible to CO_2 , despite the fact that the latter is a larger molecule than the former. This is because diffusion on the micropore level is activated, meaning that thermal motion of the coal structure is required in order for the gas molecules to be able to penetrate the gaps between the molecules. N_2 is apparently less able to penetrate the structure than CO_2 because the experiments with N_2 must normally be performed at very low temperatures (i.e. liquid nitrogen temperatures), and the magnitude of the vibrations in the coal structure are not large enough at this temperature to open up sufficiently large gaps for large amounts of N_2 to penetrate. The magnitude of motions required for penetration by molecules depends upon the size of the penetrant species, and the nature of interactions between the coal and the species. Thus what may appear to be impenetrable bulk solid to one molecule may appear to be porosity to another.

It is the process of activated diffusion in coals that is of principal interest in this paper. There have been a limited number of other earlier studies of activated diffusion processes in coals, particularly concerning the diffusion of small gas molecules (e.g. CH_4 , CO_2 , light hydrocarbons, noble gases), through bulk coals. This study is, however, mainly concerned with the activated diffusion of larger organic species in coals. In the present case, common "swelling solvents" such as water, pyridine, tetrahydrofuran (THF) are of interest. These are termed swelling solvents because when a dried coal sample is immersed in them, it will physically swell as the solvents are imbedded. The theory of solvent swelling in coals has been well described elsewhere¹, and is based on the classic technique as developed for characterization of crosslinked polymers². The simplest relationship that embodies the essence of the technique is the Flory-Rehner equation, a relationship between the molecular weight between crosslinks in a polymer (M) and the extent to which the polymer is volumetrically swollen by a particular solvent (Q):

$$M = \left[\frac{\rho_c M_s}{\rho_s} \right] \left[\frac{(1/2Q) - (1/Q)^{1/3}}{\ln [1 - (1/Q)] + (1/Q) + \chi(1/Q)^2} \right]$$

where ρ_c is the density of the original coal, ρ_s is the density of the solvent, M_s is the molecular weight of the solvent and χ is the solvent-network interaction parameter. The measurement of χ is difficult, as is its estimation for specifically interacting solvents such as pyridine. Values range between 0.3 and 0.6 for typical pairs of solvents and coals. It has been suggested that the Flory-Rehner equation does not hold particularly well for coals, which are highly crosslinked rigid networks^{3,4}. Its use here is only illustrative, and more sophisticated approaches have been developed⁵⁻⁶; unfortunately these new models require more information about the structure of the coal-- namely, the molecular weight of repeat units within the coal structure. Since such information is not readily available at present, this will tend to restrict somewhat the use of these more realistic models.

The nature of the combined diffusion and solvent swelling process has also received attention in the literature in recent years⁷⁻⁹. This process, observed in "good" solvents-- those that swell the coal structure significantly -- is often non-Fickian in nature. Instead, it is often controlled by what is termed as relaxation of the coal macromolecules, and the process is characterized as exhibiting "Case-II" diffusional behavior. This behavior is well known in polymer systems that are below their glass transition temperatures. It is normally identified by noting that the rate of solvent uptake, or alternatively polymer swelling, is proportional to time, rather than square root of time as in Fickian processes.

What has received relatively little attention thus far in the literature on this topic is the activation energy for the combined diffusion and swelling process. This activation energy will depend upon the nature of the relaxation process that occurs in the glassy coal structure. Below its decomposition temperature, an unswollen coal is below its glass transition temperature¹, but solvent imbibition lowers the glass transition temperature significantly¹⁰. For the temperatures of interest in this study, the coal will always initially be in the glassy regime.

It is likely that the diffusion rate of a swelling solvent in a glassy material (coal) will be significantly altered by the presence of another swelling solvent. The swelling of coals in mixed solvents has been previously studied in binary mixtures, and co-operative effects noted¹¹. But a special case of this effect might involve diffusion in coals that are undried or incompletely dried. In such a case, the water present in the coal may influence the diffusion process, by virtue of being a swelling solvent itself. The swelling and shrinkage behavior of lignites with respect to moisture gain and loss has been reported on in some detail^{12,13}, and other recent results suggest that even bituminous coals behave similarly, as colloidal materials, with respect to water as a solvent¹⁴. In the present study, the effect of moisture content on the diffusion behavior of solvents, in various ranks of coal, is considered.

EXPERIMENTAL

The analyses of the coals examined in this study are provided in Table 1. Except where otherwise noted, the coals were ground and sieved to the size range 53-88 μ m. Special care was given to the lignites to avoid any more drying than necessary while processing. The first four samples in Table 1 were judged to have dried to only a limited extent since mining, and all were crushed in-house from large lumps. To prevent drying, these four samples were stored at 100% relative humidity conditions, at room temperature, by suspending the samples above a large reservoir of clean water, in a sealed container. It is of course difficult in practice to maintain truly 100% relative humidity conditions in such a manner, particularly if the chamber must be occasionally opened for sample removal. There was consequently a small difference in measured moisture contents between bed-moist samples (which are effectively immersed storage samples) and those used in this study. The difficulty in characterizing the initial moisture contents of immersed samples was what prompted us to use this slightly different storage method. Related sample storage and characterization information concerning these lignites can be found elsewhere¹³.

The principal experimental technique employed throughout this study was solvent swelling. The technique involves immersion of prepared, sized, coal samples in pure solvents. The measurements were performed in tubes of only a few millimeters inner diameter, and less than 5 cm in length. This technique permitted such measurements to be made with modest quantities of sample. The sample and solvent is frequently stirred during the first phases of the swelling process to prevent plugging in the bottom of the tubes. The tubes are immediately immersed in thermostatted water baths, after mixing coal and solvent. The small diameter of the tubes and the frequent stirring of their contents assure isothermality in the tubes, a necessary prerequisite for obtaining good rate data.

Rate data for swelling are obtained from measurements of the height of the column of coal as a function of time. Since the tubes are of uniform cross-section, the height change of the column of coal is proportional to the volume change in the sample. It is necessary to centrifuge the column of coal in order to obtain reliable measurements. The initial height is obtained by centrifuging the dry sample. Subsequent readings are obtained by first quenching the sample in an ice bath (if necessary because of rapid swelling kinetics) and then centrifuging the partially swollen coal sample for about ten minutes before taking readings. For this purpose, a high speed centrifuge with internal cooling has proven useful.

Thus the raw data of this study are swelling ratios as a function of time, temperature, solvent and coal. Standard Arrhenius plots of log of the swelling rate vs. inverse temperature provide the activation energies for the diffusion/swelling processes.

RESULTS AND DISCUSSION

It has recently been reported that a wide range of coal ranks seem to obey a common relationship between moisture loss and volumetric shrinkage¹⁴. A correlation was developed for the set of coals shown in Table 1:

$$\% \text{ Volumetric Shrinkage} = 0.94 (\text{Moisture Loss, wt } \%) - 0.6$$

It was noted that even high volatile bituminous coals, with only a percent or two moisture content, follow this correlation. It is interesting to note that the bituminous coals that show such weakly swelling gel behavior with water as a solvent may typically swell to double their original volume in pyridine. The lignites swell to about 30% extent in water, and also can roughly double their volume in pyridine. The reason for this difference in behaviors is not fully understood. It is obvious that lignites possess much higher amounts of surface oxygen functional groups than do bituminous coals. This would suggest that the value of χ in the Flory-Rehner equation is higher for lignite-water interactions than for bituminous coal-water interactions. But the differences in water swelling behavior may only be partly based on differences in χ values. Another possible explanation is that the apparent molecular weight (M) between crosslinks in bituminous coals is lower than in lignites, because water is unable to disrupt some kind of non-covalent crosslinking interactions that pyridine is able to disrupt (e.g. interactions between neighboring aromatic clusters). Which of these effects is predominant is, at present, not clear, and indeed both may play some role.

The effect that moisture content in coals may have on diffusion rates of other solvents in the coals is illustrated in Figures 1 and 2, in which the rate of swelling in pyridine is compared for both "wet" and "dry" coal samples. The data in Figure 1 show the 25°C pyridine swelling behavior of the dry and partially moist Texas lignite samples (particle size 212-300 μ m). The top panel shows the actual raw data, and the lower panel shows the same data, with a correction applied to the data for the moist lignite. The moist lignite has already been partially swollen by water, and in order to compare the data for the moist lignite with those for the dried lignite, it is necessary to express them on a common dry lignite basis. This has been accomplished in the bottom part of Fig. 1 by multiplying the actual swelling ratio (relative to the moist lignite volume) by the swelling ratio observed in going from a dry state to a 9% moisture condition. It is apparent that after such a correction, the final equilibrium swelling ratios in pyridine are identical for the two samples.

The rate of swelling in the case of the wet lignite is, however, considerably higher than the rate of swelling

of the dried lignite. Similar behavior has been noted in the swelling behavior of dried and wet lignites in THF; the swelling of a wet sample is faster than that of a dried sample.

Figure 2 shows that the same conclusion may be drawn in the case of the Powhatan #5 bituminous coal. The particle size range (212-300 μ m) and temperature (25 $^{\circ}$ C) were identical to those employed in the case of the lignite tests. The presence of moisture accelerates the rate of swelling of the coal by other solvents. Note, however, from the very different timescales in Figs. 1 and 2 that the diffusion and swelling processes in the two coals must be quite different. The swelling rate in the case of the bituminous coal is much higher than that in the lignite. This is consistent with earlier results on the diffusion of pyridine in dried bituminous coals and lignites, in which the activation energy for diffusion/swelling in several bituminous coals was about 13 kcal/mol, and in another lignite it was 18 kcal/mol¹⁴. Thus it seems in some sense easier for the pyridine to diffuse in and swell the bituminous coal than the lignite. The reasons for this are not yet understood. The effect does not, however, appear related to the presence or absence of moisture in the coals, since the timescale difference exists for both wet and dried samples. In fact, the difference in the rates of the diffusion and swelling processes appears to be a characteristic of the structure of the coals, since, the timescale for THF swelling of the Texas lignite is comparable to that for pyridine swelling of the lignite. Thus, one may conclude that the swelling processes are inherently slower in lignites than in bituminous coals, but that they are affected in the same way by moisture in both cases.

There may be concern that the apparent effect of moisture content on diffusion rates is an artifact, due to some kind of irreversible collapse of the structure upon drying. This was proven to not be the case in an experiment in which samples of the Beulah lignite were dried at vacuum for 3 hours, at 100 $^{\circ}$ C, and then allowed to regain varying amounts of moisture, by exposure to different relative humidity environments. The samples were then subjected to pyridine swelling at 35 $^{\circ}$ C. The effect of moisture content was as noted previously in the case of the Texas lignite. Figure 3 presents a summary of results. The curves show the times required for the samples to reach 30 and 50% of their final extents of swelling (relative to the particular initial volumes of each sample). The conclusion is that the more swollen the coal is to start with, the less time is required to reach any additional extent of swelling.

Indicated for each data point in Figure 3 are the activation energies for pyridine swelling, calculated for each sample at a constant extent of swelling, i.e. either 30% or 50%. These were determined for the range of temperatures 25 $^{\circ}$ C to 58 $^{\circ}$ C. It is interesting to note that while additional moisture appears to accelerate the rate of swelling in pyridine, the presence of moisture also seems to increase the activation energy for additional swelling.

It has been noted in the polymer literature that the higher the glass transition temperature a polymer exhibits, the lower the activation for ordinary diffusion of light gas molecules in that polymer¹⁵. While the combined swelling and diffusion process in coals is considerably more complex than the diffusion of light gases in polymers, the trends may indeed be related. In Figure 3 it is observed that the activation energy for swelling and diffusion is highest in the highest water content samples. It is well known that the addition of a swelling solvent to a glassy structure will lower its glass transition temperature, and thus the moister the coal, the lower its glass transition temperature. The data are thus in qualitative agreement with trends observed in the polymer literature.

To explore more fully the question of effect of crosslinking and reduced mobility of the coal structure on the rate of diffusion of pyridine in coals, a separate set of experiments was performed at various sets of heat treatment conditions. It has been shown previously that heat treatment of lignites at temperatures in the range 100 $^{\circ}$ C to 300 $^{\circ}$ C results in significant irreversible changes in the structure of the materials, both in terms of collapse of porosity and crosslinking of the structure^{15,14}. Based on the trends reported above, one would expect that increasing the severity of heat treatment would lead to increasing crosslinking of the structure, and thus to decreasing activation energy for the swelling and diffusion process. (This is because increased crosslinking in highly crosslinked materials will lead to further increases in the glass transition temperature). The results in Table 2 confirm this hypothesis, and thus lend support to the view that the role of

water in raising the activation energy for the diffusion process is merely in decreasing the glassy character of the coal.

The above observations of decreased activation energy for diffusion and swelling of the coals or polymers, with increased rigidity of the structure (due to crosslinking) might be initially counterintuitive. But it should be noted that the more highly crosslinked and rigid the network structure, the more the activation energy is concentrated in a smaller number of degrees of freedom, in the area in which the activated process is occurring¹⁶. Thus an increase in activation energy with increased extent of preswelling is likely to be reflecting the fact that there is progressively more mobility in the coal macromolecule, the more it is swollen. Hand-in-hand with increased mobility is the requirement for greater thermal energy to access progressively less probable configurations, which will allow for further swelling. To keep this physical picture in perspective, it should be recalled that the individual "chains" in the coal macromolecule are probably behaving mainly as "entropy springs"- the free energy change associated with swelling, or stretching the chains in the coal macromolecule is positive, due to entropic losses. The negative free energy change that balances this positive free energy change, in the Flory-Rehner analysis, arises from the decrease in chemical potential of the solvent, as it interacts with the structure. The activation energy of the process reflects the need to assume the progressively less probable chain configurations, via thermal motions of the chain segments, as the structure swells.

CONCLUSIONS

The results of the present study confirm the importance of establishing and reporting carefully the moisture content of any coal that is the subject of diffusion rate and/or swelling rate measurements. Likewise, it is important to report carefully how a sample may have been dried, prior to these measurements, since such low temperature procedures also may influence the results.

It may be concluded from the present work that moisture will swell coals of bituminous, subbituminous, and lignite ranks. This swelling will permit faster penetration and swelling of the coal structure by organic liquid diffusants. The activation energies observed for such swelling processes are reduced, as the effective glass transition temperature of the coals are increased, either by drying or pyrolysis.

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Table 1-Coals Studied

<u>sSAMPLE</u>	<u>C</u>	<u>H</u>	<u>N</u>	<u>S</u>	<u>ASH</u>	<u>O</u>	<u>Moisture</u>
Beulah lignite ^a	65.6	3.6	1.1	0.8	11.0	17.9	26.0
Freedom lignite ^a	63.5	3.8	0.9	1.4	6.1	24.3	27.9
Glenn Harold lignite ^a	61.1	4.4	0.8	0.4	7.4	25.9	28.9
Gascoyne lignite ^a	60.9	4.2	0.6	1.4	8.2	24.7	30.7
Beulah lignite ^b	65.9	4.4	1.0	0.8	9.7	18.2	32.2
Texas lignite (PSOC1036) ^c	61.5	4.7	1.4	1.3	12.5	18.5	31.8
Belle Ayr Subbit.	69.3	4.4	1.0	0.5	10.3	14.5	30.3
Big Brown Subbit.(PSOC785) ^c	62.8	4.6	1.1	1.1	12.6	17.8	27.8
Montana Subbit.(PSOC837) ^c	57.8	4.3	0.8	0.7	11.9	24.6	17.0
Pittsburgh No.8 (HVBit.) ^b	74.2	4.1	1.4	2.3	13.2	4.8	1.7
Bruceton HVBit. ^d	80.4	5.3	1.6	1.0	4.6	6.7	1.7
Powhatan HVBit.	72.3	5.1	1.5	3.6	9.7	7.8	1.1

•All results on a dry weight percent basis, except moisture which is ASTM value on an as-received, bed moist basis.

•Oxygen by difference.

a- Grand Forks Energy Research Center lignite sample bank.

b- Argonne National Laboratory Premium Coal Samples.

c- Pennsylvania State University Coal Sample Bank.

d- U.S. Bureau of Mines Standard Sample.

Table 2- Effect of Drying Temperature on the Activation Energy for Pyridine Diffusion/Swelling Processes in Beulah Lignite

<u>Drying Temperature (°C)</u>	<u>Q(equilibrium)</u>	<u>Activation Energy (kcal/mol)</u>
100	1.86	17.7
200	1.78	16.5
320	1.70	13.9

•All samples were predried in vacuum for 3 hours, and then subsequently dried at the indicated temperatures for 1 hour additional, under nitrogen.

•All swelling ratios determined in pyridine, at 35°C.

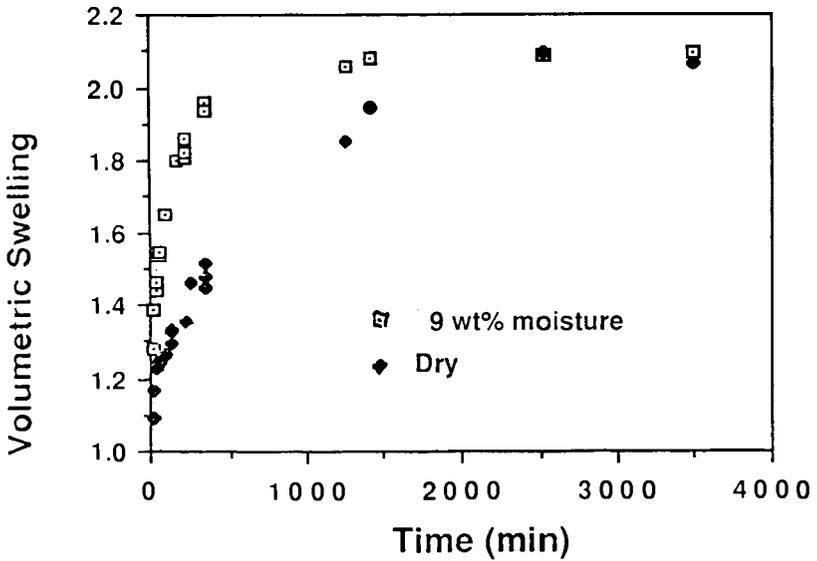
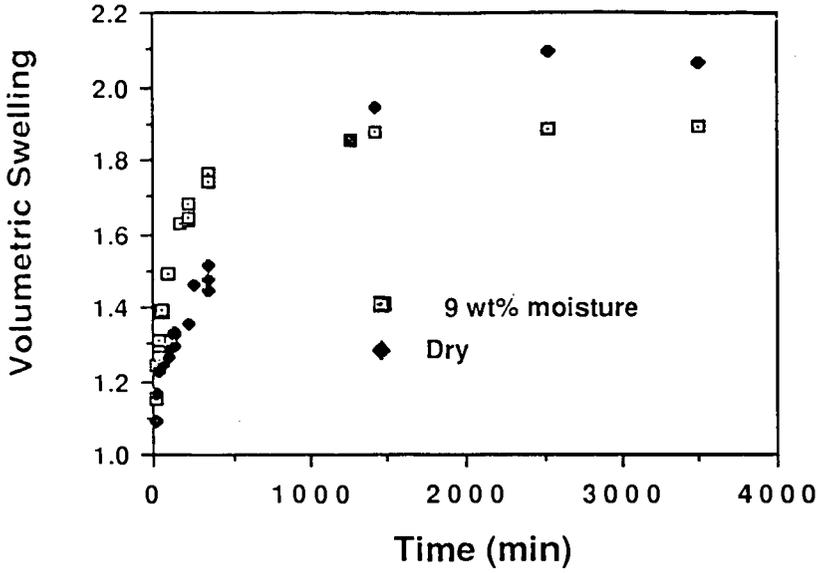


Figure 1. Volumetric swelling ratios (Q) in pyridine, at 25°C, of Texas lignite of 212 - 300 μm particle size. Top panel--raw data; lower panel - raw data for moist lignite corrected for water swelling (see text).

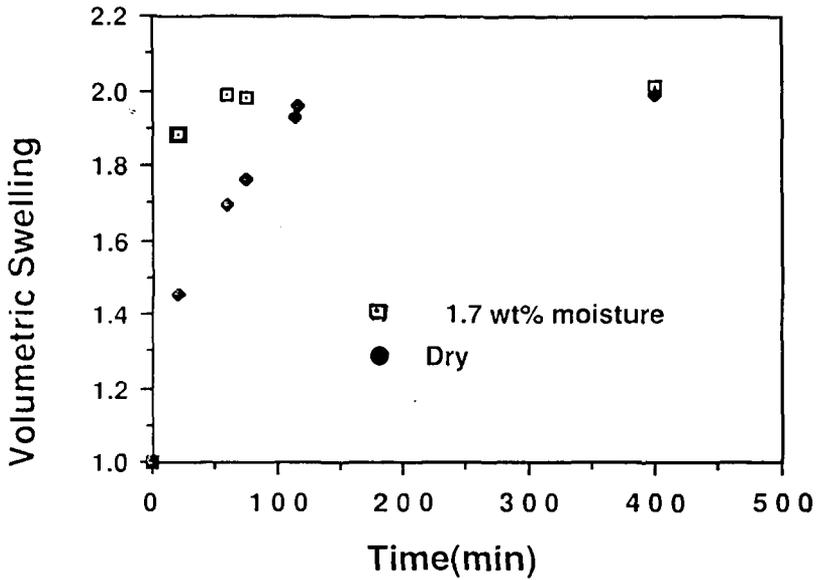


Figure 2. Volumetric swelling ratios (Q) in pyridine, at 25°C, of Powhatan No. 5 high volatile bituminous coal.

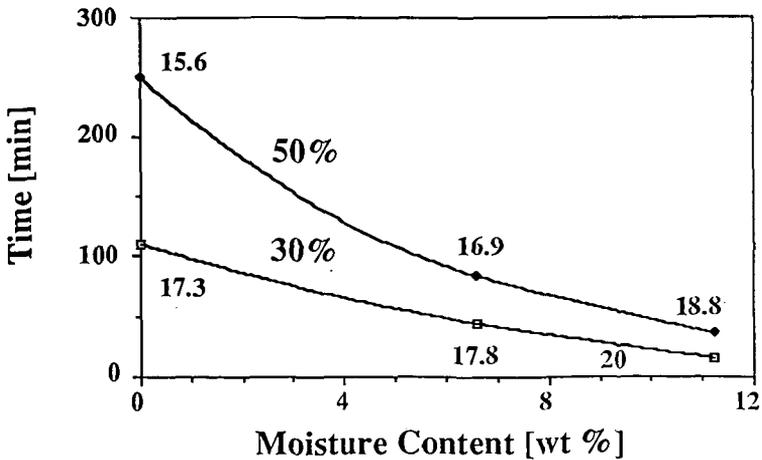


Figure 3. Swelling behavior of Beulah lignite in pyridine at 35°C. The ordinate shows the time required to achieve 30% or 50% of final extent of swelling, as a function of the initial moisture content of the samples. The values next to data points are activation energies for swelling (Kcal/mol).