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New Analytical Methods for Characterizing
Fossil Fuels and Derived Products
Direct Coal Liquefaction
Biomass Fuels

INFLUENCE OF BINARY SWELLING SOLVENTS: MECHANISM OF ACTION

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ABSTRACT

This study addresses the dramatic up-take of a poor swelling solvent in Argonne Premium Coal Samples (APCS), Illinois #6, Beulah-Zap and Lewiston-Stockton when such a solvent is spiked with various amounts of the strong swelling solvent, pyridine. The unexpected up-take can be explained in terms of four different processes: (1) disruption of weak hydrogen bonds which isolate the interconnected micropore system; (2) disruption of weak hydrogen bonds which protect individual micropores; (3) competition of pyridine for the active sites involved in the hydrogen bonds or the "poisoning" of active sites; and (4) disruption of stronger hydrogen bonds within the macromolecules which causes an opening of the structure. When more than 5% pyridine is used, no additional disruption of the hydrogen-bonded network occurs. The structural changes were monitored by spin probe incorporation which was measured by EPR spectroscopy.

INTRODUCTION

In swelling coals with chlorobenzene, it has been observed by Green and Larsen that when small amounts (0.35 mmol/g coal) of pyridine are added to chlorobenzene, the up-take of chlorobenzene by the coal is dramatically increased.[1] Since the EPR spin probe method has been shown to be very sensitive to changes in the physical and chemical structure of coal during this swelling process,[2] it was thought that some insight into the effect of pyridine on the coal structure could be gained by applying this method to a binary swelling solvent. Toluene was used as the swelling solvent because it does not significantly swell the coal or disturb any cross-linking, so that the interactions between the coal structure and pyridine can be studied.

Previously, Painter has asserted that hydrogen bonds in coal are short lived and do not make major contributions to the cross-linked structure.[3] A recent model assumes that coal is made up of interconnected chains which are solubilized during this swelling process.[4] These connected chains have segments referred to as dangling ends, whose mobility is limited by the surrounding solubilized chain segments suggesting a dynamic structure for coal during the swelling process. The same conclusion can be reached from the results of short term oxidation studies,[5] where removal of water during exposure to dry gas causes changes in as little as 30 seconds. It is possible that hydrogen bonding can establish cross-linking within a macromolecule causing a blockage of the micropore areas, making them inaccessible to guest molecules until they are disrupted by a swelling solvent as supported by observations of Larsen and Wernett.[6] It was observed that the surface area measured for Beulah Zap lignite by N_2 or hydrocarbon surface analysis was 30 times less than by CO_2 surface analysis. This was attributed to the greater solubility of CO_2 in coal and it was concluded that an interconnected micropore network does not exist.

Two assumptions are necessary to explain the observations made in the current study: one, that coal has a dynamic structure and two, that hydrogen bond interactions form cross-links which inhibit accessibility of guest molecules to the coal micropores. The two spin probes used in this study were TEMPAMINE (VII) and TEMPO (VIII) (Figure 1). These compounds have similar molecular volumes, but VII contains an amino group which can interact with hydrogen bonding sites in the coal structure.

EXPERIMENTAL

Swelling solvent/spin probe solutions were prepared in 1 millimolar concentrations of VII or VIII in toluene. Each spin probe solution was split into 16 aliquots of 10 mL and spiked with 0% to 9% pyridine.

APCS coal samples (Beulah-Zap, Illinois #6 and Lewiston-Stockton) were opened under argon and 30 mg portions were immediately placed into vials and covered with 2 mL of a toluene spin probe solution spiked with pyridine. Each sample was then swelled for 18 hours and worked up as previously described.[7] The concentration of the incorporated spin probes was determined by EPR spectroscopy.

RESULTS AND DISCUSSION

Illinois #6 Subbituminous Coal

The retention of spin probe VII (amine substitutent) in Illinois #6 is shown in Figure 2. It can be seen that oscillations occur in the concentration of spin probe retained as the amount of pyridine that is added to the swelling solvent is increased. These oscillations decrease in intensity as the concentration of pyridine in the solvent solution is increased up to 2% pyridine in toluene. From a 2% up to 5% pyridine concentration (not shown) there is no significant change in the retention of spin probe VII. The largest changes in spin probe retention are observed for concentrations of pyridine less than 0.5%. A three fold increase in spin probe retention is observed upon the addition of 500 ppm pyridine (0.05%) to the toluene swelling solvent.

Figure 3 illustrates the effect of pyridine concentration in toluene on the retention of spin probe VIII in Illinois #6, where the size of the probe is the controlling factor. The effects are similar to those observed for the retention of spin probe VII, although the extent of retention is decreased by 90%. Significant oscillations in spin probe retention are observed for concentrations of pyridine less than 2%. As above, increases in pyridine concentration beyond 2% have very little effect on the retention of spin probe VIII.

Since retention of spin probe VII was much greater than that observed for spin probe VIII, it seems that structural changes, brought about by small amounts of pyridine, provide for significantly increased accessibility of the spin probe to active sites in Illinois #6 APCS coal. The enhanced retention of VII indicates that the active sites are capable of strong interactions with the amino group.

The fact that the addition of 0.1% pyridine causes a large decrease in retention for both spin probes shows that a structural change is primarily responsible since spin probe VIII has no functional interactions. The decrease in retention of spin probe VIII indicates either that the structure of the coal collapsed, blocking access to the coal micropores, or that the structure opened up to such a large extent that the spin probes could not be trapped. It seems likely at this point that the structure is opened to an extent such that the spin probes are removed during the cyclohexane wash since the concentration of spin probe VII is still greater than the retention observed in the absence of pyridine. Evidently very small amounts of pyridine open the structure of the coal enough so that "pockets" of active sites are made accessible to the spin probes.

It is possible that opening the structure only slightly allows for diffusion of the spin probes into the structure, while somewhat greater opening of the structure allows for pockets to be formed which trap the spin probes more effectively. In this way, the coal pockets could trap polar spin probes of the requisite size with hydrogen bond interactions exactly like an inclusion compound (as opposed to a simple intercalation process). As the structure is opened further, the larger pockets can no longer trap the guest molecules, and so the retention of the spin probes in the structure decreases.

At 0.2% pyridine, the concentration of the retained spin probe VIII drops even further; however, the retention of spin probe VII increases again. This shows that the structure has opened even further (decrease in spin probe VIII), allowing greater accessibility to hydrogen-bonding sites (increase in spin probe VII), but not creating any additional pockets which might trap the non-hydrogen bonding probes (spin probe VIII).

As the amount of pyridine is increased to 0.4%, a decrease in retention is observed for spin probe VII while an increase in retention is observed for spin probe VIII. This indicates that pyridine causes a poisoning of the active sites available for interaction with the polar spin probe, while at the same time opening the structure to create more areas that are able to trap small spin probes. It should be noted that the amount of amino substituted spin probes retained at this pyridine concentration is still much greater than that of the non-substituted spin probes, indicating that there is still a significant number of active sites available for trapping polar spin probes.

At 0.6% pyridine, an increase in retention is observed for spin probe VII while a decrease is observed for spin probe VIII. At this point and beyond, further oscillations in the retention of each spin probe appear to be due to competing processes of opening micropores, opening larger structural areas, and poisoning of active sites with pyridine.

With higher concentrations of pyridine both the period and the amplitude of the oscillations decreased. After the concentration of pyridine reached 10%, the spin retention observed is similar to that observed for pure pyridine. The data suggest that complete structural opening occurs so that if this is desired, it may be possible to achieve this goal without wasting large amounts of an expensive, toxic, strong swelling solvent.

Beulap-Zap Lignite

Spin probe VII retention in Beulah-Zap lignite swelled in toluene spiked with up to 1.2% of pyridine is expressed as a function of pyridine concentration in Figure 4. Again an oscillatory behavior is observed for spin probe retention as the concentration of pyridine in the swelling solvent solution is increased. Similar to the behavior of Illinois #6, the oscillations observed for the retention of spin probe VII in Beulah-Zap have decreasing periods as the concentration of pyridine is increased. Increasing the pyridine concentration above 4% has little effect on the amount of spin probe retention. It is likely that the structure of the lignite has then been completely opened by disrupting all hydrogen bonded networks, as was observed when pure pyridine was used as the swelling solvent.

The retention of spin probe VIII (size dependence) in Beulah-Zap lignite as a function of pyridine concentration in the toluene swelling solvent is shown in Figure 5. Oscillatory behavior similar to that of Illinois #6 is observed. However, after 0.6%, additional pyridine has a negligible effect on the incorporation of the spin probe. Addition of 100 ppm pyridine (0.01%) to the swelling solvent for Beulah-Zap has almost no effect on the retention of spin probe VIII. When the concentration of pyridine is increased to 200 ppm (0.02%), a large increase in the retention of spin probe VIII is observed, while a small, yet significant decrease in the retention of spin probe VII is observed. The large increase in spin probe VIII retention indicates that hydrogen bonds which block access to the interconnected micropore network have been disrupted without significantly affecting the macromolecular structure. Although a greater number of micropores was made available, a decrease in the retention of spin probe VII was observed. This would seem to indicate that in Beulah-Zap the pyridine necessary to provide initial access to the micropore structure competes significantly for the active hydrogen bonding sites available to the amino spin probes.

As the concentration of the pyridine in the swelling solvent is increased from 200 ppm to 500 ppm (0.05%), a large decrease in the retention of spin probe VIII occurs, but a corresponding increase in the retention of spin probe VII is observed. The large decrease in retention of spin probe VIII indicates that the macromolecular structure was opened to a significant extent. This disruption of hydrogen bonds in the macromolecular structure caused a dramatic increase in the available active sites for hydrogen-bonded interactions, as evidenced by the large increase in retention of spin probe VII.

A further increase in the concentration of pyridine to 700 ppm (0.07%) results in an increase in retention of spin probe VIII and a huge decrease in retention of spin

probe VII. Again, additional micropore structure is made available to guest molecules (indicated by an increase in spin probe VIII retention), but as the concentration of pyridine approaches the concentration of the spin probes, a large percentage of the active sites in the micropore system is poisoned (indicated by the large decrease in spin probe VII retention).

When the concentration of pyridine is 0.1%, a decrease in retention of both spin probes is observed. At this point, the macromolecular structure is opened to such an extent that the spin probes can no longer be trapped in the available micropores.

Further increases in pyridine concentration do not significantly affect the retention of spin probe VIII. The retention of spin probe VII continues to oscillate as the concentration of pyridine increases. At this point the structure of the coal is opened extensively. Variations in the retention of spin probe VII are primarily due to increases in available micropore structure and decreases in active sites due to pyridine site competition.

The observed data can be explained in terms of the following four processes: one, disruption of weak hydrogen bonds which protect or isolate the interconnected micropore system; two, disruption of weak hydrogen bonds which protect individual micropores; three, competition of pyridine for the active sites capable of establishing hydrogen bonds or the "poisoning" of active sites; four, disruption of stronger hydrogen bonds within the macromolecular structure which causes more extensive opening of the structure. The contributions of each of these factors to the spin probe retention with increasing concentrations of pyridine vary to a significant extent up to 1% pyridine. At concentrations above 1% pyridine, the first factor becomes less significant, and variations in the others require greater change in pyridine concentration.

The spin probe retention does not vary to such a degree with percent added pyridine in a higher rank coal such as Lewiston-Stockton where a larger amount of covalent cross-linking and a smaller degree of hydrogen bonding occur. Furthermore, it was found that the spin probe VIII retention as a function of % added pyridine decreased nearly exponentially. The reduced hydrogen bonding in the higher rank coals is reflected by the reduced number of available micropore structures and decreases in active sites due to pyridine site competition.

CONCLUSION

Inclusion of guest molecules into the macromolecular structure of coal can be achieved by spiking a "poor" swelling solvent with as little as 100 ppm of a strong swelling solvent. The optimum amount varies with rank. Dramatic oscillations in spin probe retention are most severe below 0.5% for IL and below 0.1% pyridine for BZ and LS. Above this amount any additional break-up of the hydrogen-bonded structure is not detectable by use of spin probes.

ACKNOWLEDGMENT

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Figure 1
Spin probes VII and VIII.

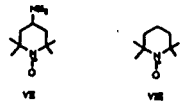


Figure 2
The retention of spin probe VII in Illinois #6 APCS coal after swelling with toluene spiked with pyridine.

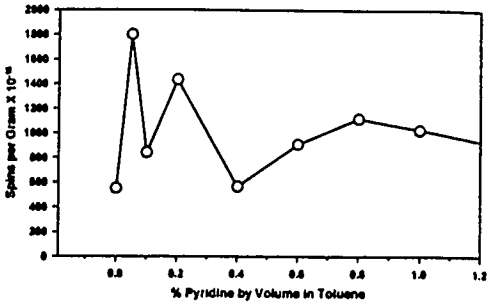


Figure 3
The retention of spin probe VIII in similarly swelled Illinois #6 APCS coal.

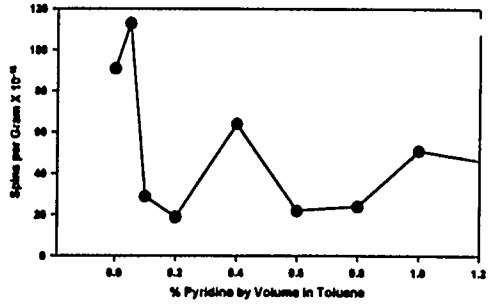


Figure 4
The retention of spin probe VII in similarly swelled Beulah-Zap APCS coal.

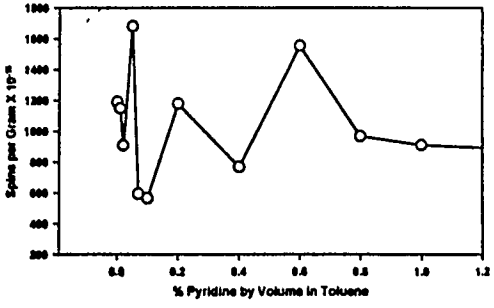
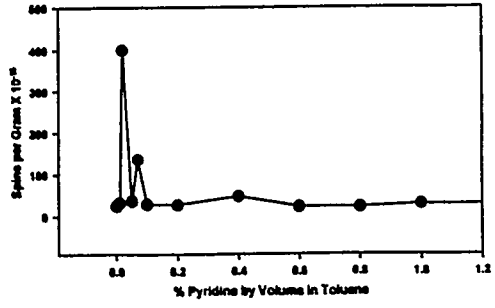


Figure 5
The retention of spin probe VIII in similarly swelled Beulah-Zap APCS coal.



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