SOLVENT AND PRETREATMENT EFFECTS ON COAL SWELLING

Rowena J. Torres-Ordonez, Elaine M. Quinga, and Donald C. Cronauer
Amoco Oil Company, PO Box 3011, Naperville, IL 60566

Keywords: Coal, solvent swelling.

ABSTRACT

Swelling ratios were determined with a wide variety of solvents and solvent blends using pulverized samples of Black Thunder, (WY) subbituminous, Burning Star (IL) bituminous, and Martin Lake (TX) lignite. Experiments were also conducted with 8 x 60 mesh raw and sulfurous acid-treated Black Thunder coal. Only marginal levels of swelling were observed for the hydrocarbon solvents, while hetero-functional solvents enhanced swelling ratios. Oxygenates gave equilibrium swelling ratios, Q, in the range of 1.15 to 1.6, with tetrahydrofuran as the most effective. Selected nitrogen-containing solvents and dimethyl disulfide were also effective, with Q ratios ranging from 1.6 to 2.7. As a result of sulfurous acid-treatment to remove the alkali and alkaline earth ions, the selling of Black Thunder coal was enhanced. The effects of coal type may be attributed to the interaction of the solvent with the bonds present in both the raw and acid-treated coals. Experiments with blends of effective and non-effective solvents gave much greater Q ratios than those expected from an linear combination of the two solvents. The greatest synergisms were observed with Black Thunder and Burning Star coals.

INTRODUCTION

Van Krevelen[1] proposed that coals are three-dimensionally cross-linked macromolecular networks. The area was expanded upon.[2-5] When brought into contact with most organic solvents, coals absorb the solvent and swell. The two factors which control the amount of swelling are the magnitude of the solvent-coal interactions and the cross-link density of the coal. Another aspect is that coals can behave as either a glass or rubber with a transition zone. In a glassy state, the macromolecular chains are constrained and diffusion through the coal matrix is quite slow. In the rubbery state, the macromolecular chains can move relatively freely, and diffusion rates in the solid approach those in liquids. Some solvents can cause a glass-to-rubber transition to occur in coals.

Coal swelling solvents can be divided into two classes: non-hydrogen bonding and hydrogen bonding. The swelling ratios of the coal samples in non-hydrogen bonding solvents are significantly less than those in hydrogen bonding solvents. The most effective solvents are those containing a nitrogen or oxygen atom possessing an unshared pair of electrons. The strong hydrogen bonding solvents replace the coal-coal hydrogen bonds with new coal-solvent hydrogen bonds. If the coal-coal hydrogen bonds are active cross-links, the replacement would result in a lower cross-link density which would cause swelling to increase. The weak hydrogen bonding solvents result in less swelling since more coal-coal hydrogen bonds remain intact.

EXPERIMENTAL

Coal swelling experiments were made using (1) Martin Lake lignite, (2) Black Thunder subbituminous, and (3) Illinois No. 6 bituminous coals. The coals were dryed and handled in nitrogen whenever possible. The coals were either sieved and ground to -325 mesh under nitrogen, or used as coarse (8 x 60 mesh) material. Samples of raw and SO_2-treated Black Thunder coal, that were partially dried to 8 wt% moisture content at ambient temperature in nitrogen, were also used.

The experimental procedure for the first set of samples consisted of placing samples of dry coal in a 1 mm. o.d. tube followed by centrifuging for 60 minutes. The height of the coal was measured as h_1. After breaking up the column of packed coal, solvent in excess was introduced and the tube was vigorously shaken to ensure thorough mixing. The slurry was centrifuged after specified times and the height was measured as h_2. The swelling ratio was defined as the ratio of the resulting heights of swelled and raw coal ($Q = h_2/h_1$). In the experiments with the coarse coal samples, 10 ml conical centrifuge tubes were used.

RESULTS AND DISCUSSION

Reproducibility: Experiments were made to determine reproducibility using two technicians to make multiple parallel tests. Reproducibility was good. At low swelling ratios, such as those of the methanol runs (average Q of 1.28), the standard deviation averaged about ±0.06. At high swelling ratios (tetrabutyl ammonium hydroxide, Q averaging about 2.5), the standard deviation averaged about ±0.14.

Effect of Solvent Type and the Interaction with Coal Pretreatment: The results of swelling ratio experiments using finely pulverized (through 325 mesh) coal samples are given in Table I. Only marginal levels of coal swelling were observed for the hydrocarbon solvents including hexane, cyclohexane, single-ring aromatics, and tetralin.

Swelling greatly increased with the introduction of hetero-functionality. Equilibrium (96 hour contact) swelling ratios of the three coals with alcohols and ketones fell in the range of 1.15 to 1.4. There appeared to be no consistent effect of the type (molecular weight) of alcohol or ketone, but the Black Thunder coal swelled to a greater extent than the other coals. Cresol was a more effective swelling agent than the above oxygenates in the case of Illinois No. 6 coal, but it was the same for the other coals. The results with methyl acetate were the same as those of the above oxygenates. Tetrahydrofuran (THF) was a significantly more effective coal swelling solvent than the other oxygenates. The Q ratios ranged from 1.38 to 1.63.

The nitrogen-containing compounds varied greatly in their effectiveness to swell these coals. The highly polar compound, tetrabutylammonium hydroxide (TBAH), was very effective with a range of Q ratios of 2.18 to 2.66. Aniline was quite effective for Illinois No. 6 and Black Thunder coals (1.94 and 1.64, respectively), but it was essentially ineffective (1.19) for Martin Lake lignite. Nitrobenzene was poor for all three coals (1.11 to 1.19).

Dimethylsulfoxide was tested due to its unusual solvent properties in other systems. It was found to be particularly effective for the Black Thunder and Illinois No. 6 coals and moderately effective for Martin Lake lignite (2.39, 2.15, and 1.63, respectively).

The results of coal swelling experiments carried out with 8X60 mesh size fractions of both raw and SO_2-treated Black Thunder coal are given in Table II. There appeared to be little or no effect of coal particle size upon the swelling ratio. However, the SO_2-treated coal swelling was significantly greater than that of the raw coal. The removal of alkali and alkaline earth ions from the subbituminous coal reduced the interaction of coal species with each other.

The above differences in swelling are attributed to the interaction of the solvent with the various bonds present in coal. The low rank coals contain significant amounts of ionic and hydrogen bonds due to the presence of a relatively large number of polar functional groups, while the high rank coals contain more charge transfer complexes because of their higher aromatic content. TBAH, which is a very basic solvent, interacts with the ionic and hydrogen bonds readily, thus swelling the Martin Lake lignite to the greatest extent. This is followed by Black Thunder coal and Illinois No. 6. On the other hand, THF disrupts charge transfer complexes, which are predominant in Illinois No. 6, a higher rank coal, thus resulting in a swelling trend opposite to that of TBAH. The increase of swelling ratio in the case of SO_2 treatment is an obvious extension of this theory, especially with the removal of divalent metal ions, such as calcium.

Effect of Solvent Blends: The results of experiments made with 325 mesh coal samples and blends of tetralin (TET) and isopropanol (IPA) are shown in Table I and Figure 1. There was a high level of synergism with an advantage of using these blends over the pure solvents. In all cases, the swelling ratios were much greater than those derived from a linear correlation between the pure solvents.
As shown in Figures 2 and 3, the synergism of coal swelling solvents also was demonstrated for methanol/water, dimethyl sulfoxide/tetralin, methanol/tetralin, and isopropanol/water. Experimentation was also carried out with the 8X60 mesh fractions of raw and SO_2-treated Black Thunder coal, as given in Table II. Again, there were high levels of synergism of solvent blends with both samples of coal.
There is a distinct advantage of using solvent blends to swell coal, because relatively low levels of swelling agent would be needed to be effective in treating coal feed slurries for a liquefaction plant.

CONCLUSIONS

The following conclusions are drawn from the coal swelling studies:
1. Only marginal levels of coal swelling were observed for the hydrocarbon solvents including paraffins, cycloparaffins, and aromatics.
2. Swelling ratios were greatly increased with the use of solvents having heteroatom functionality.
3. The effectiveness of the oxygenates increased in the following order: alcohols, ketones, methyl acetate < cresol < tetrahydrofuran.
4. The swelling ratios generated by nitrogen-containing compounds increased as follows: nitrobenzene < aniline < tetrabutylammonium hydroxide.
5. High coal swelling ratios were observed with dimethylsulfoxide.
6. Solvent synergism was observed in that the swelling ratios of solvent blends were much greater than those derived from a linear correlation between the pure solvents.

ACKNOWLEDGMENT

This project was supported in part by DOE under Project DE-AC22-91PC91051, entitled "Advanced Liquefaction Using Coal Swelling and Catalyst Dispersion Techniques."

REFERENCES

1. Van Krevelen, D. W., Coal; Elsevier; Amsterdam, 1961, and Fuel 1966 45, 99, 229.
2. Vahrman, M., Fuel 1970, 49, 5.
3. Palmer, T. J., Vahrmen, M., Fuel 1972, 51, 22.
4. Shapiro, L-L. D.; Al'terman, L. S., Solid Fuel Chem. 1977 11(3), 13.
5. Larson, J. W., Lee, D., Shawver, S. E., Fuel Process. Techn. 1986 12, 51.

Table I
SWELLING RATIO OF COAL/SOLVENT BLENDS
(325 Mesh Coal with 1 ml Winthrobe Tubes)

	Black Thunder		Illinois No. 6		Martin Lake Lignite	
Solvent/Time	24 Hr	96 Hr	24 Hr	96 Hr	24 Hr	96 Hr
Hexane	--	1.01	--	1.00	--	0.95
Cyclohexane	--	1.00	1.00	1.00	--	--
Benzene	--	1.12	--	1.06	--	1.14
Toluene	--	1.04	--	1.16	--	1.00
Xylene	--	1.02	--	1.04	--	1.05
Tetralin	1.00	1.04	0.96	1.02	1.02	1.03
Methanol	1.28	1.35	1.16	1.23	1.43	1.36
Ethanol	--	1.31	--	1.26	--	1.24
Isopropanol	1.30	1.39	1.06	1.15	1.14	1.25
Isopropanol	1.30	1.39	1.06	1.15	1.14	1.25
33% Tetralin/67% IPA	1.40	1.53	1.31	1.43	1.18	1.37
67% Tetralin/33% IPA	1.39	1.47	1.34	1.49	1.18	1.36
80% Tetralin/20% IPA	1.34	1.42	1.22	1.35	1.10	1.23
90% Tetralin/10% IPA	1.22	1.33	1.13	1.19	1.10	1.18
Tetralin	1.00	1.04	0.96	1.02	1.02	1.03
Cresol	1.16	1.29	1.28	1.48	1.13	1.20
Acetone	--	1.32	--	1.24	--	1.25
Methyl Ethyl Ketone	1.32	1.34	1.29	1.29	1.27	1.3
Methyl Acetate	1.28	1.34	1.20	1.20	1.25	1.25
Tetrahydrofuran	1.45	1.53	1.50	1.63	1.36	1.38
Chloroform	--	1.17	--	1.19	--	1.03
Chlorobenzene	1.08	1.08	1.07	1.16	1.09	1.12
Nitrobenzene	1.11	1.15	1.18	1.19	1.08	1.11
Aniline	1.41	1.64	1.71	1.94	1.12	1.19
Tetrabutylammonium Hydroxide	2.05	2.45	1.59	2.18	2.04	2.66
Dimethyl Sulfoxide	2.19	2.39	2.08	2.15	1.52	1.63

Table II

SWELLING RATIO OF THREE SAMPLES OF BLACK THUNDER COAL
(10 ml Conical Centrifuge Tubes)

	Untreated -325 Mesh				Untreated 8 x 60 Mesh				SO_2-Treated 8 x 60 Mesh			
Solvent/Time	2 Hr	4 Hr	24 H4	96 Hr	2 Hr	4 Hr	24 Hr	96 Hr	2 Hr	4 Hr	24 Hr	96 Hr
Isopropanol	--	--	--	--	1.20	--	1.25	--	1.27	--	1.42	--
50% IPA/50% H_2O	--	--	--	1.38	--	--	--	--	--	--	1.40	1.40
20% IPA/80% Tetralin	1.16	--	1.24	--	1.25	--	1.48	--	1.33	1.38	1.41	1.41
20% IPA/80% Toluene	--	--	--	--	1.18	--	1.21	--	1.26	--	1.42	--
30% IPA/70% Toluene	--	--	--	--	1.20	--	1.24	--	1.38	--	1.51	--
40% IPA/60% Toluene	--	--	--	--	1.18	--	1.30	--	1.32	--	1.56	--
Methanol	1.34	1.43	1.43	--	--	--	1.26	1.26	1.24	--	--	--
(repeat)	--	--	1.19	1.33	--	--	--	--	1.18	--	--	--
70% MeOH/30% H_2O	--	--	1.32	1.40	1.24	--	1.24	--	--	--	1.25	--
50% MeOH/50% H_2O	--	--	1.38	1.36	--	--	--	--	--	--	1.21	--
30% MeOH/70% H_2O	--	--	1.21	1.28	--	--	--	--	--	--	--	--
25% MeOH/75% Tetralin	1.43	1.46	1.49	--	--	--	--	--	--	--	--	--
Acetone	--	--	--	--	1.23	--	1.24	--	1.52	--	1.52	--
Tetrahydrofuran	--	--	1.42	1.55	--	--	1.54	1.59	1.83	1.94	2.07	2.08
70% THF/30% H_2O	--	--	1.87	1.91	1.71	--	1.86	--	1.93	--	2.15	--
50% THF/50% H_2O	--	--	1.78	1.85	--	--	--	--	--	--	--	--
30% THF/70% H_2O	--	--	1.52	1.60	1.36	--	1.49	--	1.43	--	1.52	--
20% THF/80% H_2O	1.40	1.46	1.46	--	--	--	--	--	--	--	--	--
10% THF/90% H_2O	1.24	1.24	1.31	--	--	--	--	--	--	--	--	--
5% THF/95% H_2O	1.40	1.38	1.41	--	1.14	--	1.16	--	1.16	--	1.16	--
(repeat)									1.17	--	1.15	--
Aniline	--	--	--	--	1.17	--	1.37	--	1.22	--	1.68	--
(repeat)									1.21	--	1.97	--
Dimethyl Sulfoxide	2.05	2.37	2.37	2.37	1.60	--	2.09	--	2.28	2.35	2.41	2.58
10% DMSO/90% Tetralin	1.39	1.49	1.58	--	1.21	--	1.60	--	1.41	--	1.83	--
5% DMSO/95% Tetralin	1.19	1.27	1.32	--	1.13	--	1.43	--	1.23	--	1.44	--
												--

Figure 1
Swelling Ratios of 325-mesh Coal with the IPA/Tetralin System

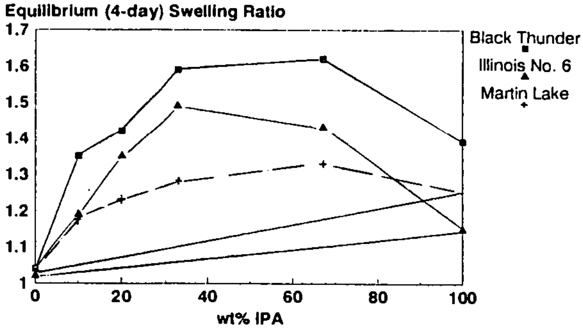

Figure 2
Swelling Ratios of 325-mesh Black Thunder Coal with the THF/Water System

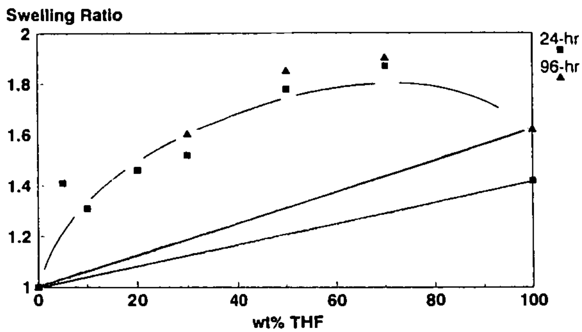

Figure 3
Swelling Ratios of 325-mesh Black Thunder Coal with Solvent Blends