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LIQUID CHROMATOGRAPHIC ANALYSIS OF COAL SURFACE
PROPERTIES

Final Report for the Period
September 1991 to February 1995

By
K. C. Kwon

March 1996

Work Performed Under Contract no DE-FG22-91PC91283

For
U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

By
Tuskegee University
Tuskegee, Alabama

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Liquid Chromatographic Analysis of Coal Surface Properties

Final Report

For the Period September 1991 - February 1995

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ABSTRACT

Experiments on equilibrium adsorption loadings of various probe compounds on 60 - 200 mesh Illinois #6 coal (PSOC-1539), Adaville #1 coal (PSOC-1544), Wyodak coal (PSOC-1545) and Pittsburgh #8 coal (PSOC-1549) were performed. The probe compounds include m-cresol, p-cresol, o-cresol, phenol, n-octanol, n-heptanol, n-propanol, isopropanol, n-butanol, s-butanol, 2-butanol, t-butanol, 2-naphthol, cyclohexanol, 2-methyl-1-pentanol (2M1P), 4-methyl-2-pentanol (4M2P), benzene and toluene. Equilibrium adsorption of various probe compounds on the coals was measured with the inverse liquid chromatography method.

Experiments on flotation of various 60 - 200 mesh treated coals such as Illinois #6 coal (PSOC-1539), Adaville #1 coal (PSOC-1544), Wyodak coal (PSOC-1545) and Pittsburgh #8 coal (PSOC-1549) were performed. The chosen coals were treated with steam, nitrogen and air at 1 atm and 125 - 225°C for 24 hours. The coals were treated with water as well as 20 - 1000 ppm aqueous alcohol solutions for 3-24 hours at 150 - 225°C. The coals also were treated with 20-ppm alcohol aqueous solutions for 1-24 hours at the 0.002-g/min mass flow rate of alcohol aqueous solutions and at 225°C. Flotation experiments were conducted with a 500-cm³ batch-type micro flotation apparatus, introducing nitrogen at the bottom of the apparatus.

This final report was prepared with the experimental data obtained during the period of September 1991 - March 1994.

INTRODUCTION

The main objectives of this research project are to refine further the inverse liquid chromatography technique for the study of surface properties of raw coals and treated coals in water, to evaluate relatively surface properties of raw coals, and treated coals by inverse liquid chromatography, and to investigate mechanisms on equilibrium adsorption loadings of probe compounds on various coals.

Coals such as Pittsburgh #8 coal, Illinois #6 coal, Adaville #1 coal and Smith-Roland Wyodak coal are chosen as representatives of high-rank bituminous coal, high volatile bituminous coals and subbituminous coal, respectively. Their proximate analysis, ultimate analysis, and sulfur analysis of the chosen coals are shown in Table 1.

Table 1. Proximate analysis (as received), ultimate analysis (dry basis), and sulfur analysis

PSU #	DECS-2	DECS-7	DECS-8	DECS-12
Seam Name	Illinois #6	Adaville #1	Smith-Roland	Pittsburgh #8
Coal Rank	HVC	HVC	Subbit C	HVA
<u>Proximate Analysis</u>				
Moisture	10.43	17.34	28.42	2.40
Ash	14.47	3.45	9.90	10.00
Volatile	34.16	38.11	32.38	35.16
Fixed Carbon	40.93	41.11	29.30	52.44
<u>Ultimate Analysis Dry, wt %</u>				
Ash	16.16	4.17	13.83	10.25
Carbon	65.49	73.90	64.14	74.78
Hydrogen	4.56	5.30	4.51	5.11
nitrogen	1.11	0.99	0.86	1.23
Total Sulfur	4.52	0.98	0.73	1.12
Oxygen (Diff)	8.16	14.66	15.93	7.51
<u>Sulfur Forms, wt %</u>				
Pyritic	2.27	0.10	0.28	0.38
Sulfatic	0.01	0.01	0.02	0.01
Organic	2.24	0.87	0.43	0.73
Total	4.52	0.98	0.73	1.12

Hydrophilicity, hydrophobicity and aromaticity of surfaces for either raw coals or treated coals in water are relatively determined by evaluating equilibrium physical/chemical adsorption of probe compounds on various raw coals and treated coals to compare affinities of coals for water.

Alcohols such as ethanol, isopropanol, isobutanol, tert-butanol, heptanol, 2-methyl-1-pentanol, 4-methyl-2-pentanol (methyisobutyl carbinol), n-octanol, and cyclohexanol as probe compounds are utilized to evaluate hydrophilicity of coals.

Effects of molecular structures of probe compounds on their adsorption on the chosen coals were investigated by using isomers such as propanols, butanols and pentanols.

Experiments on equilibrium adsorption loadings of aliphatic alcohols such as 2-methyl-1-pentanol and 1-heptanol on Illinois #6 coal, Adaville #1 coal, Smith-Roland Wyodak coal and Pittsburgh #8 coal were performed in aqueous solutions at room temperature to relate adsorption loadings of these compounds to flotation percentages of these coals equilibrated with their aqueous solutions at room temperature.

Higher alcohols such as 1-heptanol and 1-octanol were used to investigate adsorption mechanisms as well as adsorption models on their equilibrium adsorption loadings on Illinois #6 coal in 5 - 320 ppm aqueous solutions. Aromatic compounds such as benzene and toluene as probe compounds are used to examine aromaticity of coal surface. Aromatic acids such as o-cresol, m-cresol, p-cresol, phenol and β -naphthol are used to detect aromatic acidic sites of coal surface.

Aromatic compounds such as benzene and toluene are used in studying mechanisms on their adsorption on the coals. Phenol was employed to identify an adsorption model on its equilibrium adsorption on Adaville #1 coal, Smith-Roland Wyodak coal, Illinois #6 coal, and Pittsburgh #8 coal in 5 - 320 ppm aqueous solutions.

Cresols such as m-cresol, p-cresol and o-cresol were utilized as probe compounds to investigate aromatic acidities of Illinois #6 coal. P-cresol was used to find an adsorption model on its equilibrium adsorption loadings on Illinois #6 coal in 5 - 320 ppm aqueous solutions.

The research was focused on evaluating relatively change in surface properties of treated coals, and evaluating floatabilities of treated coals in water only as a flotation medium in conjunction with equilibrium adsorption loadings of probe compounds on various coals. The coals were treated with steam, nitrogen and air at 125 - 225°C. Experiments on flotation of treated coals were conducted in a 500-cm³ batch-type flotation apparatus at room temperature, using water only as a flotation medium.

This research also was centered on pursuing for optimum treatment conditions of enhancing floatability of Illinois #6 coal and examining various prospective treatment reagents by testing floatability of the treated coal in water only. The coal was treated with water, 1-propanol and isopropanol and 1-heptanol at 150 - 225°C. Concentrations of alcohols in aqueous solutions are 5-1000 ppm. Mass flow rates of aqueous solutions during treatment experiments are 0.001 - 0.05 g/min. These chosen coals were treated with 20-ppm alcohol aqueous solutions for 1-24 hours at the 0.002-g/min mass flow rate of alcohol aqueous solutions and at 225°C.

Effects of molecular structures of treatment reagents on floatability of treated coals were investigated with the flotation method. Illinois #6 coal and Wyodak coal were treated with 20-ppm aqueous solutions of various reagents such as water, 1-propanol, isopropanol, 1-butanol, 2-butanol, isobutanol, t-butanol, and hydrogen chloride at 0.002 g/min mass flow rate and 225°C, using nitrogen as a carrier gas for a selected solution. Experiments on flotation of treated coals also were conducted in a micro batch-type flotation apparatus at room temperature to examine change in floatability of the treated coals. Water treatment improves significantly floatability of Wyodak coal.

EXPERIMENTS

Hydrophilicity, hydrophobicity and aromaticity of surfaces for either raw coals or treated coals in water are relatively determined by evaluating equilibrium physical/chemical adsorption of probe compounds on various raw coals and treated coals to compare affinities of coals for water. Concentrations of probe compounds at various contact durations are determined with a

high pressure liquid chromatograph (HPLC), equipped with a RI detector. Equilibrium adsorption experiments are performed in a packed column at room temperature. A given amount of coal particles is packed in an empty HPLC column. An aqueous solution of a probe compound of interest is passed through the bed packed in the column. Concentrations of the effluent from the column are evaluated with the RI detector

Experiments on equilibrium adsorption of various alcohols on the chosen coals were performed in aqueous solutions at 25°C. The coals were pulverized and sieved to obtain 60-200 mesh coal particles. Sieved 60-200 mesh coal particles were washed with distilled water (DW) to get rid of any water-soluble organic compounds on the surfaces of the coal particles. Coal particles were submerged under water overnight, and then filtered next day to remove organics-dissolved water from coal particles. These washing processes continued for 3 weeks. Washed coal particles were dried at 110°C for 4 hours.

Dry coal particles of 0.75 - 2.5-g were introduced into an empty column. The coal particles packed in the column were washed with DW for 10 hours to eliminate any water-soluble contaminants introduced in the coal-packed column during the process of packing dry coal particles into the column.

Experiments on equilibrium adsorption loadings of aromatic compounds such as benzene and toluene on Illinois #6 coal, Adaville #1 coal, Smith-Roland Wyodak coal and Pittsburgh #8 coal were performed in aqueous solutions at room temperature to identify the role of methyl group of toluene in the adsorption process.

An empty LC column was filled with 2.5-g 60 - 200 mesh coal, and then placed in an oven to maintain the coal sample at a desired temperature. The coals were treated with steam, nitrogen and air for 24 hours at 125 -225°C. Flotation experiments of the treated coals were conducted at room temperature, using distilled water only as a flotation medium.

Water, methanol, 1-propanol, isopropanol and 1-heptanol were selected as treatment reagents. Various treatment conditions were examined to identify optimum treatment conditions of Illinois #6 coal. Concentrations of treatment reagents in aqueous solutions vary

from 5 ppm to 1000 ppm. Treatment temperatures are 150 - 225°C. Ranges of treatment durations are 3 -24 hours. Mass flow rates of aqueous solutions are 0.001 - 0.050 g/min. An empty LC column was filled with 1-g 60 - 200 mesh Illinois #6 coal, and then placed in an oven to maintain the coal sample at a desired temperature, introducing aqueous solutions of treatment additives in the coal-loaded column at desired mass flow rates.

Water, 1-propanol, isopropanol, 1-butanol, 2-butanol, isobutanol and t-butanol were selected as treatment reagents. The coals were treated with 20-ppm reagents for 1-25 hours at 225°C, feeding reagent solutions into coal at 0.002 g/min. Nitrogen gas was used as a carrier gas for reagent solutions.

Experiments on flotation of the treated coals were conducted at room temperature, using distilled water only as a flotation medium. Experiments on flotation of the coals were carried on with a 500-cc batch-type micro flotation apparatus at room temperature. Nitrogen gas was introduced at the bottom of the flotation apparatus. Distilled water was used to soak 1-g treated coal overnight prior to flotation experiments.

DISCUSSION ON EXPERIMENTAL RESULTS

Experimental data on equilibrium adsorption loadings of alcohols and ring compounds on 60 -200 mesh Illinois #6 coal were shown in Figures 1 through 6.

Equilibrium adsorption loadings of normal alcohols on Illinois #6 coal are plotted against their equilibrium concentrations of 3 - 40 ppm (see Figure 1). Equilibrium adsorption loadings of higher alcohols such as n-heptanol and n-octanol on the coal are much higher than low molecular-weight alcohols such as ethanol, n-propanol and n-butanol.

Relationships between equilibrium loadings and equilibrium concentrations of alcohols are shown to be linear. Equilibrium adsorption loadings of ethanol on the coal are $5 - 20 \times 10^{-6}$ mg/g-coal. Equilibrium adsorption loadings of propanols on the coal are $1 - 100 \times 10^{-6}$ mg/g-coal, while equilibrium adsorption loadings of butanols on the coal are $2 - 190 \times 10^{-6}$ mg/g-coal. Equilibrium adsorption loadings of normal alcohols on the coal increase with increased

numbers of carbons in their molecular formulas, as their aqueous solubilities decrease with increased carbon numbers of molecular fomulas.

Equilibrium adsorption loadings of n-propanol on the coal are $9 - 100 \times 10^{-6}$ mg/g-coal, whereas equilibrium adsorption loadings of isopropanol on the coal are $1 - 38 \times 10^{-6}$ mg/g-coal

(see Figure 2). These observations suggest that the branched alcohol isopropanol is less active than the straight-chain alcohol n-propanol with Illinois #6 coal. Hydroxyl groups of alcohols may be attached to the coal surface rather than hydrocarbon groups of alcohols.

Equilibrium adsorption loadings of butanols on 60 - 200 mesh Illinois #6 coal are 2 - 190×10^{-6} mg/g-coal (see Figure 3). Equilibrium adsorption loadings of n-butanol on the coal are 17 - 184×10^{-6} mg/g-coal, while equilibrium adsorption loadings of s-butanol are 14 - 103×10^{-6} mg/g-coal. Equilibrium adsorption loadings of isobutanol on the coal are 3 - 55×10^{-6} mg/g-coal, whereas equilibrium adsorption loadings of t-butanol on the coal are 2 - 8×10^{-6} mg/g-coal. These data suggest that the straight-chain n-butanol are more active than the branched butanols such as s-butanol, isobutanol and t-butanol with Illinois #6 coal. These facts also reveal that equilibrium adsorption loadings of butanols on the coal increase with reactivities of hydroxyl groups in butanols.

Equilibrium adsorption loadings of ring-containing compounds on Illinois #6 coal are compared in Figure 4. Equilibrium adsorption loadings of double-ring compound 2-naphthol on the coal are 200 - 1200×10^{-6} mg/g-coal, whereas equilibrium adsorption loadings of single-ring compound phenol on the coal are 32 - 276×10^{-6} mg/g-coal. Equilibrium adsorption loadings of o-cresol on the coal are 64 - 166×10^{-6} mg/g-coal. Equilibrium adsorption loadings of cyclohexanol on the coal are 17 - 115×10^{-6} mg/g-coal. Equilibrium adsorption loadings of toluene are much higher than those of the other ring compounds such as 2-naphthol, phenols and cyclohexanol (see Figure 4). This fact may suggest that toluene, the least water-soluble

compound among these ring compound, is chemically adsorbed on the coal. Adsorption of cyclohexanol, the aliphatic ring compound, is lower than the aromatic ring compounds.

Equilibrium adsorption loadings of 2-methyl-1-pentanol on the coal are $5 - 240 \times 10^{-6}$ mg/g-coal with its 5 - 40 ppm equilibrium concentrations, whereas equilibrium loadings of 4-methyl-2-pentanol on the coal are $10 - 90 \times 10^{-6}$ mg/g-coal with its 3 - 30 ppm equilibrium concentrations. Equilibrium loadings of 2M1P on the coal is much higher than those of 4M2P (see Figure 5).

Figure 4. Equilibrium concentration of various ring-containing compounds and their equilibrium adsorption on 2.5-g 60-200 mesh Illinois #6 coal in aqueous solutions at 25°C.

Figure 5. Equilibrium concentration of methyl pentanols and their equilibrium adsorption on 2.5-g 60-200 mesh Illinois #6 coal in aqueous solutions at 25°C.

Experiments on equilibrium adsorption loadings of n-butanol, n-heptanol, n-octanol, phenol, p-cresol and m-cresol on the coals were performed. Equilibrium adsorption loadings of o-cresol are much lower than those of both m-cresol and p-cresol on Illinois #6 coal (see Figures 6).

Experiments on equilibrium adsorption loadings of probe compounds on various coals were performed in the presence of probe compounds with their 5 - 320 ppm equilibrium

concentrations to identify models for adsorption of probe compounds on coals. Probe compounds include 1-butanol, 1-heptanol, phenol and cresol.

Equilibrium adsorption loadings of n-alcohols such as 1-butanol and 1-heptanol on Illinois #6 coal follow the Freundlich adsorption model at relatively low concentrations of the alcohols (up to 150 ppm), as shown in Figure 7.

Equilibrium adsorption loadings of 1-butanol on both Illinois #6 coal and Adaville #1 coal obey the Freundlich model at relatively low concentrations of 1-butanol, whereas equilibrium adsorption loadings of 1-butanol on Smith-Roland Wyodak follows the Langmuir isotherm model (see Figure 8).

Equilibrium adsorption loadings of phenol on Adaville #1 coal, Smith-Roland Wyodak coal, Illinois #6 coal and Pittsburgh #8 coal obey the Langmuir isotherm model for single layer at relatively low concentrations (see figure 9). Equilibrium adsorption loadings of p-cresol also follow the Langmuir isotherm model (see Figure 10).

Equilibrium adsorption loadings of benzene are lower than those of toluene on the four chosen coals. Equilibrium adsorption loadings of both benzene and toluene on Adaville #1 coal and Wyodak coal are higher than those on Illinois #6 coal and Pittsburgh #8 coal. Equilibrium adsorption loadings of aromatic compounds such as toluene and benzene on the four chosen coals obey the Langmuir isotherm model for single-layer adsorption up to 100 ppm in concentrations of probe compounds. (see Figures 11 and 12).

Equilibrium adsorption loadings of both 2M1P and 1-heptanol on Adaville #1 coal are highest, whereas equilibrium adsorption loadings of both 2M1P and 1-heptanol on Pittsburgh #8 coal are lowest among those on the four chosen coals (see Figures 13 and 14). Flotation of Pittsburgh #8 coal with aqueous solutions of both 2M1P and 1-heptanol is highest among the coals, and flotation of Wyodak coal is lowest among the coals. (see Figures 15 and 16).

Figure 11. Equilibrium concentration of benzene and its equilibrium adsorption on 0.75-g 60-200 mesh various coals in aqueous solutions at 25°C.

Figure 12. Equilibrium concentration of toluene and its equilibrium adsorption on 0.75-g 60-200 mesh various coals in aqueous solutions at 25°C.

Figure 13. Equilibrium concentration of 2-methyl-1-pentanol and its equilibrium adsorption on 0.75-g 60-200 mesh various coals in aqueous solutions at 25°C.

Flotation of the coals, equilibrated with aqueous solutions of both 2M1P and 1-heptanol, is plotted against equilibrium adsorption of both 2M1P and 1-heptanol on the coals. Flotation of coal increase with increased adsorption loadings of both 2M1P and 1-heptanol on the coals (see Figures 17 and 18).

Adsorption loadings of 1-heptanol on Illinois #6 coal appear to increase with decreased adsorption temperatures (see Figure 19). These data show that temperature itself significantly affect flotation of Illinois #6 coal.

Figure 16. Flotation of 60-200 mesh various coals, equilibrated with 1-heptanol of various aqueous concentrations at 25°C.

Figure 17. Flotation of 2-methyl-1-pentanol-equilibrated 60-200 mesh various coals, and their equilibrium adsorption of 2-methyl-1-pentanol at 25°C.

Figure 18. Flotation of 1-heptanol-equilibrated 60-200 mesh various coals, and their equilibrium adsorption of 1-heptanol at room temperature.

Experiments on flotation of various 60 - 200 mesh treated coals such as Illinois #6 coal (PSOC-1539), Adaville #1 coal (PSOC-1544), Wyodak coal (PSOC-1545) and Pittsburgh #8 coal (PSOC-1549) were performed. The chosen coals were treated with steam, nitrogen and air at 1 atm and 125 - 225°C for 24 hours.

Flotation experiments of the treated coals were conducted at room temperature, using distilled water only as a flotation medium. Flotation of Wyodak coal, treated with nitrogen gas, is higher than that of untreated coal, and increases with treatment temperatures (see Figure 20). These data may explain that hydrophilic labile functional groups such as hydroxyl group and carboxyl group on the coal surface are detached from the coal during the treatment of the coal with nitrogen.

Flotation of Adaville #1 coal, treated with nitrogen, is higher than that of untreated coal, and increases with treatment temperatures. Flotation of Adaville #1 coal, treated with air at 125 - 150°C, is slightly higher than that of untreated coal, whereas flotation of Adaville #1 coal, treated with air at 175 - 225°C, is slightly lower than that of untreated coal (see Figure 21). These data may indicate that hydrophilic labile functional groups such as hydroxyl group and carboxyl group on the coal surface are detached from the coal during the treatment of the coal with nitrogen. The increase in flotation of Adaville #1 coal is much higher than that of

Wyodak coal by treating these coals with nitrogen. This fact may indicate that there are less detachable labile functional groups on the Adaville #1 coal surface than on the Wyodak coal surface.

Flotation of Illinois #6 coal, treated with nitrogen, is higher than that of untreated coal. Flotation of Illinois #6 coal, treated with nitrogen at 125 - 175°C, increases with treatment temperatures, whereas flotation of Illinois #6 coal, treated with nitrogen at 175 - 225°C, decreases with treatment temperatures (see Figure 22). This observation may indicate that

significant amounts of hydrophilic labile functional groups are not detached from the surface of Illinois #6 coal to improve its flotability by the treatment of the coal with nitrogen.

Flotation of Pittsburgh #8 coal, treated with air, is lower than that of untreated coal, and decreases with treatment temperatures (see Figure 23). These experimental data may show that generation of hydrophilic labile functional groups by oxygen from air is higher than detachment of hydrophilic labile functional groups by nitrogen from air.

A series of experiments on flotation of 60 - 200 mesh treated Illinois #6 coal (PSOC-1539) were performed. The coal was treated with various treatment reagents such as water, methanol, 1-propanol and isopropanol and 1-heptanol for 3 - 24 hours at 150 - 225°C.

Flotation experiments of the treated coal were conducted at room temperature, using distilled water only as a flotation medium. Flotation of Illinois #6 coal, treated with 0.002-g/min 1000-ppm methanol aqueous solution for 3 hours, increases with treatment temperatures (see Figure 24). Flotation of Illinois #6 coal, treated with 0.002-g/min water only for 3-4 hours, also increases with treatment temperatures. These data may suggest that hydroxyl

groups of methanol are reacted with hydrophilic functional groups on the coal surface and hydrophilic functional groups on the coal surface are detached by steam.

Mass flow rates of 1000-ppm methanol aqueous solution, during treating Illinois #6 coal with the solution, increase with decreased flotation of the coal treated at 225°C for 3 hours (see Figure 25). However, mass flow rates of 1000-ppm n-heptanol aqueous solution, during treating Illinois #6 coal with the solution, do not affect significantly flotation of the coal treated for 3 hours at 225°C. This observation may show that some methanol is chemically absorbed into the Illinois #6 coal matrix to increase hydrophilicity of the coal.

Concentrations of alcohols such as methanol and isopropanol in water do not affect significantly flotation of Illinois #6 coal treated for 3 hours at 225°C and 0.002 g/min (see Figure 26).

Experiments on flotation of 60 - 200 mesh treated Illinois #6 coal (PSOC-1539) and Wyodak coal (PSOC-1545) were performed. These coals were treated with 20-ppm reagent aqueous solutions for 1-24 hours at the 0.002-g/min mass flow rate of reagent aqueous solutions and at 225°C.

Flotation of Illinois #6 coal, treated with 1-propanol aqueous solution, increases with treatment durations for the first 10-hour treatment duration, and then decreases with treatment

durations after durations. Flotation of Illinois #6 coal, treated with I-propanol, increases more drastically than that of isopropanol-treated one for the first 13-hour treatment duration. Some 1-propanol itself may be absorbed into the coal matrix so as to increase hydrophilicity of the coal, and hydroxyl groups of some 1-propanol may be adsorbed on the coal surface so as to decrease hydrophilicity of the coal.

Flotation of Illinois #6 coal, treated with butanol aqueous solutions, increases with

treatment durations. Flotation of Illinois #6 coal, treated with 1-butanol and isobutanol, is higher than that of t-butanol-treated Illinois #6 coal (see Figure 28). These data may show that

interactions between butanol isomers and functional groups such as carboxyl groups, hydroxyl groups and others on the coal surface appear to be different according to their molecular structures and reactivities at the elevated temperature. Flotation of butanols increases linearly with treatment durations. Hydroxyl groups of butanol may be reacted with hydrophilic functional groups of the coal surface.

Flotation of Illinois #6 coal, treated with 20-ppm-isobutanol 20-ppm-HCl aqueous solution, increases with treatment durations for the first 10-hour treatment period, and then decreases sharply with treatment durations, resulting in a formation of a sharp peak on the flotation-vs-

treatment duration plot (see Figure 29). Hydrogen chloride appears to act as a catalyst for the interaction between isobutanol and carboxyl group on the surface of the coal

Flotation of Wyodak coal, treated with water only, increases with treatment durations. Effects of water treatment on flotation of Wyodak coal are significantly pronounced in comparison with that of Illinois #6 coal (see Figure 30). Flotation of Wyodak coal, treated with isobutanol aqueous solution, increases more drastically than that of the water-treated Wyodak coal for the first 5-hour treatment duration. Flotation of the water-treated coal is as high as that of the isobutanol-HCl-treated coal. Hydrogen chloride does not enhance floatability of Wyodak coal, treated with 0.002-g/min-isobutanol 20-ppm 20-ppm-HCl aqueous solution at 225°C. Floatability of Wyodak coal, treated with the 20-ppm isobutanol aqueous solution at 225°C, is as high as that of untreated Pittsburgh #8 coal.

CONCLUSIONS

The following conclusions were drawn from experimental results on equilibrium adsorption of probe compounds and flotation of various treated coals.

- o Equilibrium adsorption loadings of m-cresol are higher than those of both o-cresol and p-cresol on Illinois #6 coal. Equilibrium adsorption loadings of 1-butanol on Smith-Roland Wyodak coal obey the Langmuir isotherm model for single-layer adsorption, whereas equilibrium adsorption loadings of 1-butanol on both Adaville #1 coal and Illinois #6 coal follow the Freundlich model at low concentrations of probe compounds (up to 80 ppm). Equilibrium adsorption loadings of phenol on Adaville #1 coal, Wyodak coal and Illinois #6 coal follow the Langmuir isotherm model. Equilibrium adsorption loadings of phenol on Pittsburgh #8 coal are almost negligible.
- o Equilibrium adsorption loadings of normal alcohols on 60 - 200 mesh Illinois #6 coal increase with increased numbers of carbons in their molecular formulas. Normal alcohols are more adsorbed on the coal than their branched alcohols. Adsorption loadings of single-ring compound phenol on the coal is higher than that of cyclohexanol. Adsorption

loadings of double-ring compound 2-naphthol on the coal is much higher than that of single-ring compound phenol.

- o Equilibrium adsorption loadings of toluene are higher than those of benzene on the four chosen coals. Equilibrium adsorption loadings of aromatic compounds such as toluene and benzene on the four chosen coals obey the Langmuir isotherm model for single-layer adsorption up to 100 ppm in concentrations of probe compounds.
- o Equilibrium adsorption loadings of higher aliphatic alcohols such as 2M1P and 1-heptanol on the four chosen coals do not follow both the Langmuir isotherm model and the Freundlich empirical adsorption model.
- o Flotation of the coals, equilibrated with aqueous solutions of 2M1P and 1-heptanol, increase linearly with equilibrium adsorption loadings of these probe compounds on the coals. Equilibrium adsorption loadings of 1-heptanol on Illinois #6 coal increase with decreased adsorption temperatures.
- o Flotation of Wyodak coal, treated with nitrogen gas, is higher than that of untreated coal, and increases with treatment temperatures.
- o Flotation of Adaville #1 coal, treated with nitrogen, is higher than that of untreated coal, and increases with treatment temperatures. Flotation of Adaville #1 coal, treated with air at 125 - 150°C, is slightly higher than that of untreated coal, whereas flotation of Adaville #1 coal, treated with air at 175 - 225°C, is slightly lower than that of untreated coal.
- o Flotation of Illinois #6 coal, treated with nitrogen, is higher than that of untreated coal. Flotation of Illinois #6 coal, treated with nitrogen at 125 - 175°C, increases with treatment temperatures, whereas flotation of Illinois #6 coal, treated with nitrogen at 175 - 225°C, decreases with treatment temperatures.
- o Flotation of Pittsburgh #8 coal, treated with air, is lower than that of untreated coal, and decreases with treatment temperatures. Mass flow rates of 1000-ppm methanol aqueous solution, during treating Illinois #6 coal with the methanol solution for 3 hours at 225°C, increase with decreased flotation of the treated Illinois coal. However, mass flow rates of

1000-ppm n-heptanol aqueous solution, during treating Illinois #6 coal with the solution under the same treatment condition, do not affect flotation of the treated coal.

- o Concentrations of alcohols such as methanol and isopropanol in water do not affect flotation of Illinois #6 coal treated for 3 hours at 225°C and 0.002 g/min, whereas concentrations of isopropanol, during treating Illinois #6 coal with isopropanol aqueous solutions, increase with decreased flotation of the coal treated for 24 hours at 225°C and 0.002 g/min.
- o Flotation of Illinois #6 coal, treated with 1-propanol aqueous solution, increases with treatment durations for the first 10-hour treatment period, and then decreases with treatment durations after that period. Flotation of Illinois #6 coal, treated with isopropanol aqueous solution, increases with treatment durations for the first 18-hour treatment period, and then levels off.
- o Flotation of Illinois #6 coal, treated with butanol aqueous solutions, increases with treatment durations. Flotation of 1-butanol-treated Illinois #6 coal is higher than that of t-butanol-treated Illinois #6 coal. Flotation of Illinois #6 coal, treated with 20-ppm-isobutanol 20-ppm-HCl aqueous solution, increases with treatment durations for the first 10-hour treatment period, and then decreases sharply with treatment durations.
- o Flotation of Wyodak coal, treated with water only, increases with treatment durations. Effects of water treatment on flotation of Wyodak coal are significantly pronounced in comparison with that of Illinois #6 coal.

PUBLICATIONS/PRESENTATIONS

- o "Study on Relationships between Adsorption of Probe Compounds on Treated Coal and its Flotation in Aqueous Solutions", presented at the AIChE 1994 Spring National Meeting, Hyatt Regency Hotel, Atlanta, Georgia, April 17-21, 1994.
- o "Effects of Molecular Structures of Probe Compounds on Their Adsorption on Coal", presented at the U.S. Department of Energy's Second Annual HBCU/Private

Sector/Energy Research and Development Technology Transfer Symposium, Sheraton Civic Center Hotel, Birmingham, Alabama, April 18-22, 1994.

- o "Adsorption of various alcohols on Illinois #6 coal in aqueous solutions", presented to the Miami AIChE annual meeting in November 1992.
- o "Analysis of Surface Properties of Coal by Inverse Liquid Chromatography", presented at the 18th International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, Florida, April 26-29, 1993. The paper has been published at the Proceedings of the conference, Pg. 563 - 574.
- o "Investigation of Surface Properties of Coal with Probe Compounds in Aqueous Solution", presented at the Eighth Symposium on Separation Science and Technology for Energy Applications", Getlinburg, Tennessee, October 24 - 28, 1993.
- o "Adsorption of Various Probe Compounds on Coal in Aqueous Solutions", presented at the 1993 AIChE Annual Meeting, St. Louis, Missouri, November 7 - 12, 1993.
- o "Floatability of Treated Coal in Water at Room Temperature", published in the Separation Science and Technology Journal, 30(7-9), pp. 1997-2020, 1995.
- o "Study on Relationships between Adsorption of Probe Compounds on Treated Coal and Its Flotation in Aqueous Solutions", presented at the AIChE 1994 Spring National Meeting, Hyatt Regency Hotel, Atlanta, Georgia, April 17-21, 1994.
- o "Mechanisms on Equilibrium Adsorption of Probe Compounds on Coal", presented at the 1993 University Coal Research (UCR) Annual Contractors' Review Conference, Westin William Penn Hotel, Pittsburgh, June 23 - 25, 1993.