

THE ROLE OF HEAT OF IMMERSION CALORIMETRY AND GAS ADSORPTION IN
DETERMINING THE SURFACE AREAS OF A THERMALLY
TREATED LIGNITE AND SUPERCRITICALLY SOLVENT EXTRACTED
LOW-RANK COAL RESIDUES

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ABSTRACT

Comparative surface area data can be obtained from the exothermic heat liberated when a solid substance is immersed in a suitable liquid penetrant. This heat of immersion is dependent on the heat of wetting plus other effects. The apparent surface of a sample is proportional to the heat of wetting term. The surface areas determined by this method provide an explanation of results of thermal treatment and supercritical solvent extraction of low-rank coal.

The thermally treated samples were prepared by drying Indian Head (North Dakota) lignite at 330°C with hot nitrogen gas at atmospheric pressure or with hot water under pressure. Lignite and subbituminous coal samples were also supercritically solvent extracted in a semicontinuous extraction system at temperatures of 250° to 380°C and reduced pressures between 1.05 and 2.00 in methanol, benzene, and cyclohexane. These samples were then tested in a specially constructed heat of immersion calorimeter. Nitrogen Brunauer Emmett and Teller (BET) gaseous adsorption derived surface areas were also compared with the results from the calorimeter.

INTRODUCTION AND EXPERIMENTAL

The surface areas determined in this study served as a valuable tool with which to explain the results obtained from thermal, and supercritical, low-rank coal treatments. Two techniques were used to determine the surface area of coal before and after processing. Heat of immersion calorimetry was used extensively to obtain coal surface areas and results were compared to those from the more standard gaseous adsorption method for the thermally treated samples.

Determination of Surface Area by Heat of Immersion

Differential heat of immersion calorimetry (1) is a way to find specific surface, in square meters per gram, by measurement of the heat released when the surface is wetted by a liquid. This fairly precise measurement is an indication of the number of molecules needed to coat the surfaces of cracks or pores. Since smaller pores limit the accessibility of molecules of increasing size and complexity, the rate and extent of heat released by the wetting process can be used as a measure of pore size distribution and hence a surface area determination.

The differential heat of immersion calorimeter consists of two Dewar flasks, each with its own stirrer, heater, and temperature sensor. An equal amount of liquid is put into each Dewar flask, both imbedded in a massive aluminum heat sink, and the coal or carbon sample is added to one Dewar only. Temperature is measured by a matched pair of thermistors forming opposing arms of a Wheatstone bridge. The heat liberated when the solid sample is added to the working Dewar produces a current imbalance which is recorded directly. Figure 1 shows a cross-sectional view of one calorimeter.

Determination of Surface Areas by Gaseous Adsorption

Historically, it has been known that a porous solid can take up relatively large volumes of a condensable gas. Freshly calcinated charcoal, cooled under mercury, has the property of adsorbing several times its own volume of various gases. This is because the molecules in the surface layer of a solid are bound on one side to inner molecules of the solid and bound to nothing on the surface side, creating an imbalance of atomic and molecular bonding forces on the surface side. Therefore, surface molecules attract gas, vapor, or liquid molecules in order to satisfy these unbalanced, bonding forces. The attraction may be either physical or chemical, depending on the system involved and the temperature employed.

Physical adsorption (Van der Waal's adsorption) is the result of a relatively weak interaction between a solid and a gas. This type of adsorption has one primary characteristic. Essentially all of a gas adsorbed can be removed by evacuation at the same temperature at which it was adsorbed, but the quantity of physically adsorbed gas at a given pressure increases with decreasing temperature. Consequently, adsorption measurements for the purpose of determining surface area of pore size distributions are made at a low temperature.

The physical adsorption of a gas on a smooth surface will continue as the gas pressure is increased at a constant temperature until a condensed layer, 5 or 6 molecules thick, is formed. If the surface contains cracks, crevices, or pores, the adsorbed layer will fill these as its thickness increases. The smaller pores will be engulfed first and, progressively, the larger ones will fill. Filling occurs because a concave liquid surface has a lower vapor pressure than a flat surface. When a pore fills, its surface area becomes a negligible contribution to the measured surface area. Conversely, the pore surface contribution again comes into play as adsorbed gas layers are removed (desorbed) and pore walls are re-exposed.

Continuing the adsorption by incremental steps as described earlier to, or nearly to, the saturation point yields a complete adsorption isotherm. Reversing the procedure by subjecting the sample to stepwise reductions in pressure while continuing to record volumes and equilibrium pressures permits obtaining the desorption isotherm. Adsorption and desorption isotherms coincide precisely only when the solid is completely nonporous and there are no contact points among particles creating the effect of pores.

Thermal Treatments of Coal

Raw lignite from the Indian Head Mine in North Dakota was thermally dewatered using hot nitrogen at atmospheric pressure and hot water under pressure to investigate the amenability of fuel slurry preparation of the dried product (2, 3). Products dried at 330°C and 340°C were used in the present study. Results of the proximate and ultimate analyses of the raw coal and the thermally dewatered samples are given in Table 1.

The hot-gas-dried sample was prepared by treating the Indian Head lignite, sized to 7mm x 10mm, at 330°C under a nitrogen atmosphere, and was conducted using a laboratory-scale fixed-bed coal dryer at atmospheric pressure. This drying apparatus consisted of a 3.8 cm ID by 152 cm long vertical drying chamber that was jacketed for rapid heat-up and cooldown using steam and cold water, respectively. Experimental details have been published elsewhere (2).

The objective of the hot-water drying process, (HWD) as with the hot-gas drying process, is to increase the energy density of low-rank coal/water slurries by changing the chemical and physical surface characteristics of the coal, allowing significantly higher solids content in a water slurry. Surface area measurements of the raw and treated coals are important, since a decreased coal surface means less water is required to wet the coal during slurry preparation.

TABLE 1
PERTINENT TEST DATA AND ANALYSIS OF RAW AND
THERMALLY DEWATERED INDIAN HEAD LIGNITE

Treatment	Raw	Hot Nitrogen	Hot Water
Drying Temperature °C ¹	---	328	340
Drying Pressure, psia	---	4	2400
Drying Apparatus		1.0 litres Fixed Bed	2.2 mt/day Pilot Plant
Equilibrium Moisture Content, Wt %	35.0	27.3	16.2
Proximate Analysis, wt % moisture free (mf) basis			
Ash	14.5	13.0	22.0 ²
Volatile matter	47.5	39.7	34.6
Fixed Carbon (by diff.)	38.0	47.3	43.4
Ultimate Analysis, wt % moisture ash free (maf)			
Carbon	72.1	74.1	75.2
Hydrogen	4.9	4.9	4.8
Nitrogen	1.5	1.4	1.4
Sulfur	1.5	1.4	1.6
Oxygen (by diff)	20.0	18.2	17.0
Heating Value, maf basis			
MJ/kg	28.7	29.1	29.6
Btu/lb	12,350	12,500	12,700

² Feed coal for the pilot-plant test was a high ash Indian Head lignite.

Process development unit (PDU) runs, using the HWD principle, were typically 120 hours in duration including start-up and shutdown; three tons of coal were usually processed. A schematic of the PDU is shown in Figure 2. The feed to the PDU was a slurry containing a 50/50 mixture, by weight, of deionized water and pulverized coal (80% less than 75 microns). The products, after treatment for 5 minutes at temperatures between 270° to 340°C and corresponding pressures between 800 and 2400 psig, were concentrated and formulated into fuel slurries containing between 55 and 65 wt% coal solids on a dry basis. The sample used in this study was treated at 330°C. A more detailed description of the PDU operation has been published elsewhere (4).

Supercritical Solvent Extractions

Supercritical solvent extractions were performed using a semicontinuous extraction system in which the HPLC grade solvent, i.e. methanol, benzene, cyclohexane, etc., was passed through a fixed bed of coal while under supercritical conditions. The coals extracted in these experiments were Indian Head lignite and Wyodak subbituminous coal (Campbell Co., WY) which had been sized between -60 and +325 mesh. Proximate and ultimate analyses for these coals are given in Table 2. The flowsheet for this test system is shown in Figure 3. The fixed bed of coal was contained in a 25.4 cm by 1.75 cm ID section of high-pressure tubing which held approximately 50 gm of coal between two one-micron sintered metal frits. Supercritical conditions were achieved in approximately seven minutes by immersing the solvent preheating coils and the fixed bed of coal in a preheated fluidized sand bath in a such manner that no solvent flow through the bed of coal occurred during start-up. A Ruska positive displacement pump and high-pressure piston accumulator were used to provide a pulseless flow of solvent through the system once supercritical conditions were obtained. An extraction time of two hours and a solvent flow rate of 120 cc/hr were typically used in these experiments. The pressure of the supercritical solvent and the extracted material was reduced to atmospheric pressure after passing through a back pressure regulator where the extract and solvent were collected in a chilled sample vessel. The volume of noncondensable product gas was measured and collected for analysis by gas

TABLE 2
PROXIMATE AND ULTIMATE ANALYSES OF COALS USED IN
SUPERCRITICAL SOLVENT EXTRACTION EXPERIMENTS

	Sample Name and Location	
	Indian Head Mercer Co., ND	Wyodak Campbell Co., WY
<u>Proximate Analysis, MF, (wt%)</u>		
Volatile Matter	43.8	43.5
Fixed Carbon	48.0	50.0
Ash	8.2	6.5
<u>Ultimate Analysis, MF, (wt%)</u>		
Hydrogen	4.74	4.26
Carbon	66.20	64.62
Nitrogen	0.96	1.01
Sulfur	0.72	0.58
Oxygen (Ind)	19.19	23.04
Ash	8.2	6.5

chromatography. After each experiment, the extracted residue and the solvent extract mixture were rotary vacuum distilled at 0.6 psia and 80°C and weighed. This procedure allowed solvent and moisture-free products to be obtained for material balance purposes.

Table 3 summarizes the operating conditions and results from supercritical solvent extraction experiments performed on Indian Head lignite and Wyodak subbituminous coal using three solvents: methanol, benzene, and cyclohexane. The results indicate that the weight loss of the original coal (and the corresponding extract yield) increased with increasing pressure. This would be expected due to the rapidly increasing solvent density experienced by solvents in the supercritical region. However, the increasing weight loss of the coal observed with increasing temperature resulted in spite of a decreasing solvent density. This indicates that temperature has a larger effect on conversions than on solvent densities, particularly at temperatures between 300° to 350°C. Thus, in this temperature range, thermal decomposition of the coal becomes significant, resulting in the liberation of smaller and more soluble fractions from the coal.

RESULTS AND DISCUSSION

Thermally Treated Samples

Table 4 shows the results of the surface area determinations by heat of immersion calorimetry for raw Indian Head lignite and the two thermally treated samples.

TABLE 4

Sample	Heat of Immersion (cal/gm)	Surface Area (m ² /gm)
As-mined Coal	14.3	153
340°C Hot-water-dried Coal ^a	9.2	98
330°C Hot-nitrogen-dried Coal	24.5	263
340°C Hot-water-dried (freeze dried)	16.0	171

^a The HWD coal was separated from slurry by filtration; the filter cake was then air dried to remove surface moisture.

The surface area for the raw lignite sample was determined to be 153 sq. meters/gram. A similar determination on the 340°C HWD Indian Head coal showed a surface area of 98 sq. meters/gram. The hot-nitrogen-dried (HND) sample (evaporatively dried) showed a surface area value of 263 sq. meters/gram.

Evaporatively drying the coal with nitrogen at 330°C, but at atmospheric pressure, increased the apparent surface area of the coal. This increase was probably due to the volatilization and removal of coal tars and waxes which otherwise may have been filling or sealing some of the coal micropores. This explanation is in accordance with observations made during the drying experiments. Accumulations of waxes and tars were apparent in the outlet piping of the fixed-bed coal dryer, and in the condensate recovered when the hot-nitrogen was quenched (5). Therefore, drying low-rank coal with 330°C nitrogen increased the coal surface areas because tars were extracted with the hot-gas stream. Vacuum freeze drying and air drying were both used for sample preparation on the HWD coal.

TABLE 3

OPERATING CONDITIONS AND RESULTS FROM SUPERCRITICAL EXTRACTION EXPERIMENTS
ON INDIAN HEAD AND WYODAK COALS USING SELECTED SOLVENTS

Coal	Temp. (°C)	T_r^a	Pressure (psia)	P_r^b	Calc. Solvent Density (g/ml) ^c	Pct. Conv. (maf) ^d	Pct Yield, maf	
							Extract	Gas
Solvent: Methanol								
Indian Head	250	1.021	1760	1.50	0.368	4.17	3.05	1.36
Indian Head	250	1.021	2350	2.00	0.412	5.49	3.80	1.66
Indian Head	250	1.021	2935	2.50	0.434	6.13	4.43	2.23
Indian Head	300	1.118	2350	2.00	0.224	9.55	4.74	6.91
Indian Head	350	1.216	2350	2.00	0.144	23.30	12.43	22.04
Solvent: Cyclohexane								
Indian Head	291	1.020	885	1.50	0.421	6.7	2.14	4.7
Indian Head	291	1.020	1180	2.00	0.465	9.1	2.50	4.6
Indian Head	291	1.020	1480	2.50	0.489	9.1	2.68	4.9
Indian Head	307	1.048	1180	2.00	0.425	10.8	2.64	4.6
Solvent: Benzene								
Wyodak	300	1.020	745	1.05	0.185	10.8	4.62	2.0
Wyodak	300	1.020	1420	2.00	0.511	11.1	7.57	1.8
Wyodak	350	1.109	745	1.05	0.112	15.9	6.31	4.0
Wyodak	350	1.109	1420	2.00	0.345	17.2	10.8	4.4

$$a_{T_r} = \frac{\text{operating temperature of solvent } (^\circ\text{K})}{\text{critical temperature of solvent } (^\circ\text{K})};$$

$$b_{P_r} = \frac{\text{operating pressure of solvent (psia)}}{\text{critical pressure of solvent (psia)}}$$

^c Calculated using Lee-Kesler generalization of the Benedict-Webb-Rubin Equation of state.

$$d\% \text{ conversion} = \frac{\text{wt maf coal} - \text{wt maf residue}}{\text{wt maf coal}} (100); \quad \% \text{ yield} = \frac{\text{wt maf product}}{\text{wt maf coal}} (100)$$

The process of vacuum freeze drying was found to increase the surface area of the HWD coal; and in fact, the surface area determined was found to be in excess of that determined for the raw coal (171 sq meters/gram versus 153 sq meters/gram). This last result indicates that the tars and waxes evolved during hot-water coal drying migrate out of the pores to the coal surface where they plug or cap micropore entrances when cooled and resolidified. Freeze drying the HWD coal in a vacuum, as compared to air drying, removes at least some of these tars and exposes the pore entrances. This is believed to occur because the gases and water trapped in the pores expand and push tar away from the pore entrance when the sample is put in a vacuum. The volume of the newly exposed pores includes the added volume vacated when the tars migrated to the surface of the coal. Additional pore volume is also created when carboxyl groups in the coal matrix decompose and liberate carbon dioxide.

Measurements of the coal surface area before and after hot-water drying at 340°C have shown that the surface area is decreased by 50% due to the hydrothermal treatment and the subsequent capping of pores. The discovery that pore capping by the exuded coal tars was occurring helped to explain the mechanism of increased energy density after hot-water drying of low-rank coal. Until this discovery, pore collapse was believed to produce the decreased surface area in the treated coal particles.

Supercritically Solvent Extracted Samples

Supercritically solvent extracting Indian Head lignite with methanol produced two major results. First, increasing the extraction pressure while keeping the temperature constant, increases the surface area of the supercritically extracted lignite residues. Secondly, an increase in the extraction temperature, while keeping the pressure constant, decreases the surface area. The data listed in Table 5 shows the effect of changing the methanol extraction pressure while keeping the temperature constant. The effect of changes in the methanol extraction temperature at a constant pressure are shown by the data listed in Table 6.

TABLE 5
EXTRACTION OF INDIAN HEAD LIGNITE WITH METHANOL

Extraction Parameters		Surface Area By Heat of Immersion, m ² /gm
Temperature, C°	Pressure, psig	
250	1761	105.6
250	2348	120.7
250	2935	138.4

TABLE 6
EXTRACTION OF INDIAN HEAD LIGNITE WITH METHANOL

Extraction Parameters		Surface Area by Heat of Immersion, m ² /gm
Pressure, psig	Temperature, °C	
250	2348	120.7
300	2348	110.5
350	2348	97.5

As presented in Table 7, the use of cyclohexane to extract Indian Head lignite at constant temperature and increasing extraction pressure increased the measured surface area. The data in Table 8 show that changes in the surface area of a subbituminous coal, after extraction with benzene, were similar to those exhibited by lignite. As extract pressure is increased at a constant temperature, the surface area increased and as extract temperature was increased at constant pressures the measured surface area decreased.

TABLE 7
EXTRACTION OF INDIAN HEAD LIGNITE WITH CYCLOHEXANE

Extraction Parameters		Surface Area By Heat of Immersion, m ² /gm
Temperature °C	Pressure, psig	
291	887	86.1
291	1182	97.7
291	1478	118.9
307	1182	97.2

TABLE 8
EXTRACTION OF WYODAK SUBBITUMINOUS COAL WITH BENZENE

Extraction Parameters		Surface Area by Heat of Immersion, m ² /gm
Pressure, psig	Temperature, °C	
300	746	109.9
300	1420	129.4
350	746	95.7
350	1420	111.8

Finally, a comparison of the heat of immersion calorimetry results was made with the gas adsorption results. The surface areas (BET) for Indian Head lignite extracted in methanol are listed in Table 9. The BET surface areas obtained by nitrogen gas adsorption correlate with the heat of immersion calorimetry-derived surface areas, but are two orders of magnitude lower in value. The higher measured coal surface areas determined by heat of wetting of methanol compared to values obtained by the BET method is a common phenomenon (8).

TABLE 9
 COMPARISON BETWEEN NITROGEN GAS ADSORPTION: BRUNAUER, EMMETT
 AND TELLER (BET) AND HEAT OF IMMERSION DERIVED SURFACE AREAS

EXTRACTION OF INDIAN HEAD LIGNITE WITH METHANOL

Extraction Parameters		Surface Area	
Temperature, °C	Pressure, psig	(BET), m ² /gm	Heat of Immersion, m ² /gm
250	1761	1.36	105.6
250	2348	1.56	120.7
250	2935	2.07	138.4
300	2348	1.47	110.5
350	2348	1.12	97.5

SUMMARY AND CONCLUSIONS

Surface area determinations of supercritical residues indicate that increasing extraction pressure increases the surface area of the extracted residues. For a solvent under supercritical conditions, solvent density increases rapidly with increasing pressure, thus the solubility of larger molecular species can be greatly enhanced with increasing pressure. The increase in surface area which occurs with pressure is probably due to the ability of the supercritical solvents to extract significantly larger molecules from the coal, opening more of the micropores to access by the penetrant. Conversely, a decrease in the residue surface area was observed with increasing extraction temperatures. Increasing methanol extraction temperatures has been shown to alter the surface functional groups left in the residue (6,7). Thus, some of this decreasing surface area could be due to the decrease in functional groups with which the penetrant can hydrogen bond. However, the nitrogen adsorption surface area determinations (which are unaffected by surface-penetrant interactions) also decreased with increasing temperature, indicating that these interactions are a small part of the measured heat of immersion. The decreased surface area is probably due to the extraction temperatures approaching the temperature where the coal tars become plastic and partially obstruct some of the micropores of the coal.

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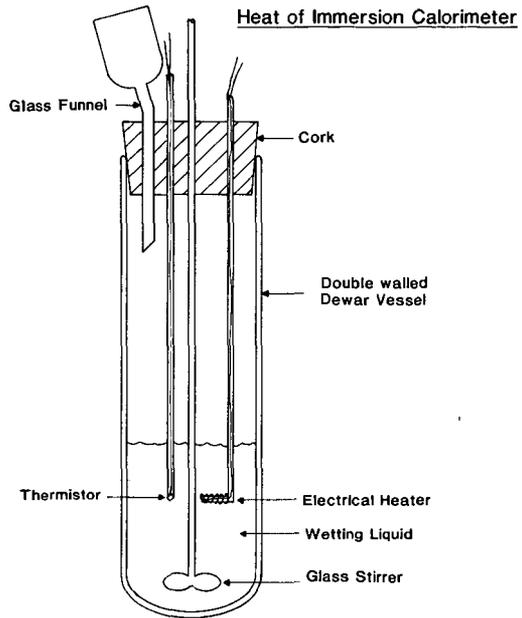


Figure 1. Heat of Immersion Calorimeter.

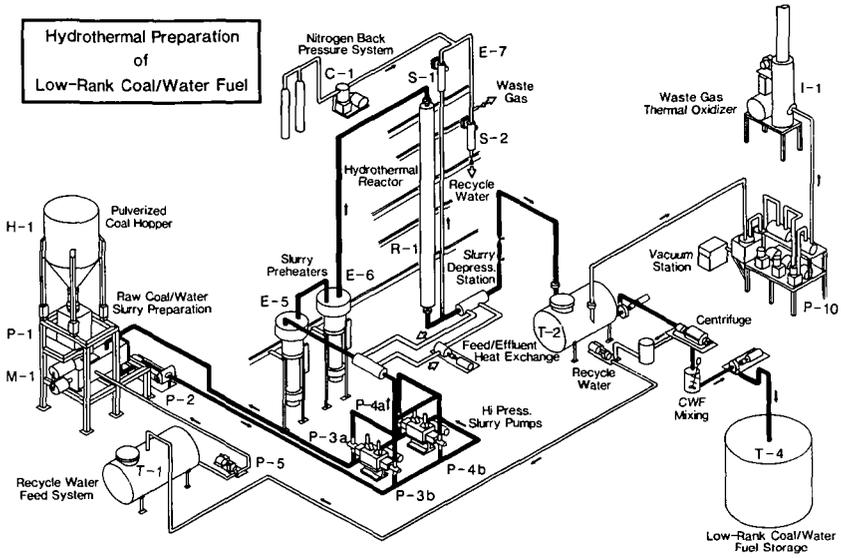


Figure 2. Hydrothermal Preparation of Low-Rank Coal/Water Fuel.

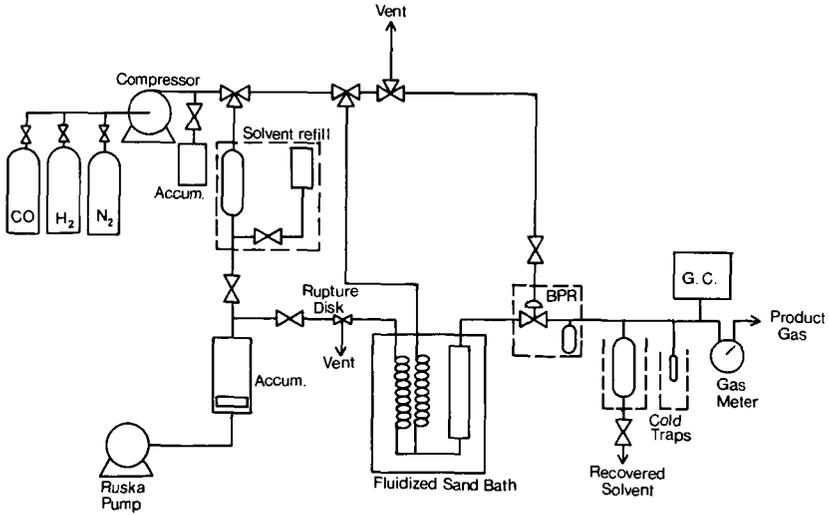


Figure 3. Supercritical Solvent Extraction Apparatus.