Title
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Surface Area Variations of Coal During Solvent Extraction

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Abstract

Changes in the surface area of a Wyoming sub-bituminous coal with progressive extraction have been investigated. Surface areas were determined from CO_2 adsorption isotherms at 196°K using the BET equation and using 23.4 $\mathring{A}^2$ for the molecular cross-sectional area of the CO_2 molecule at 196°K. Surface areas of the extracted coal varied with extraction time, yield and with the nature of the solvent. A maximum surface area of 265 m^2/g was obtained from a four-hour treatment using tetralin at 350°C as the solvent. The raw coal had a surface area of 99 m^2/g.

Introduction

Processes to utilize coal as a practical fuel are generally based upon gasification, extraction, or hydrogenation. These processes have in common that they are rate processes and the magnitudes of the rates are related directly to the surface area of the solid provided transport processes acting within the porous structure can bring reactant in and products out with small concentration gradients. Coals, as mined, is a relatively porous material having large internal surface area and consequently small pores.

The relatively high internal surface area of original coal should be preserved during processing to enable high rates of reactions or extractions. Accordingly, internal structure and area should be measured with processing to determine if the high surface area is being utilized and preserved. If not, the processing variables should be modified to do this whenever possible.

The extent of solvent interaction with the porous structure of a Wyodak, Roland seam, sub-bituminous coal have been studied in this paper. The changes in the internal structure of this coal are followed by measuring the surface areas of the raw coal and coal subsequent to extraction using the well-known Braunair-Emmett-Teller method[1].

Experimental

Samples

The extracted coal samples used in these adsorption studies were obtained from Draemel and Grens[2]. They extracted the raw Roland seam coal with tetralin, benzene, phenol, decalin, and hexane in a refluxing liquid extraction apparatus. Extractions at temperatures below 250°C were made on minus-28 Tyler mesh coal, whereas at temperatures of 250°C and above, 28 to 150 Tyler mesh coal was used.

The residues (extracted coal samples) were dried following each extraction at 130°C and 200 mm Hg for 24 hours, while N_2 was swept over the samples at 60-80 cc/min. The dried extract coal was then stored in a desiccator under 100-300 mm Hg helium pressure until needed.

The chemical analysis of the raw Roland seam coal (both minus-28 and 28 to 150 mesh sizes) were determined by Commercial Testing & Engineering, Denver Laboratory. The minus-28 mesh raw coal was analyzed four separate times whereas the 28 to 150 mesh raw coal was analyzed twice. The analysis indicate the same composition for both particle sizes. The chemical composition (dry basis) of the raw Roland seam coal is 61.7% carbon, 5.1% hydrogen, 1.1% nitrogen, 1.1% sulfur, 15.1% ash, and 15.9% oxygen (by difference).

Apparatus

A typical volumetric gas adsorption apparatus* containing four sample holders was used to measure carbon dioxide isotherms at 196°K. Samples, both raw and extracted coals, were degassed at 130°C for 16 hours at a pressure of 10^{-4} to 10^{-5} torr before measuring adsorption. Carbon dioxide adsorption isotherms at 196°K were conducted in a relative pressure range (P_2/P_o where P_2 is the equilibration pressure and P_o is the saturation pressure of the adsorbate at the temperature of adsorption). An equilibration time of 30 min. was allowed for each gas adsorption point. A value for A_m, the molecular cross-sectional area of CO_2 at 196°K, has been determined by the authors[3] using two Harshaw catalysts as the adsorbents and found to be 23.4 $Å^2$. This value was used in determining all surface-area values presented in this paper.

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* Detailed design and experimental results are presented in reference 3.

Results and Discussion

Table 1 gives a summary of the extraction results and the corresponding surface areas. Reference numbers refer to points on Figure 2 and 3. The solvent, extraction temperature and time, yield, and final areas are presented. Four area columns are presented. The specific area and the surface area history of a one gram sample of coal are listed on a dry and a dry ash free basis. The extraction data were taken from Draemel and Grens[2]. Repeat extractions and surface areas were made on raw coal at several temperatures and times using either tetralin or phenol as indicated in Table 2. The yield data and surface-area values listed in Table 1 for these repeat runs are actual values for one of the runs.

The variations of surface area with extraction yield and extraction time is shown in Figures 1, 2 and 3. The solid lines in these figures connect extractions at the same temperatures (isothermal lines) using the same solvent.

The solvents used in these experiments appear to enter the micropore structure and selectively extract parts of the coal causing an increase in the specific surface area. The extent of increase is characteristic of the solvent and the amount of material removed from the coal matrix. Thus, time and temperature appear to affect surface area only as they affect the amount extracted as is rather well demonstrated by Figure 2.

Table 1. Surface Areas of Extracted Roland Seam Coal

Reference Number	Solvent	Temperature (°C)	Time (hr.)	Extraction Yield (DAF,wt.%)	BET Surface Areas+ (S) Dry Basis m^2/g	Dry Basis m^2	DAF Basis* m^2/g	DAF Basis* m^2
1	Benzene	150	4	5.05	154	146	181	172
2	Benzene	200	4	4.23	158	151	186	178
3	Benzene 1	250	4	7.79	164	151	193	178
4	Benzene	200	72	8.30	167	153	197	181
5	Tetralin	150	4	5.66	95	96	112	106
6	Tetralin 2	200	4	6.58	84	96	99	92
7	Tetralin 1,2	250	4	8.67	144	132	170	155
8	Tetralin 1,2	300	4	15.56	201	170	237	200
9	Tetralin 1,2	350	4	31.72	225	154	265	181
10	Tetralin 1	350	8.5	34.63	221	144	260	170
11	Tetralin	200	67	9.45	131	118	154	139
12	Tetralin	200	200	8.33	118	108	139	127
13	Phenol	200	4	19.01	115	93	135	109
14	Phenol 1,2	250	4	33.99	168	111	198	131
15	Phenol 1	300	4	57.46	197	83.8	232	99
16	Phenol	200	.32	29.57	133	117	157	141
	Hexane	200	100					
17	Benzene	200	100					
	Tetralin	200	100					
			Cummulative	7.13	110		130	
18	Decalin	200	4	5.47	108		127	

* Ash content (dry basis): 15.08%

\+ Minus-28 mesh coal, S = 106 m^2/g DAF basis, used as feed except where indicated

A_m = 23.4 Å for Carbon dioxide

1 28 to 150 mesh raw coal used, S = 99 m^2/g DAF basis

2 Repeat run(s) conducted

Table 2. Surface Area Ranges for Repeated Runs

Solvent	Temperatures (°C)	Surface Area
tetralin	200	99-100
"	250	170-177
"	300	215-269
"	350	265-269
phenol	250	189-198

One interpretation of these data is based upon the lines I, II, III and IV on Figure 2. Line I represents the area as a function of the percent extraction if the solvent penetrated only the macropore structure of the coal. This, of course, makes the reasonable assumption that essentially all of the area resides in the micropore structure. Point 9 and 10 (Figures 2 and 3) are for tetralin extracted coal @ 350°C for 4 and 8.5 hours, respectively, and support the contention that the area has reached a maximum in specific surface area. Curve IV (Figure 2) is drawn tangent to these points and goes through the zero area - 100% yield point. The intersection of this line with zero yield is the specific surface area at maximum extraction. This is equally well shown by plotting the specific area versus yield on Figure 3 but Figure 2 shows that the interpretation using Lines I-IV fit the data well. The data for phenol is probably complicated by the fact that the solvent is not easily removed from the coal.

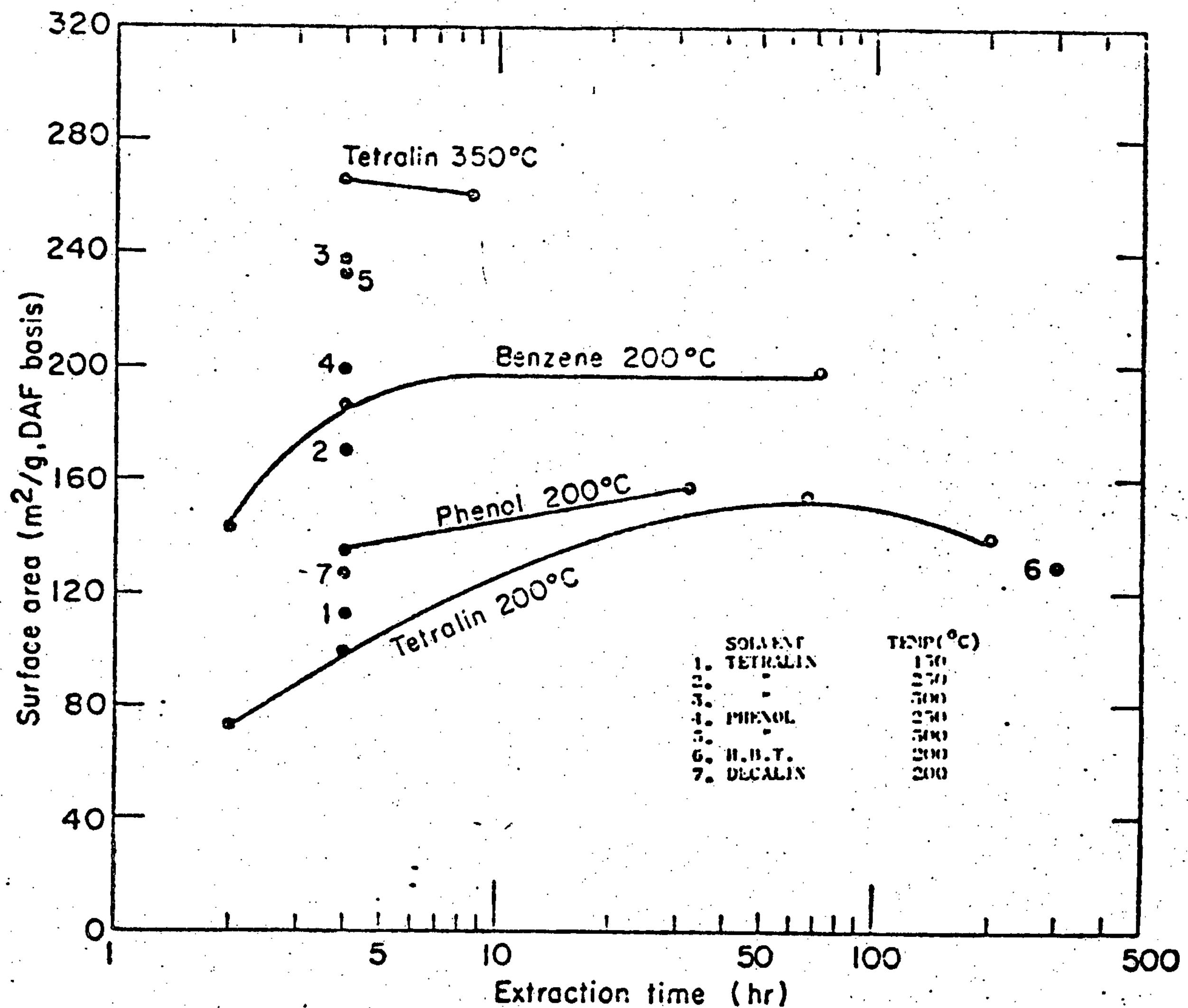

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Figure 1. Surface Area vs. Extraction Time

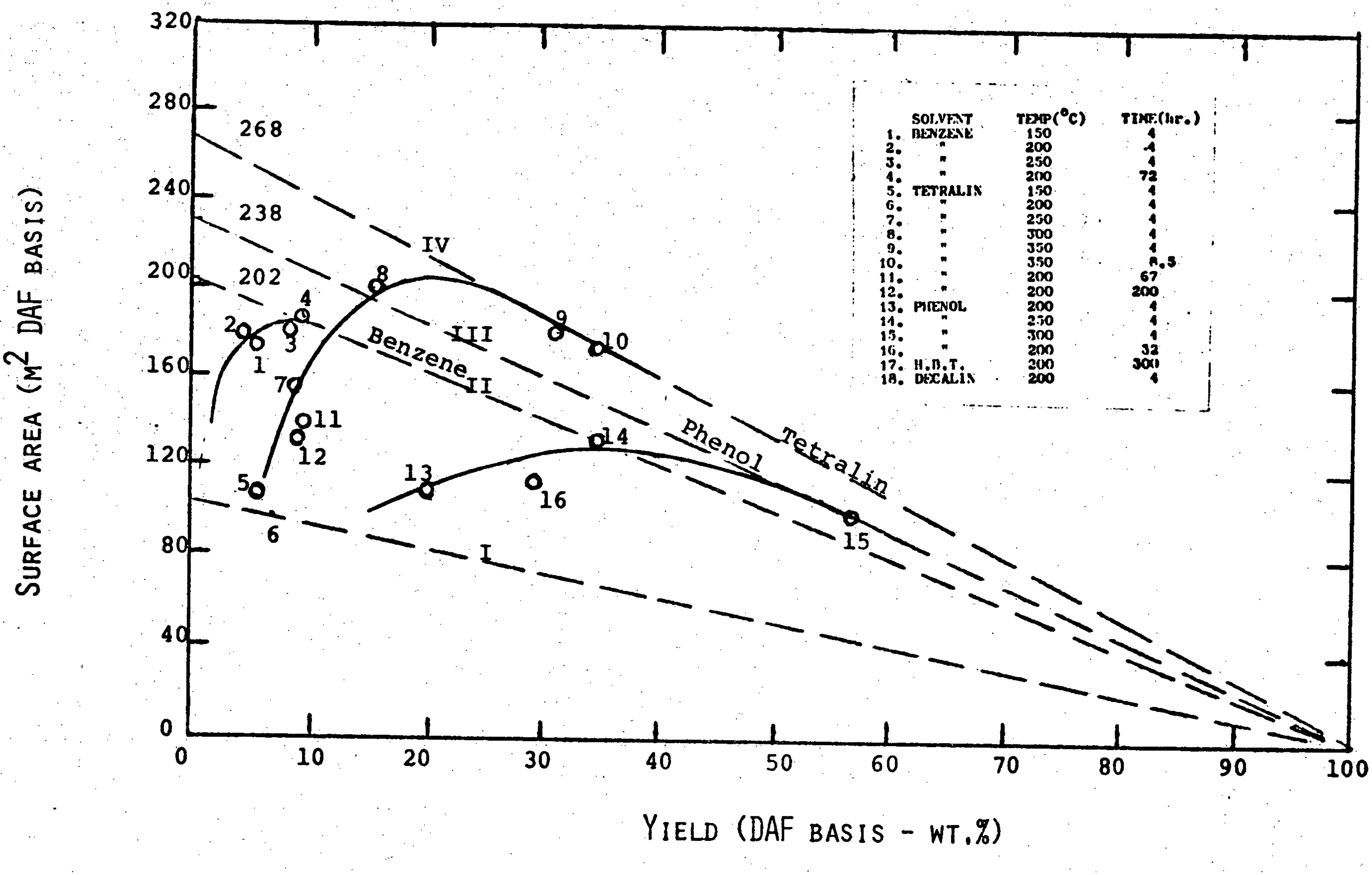

Figure 2. Surface Area vs. Extraction Yield

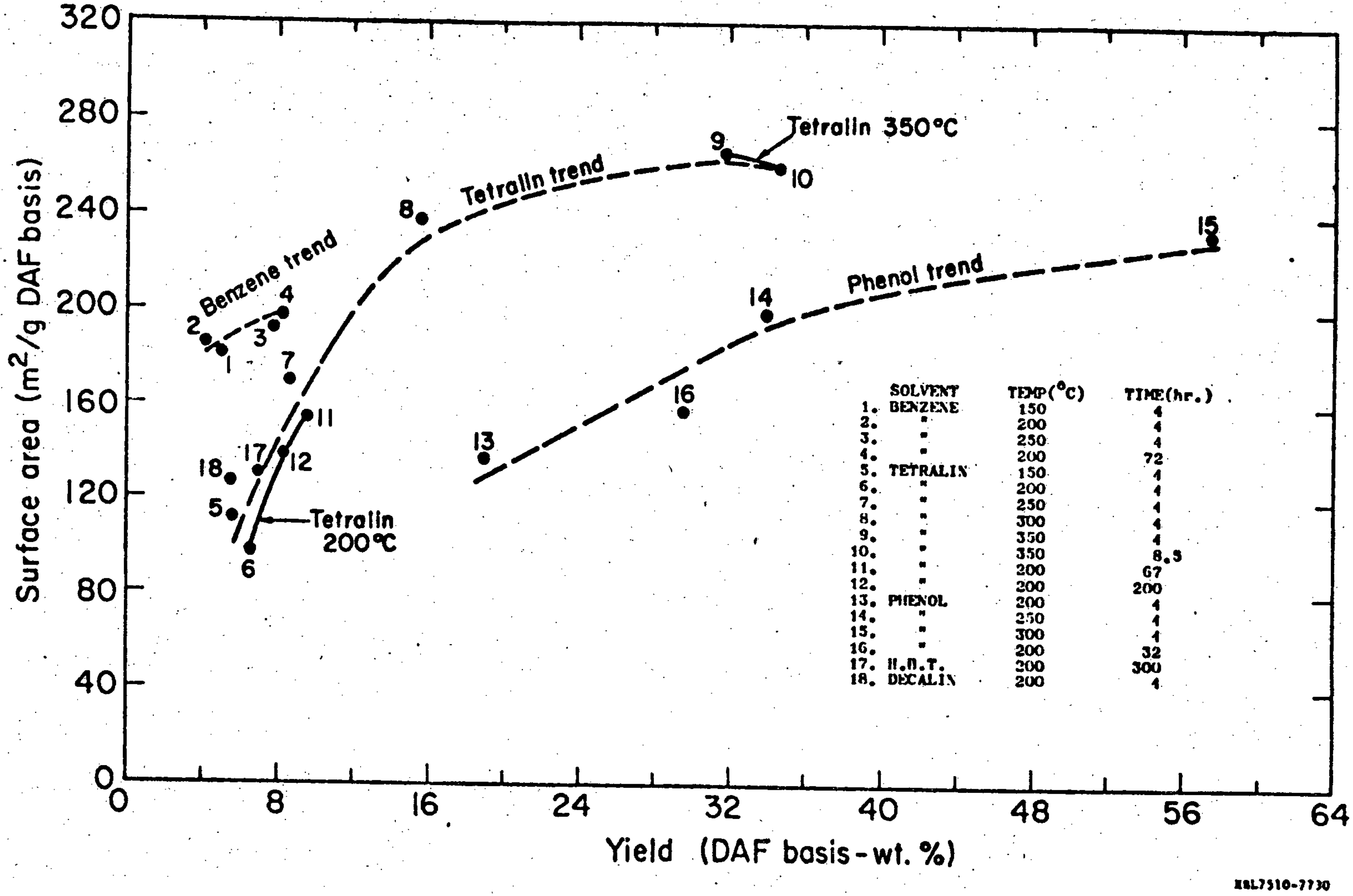

Figure 3. Surface Area vs. Extraction Yield

These results demonstrate that tetralin is a better solvent than benzene and develops a greater maximum specific surface area in this coal.

Acknowledgements

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Figure Titles

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