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AIR OXIDATION, PHENOLIC GROUP CONTENT, AND COKING PROPERTIES OF ILLINOIS COAL[1]

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Among the coals of Illinois, those which are of most promise in the manufacture of metallurgical coke are of high-volatile B bituminous rank. Experience has shown that these coals lose their coking quality rather rapidly when crushed and oxidized, even under such mild conditions as exposure to air at ordinary temperatures and pressures.

Some years ago Berl and Koerber[3] published a paper on solvent extraction of coals and the effect of such extraction on the coking properties. They stated that certain ketonic solvents removed phenolic components which "are responsible for the caking properties of coal." This statement raised the question of whether the phenolic-group content of Illinois coals, as estimated by methylation with dimethyl sulfate and subsequent methoxyl determination, would show a decrease parallel to the decrease in coking quality as oxidation proceeded.

At that time we were investigating a phase of the atmospheric oxidation of coal somewhat apart from the effect on coking properties. During the course of the experiments we exposed a sample of —100 mesh Illinois No. 6 seam coal (Laboratory No. C-2495, table 1) to the atmosphere of the laboratory and withdrew portions periodically for methylation and subsequent methoxyl determinations, the results of which are given in table 2.

Although no tests of coking power were included in this investigation, it would be expected that such values as free-swelling index and agglutinating value would drop off appreciably within a few days. Yet it can be seen from the methoxyl values in table 1 that the phenolic hydroxyl content showed no decrease, but was maintained essentially at the same value as that shown by the fresh coal.

In order to test this point further, several series of experiments were carried out by subjecting coal samples to the action of air at room temperature or to accelerated air oxidation in a drying oven. Samples were taken at intervals for methylation and for tests of coking quality. In two series the agglutinating value[4] was used to measure the change in coking quality, as this test has long been recognized as very sensitive to oxidative changes.[5] In the other two series, the change in free swelling index[6] (F.S.I.) was followed until it

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[3] Berl, E., and W. Koerber, Ind. Eng. Chem. 32, pp. 1605-7, 1940.

[4] Proc. Am. Soc. Testing Materials 34, pt. I, pp. 457-62 (1934); ASTM Tentative Standards, 1938, pt. II, Non-Metals, 95-100.

[5] See L. D. Schmidt, Chemistry of Coal Utilization, H. H. Lowry, ed., vol. I, p. 668, New York, John Wiley, 1945.

[6] ASTM Designation D 720-46. Am. Soc. Testing Materials Standards on Coal and Coke, p. 70, September 1951.

TABLE 1.—ANALYTICAL DATA ON COALS.

Lab. No.	As Received			Moisture and ash-free basis						Condition
	Moist.	Ash	F.C.	C	H	N	O	S	Btu/lb	
C-2445[a]	8.0	9.5	49.0	......	......	......	......	1.88	14516	Fresh
C-2495[a]	7.9	7.4	54.2	81.78	5.27	1.78	10.24	0.93	14368	Fresh
C-4680[b]	5.9	7.4	53.5	81.99	5.45	1.94	8.14	2.48	14654	Fresh
C-4737[b]	0.8	7.4	60.4	76.67	4.75	1.84	14.37	2.37	13166	C-4680 oven oxidized 15 days
C-4738[b]	0.4	7.3	59.6	73.82	4.37	1.82	17.70	2.29	12433	C-4680 oven oxidized 32 days
C-4752[b]	8.1	4.7	54.4	75.33	4.54	1.80	16.82	1.51	12814	C-4738 methylated
C-4758[a]	8.0	7.0	55.5	82.09	5.52	1.95	9.71	0.73	14443	Fresh
C-4787[a]	0.6	7.4	61.4	77.66	4.70	1.84	15.12	0.68	.....	C-4758 oven oxidized 13 days
C-4841[a]	2.5	7.1	58.0	74.39	4.25	1.87	18.83	0.66	12239	C-4758 oven oxidized 45 days
C-4900[a]	17.0	11.2	44.5	75.30	5.04	1.79	17.19	0.68	13323	C-4841 methylated

a) Franklin County, No. 6 seam coal.
b) Saline County, No. 5 seam coal.

TABLE 2.

Methoxyl values of coal C-2495. Methylated after exposure to air in the laboratory at room temperature.

Time of exposure (Days)	Methoxyl value[a] (Percent)
0	3.25
5	3.37
11	2.43
15	3.27
19	3.72
25	3.62
32	2.87
39	3.54
46	3.74
53	2.74
60	3.54
67	2.75

a) Determined by M.H.W. using the semimicro Zeisel method.

TABLE 3.

Coal C-2445. Exposed to laboratory atmosphere at room temperature in —40+ 60 mesh size; ground to —200 mesh prior to methylation.

Time of exposure (days)	Agglutinating value (kg.)	Methoxyl after methylation[a] (%)
0	5.1	1.40
13	3.9	1.52
35	3.1	2.01
101	2.1	3.02

a) Determined by M.H.W. using the semimicro Zeisel method.

was obvious that the coal no longer had the ability to swell.

Methylations were carried out as described in an earlier publication,[7] using the same proportions of reactants but smaller amounts of coal (5 or 10 grams). In some instances the methylation mixture was filtered while still alkaline, and the filtrate acidified to recover separately the "humic acids" resulting from the oxidation of the coal; in others the methylation mixture was acidified before filtering, so that "humic

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[7] G. R. Yohe and Eva O. Blodgett, J. Am. Chem. Soc. 69, pp. 2644-48, 1947.

TABLE 4.
Coal: A "grab" sample from the same source as C-2495; —200 mesh. "Humic acid" isolated, but not subjected to methoxyl determination.

Days in oven (100°)	Agglutinating value (kg.)	OCH_3 after methylation (%)	"Humic acid" (%)[a]
0.0	4.49	2.85	0.12
0.75	0.83	4.02	0.37
2.0	0.0	4.64	....
4.0	0.0	4.09	....
11.0	0.0	3.17	0.32
18.0	0.0	3.63	0.58
25.0	....	3.74	0.69
32.0	....	3.78	0.93
39.0	....	4.41	0.94
46.0	....	4.02	1.36
57.0	....	3.71	1.26

a) Parts by weight from 100 parts by weight of coal.

acids'' and alkali-insoluble materials were not separated, but taken together as the sample of methylated coal.

The results are reported in tables 3, 4, 5, and 6. Except where otherwise indicated, methoxyl determinations were made by H. S. Clark and Donald Dickerson in the Survey laboratory, using the micro Zeisel method.

The gradually increasing yield of ''humic acid'' in table 4 and the increasing oxygen contents (determined by difference) and decreasing calorific values in tables 5 and 6 are shown to give some indication of the extent of the oxidation.

A great difference in rate of loss of agglutinating value is evident in tables 3 and 4. Undoubtedly both differences in particle size and differences in temperature of exposure contributed to this effect, but it is probable that temperature is the more important factor. If it be assumed that the rate of loss of agglutinating value doubles for each 10°C. rise, then the loss for table 4 should be about 180 times as rapid as for table 3. Plotting the data shows that the difference in slopes of the curves is of about that order of magnitude.

It can be seen that the loss of coking quality was not accompanied by a decrease in the phenolic hydroxyl content as estimated by the methylation procedure. Rather, there seemed to be a trend toward an increase of the phenolic groups during the time that the caking power was disappearing.

We are aware that there are inherent sources of error in this method of estimating phenolic hydroxyl in such a material as coal, but, nevertheless, the results are sufficiently precise (1) to show that the presence of phenolic hydroxyl groups in a coal is not a sufficient condition to assure cokeability and (2) to establish the conclusion that the loss of coking quality by atmospheric oxidation is not due to the disappearance of phenolic structures. This does not mean, of course, that the phenolic groups originally present have remained intact, for such experimental work as this affords no means of distinguishing between original structures and groups of the same type that may have formed during the oxidation.

TABLE 5.

Coal C-4680; —200 mesh.

Days in oven (107°)	F.S.I.	OCH_3 after methylation	Moisture and ash-free	
			Oxygen (%)	Btu
0	4.0	2.0	8.14	14654
1	1.5	3.44	.....	.....
5	1.0[a]	3.90	.....	.....
6	...	3.38	.....	.....
11	...	3.90[b]	14.37	13166
18	...	4.19[b,c]	.....	.....
32	1.0[a]	4.84[b]	17.70	12433
32	...	4.24[d]	.....	.....
32	...	4.71[e]	.....	.....

a) Coal did not cohere to form a coke button.
b) Methylation reaction mixture acidified before filtering; this includes alkali-soluble and alkali-insoluble portions.
c) A parallel methylated sample gave 3.73% OCH_3.
d) The alkali-insoluble portion of the methylation mixture.
e) The alkali-soluble portion of the methylation mixture.

TABLE 6.

Coal C-4758; —200 mesh.

Days in oven (105°)	F.S.I.	OCH_3 after methylation	Moisture and ash-free	
			Oxygen (%)	Btu
0	4.5	5.08	9.71	14443
1	1.5	4.81[a]	.....	.....
3	...	3.66[a]	.....	.....
6	...	5.37[a]	.....	.....
10	...	3.11[a]	.....	.....
13	...	....	15.12	.....
17	...	5.34[a]	.....	.....
29	...	5.85[a]	.....	.....
44	...	3.07[a]	.....	.....
45	...	5.45[a]	18.83	12239
45	...	4.06[b]	.....	.....
45	...	4.90[c]	.....	.....

a) Methylation reaction mixture acidified before filtering; this includes alkali-soluble and alkali-insoluble portions.
b) The alkali-insoluble portion of the methylation mixture.
c) The alkali-soluble portion of the methylation mixture.