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THE OXIDIZING POWER OF ILLINOIS COAL. II. THE EFFECTS OF EXTENDED TIME

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The Oxidizing Power of Illinois Coal. II. The Effects of Extended Time[1]

By G. R. Yohe[2] and Myron H. Wilt[2]

Previous work[3] has shown that Illinois coals take on the ability to act as oxidizing agents toward titanous chloride upon exposure to air or oxygen, even for very short periods of time. In the present work, a similar study has been applied to another group of coals with emphasis upon the changes in oxidizing power over longer times of exposure to air.

Preparation of Samples.—The coal samples were obtained in the form of large fresh blocks at the mines, brought to the laboratory as soon as possible, and ground to pass a 100-mesh sieve. No precautions were taken to prevent atmospheric oxidation during the preparation of the samples. After grinding, portions were taken for analyses, and the remaining stocks were placed in 2-quart mason jars and deliberately exposed to air by leaving the covers loose and by occasionally mixing the contents of each jar. The time of exposure to air was measured in days from the date of grinding.

Determination of Oxidizing Power.—The determinations of oxidizing power were made by the titanous chloride–ferric chloride method previously described.[3] Parallel determinations of soluble ferric iron extractable from the coals under similar conditions were made, and the oxidizing power data reported here are corrected for soluble ferric iron. As a rule, the soluble ferric iron values were low compared to total oxidizing power. The results obtained with five whole coal samples are shown in Fig. 1 expressed in milliequivalents per gram of coal dried in contact with laboratory air, but not calculated to a moisture- and ash-free basis. Analytical data for the coals are given in Table I.

Measurement of Specific Surface.—In order to determine whether the variations in magnitude of oxidizing power were due entirely to differences in surface exposed, specific surface measurements were made. The procedure used is an adaptation of the air-permeability method of Lea and Nurse[4] with apparatus constructed according to specifications obtained from Battelle Memorial Institute.[5] Table II gives the results obtained and a comparison of the maximum oxidizing power values per unit surface.

Discussion

The mechanism of the reaction of oxygen with coal is obscure and will doubtless remain so until the chemical nature of coal is more clearly revealed. A number of workers in this field have considered that the initial step is the formation of a "coal-oxygen complex" or an unstable surface

(1) Presented before the Division of Gas and Fuel Chemistry at the Memphis meeting of the American Chemical Society, April 22, 1942.

(2) Associate Chemist and Research Assistant, respectively.

(3) Yohe and Harman, This Journal, 63, 555 (1941).

(4) Lea and Nurse, *J. Soc. Chem. Ind.*, 58, 277–83 (1939).

(5) Private communication from R. A. Sherman to O. W. Rees.

TABLE I

ANALYTICAL DATA, ILLINOIS COALS

Laboratory number	County	Seam	"As received" basis Moisture	Ash	Ash- and moisture-free basis C	H	N	O	S	Calorific value, cal. per g.[a]	Bituminous coal rank (A. S. T. M.), high volatile
C-2413	LaSalle	6	10.2	9.2	78.38	5.62	1.22	9.25	5.53	7182	C
C-2414	Fulton	5	11.7	7.4	79.93	5.57	1.47	10.43	2.60	7003	C
C-2415	Sangamon	5	11.3	6.8	78.02	5.49	1.48	9.70	5.31	7040	C
C-2422	Vermilion	6	13.1	3.2	81.05	5.65	1.76	10.05	1.49	7035[b]	C
C-2423	Gallatin	5	2.6	10.4	81.36	5.78	1.80	7.78	3.28	7832[c]	A

[a] Moist mineral-matter-free basis. Multiply by 1.8 to obtain the B. t. u. per lb. values used in A. S. T. M. classification by rank. [b] Calculated from ultimate analysis. [c] Value obtained on another sample (C-2416) from the same source.

TABLE II

SPECIFIC SURFACE DATA

Coal number	Specific surface sq. cm./gram	Maximum O. P. × 10^6 / Specific surface
C-2413	3270	5.84
C-2414	5450	2.86
C-2415	3510	4.37
C-2422	3410	3.30
C-2423	3850	1.96

combination.[6-9] Although some assume this to be adsorbed oxygen,[7] others believe it to be chemically combined, since evacuation does not lead to oxygen recovery in the way such treatment of an adsorption complex should do.[10] This "complex" has been referred to as "peroxide,"[8,11,12] yet little is known of its nature or properties.[13] Nevertheless, this loosely bound oxygen is commonly mentioned as an intermediate stage in the atmospheric oxidation of coal.[6,7,8]

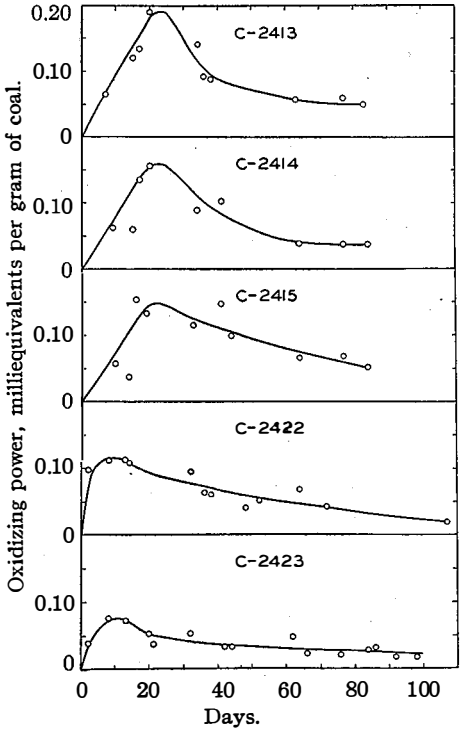

Fig. 1.—Change in oxidizing power with time of exposure to air.

In general form, the curves of Fig. 1 are suggestive of the existence of an intermediate such as B in consecutive reactions of the type

$$A \longrightarrow B \longrightarrow C^{14}$$

Although the atmospheric oxidation of coal is undoubtedly a complex process, the data presented herein may be considered as evidence supporting the hypothesis that loosely held oxygen (perhaps of a peroxide type) constitutes an intermediate stage in a part, at least, of the total change occurring in the oxidative degradation of these coals. It is of interest to note that data for the change in peroxide number of glyceryl trilinolen-

(6) Wheeler, *J. Chem. Soc.*, **113**, 945-55 (1918).
(7) Parr and Milner, *Ind. Eng. Chem.*, **17**, 117 (1925).
(8) Davis and Byrne, *ibid.*, **17**, 125 (1925).
(9) Porter and Ralston, *U. S. Bur. Mines Tech. Paper*, **65**, 21-6 (1914).
(10) Winmill, *Trans. Inst. Mining Engrs.* (London), **48**, 503-7 (1914-15).
(11) Bunte and Brückner, *Angew. Chem.*, **47**, 84-6 (1934).
(12) F. Fischer, *Ges. Abhandl. Kenntnis Kohle*, 4, 454-5 (1920).
(13) Attempts to demonstrate the presence of peroxides in coal in this Laboratory have given inconclusive results. The common potassium iodide test is rendered valueless because of the avidity with which coal combines with iodine. The chemiluminescent oxidation of magnesium phthalocyanine [Cook, *J. Chem. Soc.*, 1845 (1938); Helberger and Hever, *Ber.*, **72B**, 11-15 (1939)] was tried with magnesium phthalocyanine kindly provided by Dr. R. P. Linstead of Harvard University. This reaction is apparently inhibited by coal; a chlorobenzene solution of tetralin which produced red luminescence ceased to do so when a small amount of powdered coal was added. The use of powdered coals as catalysts in the peroxide-catalyzed side chain chlorination of toluene and the addition of chlorine to the ethylenic double bond [Kharasch and Brown, THIS JOURNAL, **61**, 2142-60, 3432 (1939)] gave results which could be explained without assuming the presence of peroxides. A modification of the Yule-Wilson ferrous sulfate test [Yule and Wilson, *Ind. Eng. Chem.*, **23**, 1254-9 (1931)] gave positive results essentially like those obtained with the titanous chloride method. Although proof of the presence of peroxide structures is lacking, such groups must still be considered as possible causes of the oxidizing power observed.
(14) Getman and Daniels, "Outlines of Theoretical Chemistry," 6th Edition, John Wiley and Sons, New York, N. Y., 1937, pp. 329-31.

ate[15] and of a soybean oil[16] give curves similar to those shown in Fig. 1.

There is no apparent correlation between the magnitude of the oxidizing power and properties within the group of coals having high-volatile C bituminous rank. It will be seen, however, that the one coal of higher rank (C-2423) exhibits a definitely lower oxidizing power per unit surface. It seems obvious from Table II that the magnitude of oxidizing power attained is not simply a function of the extent of the surface, but that the nature of the surface (which undoubtedly varies with the rank and source of the coal) is of utmost importance in this respect. It is hoped that this investigation may be extended to cover a series of coals of widely differing ranks.

It is possible that the different petrographic or "banded" ingredients of the coal may differ in their ability to take on oxidizing power. Such differences, as well as errors in sampling, might contribute to the irregularities in the curves. The present study is being continued with samples of separated banded ingredients of an Illinois coal.

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Summary

The oxidizing power exhibited by five Illinois coals has been shown to reach a maximum value and then decrease, suggesting that this "reactive oxygen" may play the role of an intermediate in the oxidative degradation of these coals.

(15) Elm, *Ind. Eng. Chem.*, **23**, 882 (1931).

(16) Clark and Rugg, *Ind. Eng. Chem., Anal. Ed.*, **13**, 243 (1941).

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