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OXIDATION OF COAL

June 16, 1976

Work Performed Under Contract No. E(11-1)-2898

North Dakota State University
Fargo, North Dakota
and
California University
Irvine, California

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Oxidation of Coal

A. VOLBORTH

North Dakota State University and University of California, Irvine

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Oxidation of Coal

Coals are rocks of organic origin consisting mainly of carbon, oxygen, hydrogen, sulfur, and nitrogen. The chemical composition and physical characteristics of coals vary greatly. In the petrographic description of coal one distinguishes certain components, called macerals (Stopes, 1919;1935). These can be best identified microscopically in polished coal sections (reflected light) and thin sections of coal (transmitted light). A parallel can be drawn between the minerals of the rocks and the coal components--macerals, with the distinction that while minerals have definite physical and chemical properties, the properties of coal macerals are not constant and vary according to the rank of coal.

Three categories or maceral groups are distinguished: according to the Stopes-Heerlen System[19]:

1) Vitrinite - the primary constituent of bright bituminous coal. Can be structureless (collinite) or has a well defined cellular structure (Telinite). Fuses into a swollen button.

2) Exinite, rare in bituminous coals, main constituent in cannels and torbanites; in cellular, compressed and stratified, often oval-shaped cerrated masses. Composed of algae remains (alginite), of waxy plant cuticles (cutinite), rod-like oval masses and films, formed from fossil plant resins and waxes (resinite), in bituminous coals, and of remains of spores (sporinite) common in dull coals. Exinite is transformed to gas and tar on heating, has a high volatile and hydrogen content.

3) Intertinite, includes the macerals which are chemically very inert, which will yield low quantities of volatiles. Four macerals are distinguished in this group:

   a) Fusinite with well-defined cellular structure with round, oval, and elongated cell cavities, opaque in transmitted light, occurring as lenses and angular inclusions, very brittle; originated in forest fires (?).

b) Micrinite, fine or coarse-granular layered materials, from decayed plants, especially in dull coals.

c) Sclerotinite, rounded bodies with filaments in stratified mass; remains of fungi (?).

d) Semifusinite, cellular, less well developed than in fusinite, occurs in lenses and inclusions.

The Stopes-Heerlen System further distinguishes lithotypes, "rock types", commonly with suffix -ain. For example, in Banded Coals we find four lithotypes: Vitrain, brilliant black, non-laminated bands of coal and lenses rich in vitrinite. Coal with over 95% of vitrinite is called vitrain. Clarain - a coal occurring in thin laminated bands of alternating bright and dull lustre containing both vitrinite, resinite, and exinite, with some micrinite. Vitrain and clarain are both bright coals. Durain, a dull hard coal consisting mainly of micrinite and exinite. Fusain, soot-like, opaque, powdery, dull, charcoal-like substance in thin bands, consisting mainly of fusinite. Non-Banded Coals have two lithotypes: Cannel coal, a sapropelite, dull black, composed of micrinite with considerable microspores, and Boghead coal, or torbanite, a sapropelite of algal origin, under microscope a dark ground mass with numerous white globules.

The above briefly described system of petrographic coal classification is based on examination of polished sections in reflected light, and is used extensively in Europe. Another petrographic classification based on the study of coal thin sections in transmitted light, the so-called Thiessen-Bureau of Mines System is currently also employed in the U.S.A.[22,23,29,40] Spackman, 1975,[3] has recently prepared a somewhat simplified system of coal classification.

This brief and incomplete description of coal macerals and lithotypes is given here in order to permit a better understanding of the complexity and variability of the chemical composition of coal. It is obvious that oxidation and decomposition studies of coal must be conducted on carefully selected material that has been identified as to the maceral group and lithotype.

Numerous comparative chemical studies of coal macerals exist. Tschamler and De Ruiter[24] have found that in a dull coal aromaticity increases in the sequence exinite → vitrinite → micrinite, while aliphatic hydrogen decreases, and hydroxylic oxygen remains constant; also, that the number of CH_2 groups in exinite is more than double that of vitrinite and six times higher than in micrinite. Exinite was found to have one CH_3 group per two CH_2 groups, and micrinite - one CH_3 per one CH_2 group. Analyses of these macerals of interest are shown in Table 4. As can be seen from this table, the atomic ratios H/C decrease remarkably from exinite-vitrinite to micrinite. It is found that this is due to the decrease of aliphatic groups and the increase of aromatic cluster size from exinite through vitrinite to micrinite. The ratio of aromatic hydrogen to total hydrogen has been also found to increase in the same sequence (see Table 5).

Austen et al., 1966,[25] conclude from results of an electron spin resonance study on fusinite, exinite, and vitrinite that fusinites were affected by elevated temperatures and pyrolysis to perhaps 400-600 °C before the incorporation into the organic sediment. This supports earlier suggestions that fusinites may be products of partial pyrolysis due to contemporaneous forest fires. The high concentration of carbon in fusinites (~90%) can be also due to thermophilic bacterial decomposition, resulting in hot spots and spontaneous combustion. In principle therefore, oxidation of organic matter by incomplete combustion could produce highly carbonaceous material. The authors, however, emphasize that such burning, in order to be effective, would have to burn off selectively the combined hydrogen leaving the skeletal carbon structures intact to be later polymerized during the metamorphism. They also suggest that some form of fungal attack may be feasible that selectively would oxidize the woody tissue.

Sun et al., 1966,[26] studied the electrokinetic properties of anthracite and found three distinct lithotypes. The eleven anthracites studied contained on the average 60-80%

Table 4

Aliphatic Group Distribution per 100 C_{total} of an Exinite, Vitrinite, and Micrinite

Sample	CH_3	CH	CH_2	H_{al}/C_{al}	f_a
Exinite	8	0	26	2.23	0.66
	7	3	26	2.11	0.64
	6	6	26	2.00	0.62
	5	9	26	1.90	0.60
	4	12	26	1.81	0.58
	3	15	26	1.73	0.56
	2	18	26	1.65	0.54
	1	21	26	1.58	0.52
	0	24	26	1.52	0.50
Vitrinite	8	1	11	2.35	0.80
	7	4	11	2.14	0.78
	6	7	11	1.96	0.76
	5	10	11	1.81	0.74
	4	13	11	1.68	0.72
	3	16	11	1.57	0.70
	2	19	11	1.47	0.68
	1	22	11	1.38	0.66
	0	25	11	1.31	0.64
Micrinite	5	0	4.3	2.54	0.90
	4	3	4.3	2.09	0.88
	3	6	4.3	1.77	0.86
	2	9	4.3	1.54	0.84
	1	12	4.3	1.36	0.82
	0	15	4.3	1.22	0.80

$$f_a = 1 - \frac{C_{al}}{C}$$

after Tschamler and De Ruiter, 1966, by proton spin resonance

Table 5

Hydrogen Distribution of an Exinite, Vitrinite, and Micrinite

Sample	% H	% H_{al}	% H_{ar}	% $H_{OH(Diff.)}$	$H_{al/H}$	$H_{ar/H}$
Exinite	7.0	5.4	1.4	0.2	0.77	0.20
Vitrinite	5.5	3.3	1.9	0.3	0.60	0.35
Micrinite	3.9	1.7	2.0	0.2	0.44	0.51

after Tschamler and De Ruiter, 1966

vitrain, 10-30% durain, and 1-10% fusain. They conclude that anthracite cannot be regarded as a homogeneous substance. Electronmicroprobe analysis reveals that the mineral matter in the vitrain was uniformly distributed while in the fusain, finely disseminated quartz in a cellular structure was found, and the durain surface was impregnated with aluminum and silicon, most likely due to a kalolinite type mineral. It is likely that the surface oxidation of each of these lithotypes would be different.

Murchison, 1966,[27] found in infrared spectral studies that resinites probably lose aliphatic groups and undergo an increase in aromaticity on carbonization and oxidation. Strengthening of the carbonyl bond was also observed. Otherwise the resinites studied showed an extremely low aromaticity and failed to give aromatic char when carbonized (see Table 5). In Table 6 Murchison's data and Tschamler's[24] data are combined. The hydrogen to carbon ratio is shown to decrease in the sequence resinite → exinite → vitrinite → micrinite.

In order to understand better the processes involved in the oxidation of coal, numerous studies of the compositional variations of coal macerals and their structure[6,7,8,9,10,11,18,20,23,24,29] have been made. These involve ultrasonics,[32] radio-frequency heating,[34,36] electronic low temperature ashing, (LTA)[37], solvent extraction, pH and Eh measurements,[18] the determination of the properties of the extracts by the classical and instrumental methods such as infrared spectroscopy,[26,27] ultraviolet absorption[18], mass spectrometry, nuclear paramagnetic resonance,[33] x-ray diffraction and scattering studies, electron spin resonance,[25] streaming potential methods (electrokinetic behavior),[26] gas and paper chromatographic techniques,[18] electrophoresis,[11,18] x-ray photoelectron spectroscopic[35] and electron- and x-ray-microprobe techniques,[27] thermogravimetric analysis, differential thermal analysis, and many complex procedures involving combinations of the instrumental techniques listed above with sophisticated organic separation and synthesis methods of analysis.[1]

Table 6

Elementary Analyses of Resinite, Exinite, Vitrinite, and Micrinite

Sample	Volatile Matter	% C	% H	% O	% N	% S (diff)	H/C
Resinite*		84.1	8.2	6.5			1.16
Resinite*		84.3	7.4	6.2			1.04
Exinite**	66.7	84.1	7.0	6.3	1.3	1.3	0.991
Vitrinite**	35.2	83.9	5.5	8.0	1.4	1.2	0.780
Micrinite**	22.9	85.7	3.9	8.0	1.2	1.2	0.542

*After Murchison, 1966 **After Tschamler and De Ruiter, 1966

These studies have shown that during the metamorphism of organic matter from peat to lignite and bituminous and brown coal to anthracite, condensation of aromatic nuclei seems to occur. This is accompanied by a loss of oxygen and hydrogen and an increase of carbon. In this process the functional groups such as carboxyl (-COOH), hydroxyl (-OH), methoxyl ($-OCH_3$), and the carbonyl (=C=O) are progressively depleted in the coal[30,31] but are not entirely lost even in the high rank coals.

In general, early work in this field in the 1940-1950's[18] has established that 1) the quantity of these oxygen functional groups is reduced with the increasing rank and is higher in the younger coals; 2) the hydroxyl groups account one-fourth to one-eighth of the total oxygen in the coal, with lignites containing about 10 percent by weight of the -OH groups; 3) in high rank coals of 80 percent carbon, only about 7 percent of functional groups remain and drop to near zero in coals with 90 percent carbon; 4) the carboxyl groups are present in brown coals and lignite but are practically absent in bituminous coals, with brown coal containing about 5 to 6 percent carboxyl,[31] and coal with 85 percent carbon none; 5) the carbonyl groups are found generally in coals of all ranks, but their concentration is low in bituminous coal. Brown coal contains about 3.5 percent carbonyl groups, coals with 85 percent or more of carbon average 0.6 percent carbonyl associated mainly with quinoid structures.[30] 6) The methoxyl groups while forming a large part of the "fresh" lignin (7-17% according to Flaig's data [4]), represent only an insignificant percentage in coal. This decreases from 0.8 percent in the brown coal to about 0.4 percent in coal with 70 percent carbon, and drops to about 0.2 percent or less methoxyl in a coal with 80 percent carbon.[18]

Van Krevelen[30] emphasized that not all oxygen in coal is detected by the determination of the functional groups. Like nitrogen, as proposed by Francis,[29] part of the oxygen can be built into the heterocyclic rings and thus may be liberated only by the hydrolysis of coal.

Quantitative determination of functional groups in coal presents considerable difficulties, however, Manskaya[18] has compiled data (up till 1965) and compared the oxygen contained in the different functional groups in coal to the total oxygen and the carbon content in different coals (Table 7).

Factors further complicating the study of the structure and oxidation of coal are the presence of water of crystallization and of the OH groups in the mineral matter associated with coal and the oxidation of iron sulfides pyrite and marcasite upon heating in air. These are causes for evolution of water from coal and also for consumption of oxygen. It is very difficult to distinguish water evolved from mineral matter from the water evolved due to the pyrolytic reaction and destruction of the oxygen functional groups of the organic matter. Decomposition of coal by radio-frequency techniques often permits better retention of mineral matter, such as sulfide and carbonate minerals, for example,[36] and thus may lead to a better understanding of the composition of the organic coal material. Low temperature ashing techniques (LTA) developed by Gluskoter, 1965,[37] permit a decomposition of coal at temperatures between 150 and 200 °C with residues composed primarily of calcite, pyrite, kaolinite, and undecomposed clay minerals. This technique combined with fast-neutron activation determination of oxygen shows promise for more accurate interpretation of the true organic oxygen content in coal.[38,39]

Oxidation reactions of coal with atmospheric oxygen, oxygen, hydrogen peroxide, nitric acid, potassium permanganate, sulfuric acid, and other reagents[41,42,43,44] produces a mixture of water-soluble acids. Chromatographic and mass spectrometric studies of these acids, obtained from oxidation of bituminous coal, have detected[42,43] mainly benzoic acid, phthalic acid and its isomers, but also mellitic acid, trimellitic acid and its isomers.

Table 7

Functional Groups in Coal

(in % per functional group*)

C	O_{COOH}	O_{OCH_3}	O_{OH}	$O_{C=O}$	O unreactive	O_{total} *
65.2	9.0	0.4	10.2	4.7	4.3	28.7
69.9	3.6	0.9	9.6	3.9	5.3	23.4
74.6	1.5	0	8.1	2.7	3.8	16.8
77.3	1.2	0	8.0	2.9	3.2	15.4
80.0	0.5	0	7.0	1.3	4.9	13.4
82.8	0.1	0	1.2	0.6	8.3	10.7
85.0	0	0	0.4	0.35	7.3	8.2
89.7	0	0	0.1	0.55	3.0	3.7
90.3	0	0	0	0.5	2.9	3.4
92.8	0	0	0	0.4	2.0	2.5
65.5	8.0	1.1	7.2	1.9	9.6	27.8
70.5	5.1	0.4	7.8	1.1	8.2	22.6
75.5	0.6	0.3	7.5	1.4	6.4	16.2
81.5	0.3	0	6.1	0.5	4.2	11.1
85.5	0.05	0	5.6	0.5	1.75	7.9
87.0	0	0	3.2	0.6	1.3	5.1
88.6	0	0	1.9	0.25	0.85	3.0
90.3	0	0	0.5	0.2	2.2	2.9

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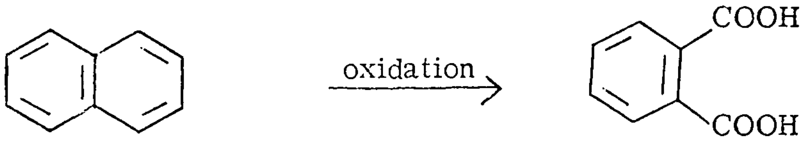
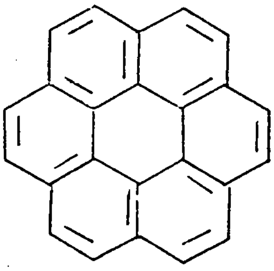
* According to Manskaya and Drozdova, 1968[18]

The detection of phthalic acid in oxidized bituminous coal may be an indication of naphthalene, anthracene, and phenanthrene type polycyclic aromatic nuclei in coal:



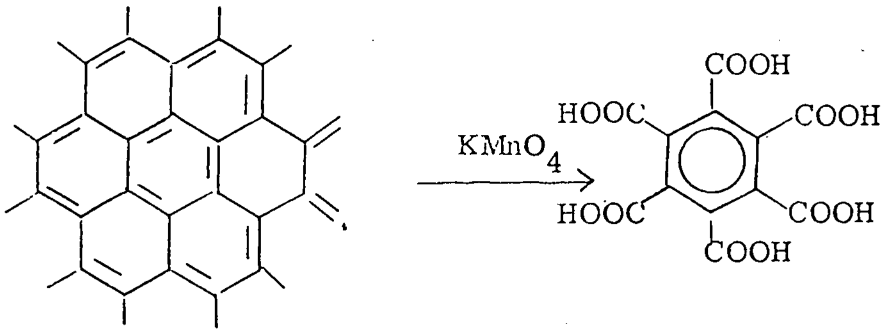
naphthalene   phthalic acid

The presence of mellitic acids in oxidized coal products is significant because it indicates that the original material has probably contained larger aromatic clusters such as coronene:



coronene

Since mellitic acids are obtained also from the oxidation of graphite:

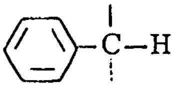
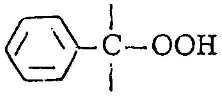


graphite mellitic acid

coal can be assumed to have aromatic structural units similar to the graphite structure. It was also found that the yield of the mellitic acid increases with the rank of coal.[30] The yield of aromatic acids in general increases when oxidizing lignin → peat → brown coal → lignite → bituminous coal → anthracite, with anthracite yielding about 50 percent.[45] This indicates increasing aromaticity and an increasing size of the aromatic clusters or nuclei. Based on these studies, models of the chemical structure of coal have been proposed. These consist of polyaromatic clusters bound together by heterocyclic rings containing oxygen, nitrogen and sulfur, with occasional carbonyl groups, as shown in the model proposed by Fuchs and van Krevelen, in 1957[30] (Figure 1).

Comparison of the ultimate analyses of subbituminous and low to high rank bituminous coals to the composition of hypericin, anthraquinone, anthrone, benzanthrone and dibenzanthrone (see Tables 1,3) indicates very similar composition, supporting Fuchs' and van Krevelen's[30] proposed model for the chemical structure of coal (Fig. 1), which contains polycyclic aromatic clusters interconnected by heterocyclic rings containing oxygen, sulfur, and nitrogen, as well as a few aliphatic chains, carbonyl, carboxyl, hydroxy, and methoxy functional groups, which seem to decrease in abundance with the increase of the rank of coal, while the rise of the aromatic clusters seems to increase.

Certain organic compounds are oxidized more readily than others. The ease with which an organic substance will oxidize depends on the functional groups present in the molecule. Oxidation of coal is affected by incorporation of oxygen functional groups, such as the peroxide, the hydroxyl, the aldehyde, the carbonyl, the carboxyl, the ether linkage, and the methoxyl groups. Once oxygen has been combined with an organic molecule, further oxidation may occur more readily. Compounds with oxygen functional groups attached are more susceptible to further oxidation than their progenitors. For example, alcohol and acetaldehyde oxidize more readily than ethane, phenol and naphthol more easily than benzene and naphthalene, and benzaldehyde more readily than toluene. Saturated and purely aromatic hydrocarbons are more difficult to oxidize than their derivatives containing oxygen functional groups. Some unsaturated structures and ethers are known to form peroxides easily, Yohe, 1958, p. 17[75]:

Group	Structure	Peroxide Formed
methyl	CH_3	$-OOCH_3$
ether	C—O—C—H	—C—O—C—OOH
olefin	C:C—C—H	—C:C—C—OOH
alkylated aromatic		

The formation of peroxide appears to be one of the initial steps of coal oxidation (see p.   ); it can lead then to the formation of other oxygen functional groups.

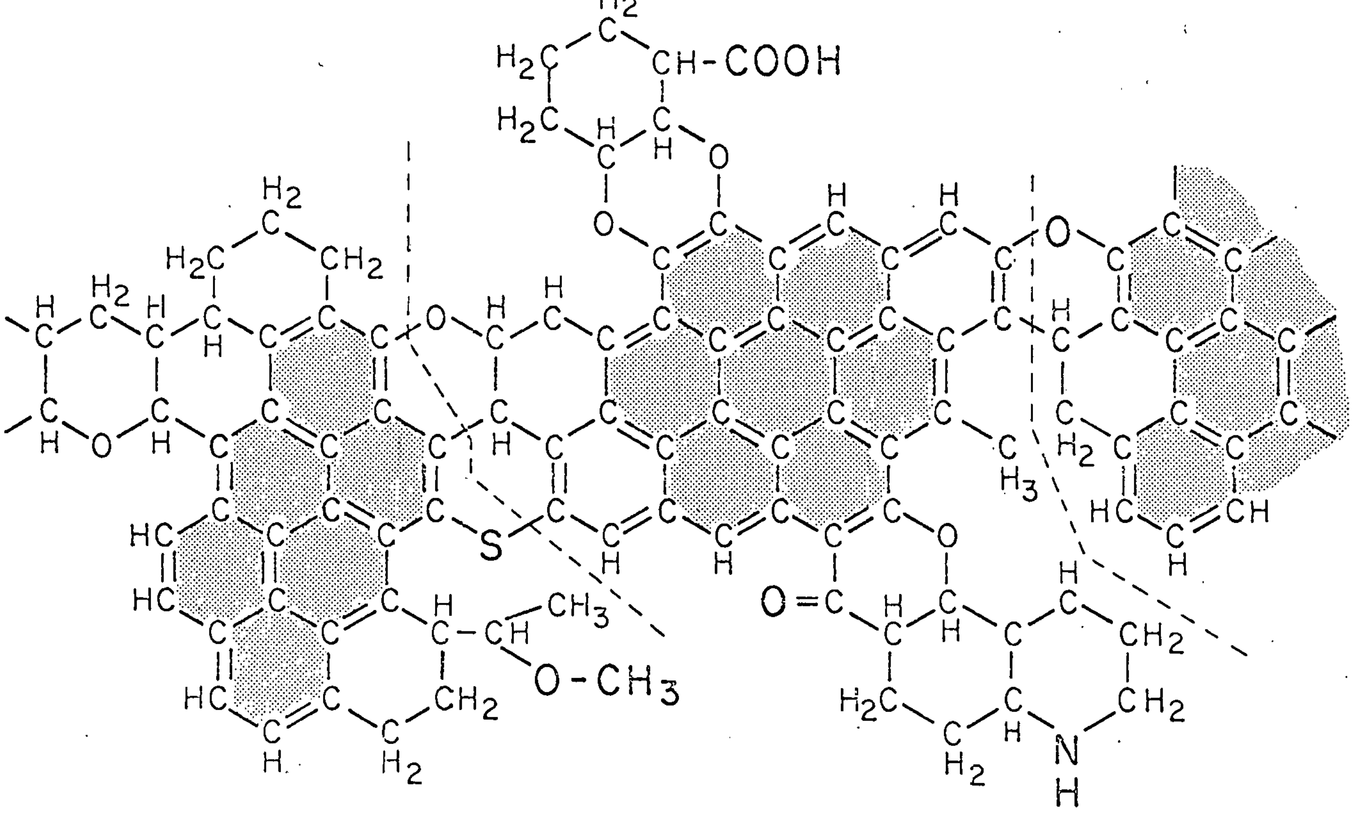


FIG. I Model of chemical structure of coal modified after Fuchs and van Krevelen (van Krevelen, 1957).

The weathering of coal increases the concentration of the oxygen functional groups,[46,47] and some reduction of carbon content results,[41] technological quality of coal changes, water content increases, and alkali-soluble products similar to the humic acids form (see p.   ), as well as water-soluble lower molecular weight acids. In the early stages of oxidation oxygen is being added to the coal bulk composition and water is lost, while during the later stages of humification of coal, CO_2, CO, and H_2O evolve. The oxidation proceeds along the periphery of the macromolecule clusters in coal and affects the C—C bonds, rupturing the aromatic rings.

The terms "coal-oxygen-complex" or "unstable surface combination" have been used by a number of early workers in the field of coal oxidation and weathering Yohe, 1958, p. 11.[75] The types of interaction between the solid coal and the gaseous oxygen are dual in nature. First, the preferential adsorption of oxygen rather than that of nitrogen on the surface boundary of coal particles may produce an increased concentration of it on the surface. This attraction is not of chemical nature and the gas may be desorbed by increasing the temperature, or evacuation in vacuum. Second, a process of chemisorption may occur in connection with adsorption. This would involve initial oxidation of coal surfaces and the formation of hydroperoxides (—C-O-O-H by the interaction of molecular oxygen with the —C—H groups. Such process is well known to occur in the "drying" or aging of oil paints and the development of rancidity of butter. Such reacted oxygen cannot be removed by heating or evacuation as oxygen, but evolves as H_2O or CO_2. Both processes described above probably occur simultaneously. The chemisorbed oxygen of the hydroperoxides as well as the adsorbed oxygen can further react with the coal "molecules" forming more stable and permanent organic groups. Yohe and Harmon[90] have studied the surface oxidizing power of Illinois coals and suggested that both processes exist. They emphasize that the rapid formation of the coal oxygen complex in only a few minutes is indicative of the adsorption type reactions, while the fact that simple evacuation does not lead to full recovery of adsorbed oxygen implies that chemical combination also occurs. Yohe, 1950, also demonstrated using the darkening effect on a photographic plate (Russell Effect) that peroxide compounds do exist on coal surfaces. In earlier work Yohe and Wilt, 1942[91,92] have found that the surface oxidizing power of several high-voltaile bituminous coals reached a maximum in 10 to 25 days of exposure, then diminished slowly. They interpreted this phenomenon by suggesting that after the fast initial adsorption of oxygen, the hydroxyperoxide phase is intermediate and leads to the formation of more stable oxidation products.

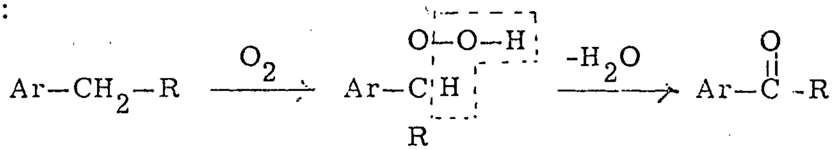
Oreshko, 1949[93,94,95] found in heating studies of Donets Basin coals in air and oxygen that in all cases there was first a gain in weight, then a drop, then another gain and yet a higher weight gain before a sharp drop when combustion occurred. He was able to distinguish three stages of reaction depending on the temperature:

70-80°	Formation of peroxide type complexes
80-130°	Decomposition of peroxide complexes
130-160° or 180-290°	Formation of "stable" coal-oxygen complexes destroyed only by ignition.

Jones and Townsend, 1949[96] studied oxidation of British coals and Chakravorty *et al*., 1950[97], British and Indian coals. These authors also found that the "peroxide" complex started to decompose at 80 °C. Chakravorty *et al*. found that the decompostion of this complex approximates a first-order reaction and were able to determine that the activation energy is approximately that for hydroperoxide decomposition. Higushi and Shibuya, 1954[98] have also detected peroxides in nonvolatile air-oxidized lignite.

Yamasaki, 1953[99] oxidized coal of different screen sizes and determined oxygen absorbed at temperatures under 100 °C. He found a linear relationship between oxygen absorbed and temperature between 30° to 100 °C. Below 30° values obtained for oxygen deviated greatly from his empirical equation. Yamasaki suggested that this phenomenon is due to van der Waal's adsorption of oxygen on the surface of coal which occurred predominantly under 30°C, whereas chemisorption occurred predominantly between 30° and 100 °C.

In recent oxidation studies of coal Albers, Lenard and Oelert, 1974,[59] have shown that autooxidation of coal can proceed through the formation of hydroperoxides to ketones:

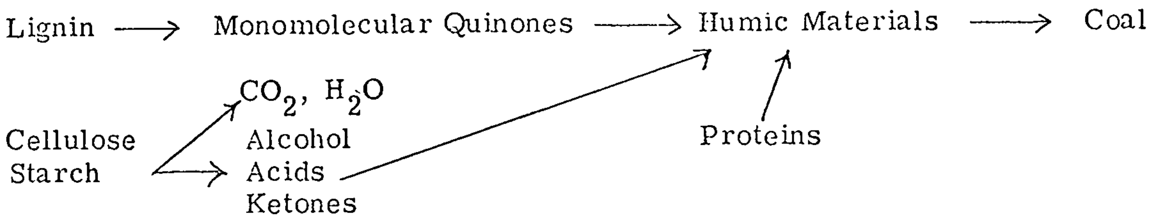


$$\mathrm{Ar{-}CH_2{-}R} \xrightarrow{O_2} \mathrm{Ar{-}\underset{R}{\overset{O-O-H}{C}}H} \xrightarrow{-H_2O} \mathrm{Ar{-}\overset{O}{\overset{\|}{C}}{-}R}$$

Molecular oxygen is an efficient breaker of chain reactions. The formation of the peroxy radical (R—O—O—) by autooxidation of coal with atmospheric oxygen may first attack, cleave, and weaken the aliphatic domains of the coal miscelles, then gradually destroy the heterocyclic and hydroaromatic regions, thus exposing the aromatic clusters to further degradation.

Chakrabratty, 1975,[2] has recently raised, however, serious questions concerning the evidence/and probability of lignin decomposition through the formation of quinones which he points out, if formed, would certainly react first with other reactive compounds available in the decomposing peat rather than get concentrated so that they could interact to form larger aggregates. He also emphasizes that before the cellulose can be degraded bacterially, it has to be transformed to non-crystalline forms.

Chakrabratty presents a simplified scheme for coal formation:



He considers the present concept of an average coal "molecule" having polycondensed aromatic ring clusters as predominant structural feature of coal unsatisfactory, because oxidation studies with hypohalite revealed reactivities and oxidative properties inconsistent with that widely accepted structure.

Kinetic studies of oxidation of coal are complicated considerably by the fact that several different reactions seem to occur concurrently; chemically different structural units and different functional groups are involved, and the nature of coal is very variable. The measurement of reaction rates on coal surfaces is therefore very difficult. Whether one determines the oxygen adsorbed, the heat produced, or the concentration of compounds formed, one tends to measure the result of a series of complex processes often unrelated and which are difficult or impossible to separate. This explains why attempts at accurate and consistent kinetic measurements have produced somewhat inconsistent results. Nevertheless, the general agreement considering these difficulties is remarkably good.

Oxidation of coal may then be represented by a scheme proposed by Oreshko in 1953:[51]

$$\text{Coal} + O_2 \longrightarrow \text{Coal-oxygen complex} \xrightarrow{O_2} \text{Humic acid} + CO_2 + CO + H_2O$$

Oreshko emphasized the importance of the "coal-oxygen complex", the nature of which changes with progressing oxidation. Howard, 1945,[52] notes that the "regenerated" humic acids from oxidation of coal of higher rank have fewer active acidic groups, fewer ether links, and a higher degree of condensation of aromatic nuclei. Humic acids extracted from different types of coal have different optical density, depending on the degree of condensation of the aromatic clusters and the concentration of the oxygen groups, according to Kucharenko, 1953, 1955.[53,54].

Gillett, 1951,[67] has proposed that about 80 percent of the coal substance is more or less homogeneous and has the approximate "fundamental" composition of $C_{29}H_{22}O_2$. By oxidizing coal in oxygen atmosphere at 220°, Gillet, 1958,[55] obtained a humic acid with a molecular weight of 376 and proposed the formula $C_{20}H_8O_8$ for the dry material. In 1960[56] he was able also to separate the anthraxylic acid of idential composition ($C_{20}H_8O_8$) from peat, coal, and lignite (see p.). Humic acids obtained from anthracite were labeled "regenerated" by Gillet.[55]

Among the acids formed in extracts from oxidized bituminous coal mellitic, trimellitic, and phthalic acids as well as condensed aromatic acids dominate. The oxidation end-products are the oxalic, malonic, and the acetic acids, indicating that the phenol ring is broken during the final stages of oxidation.

We have selected a representative array of aromatic and aliphatic acids and other compounds actually found in coal oxidation studies[1,2,4,10,11,13,18,72,75] and plotted them in a sequence representing advancing oxidation of coal (Table 8). In this table, we have included also gluconolactone and gluconic acid, because recent infrared

Table 8. Organic compounds detected in coal oxidation studies plotted according to increasing oxygen content

	C	H	O	%N
Anthracene: $C_{14}H_{10}$	94.34	5.66	0.00	
Squalene: $C_{30}H_{30}$	87.73	12.27	0.00	
Anthracite, Mason, p. 227[16]	93.50	2.81	2.72	.97
Friedeline: $C_{30}H_{50}O$	84.44	11.81	3.75	
Cholesterol: $C_{27}H_{45}(OH)$	83.87	11.99	4.14	
Phytol: $C_{20}H_{39}(OH)$	81.01	13.60	5.40	
Betuline: $C_{30}H_{50}O_2$	81.39	11.38	7.23	
Gillet's "fundamental coal formula":[67] $C_{29}H_{22}O_2$	86.54	5.51	7.95	
Anthranol: $C_{14}H_9(OH)$	86.57	5.19	8.24	
Bituminous coal, Mason, p. 227[16]	84.24	5.55	8.69	1.52
Abietic acid: $C_{20}H_{30}O_2$	79.42	9.99	10.58	
Naphthol: $C_{10}H_7(OH)$	83.31	5.59	11.10	
Anthraquinone: $C_{15}H_{10}O_2$	80.76	3.87	15.37	
Phenol: $C_6H_5(OH)$	76.57	6.43	17.00	
Naphthoic acid: $C_{10}H_7(COOH)$	76.73	4.68	18.58	
Naphthoquinone: $C_{10}H_6O_2$	75.94	3.82	20.23	
Lignite, Mason, p. 227[16]	72.95	5.24	20.50	1.31
Cinnamic acid: $C_6H_5CH{:}CH(COOH)$	72.96	5.44	21.60	
Toluic acid: $CH_3C_6H_4(COOH)$	70.57	5.92	23.50	
Benzoic acid: $C_6H_5(COOH)$	68.84	4.95	26.20	
Vanillin: $CH_3OC_6H_3(OH)CHO$	63.15	5.30	31.55	
Anthraxylic Acid: $C_{20}H_8O_8$	63.84	2.14	34.02	
p-Hydroxybenzoic acid: $C_6H_4(OH)(COOH)$	60.86	4.38	34.75	
Purpurogallin: $C_{11}H_8O_5$	60.00	3.66	36.33	
Peat, Mason, p. 227[16]	55.44	6.28	36.56	1.72
Phthalic acid: $C_6H_4(COOH)_2$	57.83	3.64	38.52	
Syringic acid: $(CH_3O)_2C_6H_2(OH)(COOH)$	54.55	5.09	40.37	
Mevalonic acid: $C_5H_9(OH)_2(COOH)$ (also in lactone form)	48.64	8.16	43.20	
Wood, Mason, p. 227[16]	49.65	6.23	43.20	.92
Adipic acid: $(CH_2)_4(COOH)_2$	49.31	6.90	43.79	
Trimellitic acid: $C_6H_3(COOH)_3$	51.44	2.88	45.68	
Gallic acid: $C_6H_2(OH)_3(CCOH)$	49.42	3.55	47.02	
Pyromellitic acid: $C_6H_2(COOH)_4$	47.26	2.38	50.36	
Acetic acid: CH_3COOH	40.00	6.71	53.29	
Gluconolactone: $C_6H_{10}O_6$	40.45	5.66	53.89	
Succinic acid: $(CH_2)_2(COOH)_2$	40.68	5.12	54.20	
Mellitic acid: $C_6(COOH)_6$	42.12	1.77	56.11	
Gluconic acid: $C_6H_{12}O_7$	36.74	6.17	57.10	
Malonic acid: $CH_2(COOH)_2$	34.62	3.87	61.50	
Formic acid: HCOOH	26.10	4.38	69.52	
Oxalic acid $(COOH)_2$	26.68	2.24	71.08	
Carbon dioxide	27.29	----	72.91	

reflection spectrometry and mass spectrometry studies have shown that lactones may form on the surface of oxidized graphite, char, and coal (Yang, 1975[57]; Barton, 1975[58]). It may be significant that plotted according to the increasing oxygen content, these compounds form distinct groups in the sequence polyaromatic acids--carboxyl phenolic acids --polycarboxylic phenolic acids--polycarboxylic heterocyclic polyaromatic acids (humic acids)--carboxylic acids and glycosides.

In the oxidation of coal the coalification sequence represented in Tables 1 and 3 is reversed (see Table 8). The important intermediate products in both cases are the humic acids. In coalification these acids are decarboxylated, dehydroxylated, and further aromatization results. In the oxidation of coal they are then reconstituted, cleaved stepwise into smaller units, and carboxyl and hydroxyl groups are added to the phenolic nuclei which are broken in the final stages of oxidation to form smaller aliphatic molecules rich in carboxyl oxygen. The sequence in which the compounds are listed in Tables 1, 3, and 8 is intended not in the sense that the compounds are necessarily immediate precursors or are formed directly from the compounds listed above. Such constrains as equilibria, and the fact that the oxidation reactions must proceed simultaneously in a variety of complex organic molecules and aromatic heterocyclic clusters affecting different active sites makes such a simple scheme very inadequate. However, we believe that the general path of coal weathering, degradation, and oxidation is well represented by plotting the products of these processes according to the increasing oxygen content of their molecules actually identified by modern techniques.

When compounds found in coal oxidation studies are plotted and their composition compared in the sequence of increasing oxygen content as in Table 8, a few observations may be made which could be useful.

First, the increase in oxygen and the decrease in carbon seem to follow a similar pattern as when different rank coals are grouped in a sequence of decreasing rank.

While oxygen decreases some ten to twentyfold as compared with a high rank anthracite versus oxygen in wood, the carbon concentration is only changing by about a factor of two, and the bulk hydrogen concentration remains about the same while fluctuating within relatively narrow limits of about 3 to 5 percent total. The wide range of the oxygen content being between about 3 to 72 weight percent, demonstrating the important role of this element in the oxidation processes of coal. These lead from pure hydrocarbons and anthracite to carbon dioxide. Determination of oxygen in these products should therefore provide more diagnostic information concerning the rank of coal or the degree of oxidation of the derivative products than the analysis for hydrogen or even carbon.

Second, even a fleeting comparison of composition of coals and their derivatives, when plotted in this manner, groups together the saturated cyclic hydrocarbons, the steroids, the terpenes and their derivatives according to their low oxygen and high hydrogen content. When these compounds are compared with the composition of coal, the abnormally high content of hydrogen, about double that of the typical coals, is obvious. Coals do not have nearly enough hydrogen should they be assumed to contain considerable quantities of such compounds or similar saturated structures.

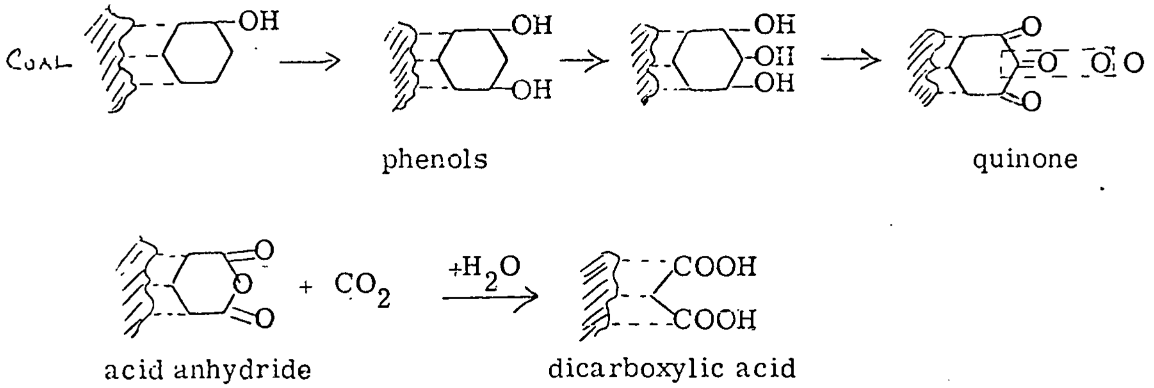
Third, the comparison of compositions of several aromatic and polyaromatic as well as heterocyclic compounds of coal decomposition products with coals reveals remarkable similarities in oxygen, hydrogen, and carbon content.

Fourth, the arrangement of this plot coincides with the general sequence of oxidation and decomposition products formed from coal, lignite, peat, and organic material.

The formation of phenols and quinones from lignin, cellulose, and sugars, and their dimerization, polymerization and fusion products as precursors of polyaromatic heterocyclic humic acids has been demonstrated above (pp.). Below, a few proposed oxidation schemes will be discussed.

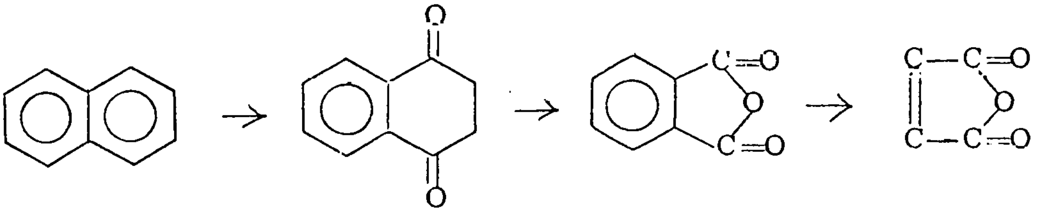
Referring to the model coal structure (Fig. 1) proposed by Van Krevelen[30], one could easily imagine that a relatively mild degree of oxidation could have a strong effect on the physical properties of the whole coal. As the heterocyclic structures are more affected by oxidation, additional aliphatic chains with carbonyl, carboxyl groups, and ether linkages are formed and the nature of internal surface changes and swelling takes place. Recent studies using $^{18}O_2$, by Ignasiak and coworkers, 1972,[60] have shown that indeed even mild weathering introduces sufficient crosslinks to have a profound influence on the physical properties of the coal. Ignasiak et al., 1974,[61,62] have further demonstrated that weathering does influence the plasticity and dilatation properties of weathered coking coal. Washowska <u>et al.</u>, 1974,[63] have also found the dilatation effect and demonstrated that the ether linkages are also broken in the coal's internal structure by progressing oxidation at low temperatures (85°) in air for three days. Swann <u>et al.</u>, 1974[64] have detected notable changes in the internal surface properties of brown coal after low temperature oxidation.

In 1940 Tronov[65,66] has proposed an oxidation sequence of coal starting with formation of polyhydric phenols and proceeding through carbonyl compounds (quinones) to acid anhydrides and carboxylic acids that is still valid today:



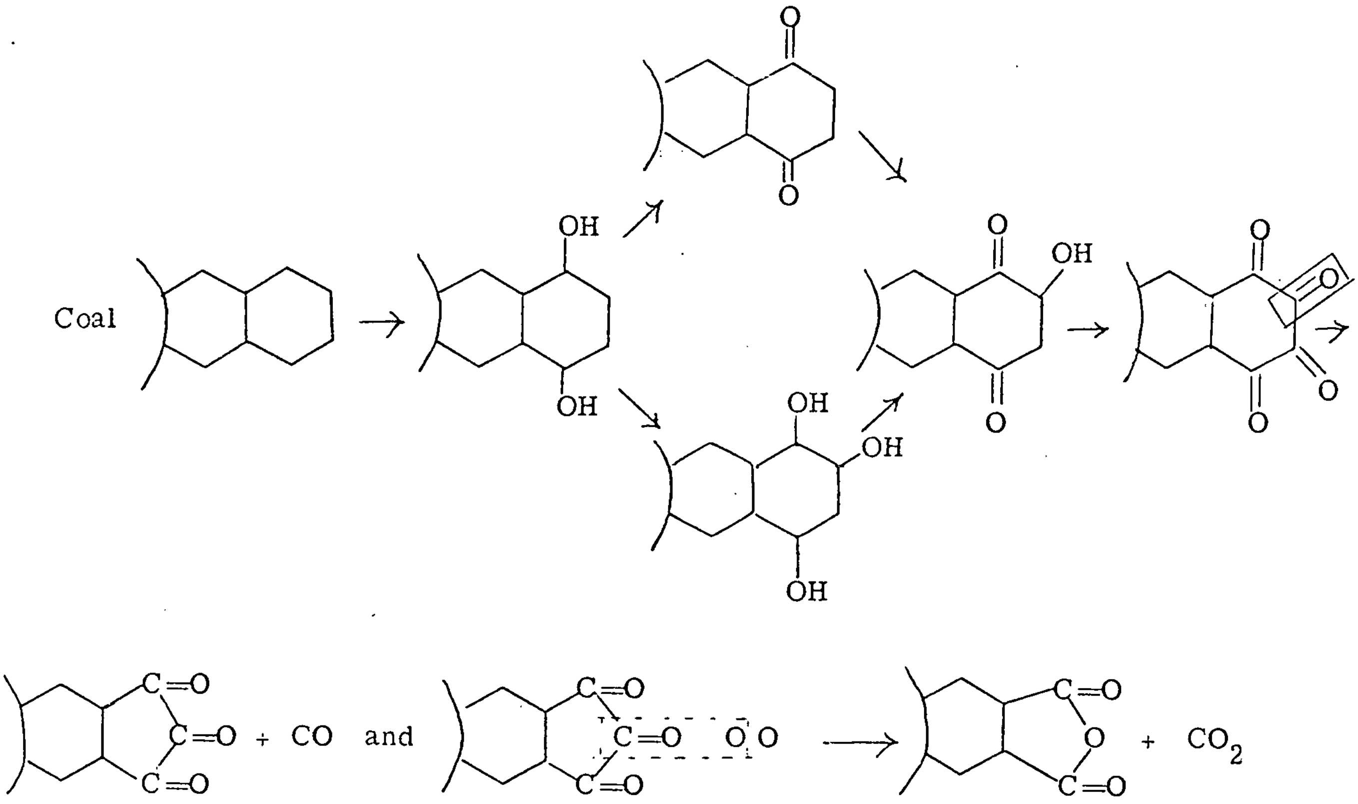
Modified after Tronov, 1940

Yohe and Blodgett, 1947,[68] concluded from studies of oxidation of various coals methylated with dimethyl sulfate that the content of phenolic structures in lower rank medium volatile bituminous coals decreased with the increase of coal rank. This was confirmed by infrared studies, Brown, 1955[69]. Vucht et al., 1955,[70] also found an increase in OH groups during the oxidation of coal. Atmospheric oxidation of Illinois coals at 100 °C for about 100 days yielded essentially constant concentration of the phenolic group (Yohe et al., 1955).[71] These studies confirmed Tronov's postulation concerning the presence of phenolic structures in oxidizing coal. Dry oxidation studies of subbituminous coal by Jensen et al., 1966,[72] have shown that phenolic structures appear well before appreciable amounts of the carboxylic acids are detected. Jensen et al.,[72] have also detected the acid anhydrides by infrared spectroscopy, but after the appearance of carboxylic acid. This is explained by the fact that aliphatic structures in coal are the more probable loci for the initial carboxyl formation. Referring to the commercially used gas-phase oxidation of naphthalene to produce phthalic acid and maleic anhydrides:



Modified after Jensen, 1966

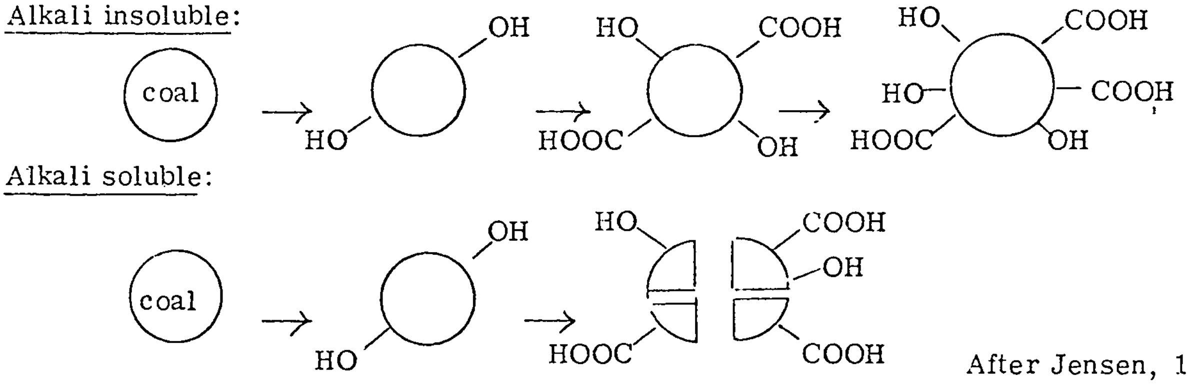
Jensen and coworkers[72] propose a scheme for coal oxidation similar to Tronov's:



after Jensen et al., 1966

The scheme above is partially based on work by Moshopedis, 1962,[73] and Wood et al., 1961.[74] Moshopedis has also shown that quinones and hydroxyquinones are actually present in coal and in humic acids derived from it.

The actual process of coal oxidation is much more complex. The recent detection of lactones on the surface of oxidizing graphite, char, and coal by Yang, 1975,[57] and Barton, 1975,[58] further complicates the scheme presented above. If glycosides indeed seem to form on the surface in the so-called "coal-oxygen complex" in the early stages of oxidation of coals, further oxidation and breaking of the glycoside bond could lead directly to aliphatic small chain carboxylic acids bypassing the phenyl and the hydroxyquinone stages. This oxidation path may further elucidate the early appearance of the carboxyl acids in coal oxidation before the acid anhydrides which later could be the products of dehydration (see Jensen, 1966, p. 639[72]). To emphasize the complexity of coal oxidation processes, Jensen[72] does point out that coal breaks down on oxidation by two simultaneously progressing types of reactions. One of these involves the physical skeletal breakdown and degradation of the coal infrastructure into progressively smaller fragments, which in itself results in increased alkali solubility whereas fresh coal is alkali insoluble. The other process is chemical in nature, causing increased acidity and the gradual evolution of "humic acids". Jensen notes that the "acidity" builds up more rapidly than the alkali soluble material and suggests therefore that alkali solubility of coal is not a good measure of the acidity and therefore should not be used as covariant with the accepted definition of "humic acid". To demonstrate this Jensen[72] et al., propose the following scheme for the skeletal breakdown during oxidation of coal:



After Jensen, 1966

The above qualitative scheme also illustrates the wide spread in molecular weights of humic acids in the literature, indicating that 600 may be as valid as 10,000. Jensen emphasizes that attempts to give kinetic expression to directly measured humic acid concentrations based on alkali solubility are unjustified.

Yohe, 1958,[75] gives a detailed summary and a literature review of coal oxidation. Oxidation studies of coal have shed considerable light on the chemical structure of coal. Such work is of great value to the coal mining and utilization industry. Much practical information concerning the nature and the effects of atmospheric oxygen on coal exists.

Coal is susceptible to spontaneous combustion when stored in piles, especially when fines are intermixed with coarse material. The initial absorption of oxygen is relatively rapid on fresh coal surface and ignition temperatures can be very low. High percentage of iron in coal may accelerate oxidation whereas high percentage of mineral matter (ash) retards oxidation. Coal in storage piles can oxidize rapidly and its properties as well as value as heating material will deteriorate with time. Especially low rank coals are affected by storage. High temperature, fine particle size, high percentage of bright constituents and high oxygen concentration in the storage area all have an accelerating effect on coal degradation. Storage in covered piles under water or in "compacted layer piling", as well as addition of anti-oxidants prevents fast weathering of coal. Very dry coals and very moist coals oxidize slowly, whereas coals with intermediate moisture content tend to oxidize faster. Time is an important factor in coal oxidation.

Oxidation generally impairs or even destroys the coking properties of coal, especially in marginal low rank coking coals. The extent of oxidation of coal can be measured because it affects the plastic and coking properties of coal as well as the ignition temperatures. Progressing oxidation of coal stored near power plants decreases the heating value of the fuel, thus increasing the costs. Coal stored for coking purposes if not protected may deteriorate to the point where coke of inferior quality is produced (Jackman et al., 1957[78]; Ignaziak et al., 1970[79]). Spontaneous ignition of coal piles and coal in ships' holds can cause major losses and accidents.

Controlled oxidation studies of coal permit us to learn how to utilize more economically this fuel, how to convert it to new useful products, how to prevent the undesired attack of oxidizing media, how to store it better, how to get the highest heating values, how to control its combustion, how to best fluidize it, gasify it, or produce synthetic oils from it by reacting it with oxygen, carbon monoxide, hydrogen and water.

Coal surface reacts with oxygen the moment coal is mined. Coal absorbs oxygen at a rate that is first rapid then falls off if the temperature remains constant. According to Arrhenius' equation the logarithm of the oxidation rate varies in a linear manner with reciprocal of the absolute temperature (see below). Oxygen absorption in coal varies directly with the 0.4 power of the surface area (Yamasaki, 1953,[99]) and with somewhat less than the first power of the oxygen concentration (Howard, 1947[89]; Yohe, 1958,[75] p. 7). Kramers, 1946,[76] and Waard, 1941,[77] have found that this rate depends on a number of factors, such as particle size, rank, time of exposure, temperature, moisture, concentration of oxygen, as well as on the nature of coal macerals (petrographic properties). The oxidation rate of coal approximately doubles with each 10 °C rise in temperature, Schmidt, 1945, pp 642-5[80]. This fits an Arrhenius type relation, Howard, 1947,[89] but time effects make the measurements difficult. This empirically established rate increase with temperature is typical for numerous chemical reactions that occur near room temperature. Arrhenius has proposed the following equation which quantitatively describes the effect of temperature on the rate of a reaction:

$$k = se^{-\Delta Ha/RT}$$

where s is a constant and ΔH_a, or the heat of activation, is another constant.

In logarithmic form: $\log k = \dfrac{-\Delta Ha}{2.303R} \times \dfrac{1}{T} + \text{constant}$

In oxidation of coal this relation is complicated by the increasing rate of removal of the oxidation products in gaseous form from the coal surface at increasing temperature. This has been first shown by Veselovskii and Terpogosova, 1953,[81] and Bostick, 1954.[82]

Oxidation of coal stored under constant temperature is first rapid then falls off and the decrease of the rate of oxidation or absorption of oxygen appears to be faster when the initial rate of absorption is high, Scott and Jones, 1941[83]; Elder et al., 1945[84]; Schmidt, 1945, pp. 642-5.[80] Oxidation of coal is faster in an aerated storage and may be very slow in covered or unventilated storage piles, Graham and Raybould, 1932;[85] Drewry, 1937;[86] Jackman, 1957[78].

The different banded components or lithotypes of coal have a different affinity to oxidation. Jüttner, 1956,[100] has found that one can list the petrographic constituents of coal in the sequence:

fusain → durain → clarain → vitrain

with increasing susceptibility to oxygen uptake. Fusain appears to be most resistant to oxidation, but being probably a product of ancient forest fires and thus charcoal-like, it may absorb oxygen very rapidly after being mined, Yohe, 1950.[87] Kukharenko and Ryzhova, 1956,[88] have also found that vitrain oxidizes more readily than fusain.

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COMPOSITION OF COALS AND COAL OXIDATION PRODUCTS PLOTTED IN THE SEQUENCE OF INCREASING OXYGEN CONTENT

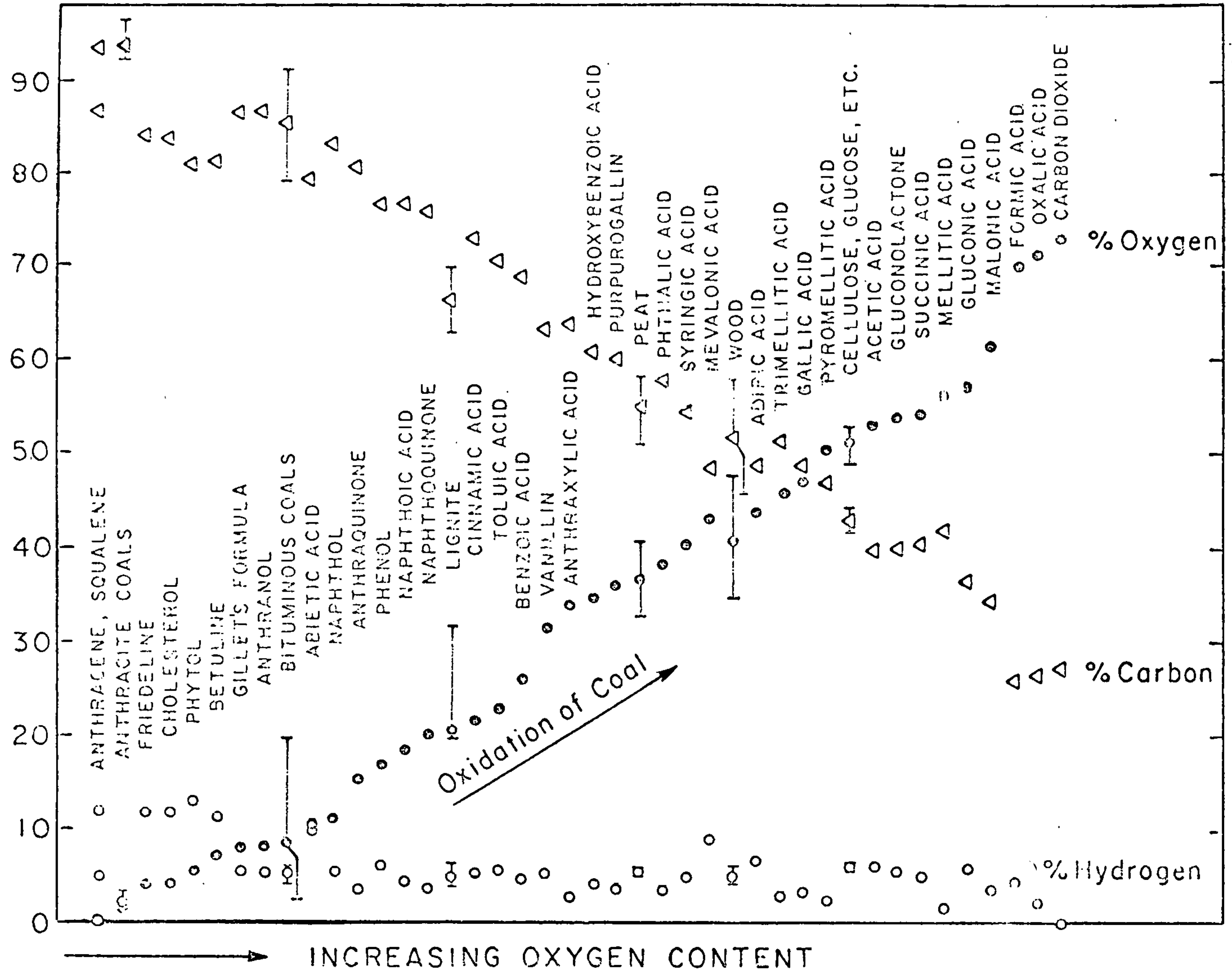

Figure 2

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