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OXIDATION OF COAL

G. R. Yohe

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ILLINOIS STATE GEOLOGICAL SURVEY
JOHN C. FRYE, *Chief* URBANA, ILLINOIS

OXIDATION OF COAL

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OXIDATION OF COAL

G. R. YOHE

ABSTRACT

A summary and review of the literature on coal oxidation, with emphasis on results published since the appearance of Lowry's "Chemistry of Coal Utilization," in 1945, is presented.

The major topics discussed are the initial attack of oxygen, oxidation kinetics, oxidation results and the chemical nature of coal, storage and spontaneous combustion, determination of the extent of oxidation, and the effect of oxidation on coking properties. Gasification and combustion of coal are mentioned but not discussed in detail as they are phases of coal oxidation beyond the scope of this work. A bibliography of 315 references is appended.

SUMMARY

Reasons for the Study of Coal Oxidation.

The oxidation of coal is studied in order to learn more about the intimate chemical nature of this important resource; to understand better the processes of deterioration and spontaneous heating in stored coals; to gain knowledge which may be of value in the utilization of coal, either as a fuel or as a chemical raw material.

Initial Attack of Oxygen.—The following factors favor rapid initial oxidation: small particle size, low rank, high percentage of bright constituents, high storage temperatures, and high concentration of oxygen. The rate of oxidation diminishes with the time of exposure. The effect of moisture varies with different coals, but oxidation appears to be retarded if the moisture content is very low or very high. Oxygen is initially taken up as a "coal-oxygen complex" which is probably peroxidic in nature.

Oxidation Kinetics. — The logarithm of the oxidation rate varies in an approximately linear manner with the reciprocal of the absolute temperature (Arrhenius equation). Oxygen absorption has been reported as varying directly with the 0.4 power of the surface area (from screen analysis) and with somewhat less than the first power of the oxygen concentration.

Chemical Nature. — Coal contains aromatic (benzene) ring systems and condensed aromatic structures; these nuclei increase in size and form an increasingly greater part of the total substance as the rank of the coal increases. Aliphatic structures are probably present as side chains of one or more carbon atoms, as connecting chains between aromatic nuclei, or as hydroaromatic rings. Phenolic groups are present in low and medium rank coals, but essentially absent in coals of more than 89 percent carbon. Part of the nitrogen is probably present in heterocyclic structures.

Storage and Spontaneous Combustion.—Coals generally are susceptible to spontaneous combustion in storage piles. The danger is lessened by storing higher rank coals, by avoiding storing fines, and especially by avoiding a mixture of fine and coarse sizes in which careless piling may bring about segregation of sizes. Covering of piles, compacted layer piling, or storage under water largely eliminates the danger.

Coals that absorb oxygen avidly and have low ignition temperatures are dangerous; high ash content inhibits oxidation unless the mineral matter contains a high percentage of iron which seems to accelerate oxidation. Arguments still rage concerning the hazards of pyrite, but some evidence seems to indicate that it has in the past received unwarranted blame for spontaneous fires.

Exclusion of oxygen is the only practical method of preventing deterioration of stored coal; the use of added antioxidants is practically untested, but would probably prove too expensive to be feasible.

Determination of Extent of Oxidation. Changes in plastic and coking properties appear to be the most useful tests in determining to what extent a coal has been oxidized; ignition temperature and other methods have been used by some experimenters.

Effect on Coking Properties.—Except for some strongly coking coals which may show slight improvement by a little oxidation, the general effect of oxidation is to lessen or destroy the coking qualities of coal. The effect is more marked in the marginal (lower rank) coking coals.

Gasification and Combustion. — These topics are mentioned only as applications of oxidation; their full discussion is beyond the scope of this paper.

INTRODUCTION

SEARCH OF LITERATURE

The following paper summarizes the findings of many investigators who have studied coal oxidation since the appearance of the two-volume work entitled "Chemistry of Coal Utilization," edited by H. H. Lowry and published in 1945 by John Wiley and Sons, New York. Two chapters in that work are of special interest to those concerned with various phases of the oxidation of coal—Chapter 9, "Chemical Constitution of Coal: As Determined by Oxidation Reactions," by H. C. Howard, and Chapter 18, "Changes in Coal During Storage," by L. D. Schmidt.

This report contains some references to the earlier work in order to tie the recent to the older results, but no attempt has been made to cite all publications that have appeared on this topic during the intervening years. The writer believes, however, that the report is comprehensive enough to give a fair picture of the recent accomplishments in this field.

The original papers have been consulted where they have been available. In numerous cases, however, because of inaccessibility of the journals or because of language difficulties (for example, Russian and Japanese), the information has been taken from *Chemical Abstracts.* For such articles the *Chemical Abstracts* references are given.

The writer wishes to thank Earle C. Smith and Mrs. Marjory Herder for assistance in the literature search.

IMPORTANCE OF COAL OXIDATION

The reaction of coal with oxygen is fundamental to its importance in the economy of modern civilization, because the value of a fuel lies merely in its oxidation at such a rapid rate and under such conditions that the heat produced is useful. Nevertheless, a study of the oxidation of coal is of interest and importance from other viewpoints than those connected with its use as a fuel.

For example, undesired and uncontrolled oxidation may be dangerous and costly, as in the case of spontaneous combustion, which is initially a slow oxidation under conditions that do not permit dissipation of the heat evolved. The result is increased temperature, accelerated oxidation, the accumulation of more heat, and still greater rise in temperature until active combustion starts. Coal piles have been destroyed and ships lost at sea because of spontaneous combustion.

Short of such catastrophic burning, however, are lesser losses to be attributed to oxidation. The reserve fuel pile at a power plant gradually loses some of its heating value—perhaps only a small percentage, but a loss, nonetheless. The stock of coking coal at a metallurgical coke plant may deteriorate, because of oxidation, to the point that there are difficulties in coke oven operation, inferior coke is produced, and there are consequent losses, or perhaps the coal becomes useless for this purpose and must be disposed of.

Yet this adventitious oxidation of coal is not always a curse. A home owner who has been annoyed at coke-tree formation in his stoker-fired furnace may find this trouble largely eliminated after his coal has aged in storage several months, because the combustion characteristics may benefit by the loss of coking properties (Schmidt et al., 1943).

There are yet other reasons for our interest in the oxidation of coal. Man has learned that the more he knows about any resource, the better are the chances that he can use that resource advantageously. And in processes of controlled oxidation we have one means of learning more about the intimate chemical nature of coal. Furthermore, controlled oxidation may lead to the conversion of the coal to new and useful products.

The research chemist is an explorer. He does not look for uncharted seas nor for unmapped lands; he searches for the minute details of molecules that he is destined never to see—to show how atom is placed upon atom to constitute these molecules. Who can live life as we live it today and not recognize the many contributions of this kind of exploration?

These, then, are some of the reasons for studying the oxidation of coal: What is the chemical nature of the material, what happens when oxygen of the air attacks it, how may we preserve coal that we want to keep, and how may we best use it when the time for utilization comes? What new and useful products may we make from coal, and how may we best proceed to make them?

The pages that follow present information that chemists have gained about various phases of coal oxidation during recent years. Some of it is technical, written in the language of the chemist. Yet it is hoped that enough of the picture is presented in nontechnical terms to give an understanding of what the chemist is seeking.

INITIAL ATTACK OF OXYGEN

As soon as coal is uncovered from its place underground and exposed to air, oxygen begins to react with it. This reaction ordinarily is slow, and its effects are not readily apparent. The rate at which it takes place varies with a number of conditions (Kramers, 1946; Waard, 1941), among which the following may be mentioned: particle size of the coal, coal rank, temperature, length of time of exposure, concentration of oxygen, moisture, and petrographic composition of the coal.

Variable Conditions

Particle Size

As oxidation occurs at or very near the surface of the coal particle, a coal which is finely crushed, and consequently exposes more surface for a given weight, will react more rapidly with oxygen than will a similar sample in lump form (Scott and Jones, 1941; Elder et al., 1945). It is in part for this reason that recommendations have been made that coke oven operators avoid using the finer sizes of certain rather easily oxidized coals (Reed et al., 1947).

Pogrebitskiĭ (1943) stated the conclusion that a solid block of coal is not subject to spontaneous combustion, but that finely divided particles are essential to start a fire.

Oreshko (1952) has stated that the low-temperature oxidation of certain Soviet coals is proportional to the volume of the coal and not to the surface. He assumed that the oxygen penetrates into the coal through various pores and capillaries and that the rate of oxidation may be correlated to the surface of these "channels." Thus it would appear that Oreshko's use of the word "volume" implies specific volume and is related to porosity; that it is not only the apparent surface of the coal grains that is involved, but the pore or "internal" surfaces as well.

The values of such surface vary with the rank and type of the coal, and may well be partly responsible for the varying rates of oxidation observed with various coals. The point, however, is that for a given coal, small particle sizes will expose greater surface areas than large particles, and the result will be increased oxygen absorption.

Rank of the Coal

In general, the lower the rank of the coal, the higher is its oxygen content, and greater its susceptibility to attack by oxygen (Schmidt 1941, 1945, p. 648-9; Stopes and Wheeler, 1923a; Wheeler and Woolhouse, 1932; Georgiadis and Gaillard, 1954; Elder et al., 1945).

The variation of oxidizability with changing yield of volatile matter may be mentioned in connection with the effects of rank of the coal. Oreshko (1951a) studied ten coals having volatile matter contents of 7 - 42 percent, and found that the oxygen consumption was at a minimum when the volatile matter of the coal was 26 percent.

Temperature

It has been found that the rate of many chemical reactions is approximately doubled for each 10°C. rise in temperature; this appears to be approximately true of the oxidation of coal (Schmidt 1945, p. 642-5), but there are difficulties in making reliable measurements because of the effects of time. (See below.) But in a qualitative way it may be said that, other conditions being equal, coal in contact with air will oxidize much more rapidly in a warm environment than in a cool one (Elder et al., 1945).

The effects of increasing the temperature are complicated by the nature of the reactions involved. Veselovskiĭ and Terpogosova (1953) found that the oxidation products first formed by the addition of oxygen decompose more readily as the temperature rises, and that ultimately this decomposition is accelerated more than their rate of formation. Thus at lower oxidation temperatures there is an accumulation of oxidation products which does not occur at higher temperatures. Bastick's (1954) report that an increase in oxidation temperature favors the formation of gaseous products agrees with this concept.

Time

Although coals start to absorb oxygen at once when fresh surfaces are exposed to air, the rate of absorption at a given temperature falls off with time of exposure (Scott and Jones, 1941; Elder et al., 1945), and this decrease in rate is greater when the rate itself is high (that is, at higher temperatures) (Schmidt 1945, p. 642-5). Thus unless the temperature is allowed to rise, the rate at which a coal will deteriorate gradually becomes less. With fine coal, it has been found that the rate of oxidation varies inversely as the 1.7 power of the extent of oxidation (Schmidt 1945, p. 642-5).

Concentration of Oxygen

Coal is oxidized more rapidly in an atmosphere of pure oxygen than it is in air (Oreshko 1949d; Elder et al., 1945), and the rate is still slower in air from which some of the oxygen has been removed (Schmidt 1945, p. 648). This fact may be of little consequence where air has free access to the coal, but it is of considerable importance in large storage piles, or in covered or protected piles where ventilation is limited or prevented, as the concentration of oxygen in the air in the interior of the pile may fall to a very low value (Graham and Raybould, 1932; Drewry, 1937).

Moisture

The fact that high-moisture coals oxidize more rapidly than low-moisture coals is not necessarily evidence that the more rapid reaction is because of the moisture present. Coals of low rank usually have a high moisture content, yet it is probably the low rank itself (high oxygen content) which is responsible for the fact that they are more susceptible to oxidation.

Katz and Porter (1917) studied the effects of changing moisture content and concluded that some coals absorbed oxygen more rapidly when dry, and others more rapidly when moist. Mukherjee and Lahiri (1957) compared two coals of different ranks at 70-120°, and found that the low rank coal absorbed oxygen more slowly from moist air than from dry, but the reverse was true of the higher rank coal. Mehta and coworkers (1952) found that with the Indian coals they investigated, oxygen absorption reached a maximum at conditions of about 40 percent relative humidity.

Under usual conditions of storage or exposure, moisture is present in both the coal and the air, so that conditions of really dry exposure are not attained.

Petrographic Composition

Examination of a lump of coal will reveal in almost all instances that it is made up of layers of differing appearance. These are the "banded ingredients" or "petrographic constituents."

Fusain, the dusty, charcoal-like friable constituent is ordinarily considered the most inert chemically and the most resistant to oxidation. It seems apparent that it is indeed less likely to undergo appreciable changes because of oxidation, particularly under rather drastic conditions (Lefebvre and Faivre, 1936; Fuchs et al., 1938; Jüttner, 1956), yet when freshly mined, or after having been evacuated, it may absorb oxygen more rapidly than the other portions of the coal (Tideswell and Wheeler, 1920; Stopes and Wheeler, 1923b; Yohe and Wilt, 1942b; Yohe, 1950). Aside from this rapid up-take of oxygen by fresh fusain, it is generally found that the banded ingredients would be listed as follows according to their ease of oxidation: vitrain, clarain, durain, and fusain (Jüttner, 1956).

Kukharenko and Ryzhova (1956) have recently stated that under natural conditions, vitrain is more easily oxidized than fusain.

Shotts (1950) studied the step-wise nitric acid oxidation of several bituminous coals after separating them into fractions on a specific gravity basis and concluded that the approximate amount of "bright" and "dull" components could be calculated from the oxidation data.

NATURE OF OXIDATION

Although it has been known for many years that coal absorbs oxygen from the air and undergoes certain changes in properties as it does so, the exact nature of this absorption and change has not been completely elucidated. The facts that coal is a solid and that it is of complicated and undefined chemical structure increase the difficulties of explaining the details of the process.

"Coal-Oxygen Complex"

A number of workers in this field have considered that this initial stage of oxygen up-take is the formation of a "coal-oxygen complex," or an unstable surface combination (Wheeler, 1918; Parr and Milner, 1925; Davis and Byrne, 1925; Porter and Ralston, 1914).

Two possibilities must be considered in explaining the nature of a "coal-oxygen complex." One of these, known as adsorption, is a process which occurs where there is a surface boundary between phases of substances, as for example, the surface of a coal particle is the boundary between the solid coal phase and the gaseous air phase in contact with it. At such an interface there may be an increased concentration of certain kinds of the molecules present in the gas—a preferential attraction of certain molecules so that in effect they form a layer coating the surface of the solid.

If the "coal-oxygen complex" is of this nature, we would picture it as a layer of oxygen molecules preferentially attracted and adhering to, but not in permanent chemical combination with, the coal surface. It is considered characteristic of simple adsorption processes that the adsorbed material may be removed or "desorbed" and recovered in its original chemical form, usually by evacuating, by heating, or by heating in a vacuum.

Peroxide Formation

The second process possibly involved in the initial oxidation is that of peroxide formation. This is considered to be more truly chemical in nature, and the existence of a surface or interface between phases is not required. Certain chemical structural units in which a hydrogen atom is attached to a carbon atom (-C-H) are capable of taking up an oxygen molecule (O_2) to form a "hydroperoxide" (-C-O-O-H). This is the initial process in the "drying" of oil paints, in the development of rancidity in butter, etc. Oxygen which has been taken up in this manner cannot be recovered as oxygen gas by heating or evacuation; if it can be removed at all it breaks carbon or hydrogen away with it and is obtained as an oxide of one of those elements, namely, as water or a carbon oxide.

Neither of these possible forms of the "coal-oxygen complex" possesses the stability that is characteristic of most chemical compounds. Both are sufficiently "loose" combinations that the oxygen involved may still oxidize certain readily oxidizable substances which may be brought into contact with it, or may indeed serve to oxidize the coal substance itself by being converted to more permanent, stable oxygen-containing combinations.

The fact that this oxygen is loosely bound initially makes it possible to detect its presence and to measure its amount, but unfortunately does not permit us to distinguish with certainty between the two possibilities mentioned above. Yohe and Harman (1941) used a method of estimating this oxygen based on the ability of the coal to oxidize titanous chloride, the amount of oxidation being determined by titration of the excess titanous chloride with standard ferric chloride solution. They found that coal which had been carefully protected from air while it was removed from the mine face, ground, and handled showed little or no "active oxygen" content, but that exposure to air for only a few minutes resulted in a marked increase in its ability to oxidize the titanous chloride.

Later Yohe and Wilt (1942a, 1942b) followed the change in content of this reactive oxygen over time periods of several months for several high-volatile bituminous coals and found that the oxidizing power reached a maximum value in from 10 to 25 days, then diminished slowly. This behavior is exactly what one would expect if this reactive oxygen is an intermediate stage in the over-all oxidation process, that is, that the oxygen is first taken up in this loosely bound condition and subsequently is converted to chemically stable oxidation products of such nature that their presence may no longer be detected by the method used.

Still later Jones and Townend (1945a, 1945b, 1946, 1949) published results of somewhat similar experiments on British coals. They used a modification of the method of Yule and Wilson (1931), and obtained results essentially similar to those of Yohe and Harman and Yohe and Wilt. They called their active oxygen "peroxide" and noted that it started to break down when the coal samples were heated to about 80°C. Further work along similar lines on British and Indian coals was published by Chakravorty et al. (1950). Their results were essentially similar to those previously published on other coals; they extended the study of the decomposition of the peroxygen complex, and found it to approximate a first-order reaction with energy of activation approximately that for hydroperoxide decomposition.

Still later Yohe (1950) noted that the Russell Effect (the darkening of or image formation on a sensitized photographic plate kept in direct contact with certain substances in the absence of light) was produced by substances capable of forming peroxides, and that the fact that coals produce this effect (Russell, 1909; Stopes, 1919) was consistent with the idea that the active oxygen, or "coal-oxygen complex" was peroxidic in nature.

Although Jones and Townend (1945a, 1945b, 1946, 1949) referred to the active oxygen in their coals as peroxide, Yohe and Wilt (1942a) took the view that the evidence at hand was not sufficient to differentiate between peroxide and adsorbed oxygen. Recently Rafikov and Sibiryakova (1956) published a method for peroxide determination in which coal is treated with aqueous hydroquinone solution, and the amount of hydroquinone converted to quinone is determined iodometrically. They claim that adsorbed oxygen is not determined by this method.

It seems, however, that the active oxygen in coals partakes of the nature of both peroxide and adsorbed oxygen, and it may be that at one time or another in the atmospheric oxidation process, both exist. The rapid formation of the "complex" (Yohe and Harman, 1941) is suggestive of adsorption, yet the fact that evacuation does not lead to oxygen recovery (Winmill, 1914-15) casts doubt on the adsorption mechanism and supports the idea of a chemical combination. Perhaps adsorption occurs first, and the adsorbed oxygen is then converted to peroxide structures.

Oreshko (1949a, 1949b, 1949c) studied the behavior of several Donets Basin coals on heating in an air or oxygen stream. He recorded rates of heating of the furnace and of the coal, and changes in weight of the coal sample during the process. In all cases there was an initial gain in weight followed by a drop, then another increase to new and still higher maximum, then a sharp drop when active combustion set in. He concluded that the process of oxidation of coal consisted of three distinct stages: (1) up to 70-80°, the formation of peroxide-type complexes; (2) the decomposition of these complexes; and (3) at 130-160° or 180-290° (depending on type of coal), the formation of stable coal-oxygen complexes which are destroyed only on ignition.

Titov and coworkers (1956) have indicated that a connection exists between the peroxide content of coals and other properties, such as hardness, inner surface, nature of gas evolution, thermal decomposition, etc., and recognized peroxide-formation and peroxide - decomposition stages in the oxidation of coal, particularly the exothermal effect of the latter.

Higuchi and Shibuya (1954) air-oxidized humic material from lignite, and reported that the analysis of the nonvolatile coal revealed that various peroxides appeared as unstable intermediates.

MECHANISM AND KINETICS OF COAL OXIDATION

The influence of various factors on the rate of coal oxidation has been studied in some detail by a number of investigators. Although qualitative statements of some of these relationships have already been presented, this section of the paper is devoted to a summary of some of the more quantitative findings and some of the mathematical expressions of the results.

Howard (1947) noted that the relationship between oxidation rate and temperature fits an Arrhenius type of equation fairly well; that is, there is an approximately linear relationship between the logarithm of the reaction rate and the reciprocal of the absolute temperature.

The Arrhenius equation*, in which k is the specific reaction rate, E is a constant (the "activation energy"), R is the gas constant, and T is the absolute temperature, is as follows:

$$\frac{d \ln k}{dT} = \frac{E}{RT^2}\dagger \qquad (1)$$

Integration of the above equation gives

$$\ln k = -\frac{E}{R} \cdot \frac{1}{T} + C \qquad (2)$$

which, in terms of logarithm of the reaction rate and the reciprocal of the absolute temperature, is a straight-line equation.

In his earlier work on the kinetics of coal oxidation, Oreshko (1943) passed oxygen through a heat-insulated pile of dry coal and measured the temperature, which he designated θ. He found that the rate of heating, $\frac{d\theta}{dt}$, followed the relationship

$$\frac{d\theta}{dt} = Ce^{-\frac{A}{R\theta}} \qquad (3)$$

where t is time, and C and A are constants. If it is considered that the rate of temperature rise is a direct measure of the reaction rate, this is equivalent to the integrated form of the Arrhenius equation given above, for by taking the logarithm of it, we have

$$\ln \frac{d\theta}{dt} = -\frac{A}{R} \cdot \frac{1}{\theta} + C' \qquad (4)$$

Oreshko found that in these experiments, A (the energy of activation) had a value of 2.7 kg. calories below 80°C., and 7 kg. calories above 85°C., and deduced that the mechanism of oxidation was different above this temperature (80-85°C.) than below it.

In later work, Oreshko (1949b) found evidence that the oxidation of coal proceeded in three stages: up to 70-80°, activation energy 3.4 kg. calories; from this temperature to 130-160°, activation energy 6-8 kg. calories; and then up to 180-290°, activation energy 12-17 kg. calories. He concluded from the nature of the constants of

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* The reader is referred to any standard textbook on physical chemistry for a detailed explanation of this equation.

† The expression ln k is the logarithm to the base e; where log k is the logarithm to the base 10, ln k = 2.303 log k.

the equation that the rate of oxidation depended on the chemical reaction itself, not on diffusion.

In still more recent work, Oreshko (1950b) has stated that under conditions where diffusion is not a rate-determining factor, a coal surface area S oxidizes at the rate

$$\frac{dx}{dt} = k' S[O_2] \qquad (5)$$

where x is a measure of extent of oxidation, t is time, $[O_2]$ is the concentration of oxygen, and k' is a constant. Under nonisothermal conditions, the equation is

$$\frac{dx}{dt} = S[O_2]\, k_o'\, e^{-\frac{E}{RT}} \qquad (6)$$

where the more conventional E and T are used for the activation energy and temperature, respectively.

If the oxygen concentration $[O_2]$ is maintained constant, and the time of oxidation is short enough that the surface area S may also be considered nonvariant,

$$\frac{dx}{dt} = k_o\, e^{-\frac{E}{RT}} \qquad (7)$$

where the new constant k_0 is the product of the previous constants
$(k_o = k_o' \; S\,[O_2]\,)$.

Equation 7 gives the rate of change with respect to time; the following derivation gives the rate of change with respect to the temperature.

If the temperature increases uniformly at the rate β,

then $$T = T_o + \beta t \qquad (8)$$

or $$t = \frac{T}{\beta} - \frac{T_o}{\beta} \qquad (9)$$

and, since T_0 (the original temperature) and β are constant,

$$\frac{dt}{dT} = \frac{1}{\beta} \qquad (10)$$

and, as

$$\frac{dx}{dT} = \frac{dx}{dt} \cdot \frac{dt}{dT}$$

the combination of equations 7 and 10, and expression in differential form gives

$$dx = \left(\frac{k_o}{\beta}\right) e^{-\frac{E}{RT}}\, dT \qquad (11)$$

The integral of this function develops into a series; Sherman (1936) gives the integral of an equation of essentially this form, and Oreshko (1950b) gives an approximate solution in which the less significant members of the series have been neglected (shown as the definite integral between limits T_1 and T_2):

$$x_2 - x_1 = \left(\frac{k_o R}{\beta E}\right)\left(T_2 e^{-\frac{E}{RT_2}} - T_1 e^{-\frac{E}{RT_1}}\right)^{*} \qquad (12)$$

It is obvious from the condition imposed in equation 8 that equation 12 is applicable only in the range where the increase in temperature is linear, and would not hold as the temperature approaches the region of self-ignition and increases at an increasing rate.

In further work of this nature, Oreshko (1950c, 1950d, 1950e) studied various coals at various stages of the oxidation process, and found that although the constants of the equations differed for different coals, for the different petrographic ingredients, and for the different oxidation stages, the equations given above were generally applicable. This holds for the stage in which peroxides are decomposing and the sample weight is decreasing as well as for periods of gain in weight as oxygen is absorbed.

Georgiadis and Gaillard (1953) considered that the oxidation of coal consisted of two consecutive reactions, the first being the formation of the oxygen complexes

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* In checking this integration by substitution of variable $z = 1/T$, integrating by parts ($\int u\,dv = uv - \int v\,du$), and retaining only the first member of the resulting series as Oreshko evidently has done, I obtain either

$$x_2 - x_1 = \frac{k_o R}{\beta E}\left[T_2^2 e^{-\frac{E}{RT_2}} - T_1^2 e^{-\frac{E}{RT_1}}\right]$$

or

$$x_2 - x_1 = \frac{k_o}{\beta}\left[T_2 e^{-\frac{E}{RT_2}} - T_1 e^{-\frac{E}{RT_1}}\right]$$

depending upon the selection of u and v in the above form. ~~The first solution is not applicable, as it has been obtained by dropping members of a divergent series which cannot be evaluated~~; the second solution differs from Oreshko's by the factor R/E, which neither I nor my mathematician friends could obtain here.—G. R. Y.

which follows the Arrhenius law between 150° and 250°C., and the second being the decomposition of these complexes. They indicated that diffusion was of importance in the first reaction. Sommers and Peters (1954) investigated many variables in their studies of oxidation of coals in the temperature range 150-260°C., and developed a theory which considers that the penetration of oxygen into the compact coal material is a process of solid body diffusion.

Schmidt (1945), and Schmidt and Elder (1940) proposed the relationship

$$x = ct^b, \text{ or } \ln x = b \ln t + \ln c \qquad (13)$$

for the data of coal oxidation, where x is the amount of oxygen consumed in percent by weight of dry coal, t is time in days, and c and b are constants. This equation has since been used by Constantinides (1946). Higuchi and Shibuya (1955) have found that the yield of CO_2, CO, and HCHO with time upon oxidation of lignite in a fluidized system at 180-220°C. obeyed the same equation, which they stated in the form:

$$\ln Y = K \ln t + c$$

where Y is the yield of the products indicated above, t is reaction time, and K and c are constants. They said that the variation of yields of these products falls into two time ranges, both of which proceed according to this equation with different values of the constants peculiar to each stage.

Yamasaki (1953) oxidized coals of varying screen sizes and measured the oxygen absorbed in cc. per gram (x) at temperatures below 100°C. He reported that between 30° and 100°C. the relationship between oxygen absorbed and the temperature was

$$\ln x = bT + c \qquad (14)$$

Starting with this equation, we see that

$$x = e^{bT} + c'$$

and

$$\frac{dx}{dT} = be^{bT}$$

In the region where temperature rise is constant (equation 9)

$$T = T_o + \beta t$$

and

$$\frac{dT}{dt} = \beta$$

therefore

$$\frac{dx}{dt} = b\beta e^{bT}$$

and

$$\ln\left(\frac{dx}{dt}\right) = \ln b + \ln \beta + bT$$

which would indicate a linear relationship between the logarithm of the reaction rate and the temperature, rather than the reciprocal of the temperature as shown by Oreshko's results. However, Yamasaki noted that below 30°C. the values of x deviated greatly from equation 14, and the implication is that this equation is applicable only within a limited temperature zone. Yamasaki suggested that van der Waals adsorption of oxygen on the surface was predominant below 30°C., whereas chemisorption became predominant between 30° and 100°C.

Yamasaki also gave a relationship between oxygen absorbed and surface area as calculated from the screen analysis:

$$x = aS^{0.4040}$$

where x is cc. of oxygen absorbed per gram of coal, S is the surface area in sq. m./kg., and a is a constant peculiar to the coal used.

Howard (1947) has stated that the rate of oxidation is proportional to somewhat less than the first power of the oxygen concentration.

In evaluating the results of kinetic studies of coal oxidation, one is impressed with several difficulties which stand in the way of precision. One of these is the likelihood that we are dealing not with just one chemical reaction, but with many different reactions taking place concurrently as different structural units or functional groups are attacked by the oxygen. There is no assurance that these separate reactions would conform to the same equation; that is, even if they obeyed the same type of equation, the constants for each separate reaction might well be different.

Another complexity occurs in the difficulty of finding a reliable means of measuring the reaction rate. In view of the probability that there are a number of concurrent reactions, the measurement of oxygen absorbed, of heat evolved, or of a certain product or type of product formed are all of questionable reliability as measures of the over-all reaction rate. It is not surprising that the results of various investigators fail to conform completely with the classical relationships of chemical kinetics; it is perhaps remarkable that the agreement found is as good as it is.

STUDIES OF THE CHEMICAL STRUCTURE OF COAL

When an organic chemist is confronted with the problem of elucidating the chemical structure of a material, he must learn many things about it.

First of all, he must know just what chemical elements are present in it. Ordinarily, this is not too difficult to learn. It has long been known that coals contain carbon, hydrogen, oxygen, nitrogen, and sulfur. Other elements that are present in the mineral matter, or ash-forming constituents, are not discussed here, as the mineral matter is considered an "impurity"; the organic chemist is concerned only with the "pure coal" material. The trace elements (Headlee and Hunter, 1955) present also are many and varied, but that, too, is another problem.

In the second place, the chemist must determine with the greatest possible accuracy the percentages of the various elements present in his unknown material. Here the coal chemist encounters his first major difficulties: (a) coal is so heterogenous and variable that it is difficult, if not impossible, to get two coal samples that are identical in percentage composition; and (b) the limits of accuracy of known methods of analysis are not narrow enough.

For example, let us consider the following three hydrocarbons:

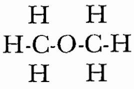
	Compound	Molecular weight	C%	H%
1.	$C_{40}H_{82}$	563.06	85.32	14.68
2.	$C_{41}H_{84}$	577.08	85.33	14.67
3.	$C_{40}H_{80}$	561.04	85.63	14.37

If an analyst knew that he had one of these three compounds, and his analysis came out 85.33 percent C and 14.67 percent H, he might be bold enough to report that he did not have compound No. 3, but he would never dare say (on the basis of the analysis alone) that he had No. 2 rather than No. 1, because he knows that his experimental error in making the analysis is almost certainly greater than the difference between them. In fact, many analysts would report values of 85.3 percent C and 14.7 percent H, recognizing that the second digit to the right of the decimal point is not reliable.

In the third place, the chemist must determine the molecular weight of his unknown. Here the coal chemist is in still more serious difficulty, for the only known methods having sufficient accuracy depend on volatilizing or dissolving the unknown. Coal cannot be converted to a gas without decomposing it, and the known methods of dissolving it are incomplete and probably attended by more or less decomposition. The molecular weight of coal has never been determined, and we know only that it is probably very large.

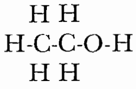
In the fourth place, for a complete clarification of chemical structure, the chemist must determine how the atoms of the various elements are arranged within the molecules of his unknown—he must be able to draw a "structural" or "graphic" formula for it, much as an architect might draw detailed plans of a house or a skyscraper. This is the most difficult of all.

To cite a simple example, there are two known compounds of formula C_2H_6O; they have the same percentage composition and the same molecular weight. An analysis alone would not show any difference between them, neither would a molecular weight determination, so the chemist must rely on an investigation of their properties. A difference would show up on oxidation in that only one of these would be converted to acetic acid, CH_3CO_2H. This one is II; the following structural formulas show the difference:



$$\begin{matrix} & H & & H & \\ H\text{-}& C & \text{-}O\text{-} & C & \text{-}H \\ & H & & H & \end{matrix}$$

I



$$\begin{matrix} & H & H & \\ H\text{-} & C & \text{-}C & \text{-}O\text{-}H \\ & H & H & \end{matrix}$$

II

It may be of interest to note that there are 75 different hydrocarbons possible with formula $C_{10}H_{22}$, 4,347 with formula $C_{15}H_{32}$, and 366,319 with formula $C_{20}H_{42}$ (Henze and Blair, 1931).

It is beyond the scope of this paper to reveal in detail how these structural studies are carried out. They may be long, arduous, baffling problems, but they are fascinatingly interesting to the chemist. Suffice it to say that even with materials whose percentage composition can not be learned accurately and whose molecular weight is undeterminable, nevertheless, much valuable information may be gained by a study of properties.

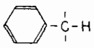
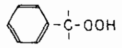
For example, all alcohols contain the characteristic or "functional" group of atoms C-OH; aldehydes the group $\underset{H}{\text{—C}}\text{:O}$, ketones $\text{C-}\underset{\ddot{O}}{\text{C}}\text{-C}$, etc. The properties of an organic substance depend to a large extent upon the functional groups which it contains, and in many materials the identification of such groups is possible even though a complete structure determination is not. So it is with coal, and this section of the paper is devoted to reporting some of the facts learned by oxidizing coal and some of the structural inferences that may be drawn from these facts.

It may be mentioned at this point that possible structural formulas for the coal substance have been presented (Gillet, 1951), yet the reader must bear in mind that such formulas are not given with the conviction that they actually depict the true structure of coal. Rather, they are proposed as the type of structures that coal *might* have; structures which would explain (but not be the only explanation of) the observed properties of the coal.

The very fact that coal is easily oxidized gives us some information, albeit meager, about its nature. For it is well known to organic chemists that the saturated and purely aromatic hydrocarbons are not as easily oxidized as are certain of their oxygen-containing derivatives. Alcohol (C_2H_5OH) and acetaldehyde (CH_3CHO) are more easily oxidized than ethane (C_2H_6); phenol (C_6H_5OH) more readily than benzene (C_6H_6); the naphthols ($C_{10}H_7OH$) more readily than naphthalene ($C_{10}H_8$); benzaldehyde (C_6H_5CHO) more readily than toluene ($C_6H_5CH_3$). It seems that, up to certain limits, once oxygen has gained a "foothold" in a molecule, further oxidation occurs more easily.

Yet other oxygen-containing structures are fairly resistant to further attack by oxidizing agents—for example certain ketones, ethers, and carboxylic acids. It has already been noted that the low-rank, high-oxygen coals are the most susceptible to oxidation. It is, therefore, in keeping with the known facts of organic chemistry that we should consider it possible that some of the oxygen present in them may be in the form of alcohol, phenol, or aldehyde groups. It must be remembered, however, that other properties of these materials may eliminate one or more of these groups from consideration.

If the reactive oxygen of the "coal-oxygen complex" (Wheeler, 1918; Parr and Milner, 1925; Davis and Byrne, 1925; Porter and Ralston, 1914; Yohe and Harman, 1941; Yohe and Wilt, 1942a; Jones and Townend, 1945a, 1945b, 1946, 1949; Chakravorty et al., 1950) is actually present as organic peroxides, certain additional hints as to structures possibly present are offered. Ethers and some types of unsaturated structures as shown below are known to form peroxides easily, and we should be alert to the possibility that these structures may be present in coals.

Group	*Structure*	*Peroxide formed*
ether	C–O–C–H	–C–O–C–OOH
olefin	C:C–C–H	C:C–C–OOH
alkylated aromatic		

These are not the only possibilities for peroxide formation, but are selected as examples deemed most probable in coal.

Gillet and Fastre (1944) used coal samples which had been ground and prepared in the absence of oxygen, then forced moist air through samples held in fritted glass crucibles. They found that during the first 48 hours, one atom of oxygen was absorbed for every 29 carbon atoms present in the coal, and that 4 atoms of hydrogen were liberated (presumably as water—G. R. Y.) simultaneously. After 10 days a second oxygen atom was combined, but no more hydrogen was released. They state that these effects occurred only in the surface layer of the coal.

Chereau (1952) found that a coal of 34 percent volatile matter gained weight upon oxidation until a maximum of 6.7 percent gain had been reached, then lost weight. As the same coal absorbed iodine from Wijs reagent in amount equivalent to 6.8 percent of oxygen, he concluded that oxygen is absorbed by coal by adding to double bonds. Ward et al. (1945) compared the behavior of a number of organic compounds of known structure with that of coal in regard to the action of alkaline permanganate, and found the results consistent with the view that bituminous coals are condensed cyclic structures, and that they possess a high "double bond character."

Kramers (1946), in his review of the oxidation of coal, has given a brief summary of the nature of the oxidation products which may be obtained from coal.

HUMIC ACIDS

The fact that many coals on mild oxidation readily yield significant amounts of the alkali-soluble '"humic acids" (Yohe and Harman, 1939; Tawada and Kawai, 1941; Chowdhury and Biswas, 1942; Kreulen, 1943; Fuchs, 1944; Eddinger and Demorest, 1947; Belcher, 1948a, 1948b, 1948c, 1948d, 1948e) indicates that one of two changes occurs: (a) that acidic structures, if present in the original coal, are part of overall structural units too large to disperse in alkali, and that these now break down to dispersable size, or (b) that previously neutral groups are now converted to acidic groups, perhaps with simultaneous degradation of molecular size.

As bituminous coals show little or no base-exchange capacity unless first oxidized (Gillet et al., 1955; Goedkoop, 1956) and/or sulfonated (Broderick and Bogard, 1941; Jurkiewicz et al., 1954; Delaroziere, 1944), we must consider the second possibility as more probable.

The formation of acidic groups by mild oxidation could presumably be caused by the conversion of alcohol or aldehyde groups to carboxyl, breaking a carbon chain at some susceptible linkage such as the olefin type to form carboxyls, or the formation of phenolic structures, possibly by such a mechanism as the peroxidation of an alkyl side chain followed by fission as is now done commercially in the manufacture of phenol from cumene (isopropyl benzene) (Plummer, 1953).

It seems obvious that new acidic groups are formed in the conversion of coal to "humic acids." These acids have been found to contain both carboxyl and phenolic groups (Howard, 1945a), although Kinney and Kerschner (1952) have cited evidence indicating that not all of the hydroxyl groups in these materials are phenolic in nature, but some are of the alcohol type.

In view of the fact that "humic acids" can be made by oxidizing relatively simple phenols, it has been pointed out that oxidative condensations as well as molecular size degradation may occur in the oxidation of coal (Yohe et al., 1953; Kharitonov, 1956). Kukharenko and Ryzhova (1956) have also suggested the idea of an oxidative condensation during coal oxidation as follows: In the initial stage, oxygen reacts with the coal to form bridges between macro-molecules, thus creating "potential" humic acids; subsequent oxidation brings about an intensive formation of humic acids and a decrease in the content of hydrogen and hydrocarbon. The final stage consists of the decomposition of the acids and condensation of aromatic nuclei.

Whether the "humic acids" are formed from coal by oxidative degradation, oxidative condensation, or (as seems more probable) a combination of both processes, it has been considered by many investigators that study of these materials constitutes a promising approach to the problems of the chemical constitution of coal itself.

Although it has been stated that the humic acids are produced from coals by "mild" oxidation, it might be well to point out that the action of air on coal at ordinary room or weather temperatures constitutes conditions too mild to bring about a rapid formation of the humic acids. A high-volatile bituminous coal, even of B or C rank, may be exposed to such air oxidation for months without developing more than a trace of alkali-solubility, but the outcrop coals, which yield appreciable amounts of humic acids on extraction with alkali, have been weathered for many years or even centuries.

Yohe and coworkers (1955) found that even at 100°C., air oxidation of a high-volatile B bituminous coal for about two months produced only a little more than one gram of humic acid from 100 grams of coal. At 150°C., however, the reaction is much more rapid (Yohe and Harman, 1939), giving yields in the neighborhood of 80 grams of humic acid from 100 grams of similar coal in three weeks. On the assumption that the rate of oxidative conversion of coal to humic acid doubles for each 10°C. rise in temperature, it may be calculated that two months exposure at 100°C. is equivalent to approximately two days at 150°, or to about 40 years at 20°C. (68°F.). On the same basis, three weeks of exposure at 150°C. would be equivalent to more than 470 years at 20°C.

Higuchi and Shibuya (1954) reported that lignite oxidized by air at 150° to 200° yielded 80 percent or more of humic acid, and Kamiya (1954), from his experiments on air oxidation of coal in a fluidized bed, concluded that the rapid destruction of the caking property involved a different reaction mechanism than the slower formation of the humic acids.

Friedman and Kinney (1950) oxidized coals of various ranks with air in electrically heated tubes, limiting the air flow at first to prevent excessive temperature rise. After 25 to 75 hours of oxidation it was possible to admit air in large excess; total oxidation times were 120 to 180 hours. Although alkali solubility increased with the temperature, the maximum yields of alkali-soluble products were obtained at 150° for lignite and sub-bituminous coal, and at 200° for bituminous coal. Acidification of the alkaline solutions gave 80-85 percent of humic acid-like products, based on the original coals. When the oxidations were carried out at 200-300°, the equivalent weights and oxygen contents of the products from the three kinds of coals tended to converge to the same values.

Gillet (1951) cited evidence of this kind in support of his idea that coals are much more homogeneous than is generally believed. He considers that 80 percent or more of the coal substance is a "fundamental" material having the approximate composition $C_{29}H_{22}O_2$, and that when this material is oxidized, 20 carbon atoms remain, giving products of empirical formula $C_{20}H_8O_8$. This, he states, appears to apply to all of the products of oxidation of the various coals.

Jüttner (1956) has stated that dry oxidation of coals leads predominantly to the humic acids, but that if low molecular weight degradation products are desired, oxidation in an aqueous medium is necessary. However, oxidation in aqueous media may be controlled so as to produce humic acids if desired. For example, Bailey, Kimberley, and Ward (1954) made use of controlled oxidation of coal with alkaline permanganate with the object of obtaining maximum yields of humic acids, and of finding out whether they could isolate a humic acid that was a single chemical entity. Although they were able to obtain acids of constant elementary composition, they concluded that this material was still a mixture rather than a single pure compound.

A recent thermographic study of coal humic acids from various sources (Klimov et al., 1953) shows that although all humic acids gave maxima at 396-426° and at 725-35°, there was no regular variation in the properties of the humic acids from coals corresponding to the transition from older to younger coals.

Roga and Ihnatowicz (1951) determined "humic acid curves" (Kreulen, 1934) of various coals, and found that the activity of the coal, as measured by the amount of humic acid formed at a given temperature, decreased with increasing rank of the coal; vitrain was found to give more humic acid than durain.

Kukharenko, Lyubimova, and Shalyapina (1956) noted that the yield and properties of humic acids produced by mild oxidation of coal depended on its organic structure, the extent of aromatic ring condensation, the relation between the aromatic and aliphatic constituents, and the oxygen bridging. They state that the rate of formation, yield, and properties of the alkaline solutions of the humic acids may be used to evaluate the "grade" of a coal, the extent of its oxidation, and its petrographic composition.

In determining the amount of humic acids in coals, peats, and lignites, Kukharenko (1956a) tried several methods, and recommended the gravimetric method as being more accurate than either the volumetric method based on further oxidation of the acids with chromic acid, or the still less reliable colorimetric determination. He observed, further, that air oxidation incidental to the extraction of the humic acids on the steam bath had no effect on the total yield, but that it did alter their structure appreciably.

Kukharenko (1949) separated coal humic acids into fractions by extraction successively with salt and base solutions (sodium oxalate, sodium fluoride, sodium carbonate, ammonium hydroxide, and sodium hydroxide) of pH that increased progressively from 6.6 to 13, and found that, in general, the higher the pH of the extracting solution, the higher were the carbon and hydrogen contents of the extracted materials. He concluded that the humic acids formed a closely interrelated family as regards chemical structures and molecular weights.

In further investigation of the properties of humic acids from various sources, Kukharenko (1956b) utilized the "coagulation threshold" determination, which is expressed in terms of the minimum concentration of a barium chloride solution required to produce a cloudiness in an alkaline humate solution prepared in a specific manner. He found that the coagulation threshold was higher (12.2 to 19.2) for the naturally occurring humic acids extracted from brown coals than it was (2.0 to 6.8) for humic acids prepared by oxidizing higher rank coals.

In another study of their properties, the humic acids were treated with metallic sodium in liquid ammonia (Kukharenko et al., 1952). Although no identifiable compounds were reported from this reaction, ether-soluble neutral and acidic fractions and traces of basic and water-soluble material were isolated; their molecular weights ranged from 200 to 273.

The oxidation of bituminous coal with nitric acid yields, among other products, an ether-insoluble fraction having the properties of humic acids (Duuren, 1951a; Fuchs et al., 1943). Duuren (1951a) found that about half the total oxygen in this material was in hydroxyl and carboxyl groups, and reported that most of the nitrogen in this substance occurred as nitro, isonitroso, or oxonium structures (and possibly a little heterocyclic nitrogen).

Later work resulted in the isolation of a fraction of composition $C_{60}H_{40}N_4O_{35}$, in which nitro and nitroso groups were shown to be present, but no valid deduction could be made regarding oxonium structures (Duuren, 1951b). This latter material was a weak acid of equivalent weight 174. Methylation reaction showed that it contained six carboxyl groups and four hydroxyls, two of which were alcoholic; carbonyl and chromophoric groups were absent. High-pressure hydrogenation gave a small yield of an oil which appeared to be hydroaromatic. Duuren (1953) has applied Krevelen's (1950) graphical method to the study of these "nitro-humic acids."

Kinney and Ockert (1956) believe that coal combines with cold nitric acid, and that on brief heating this combination is converted to nitric acid-insoluble humic acids; further boiling with nitric acid introduces additional carboxyl groups and converts these insoluble acids to the soluble type. Water-soluble acids and carbon dioxide are formed at the same time.

Higuchi and coworkers (1955, 1956) have also studied the "nitro-humic acids," which they prepared by the action of nitric acid on lignite humic acids or on lignite itself.

Mukherjee, Bhowmik, and Lahiri (1956) oxidized coals of various ranks in air at 150°-200°, and concluded that there was a correlation between the properties of the humic acids formed and the ranks of coals used. They found that (except for lignite) the higher the rank of the coal, the lower was the base-exchange capacity and the higher the molecular weight of the humic acid produced.

Ahmed and Kinney (1950a, 1950b) and Kinney and Friedman (1952) studied the behavior of humic acids towards pyrolysis and the action of ozone. Pyrolysis yielded carbon dioxide corresponding to an equivalent weight of 242; 87 percent of the carbon remained in material nonvolatile at 950° and the residue was nearly pure carbon. No volatile aromatic fragments were isolated. The action of ozone gave primarily carbon dioxide and oxalic acid and converted most of the remaining carbon to nearly colorless, water-soluble, ozone-resistant acids. They believe that their results are consistent with the idea that coals and the humic acids derived from them contain, as part of their structure, stacked planes of carbon atoms similar to those present in carbon black.

Although a number of investigators have estimated the molecular weights of the humic acids to be in the range of 1000 to 1400 (Howard, 1945a), or even as high as nearly 3000 (Higuchi and Tsuyuguchi, 1954), others have given much lower values, even down in the range of 200 to 300 when the determinations were made cryoscopically using catechol as the solvent (Belcher, 1948a; Smith and Howard, 1935, 1936; Herbert et al., 1948; Polansky and Kinney, 1952). Mukherjee and Lahiri (1956) concluded from the results of their rheological studies that the behavior of the humic acids indicated a polymeric character which conflicted with the low molecular weights just cited.

Further oxidation of the coal "humic acids" with potassium permanganate, hydrogen peroxide, or ozone under suitably mild conditions has resulted in the isolation of "subhumic acids" (Bailey et al., 1955; Brooks et al., 1956; Dobinson et al., 1956; Ward, 1956). These are apparently simpler than the "humic acids" themselves, but are still rather complex mixtures. They were separated into fractions on the basis of solubility; the following shows average compositions:

Ether soluble $C_9H_{12}O(OH)(COOH)_3$
Acetone soluble
$C_{15}H_{11}O_2(OH)_4(COOH)_3$
Ethanol soluble
$C_{32}H_{33}O_3(OH)_5(COOH)_4$

Still further oxidation gave oxalic acid as the only identifiable product (presumably in addition to CO_2 — G. R. Y.), but it is of interest to note that they record a positive test for pyrrole structures by the "pine splinter" method. Methylation of the "subhumic acids" gave products containing about 24 percent methoxyl.

The uses of humic acids, with special reference to those prepared by the mild oxidation of lignite, have been summarized by Inukai (1956); the applications include peptizing of oil drilling muds, cement slurry, cement mixtures, and pottery clays; as agents to lower the viscosity of dense media in mineral dressing; soil conditioners; organic fertilizers, etc.

Gaseous Oxidation Products

It has been found that gaseous oxidation products are formed when coal is oxidized by air, even at moderate temperatures, and Grigor'ev and Semenova (1940) found that younger coals, on oxidation, yielded larger amounts of these gaseous products than did the older coals. Khrisanfova and Soboleva (1955) observed that the most carbon dioxide and water is formed on the oxidation of "long-flame" coals, and the least from semi-anthracites and anthracites. Jones and Townend (1945a, 1945b, 1946, 1949) have pointed out that below 70-80°, carbon monoxide is the main gaseous product, whereas above this temperature carbon dioxide and water are formed in much greater proportion than CO.

This behavior signifies that there is in coal a structural group that is easily attacked by oxygen gas to give a new group which decomposes easily to give carbon monoxide. The significance of this in coal structure deductions is obscure, as functional groups which lose CO at such low temperatures have not been well cataloged. Hurd (1929) reports that α-keto esters lose carbon monoxide readily, and cites examples wherein decompositions of the type

$$-CH_2-CO-CO_2R \rightarrow CO + -CH_2-CO_2R$$

occur at temperatures as low as 160-90°. It is conceivable that such a reaction could take place, although at a much slower rate, at still lower temperatures. Perhaps a hydroperoxide forms first, then undergoes decomposition to form a new carbonyl group, as in the conversion of tetralin to α-tetralone (Thompson, 1940), so situated that it may evolve CO as a further decomposition product.

An explanation of the evolution of carbon dioxide, which predominates at temperatures above 70-80°C., is more readily given. Certain carboxylic acids, in particular those having a carbonyl group β- to the carboxyl (-C-CO-C-COOH) are easily decarboxylated, giving CO_2 and replacing the -COOH group by H.

Although it is not possible to pinpoint exact structural units which are responsible for the oxidation that results in the formation of CO and CO_2 at relatively low temperatures, it would appear most probable that "side chains" of at least two or three carbon atoms length are involved.

Water-soluble Acids: Aliphatic

The formation of acetic acid in the oxidation of coals with nitric acid-sodium dichromate has been studied by Kinney (1947). He found that the structures in coal that produced acetic acid on oxidation were largely destroyed by carbonizing to 500°, and that high-rank coals gave less acetic acid, the quantity diminishing with decreasing volatile matter. The woody or vitrain portions of low-rank coals gave less acetic acid than did the attrital portions. The amount of acetic acid formed seemed to be directly related to the amount of methane formed on carbonization, and Kinney suggests that the acetic acid-yielding structures are those which produce methane up to about 500°, whereas a different set of structures (which give approximately the same amount of additional methane on carbonizing to 1000°) does not yield acetic acid on oxidation.

From the results of his studies on the air oxidation of four types of coal at temperatures up to 200° for as long as 3000 hours, Bastick (1954) concluded that the constituent groups which produce tars and methane on the pyrolysis of coal are very sensitive to oxidation. Kinney's work on the oxidation of several pure phenols (Kinney, 1947) showed that acetic acid was produced in significant quantity only by those phenols bearing methyl side chains. It is possible, of course, that side chains longer than methyl might also produce acetic acid, but such compounds were not included in the group he tested. Thus it may be said that the evidence from the study of the formation of acetic acid by oxidation of coal favors the idea that coal contains side chains or alkyl groups of at least one carbon atom.

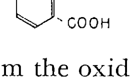
Another study of coal oxidation which supports the concept of aliphatic side chains or perhaps chains of at least two carbon atoms length coupling other nuclei together is that of Duuren and Warren (1950). They used nitric acid as the oxidizing agent, and allowed it to react 120 hours at the boiling temperature; during this time the spent acid was removed and new oxidizing agent was added every two hours. Although they obtained various aromatic acids (as have many other investigators — these are discussed later), they found succinic acid ($HO_2CCH_2CH_2CO_2H$) and its anhydride in one of the fractions. If such a 4-carbon dibasic acid had been formed by the rupture of a benzene ring, one would expect to obtain maleic acid; the fact that the saturated acid was the one found suggests that it must have been derived from a saturated structure such as an aliphatic chain, or at least a cycloalkane unit.

Macrae (1943) has suggested that the oxidative alteration of aliphatic side-chain groups of the coal substance is responsible for the lowered yield of oily volatile matter in the carbonization of oxidized coals.

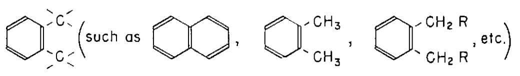
WATER-SOLUBLE ACIDS: AROMATIC

A study of the "nuclear" structure of coal has involved many oxidation experiments. Among the earliest investigators in this field were Bone and Quarendon (1926), who used potassium permanganate as the oxidizing agent, and isolated 1,2,3,4-benezenetetra- and hexa-carboxylic acids from their product. Since then Bone and his coworkers extended this work, and others elsewhere have applied this and other oxidizing agents to the problem of preparing aromatic acids from coal. As this early work has been summarized elsewhere (Bone and Himus, 1936; Howard, 1945a), the material covered in this paper will deal largely with the more recent work along these lines.

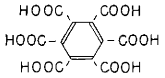
The more complete degradation of coal structure by means of these more powerful oxidizing agents, more drastic conditions, or both, points to the conclusion that coal contains an appreciable proportion of its carbon in the form of aromatic six-membered ring structures, and that the percentage of the carbon existing in this form increases with increasing rank of the coal. The formation of benzene carboxylic acids indicates (but perhaps does not, in itself, prove) the presence of benzene rings with one or more side chains or "condensed" aromatic structures containing "fused" benzene rings. For example, phthalic acid,



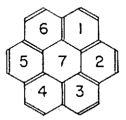
could result from the oxidation of any of a wide variety of structures in which two adjacent carbon atoms of the ring held other carbon atoms:



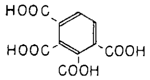
the only requisite being that the groups attached to the benzene ring should be more easily oxidized than the benzene ring itself. To carry the example further, mellitic acid,



would not be found in the oxidation products unless the original material contained structures in which all six carbon atoms of some of the rings were attached to other carbon atoms, as in coronene:



Here, if the peripheral rings (1 - 6 inclusive) were oxidized, ring 7 might be left holding the necessary six carboxyl groups. On the other hand, if rings 2 - 7 inclusive were oxidized, leaving ring 1 intact, it would hold only four carboxyl groups:



Thus, in coal oxidation, the isolation of larger amounts of mellitic acid or of benzene carboxylic acids holding a large number of carboxyl groups indicates the existence of a proportionately greater amount of "network" structure than if little or no mellitic acid is formed and the other benzene carboxylic acids isolated hold fewer carboxyl groups.

In bringing about such extensive oxidations as this, some recent investigators have used permanganate (Funasaka et al., 1952; González Sánchez, 1955), but others have employed a variety of different oxidizing agents. Jüttner (1956) and Fujimoto et al. (1956) have described the use of nitric acid; Savich and Howard (1952) used nitric acid and oxygen at elevated temperatures and pressures.

Benning (1955a) also oxidized coal with nitric acid and oxygen, using finely ground coal with 6 to 8 times its weight of 15-35 percent nitric acid at 150-60° and 5 atmospheres pressure. More than 40 percent of the carbon in the coal was converted to CO_2, and the remaining brown oxidation product was found to consist of 6.5 percent aliphatic dibasic acids (succinic, glutaric, and adipic), 3.5 percent benzenedicarboxylic acids (phthalic, isophthalic, and terephthalic), 8.0 percent benzenetricarboxylic acids (trimellitic and hemimellitic), 7.0 percent benzenetetracarboxylic acids (pyromellitic and mellophanic), 5.5 percent benzenepentacarboxylic acid, 0.5-2.0 percent mellitic acid, 8.0 percent naphthalene- to phenanthrene-carboxylic acids, 6.5 percent picric acid, 52.0 percent higher molecular-weight acids, and small amounts of benzoic acid, 2,5-furan- and 2,5-pyridinedicarboxylic acids, 1,2,3,4-tetrahydro-x-hydroxynaphthalenecarboxylic acids, and polycyclics of molecular weights 400-500. Benning believed that dilute nitric acid oxidation attacked coal structural units which contain methylene ($-CH_2-$) groups to give benzenecarboxylic acids and aliphatic acids, and he calculated, on the basis of this assumption and the yield of acids obtained, that the molecular weight of his coal was 630.

It is interesting to compare Benning's idea that nitric acid attacks the methylene groups with the report given by Bergmann and coworkers (1954), who included some oxidized coal samples in their study of the infrared absorption spectra of coals. These samples were apparently oxidized dry, as in air or oxygen, at 230°C. for periods of 3, 12, 24, and 96 hours. With this progressive oxidation there occurs first a "shoulder," then a peak at 1720 cm^{-1}, the position of which indicates the formation of C-O groups; these investigators state that an attack of methylene groups is indicated, but that aromatic structures are much less affected.

Jüttner's (1956) results on the nitric acid oxidation of a "fat" coal and a "gas-flame" coal were somewhat similar to those of Benning. He identified oxalic, succinic, a little glutaric and adipic acids as well as formic, a relatively large amount of acetic, and a little butyric acids in the aliphatic class. After a secondary oxidation of the primary products with hot concentrated sulfuric acid, he obtained pyromellitic, mellophanic, benzene pentacarboxylic, and mellitic acids. He stated that, on the average, the benzene carboxylic acids contained between three and four carboxyl groups, but that the main part of the primary oxidation product consisted of higher molecular weight acids of unknown structure.

In a study of the various petrographic constituents of coals, Schulz and Howard (1946) used nitric acid followed by alkaline permanganate; they reported yields of acids as tabulated below:

Yields of Acids, Percent

Coal	Oxalic	Total benzenoid	Mellitic
Pittsburgh seam (bright)	2.7	28.0	6.2
High Splint (dull).......	0.0	36.8	13.5
Illinois No. 6 (fusain)...	0.0	56.3	25.4
Utah Hiawatha (resins)..	11.9	21.0	1.5

Sustmann and Weinrotter (1940) oxidized brown coal and a semicoke prepared from it, using fuming nitric acid. The coal yielded 1.3 percent, and the semicoke 2.6 percent of mellitic acid.

The use of nitric acid as an oxidizing agent has been found to introduce some nitrogen-containing structures into the products (Savich and Howard, 1952), and picric acid (2,4,6-trinitrophenol) has been found among the acidic compounds formed (Jüttner, 1956). Grosskinsky (1952) also reported the isolation of picric acid from the nitric acid oxidation of coal. He reported yields of oxidation products which varied depending on the kind of coal, petrographic composition, physical and chemical pretreatment, particle size, concentration of nitric acid, presence of catalysts, reaction temperature, and pressure. He showed that the primary product contained aliphatic acids (succinic and adipic) 4.4-11.5 percent, benzene dicarboxylic acids 4.7-9 percent, benzene tricarboxylic acids 13.9-21 percent, benzene tetracarboxylic acids 9-11.3 percent, benzene pentacarboxylic acid 3.4-9.4 percent, mellitic acid 0.2 percent, and picric acid 9-20.4 percent.

Beck (1954) has applied a chromatographic method to the separation of the acids formed in the nitric acid oxidation of coal, and claims that it is an improvement over the usual analysis by fractional distillation and crystallization of the methyl esters.

Howard (1939) developed an electrolytic method for the separation and purification of the water-soluble acids from coal oxidation, and González Sánchez (1955) also used a similar procedure.

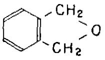
Belcher (1948a, 1948b, 1948c, 1948d, 1948e) oxidized vitrain electrolytically at a copper anode and obtained, in addition to the "humic acids," a water-soluble fraction (Belcher, 1948c) in which he identified (by distillation and crystallization of the methyl esters) oxalic, mellitic, 1,3-benzenedicarboxylic, and 1,2,3-benzenetricarboxylic acids. He found that a high proportion of the methyl esters failed to distil under conditions which favor ready distillation of the methyl esters of the benzenecarboxylic acids; decarboxylation of the sodium salts from the residual esters gave a mixture in which benzene, biphenyl, and diphenyl ketone were identified. Belcher stated that the water-soluble acids from this oxidation appeared to be similar to those obtained from the potassium permanganate oxidation of coal.

The experiments of Smith and coworkers (1939) on the oxidation of coal with oxygen and aqueous alkali at elevated temperatures and pressures was followed by the development of larger equipment for carrying out this reaction on a pilot-plant scale (Franke and Kiebler, 1946; Franke et al., 1952), using oxygen at 200-300°C. and 500-1200 lb./sq. in. total pressures, and giving yields of about 50 percent of the carbon as carbon dioxide and the remainder as water-soluble organic acids. These acids are obtained from the reaction mixture by acidification and solvent extraction. Kamiya (1956) applied a similar procedure to two bituminous coals of 84 percent and 87 percent carbon, using CuO, MnO_2, or V_2O_5 as catalyst, and obtained results similar to those just described.

The chemistry of such acids has been reviewed by González Sánchez (1954), and detailed studies of their properties (Berman and Howard, 1949, 1950; Ruof et al., 1951; Roy and Howard, 1952; Entel et al., 1953; Entel, 1955; Montgomery and Sienknecht, 1955; Holly and Montgomery, 1956; Holly, Montgomery, and Gohlke, 1956; Montgomery et al., 1956) indicate that their molecular weights range from 199 to 442 with an average of about 265 (Berman and Howard, 1949). The butyl esters of molecular weight 300 to 700 were distillable, but they left a non-distillable residue that had an average molecular weight of 900. These esters apparently contain significant amounts of nuclear structures more complex than a single benzene ring (Berman and Howard, 1950).

Further study, including hydrogenolysis of the butyl esters in such a manner as to convert carboxyl groups of the acids to methyl groups (Ruof et al., 1951; Entel, 1954), resulted in the isolation and identification of phthalan, 5-methylphthalan, 2-methylcyclohexanemethanol, and 1,2,3,4-, 1,2,3,5-, and 1,2,4,5- tetramethylbenzenes from the ester fraction boiling at 195-207° C. (760 mm.). Hydrogenation of the ester fraction boiling above 207°, permitted isolation of pentamethyl benzene and 4,5- and 4,7-dimethylphthalans, and indications were obtained that such compounds as polymethylbiphenyls, polymethylphthalans, polymethylhexahydrophthalyl alcohols, lactones of polymethyl-2-hydroxybicyclohexyl-2'-carboxylic acid and polymethylcyclohexanemethanols were present.

The isolation of phthalan derivatives is of considerable interest. Studies of phthalan itself (Entel et al., 1952) and comparisons of it with degradation products of the acids from coal resulted in the suggestion that part of the oxygen in coal may occur in phthalan-type structures.



Phthalan

Benning (1955b) proposed a paper-chromatography method for the separation and identification of the lower molecular weight constituents of the acid mixtures. Montgomery and Sienknecht (1955) found that they could partially separate the acids by stepwise acidification of their solution in aqueous alkali and extraction with butanone at each stage, and that this process was more effective than the use of graded solvent mixtures progressively richer in an effective solvent. They noted also that part of the acids (13 percent) could be obtained as a sublimate at 1 mm. of mercury pressure.

Roy and Howard (1952) also applied a solvent fractionation procedure to the mixture, which consists of approximately ⅓ benzene carboxylic acids, ⅓ bi- and tricyclic acids, and ⅓ higher polycyclic acids, and isolated the following: $1,2\text{-}C_6H_4(CO_2H)_2$, $1,3\text{-}C_6H_4(CO_2H)_2$, $1,2,4\text{-}C_6H_3(CO_2H)_3$, $1,2,4,5\text{-}C_6H_2(CO_2H)_4$, $1,2,3,4\text{-}C\ H_2\ (CO_2H)_4$, and $C\ H\ (CO_2H)_5$. The lactone of 2′-hydroxy-2-biphenylcarboxylic acid was isolated in the decarboxylation of the copper salts of the mixed acids (Entel et al., 1953), and benzene, naphthalene, biphenyl, biphenylene oxide, phenanthrene, diphenyl ketone, fluorenone, phenol, benzoic acid, the lactone of 2-hydroxybiphenyl-2′-carboxylic acid, and smaller amounts of pyridine, quinoline, a mixture of the three phenylpyridines, and β-naphthoquinoline were also formed (Entel, 1955).

Application of partition chromatography to the separation of these acids resulted in the isolation of benzoic and phthalic acids and gave a fraction whose nuclear C/H ratio suggested the presence of aliphatic or hydroaromatic structures in the original coal (Holly and Montgomery, 1956). The use of the mass spectrograph and the infrared spectrometer on the methyl esters of the acids obtained from Pocahontas No. 3 coal enabled Holly and coworkers to identify benzenetetracarboxylic, trimellitic ($1,2,4\text{-}C_6H_3(CO_2H)_3$), methylphthalic, phthalic, isophthalic ($1,3\text{-}C_6H_4(CO_2H)_2$), terephthalic ($1,4\text{-}C_6H_4(CO_2H)_2$), naphthoic, toluic, and benzoic acids. It appeared that the unidentified components of the mixture were probably the more highly condensed aromatic acids (Holly, Montgomery, and Gohlke, 1956). Further decarboxylation established the presence of benzene, naphthalene, biphenyl, indan, and phenanthrene ring systems, some of which carried alkyl substituents (Montgomery et al., 1956).

Montgomery and Holly (1957) applied the copper-quinoline method to the decarboxylation of acids obtained by the oxidation of Pocahontas coal (Franke et al., 1952), and found by the mass spectrograph that the eight most important nuclei contained in these acids were as follows: methylnaphthalene 38 percent, benzene 35 percent, biphenyl 9 percent, naphthalene 4 percent, phenanthrene 3.3 percent, benzene with five carbon atoms in side chains 1.8 percent, benzophenone 1.7 percent, and toluene 1.5 percent. Terphenyl and a fraction tentatively identified as phenylnaphthalene were also found. They state that the coal "thus consists largely of these aromatic nuclei, probably linked together by more readily oxidizable structures."

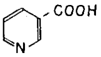
Jüttner (1956) also decarboxylated the primary acids obtained from his nitric acid oxidation of coal, and found the following in his decarboxylation product: benzene, toluene, xylene, and small amounts of naphthalene, methylnaphthalene, biphenyl, diphenyl oxide, and fluorene. Here again is evidence of the presence of alkyl groups on the ring systems of the acids formed on oxidation, and it may be presumed that these alkyl groups existed in the original coal.

Grosskinsky (1950) "pre-oxidized" coals by heating them in air at 200-300°, and stated that if these products were oxidized further in the liquid phase, they yielded cyclic acids which could be used in making lacquers, resins, plasticizers, etc.

Sufficient importance has been attached to these oxidative methods of preparing organic acids from coal that several patents have been issued relating to processes involving nitric acid, perhaps accompanied or followed by other oxidizing agents or catalysts (Juettner, 1939, 1943; Howard, 1951; Bergwerksverband, etc., 1943, 1955) and the use of oxygen and alkali at elevated temperatures and pressures (Carnegie Institute of Technology, 1950). A modification of this process involves a preliminary oxidation of the coal with nitric acid or sulfur trioxide (Kiebler, 1949). These polycarboxylic acids are considered as possible starting materials in the manufacture of synthetic plastics. The neutral esters of these acids with monohydric alcohols have been patented as hydraulic fluids (Montgomery et al., 1950).

NITROGEN IN COAL

The oxidation of coal has provided some hint as to the nature of the nitrogen which comprises approximately 0.5 to 1.5 percent of the moisture- and ash-free substance. In a study of the Kjeldahl method of nitrogen determination as applied to coals, Beet (1940) found that the sulfuric acid digestion (oxidation) of coal did not convert all of the nitrogen of the coal to ammonia unless continued for some hours beyond the point at which the reaction mixture becomes clear. Interruption of the oxidation at the "clear" stage resulted in the isolation of nicotinic acid, suggesting that the coal originally contained a part of its nitrogen in six-membered heterocyclic rings which bore at least one carbon side chain. This is confirmed by the observations of Entel (1955) who isolated pyridine and related compounds from the products obtained by decarboxylating the mixture of acids formed in the oxidation of coal with oxygen and alkali at elevated temperatures and pressures.



Nicotinic acid

Kinney et al. (1948) made a study of the fate of nitrogen in the potassium permanganate oxidation of coal and found their results suggested that "the basic nitrogen structures in the proteins have not been greatly altered by the process of coalification," although proteins, as such, were not present in coal. It was also indicated that the nitrogen of coal became more predominantly of the tertiary amine type as the rank of the coal increased.

PHENOLIC GROUPS

The gaining of information about the nature of coal is not limited to studies of the identifiable products of oxidative degradation; the course and rate of the reaction may also be revealing.

From his observations on the behavior of the humic acids, bitumens, and phenols, Tronov (1940a, 1940b) concluded that, in the oxidation of coal, oxygen attacked phenolic structures to form first polyhydric phenols, then carbonyl compounds which on further oxidation release carbon dioxide to form acid anhydride or carboxyl groups, some of which might yield CO_2 by decarboxylation.

Yohe and Blodgett (1947) studied the oxidation of various coals with oxygen in the presence of sodium hydroxide solution before and after methylating with dimethyl sulfate. They found that the methylation of coals below the rank of medium-volatile bituminous resulted in an appreciable decrease in the rate at which they absorbed oxygen, presumably because of the conversion of oxidizable phenolic groups to oxidation-resistant phenol methyl ether structures. Coals of medium-volatile rank (about 89 percent carbon) and higher were not methylated appreciably, and the dimethyl sulfate treatment had no significant effect on the rate of their oxidation. Thus it would appear that the lower rank coals contain phenolic structures which diminish in amount as the rank increases and vanish at about 89 percent carbon content. This has been confirmed by infrared studies of coals (Brown, 1955).

Some of the changes which occur in coals during oxidation have been detected by physical as well as chemical methods. Vucht, Rietveld, and Krevelen (1955) determined the infrared absorption spectra of a coal of 87 percent carbon content after oxidation for one hour, 24 hours, and 48 hours. They noted an increase in OH and C:O groups.

Adams and Pitt (1955) heated a bituminous coal 20 hours in air at 140°C., another portion in air 5.5 hours at 200°C., and a third 5.5 hours in vacuum at 200°C. Infrared spectra of these samples showed changes that they attributed to an increase in H-bonded OH, C:O, and acid dimers for the oxidized samples, but changes in the vacuum-heated sample were minor. They suggest that the major oxidation reaction has been in the formation of aromatic carboxylic acid groups, possibly at the expense of peripheral CH groups on condensed aromatic nuclei.

Brooks and Maher (1954, 1957) titrated weakly acidic groups in coal with sodium aminoethoxide in ethylenediamine (Katz and Glenn, 1952), and found an increase in total acidic groups as the coal was progressively oxidized in air. Yohe and coworkers (1955) exposed samples of Illinois coals to atmospheric oxidation at room temperature and at about 100°C. for periods of time up to about 100 days. Although the coking properties as judged by the free swelling index and agglutinating value dropped rapidly, the phenolic group content as estimated by methylation with dimethyl sulfate and subsequent methoxyl determination remained essentially constant or increased slowly.

Other effects of oxidation of coal are discussed in later sections of this paper under "Effects of Oxidation on Carbonizing Properties" and "Methods of Estimating the Extent of Weathering or Oxidation."

Thus there emerges from the studies of the oxidation reactions and products the following picture of the chemical structure of coal:

Coal is a complex, heterogeneous mixture of high molecular weight substances. Aromatic (benzene) ring systems and condensed aromatic ring systems are present, and these condensed nuclei increase in size and form an increasingly greater part of the total substance as the rank of the coal increases. Aliphatic structures exist as methyl groups and possibly as side chains containing two or more carbon atoms, as connecting chains between aromatic nuclei, or as parts of hydroaromatic units.

Part of the oxygen present in low and intermediate rank coals is present as phenolic hydroxyl, but this type of structure practically vanishes as coal attains about 89 percent carbon content.

Part of the nitrogen is probably present in heterocyclic structures.

Other methods of investigation (hydrogenation, for example) have given results consistent with this picture, but a detailed discussion of these is beyond the scope of this paper.

STORAGE AND SPONTANEOUS COMBUSTION

Taylor (1941) has given the opinion that the advantages of storing coal compensate for the losses sustained by its deterioration (except for loss of coking power) under normal conditions where the temperature rise in the pile is small and of reasonably short duration.

Yet the questions that face users of coal are not whether to store it, but where, how much, what kind, and under what conditions. The very nature of the economy and technology of our civilization requires that coal be stored by the consumer or distributor prior to its use. Such storage may be in any amount or under any condition, from a few pounds in a bag on the back porch of a modest dwelling to thousands of tons piled high adjacent to a large power plant or factory or the rail yards or docks of a trans-shipment center. And storage of coal presents problems of various kinds and magnitudes, many of them due to the oxidizability of the coal substance.

These problems, indeed, are not confined to coal in storage in the usual sense. Coal in transit in railroad cars or in the holds of ships is subject to deterioration, to loss by fire of spontaneous origin, and so also is coal in the seam where Nature deposited it, once its cover is removed and it is exposed to air and made ready for mining.

The various aspects of the deterioration of coal during storage have been ably summarized by Schmidt (1945). Scott (1944) in a publication dealing with fires in anthracite mines has also discussed many related topics, including problems encountered with coals of lower ranks and with storage piles as well as the specific problems of anthracite mines, and he has gone into the effects of various factors and conditions; he gives a bibliography of 411 references. Other resumés of the literature on spontaneous combustion of coal have been prepared by writers in other countries; among these are Sanchez Marco (126 references, 1947), Chakravorty (45 references, 1955), and Rafikov (35 references, 1956). In view of this, only some of the more recent developments are mentioned here.

The effects of conditions of storage have been considered in several publications, but new ideas are not plentiful. Although it has been indicated that, in general, spontaneous heating is less with coal of low moisture contents (Jessen, 1943; Ellis, 1943; Olpinski, 1948), Frey (1943) examined this question more carefully by means of manometric measurements of oxygen absorption. His findings were that dry coal shows the least oxygen absorption; oxidation becomes more rapid with increasing water content until a maximum value is reached, and further increase of water content results in retarding oxidation. It is for this reason that sites of ignition in coal piles after heavy rains are to be found in the interior of the piles rather than in the water-saturated zone near the surface.

It has also been reported that the presence of catalysts such as sulfur and iron compounds is important (Jessen, 1943); that fine coal is more readily ignited than coarse (Jessen, 1943; Ellis, 1943), and that a poor distribution of particle sizes may increase the probability of trouble (Ellis, 1943; Chalk, 1944). The usual recommendations for layer piling and compaction, and the admonitions for avoiding sources of heat and air drafts have been repeated (Ellis, 1943; Lange and Winzen, 1954). Oreshko (1951b) has stated that for all coals screening and classifying to remove dust and fines promotes safety of storage.

Staemmler (1954) has stated that the iron content of a brown coal, especially iron salts resulting from the weathering of pyrite, influences spontaneous ignition, and Romwalter (1947) claims that self-ignition is promoted by the presence of alkaline water derived from weathered minerals of the adjacent rock layers. Migdalski (1956) has said that iron aids the oxidation of coal, but that the role of moisture is questionable.

Whether or not a given pile of coal in storage will heat spontaneously does not depend solely upon either the conditions of storage or the inherent properties of the coal itself—both are important. An inherently "dangerous" coal may be stored safely if proper precautions are taken, or a "safe" coal may heat if carelessly piled. In line with this, Blaskett (1948) has given an approximate measure of the tendency of piled coal to heat. He indicates that the tendency is directly proportional to the initial rate of oxygen consumption, to the specific heat, and to the density of the coal, proportional to the square of the height of the pile, and inversely proportional to the thermal conductivity of the coal. In Blaskett's formula only the height of the pile is a condition of storage; the other factors are inherent properties of the coal. Such factors as size, size segregation, moisture, etc., are not mentioned, whereas properties such as the nature of the coal itself would doubtless be included in the factor involving initial rate of oxygen absorption.

Although most investigators in recent years have avoided the moot question of the effect of pyrite on spontaneous combustion, one may still find reports to back whichever side of the argument he chooses to support. For example, Mapstone has pointed out that organic peroxides may oxidize pyrite (FeS_2) to FeS (1954b). He has given a theory (1954a) for the occurrence of spontaneous combustion in pyritic coals which postulates the oxidation of pyrite by the oxygen of the coal-oxygen complex (pages 11-13) to give finely divided ferrous sulfide, which "is known to be pyrophoric."

Collet (1946) notes that pyrite is subject to oxidation in contact with air, particularly in the presence of moisture, and states that it may cause spontaneous combustion in piles of coal exposed to rain for several months. Ellis (1943) recommends selecting low-sulfur coal for storage.

Teichmann (1945) oxidized samples of pyrite, coal, and coal-pyrite mixtures at 105° in a stream of moist oxygen and concluded that although the actual amount of oxidation was small, it was appreciably greater for the coal-pyrite mixture than for the pyrite alone. The rate of oxidation was greatest during the first week, then decreased to a value which remained practically constant from the third week onward. Toledo (1954) observed that the most readily oxidizable coals are those of low rank (for example, lignite) that are friable, recently mined, have a high content of pyrite and a large proportion of fines.

Berkowitz and Schein (1951) comment that the common explanation of spontaneous heating as attributable to the oxidation of pyrite is of secondary importance except possibly for certain high-sulfur, open-structured coals.

Lemaire (1943) says that the "presence of pyrites is not to be feared when the coal is in large particles," and further that "presence of a high-ash content or other foreign bodies seems, like the pyrites, to retard oxidation provided that the iron content is very low."

Frey (1943) measured the oxygen absorption of a mixture of powdered coal with equally finely ground pyrite and found that this admixture of pyrite resulted in the inhibition of oxygen adsorption, and that the same effect was obtained with coal which has a high ash content and a low percentage of iron oxide; a high iron oxide content promotes oxidation.

These results are similar to those reported by Elder and coworkers (1945) who found that the ash and mineral constituents present in a coal appeared to diminish its tendency to heat spontaneously. They compared washed and unwashed samples of the same coals in which the unwashed samples contained larger amounts of total sulfur and pyritic sulfur, and found that washing reduced the ash and sulfur content and increased the tendency to heat spontaneously. They said that the loss in spontaneous heating tendency due to reduction of pyritic sulfur was more than compensated by the increase in concentration of the pure coal substance.

From his studies of South African coals, Sevenster (1952) concluded that pyrite played no part in the absorption of oxygen. In a summary of work done by the U. S. Bureau of Mines, Davis (1945) has written: "It is sometimes suggested that oxidation of the mineral matter, notably pyrite, may exert strong influence on the spontaneous heating of coal. Conceivably it might heat more rapidly than the coal substance at a critical point on the characteristic coal curve and thus accelerate the heating disproportionately at this point. However, none of the hundreds of curves obtained for different coals have shown inflection points and, therefore, it seems doubtful if the pyrite can exert the effect supposed."

The possibility that growth processes of micro-organisms may bring about heating that contributes to the spontaneous ignition of coals has been considered. Experiments showed, however, that in coal samples inoculated with bacteria, no temperature rise attributable to their action could be detected unless glucose was also added, and that partial sterilization of heating coal piles by injecting formalin did not retard heating (Zavarzina, 1956). It was concluded that spontaneous heating and ignition in coal piles are chemical chain processes, not bacterial.

These observations on bacterial action appear to check well with those of Dhar and Agarwal (1952), who mixed coal with carbohydrate material (sugar or straw), added this mixture to soil samples, and compared the results with experiments in which the coal and the carbohydrate were added separately to the soil. Loss of carbon from the coal was greater in the presence of the carbohydrate. It may be presumed that the carbohydrate served as nutrient material for micro-organisms of the soil samples.

The heat of wetting has been cited as a cause of the rise of temperatures to dangerously high values (Berkowitz and Schein, 1951), especially where coals of low rank have previously been dried, then brought into contact with water; this is consistent with Lemaire's (1943) statement to the effect that, up to a certain limit, hygroscopic water accelerates oxidation, and with

Frey's (1943) observation about the site of hot spots in a coal pile following rain.

EVALUATION OF SUSCEPTIBILITY

It has long been known that some coals are far more susceptible to spontaneous combustion than others, and various procedures have been devised in attempts to evaluate this tendency of coals prior to shipping or storing them.

Some of these evaluations are correlations of known properties or characteristics with susceptibility to spontaneous combustion. Olpinski (1948) has made the astute observation that the greatest tendency to spontaneous ignition was shown by coal samples from mines where underground fires are most frequent. Others have correlated petrographic composition with fire hazard; Marevich and Travin (1953) state that the durains are most stable, whereas the most oxidizable are tectonically compressed specimens of the vitrain and vitraino-fusain classes, and that aggregates where fusain and glossy coals are in direct contact with each other are particularly "dangerous."

Nötzold (1940) stated that certain vitrains are most susceptible to spontaneous combustion, and proposed a theory that the process of self-oxidation is a result of the reforming of the humus compounds which were made unstable by the loss of gases under pressure. High hydrogen content has been correlated with an increased ability of a coal to absorb oxygen (Kartvelishvili, 1946), and coals which are noncrumbling have been found to be most amenable to storage (Szadeczky-Kardoss, 1944).

Other investigators have utilized various experimental methods for judging the susceptibility of a coal to spontaneous combustion. One of these methods involves measuring the amount of oxygen absorbed by coal (Schmidt and Elder, 1940); Skochinskii and Makarov (1939a) found that the amount of oxygen absorbed by Emanzhelin brown coal, which easily undergoes spontaneous combustion, was about four times that absorbed by the more stable Lisichan coal at 25°C., and that the difference was still greater at 50° and at 75°C.

Crennan (1950) measured rates of absorption of oxygen by Australian coals and found that at the two sizes he used (−18+36 B. S. S. and −1/4+1/8 inch B. S. S.), size had little effect, but that the effect of temperature was marked, the rate being greater at 37° than at 20°. He reported that there was no clear-cut difference between coal types. Jessen (1943) and Blaskett (1948) also used oxygen absorption methods in their studies of spontaneous combustion.

Virtala and coworkers (1949) estimated tendencies toward spontaneous combustion of both liquid and solid fuels by determining the oxygen absorption, heat evolution on oxidation, and the iodine number (Wijs method), and Tronov and Grigor'ev (1940) recommended the use of the iodine numbers of coals as a measure of their spontaneous combustibility.

Chalupa and Drabek (1955) used a combination of factors to express the tendency of coal to self-ignition; these included the rate constant for the oxidation of the coal substance, the amount of oxygen consumed, thermal losses during oxidation, presence of inert gases, and composition of the ash. They stated that an increase in hydrophilic properties increased the oxidation rate.

Roga and Ihnatowicz (1951) have reported that the Kreulen (1934) method of determining the "humic acid curves" of coals can be considered a reliable indication of their affinity for oxygen.

Olpinski and Gabrys (1953); Olpinski, Pawlikowski, and Rozmus (1953); Olpinski and Pawlikowski (1953); and Olpinski (1953) investigated the specific surface of 35 coals by means of nitrogen adsorption at about −195°, and found that the lower the specific surface, the lower were the hygroscopic water, the density, and the tendency to spontaneous ignition. They studied the consumption of oxygen from air at 50-80°, and found that after an initial period of 3-4 hours the oxygen consumed approached a constant value; that the oxidation of the coal caused a decrease in mechanical strength; that washed coal heated most rapidly; that high ash and moisture contents greatly retarded spontaneous ignition; and that chemisorption increased rapidly with rise of temperature.

A number of investigators have made use of different methods of determining ignition temperatures. Oreshko (1950a) determined the temperature at which coal attained its maximum weight when heated in contact with oxygen, and defined this temperature as the "ignition temperature." Kessler (1955) used a similar procedure. Using the apparatus of Bunte and Kölmel (1922), Schroeder (1954) determined ignition temperatures. She placed the coal sample in an electrically heated vertical quartz tube, passed heated air or oxygen through the sample, measured the temperature in the coal, and recorded the temperature at which spontaneous heating occurred, raising the temperature of the coal to that of ignition.

Schroeder found that thicker layers of coal, coal of finer particle size, and the use of oxygen rather than air gave lower ignition temperature values. Ignition temperatures increased linearly as volatile matter decreased to about 15-18 percent, but rose much more rapidly as the volatile matter decreased further. Fresh coal samples had lower ignition temperatures than oxidized coals, and coals known to be susceptible to spontaneous combustion gave lower ignition temperatures than those which did not have such a tendency. Thus by suitable measurements on fresh coal samples, the relative tendencies toward spontaneous combustion may be evaluated.

Olpinski (1948, 1952) used a method (Sebastian and Mayers, 1937) similar in principle, and from the results of some 3000 determinations, reached similar conclusions.

Toledo (1954) employed two methods based on the general principles of ignition temperature determination. In the first method he placed a sample of coal in a tube, heated it to 150° and forced dry air through it at the rate of 10 liters per hour; the coal was adjudged safe, of medium oxidizability, or unsafe if the temperature fell, rose somewhat to a constant value, or rose to ignition, respectively. In the second method he heated the coal sample at 7° per minute in a current (10 liters per hour) of dry oxygen, and recorded as "flash point" the temperature at which the first glowing coal particle was detected.

Other variations of the ignition point methods have been used. A mixture of coal with an oxidizing agent, such as sodium nitrate, has been subjected to treatment with hot air, and measurements made on the temperatures of inlet air and selected points in the bed (Veselovskii and Terpogosova, 1950). It is reported that the temperature of ignition so measured is a useful index of the spontaneous ignition tendency.

Budryk (1952) used a mixture of coal dust with sodium nitrite, and reported a good correlation between volatile matter contents of coals and their ignition temperatures. Contrary to the findings of Marevich and Travin (1953), however, he stated that vitrain and durain constituents have practically identical ignition temperatures. He stated further that unoxidized coals have similar temperatures of spontaneous ignition.

Orleanskaya (1950) also used a mixture of sodium nitrite with coals, and apparently ran parallel control experiments on the coals without the oxidizing agent. He raised the temperature of the test samples 5° per minute and recorded, by means of a thermocouple, the temperature at the instant of self-ignition. He concluded that this ignition temperature was lowered by atmospheric oxidation that occurred during mining or other exposure, and reported that the addition of the oxidizing agent lowered the ignition temperature by 25-40° for an easily oxidized coal, but only 1-5° for coals that are oxidized with difficulty.

Zashkvara and Krym (1953) used the same method of determining the ignition temperature and reported that the values so obtained were lower with low rank coals and higher with high rank coals, that the ignition temperature drops with increasing time of storage or oxidation, and that a coal that undergoes less change in this respect for a given time possesses greater stability toward aging.

Orleanskaya (1952) described also the measurement of a similar drop in the ignition temperature which is brought about by a preliminary oxidation of the sample with hydrogen peroxide. He reported that a drop of less than 10° indicates a "safe" coal, whereas a 20-50° drop indicates a "dangerous" one.

Skochinskii et al. (1944) used a differential thermal analysis type of equipment where the coal sample was heated in contact with oxygen (air?), and judged the liability to spontaneous combustion from these results.

A special adiabatic calorimeter was constructed and used by Elder and coworkers (1945) for measuring the relative tendencies of various coals toward spontaneous heating. They tested a number of coals of various ranks and concluded that the tendency to heat spontaneously depended on the following factors: (a) rank—as the rank decreased the spontaneous heating tendency increased; (b) temperature—heating increased very rapidly as the temperature increased; (c) history of the coal, that is, the amount of oxygen it had already absorbed, for the reaction rate decreased rapidly as the time of storage and the quantity of oxygen consumed by the coal increased; (d) oxygen concentration — the rate of oxidation is proportional to the 0.66 power of the oxygen concentration in contact with the coal; (e) the surface exposed—the rate is proportional to the cube root of the surface area; and (f) the moisture and ash contents of the coal—ash appears to be an inert diluent which decreases the relative heating tendency, whereas the presence of appreciable moisture also reduces this tendency because of the latent heat of vaporization and high specific heat of water.

An adiabatic calorimeter was also used by Doornum (1954) to detect susceptibility to spontaneous combustion. He also explained methods of calculation which provide a means of judging the suitability of storage arrangements for coals of known characteristics.

Tanaka and Yamasaki (1955) used a simple calorimeter to measure the heat evolved when evacuated coal with fresh surfaces was placed in humid air.

Bogoyavlenskii and Petrenko (1957) crushed coal to −1.5 mm., sealed it in a steel bomb under an initial pressure of four atmospheres of oxygen, and heated it at boiling water temperature. They judged its resistance to oxidation by the length of the induction period (no formation of free methane, carbon dioxide, or carbon monoxide) and the rate of the reaction after the end of the induction period. Induction periods ranged from 7 minutes for a brown coal to 120 minutes for an anthracite, and reaction rates ranged from 0.0125 to 0.0019 atmospheres drop in pressure per minute for the same coals.

Prevention of Deterioration

The protection of coal in storage piles may be considered from two points of view, because the prevention of oxidation and the prevention of spontaneous combustion are not necessarily synonymous. If only prevention of self-ignition is desired, one method is to provide good ventilation; this permits slow oxidation but removes the heat as it is generated and thus prevents an increase in temperature which might lead to fire.

In most cases it would be more desirable, if feasible, to prevent oxidation of the coal, for this would prevent not only spontaneous combustion, but also the deterioration which causes loss of calorific value, cokeability, etc. Much has been published on the exclusion of oxygen from coal by storage in compacted and/or layered piles, covered piles, under water storage, etc., and summaries of these methods are available (Schmidt, 1945; Scott, 1944; Toledo, 1954; Allen and Parry, 1954; Bodmer, 1941; Goodman et al., 1946; Clark and Walker, 1951).

Inhibiting oxidation by the addition of small amounts of certain materials ("antioxidants") has met with outstanding success in the fields of rubber and petroleum chemistry, but has received very little attention from coal chemists. The problems of treating a heterogeneous solid rather than a homogeneous liquid, of applying sufficient and suitable protecting material to the surfaces of particles of such a friable substance as coal, and doing it for a cost of not more than a few cents per ton of coal are quite different from the problems encountered in other industries. Nevertheless, it would seem that the use of antioxidants may offer possibilities that would warrant exploration.

Gillet and Fastre (1944) found that a coal treated with a 3 percent solution of hydroquinone and then exposed to air, maintained nearly constant H/C and O/C ratios for as long as 24 days, whereas a coal not so protected showed a pronounced drop in H/C ratio and a marked rise in O/C ratio.

Skochinskii and Makarov (1939b) investigated the effects of adding certain "antipyrogenic" substances to coals. They tested the following: air with 1.76 percent of sulfur hexafluoride, a mixture of 0.5 percent solutions of calcium chloride and sodium silicate in a 0.16-0.25 percent solution of calcium bicarbonate, and a 1-5 percent suspension of calcium bicarbonate in water. It was reported that all of these substances decreased considerably the amount of oxygen adsorbed by the coal. They stated further that an "ultra-hard water" made up with calcium bicarbonate produced satisfactory results in fighting fires.

The effect of adding carbon tetrachloride vapor to oxygen passed over coal in oxidation experiments has been studied by Grigor'ev (1940) who found that it had no inhibiting action, but served only as an inert medium.

Orleanskaya (1950) hinted at possibilities of protecting coal when, after stating that treating coal with dilute aqueous solutions of surface-active agents lowered the ignition temperature, he added: "However, certain surface-active agents have the opposite effect and are inhibitors of self-ignition."

In investigations made by Terpogosova (1954), petroleum products, their emulsions, soaps, fatty acids, calcium hydroxide, and "other substances" were studied for their inhibiting action on coal oxidation. All petroleum products and their emulsions protected coal from oxidation, but the other substances mentioned were "less effective."

Yohe et al. (1951-2) immersed 10-gram samples of Illinois No. 6 seam coal from Franklin County in a 5 percent solution of an antioxidant in ether, and the volume of oxygen absorbed by this sample over several days was measured after draining and drying it. Comparison was made with control samples similarly treated with ether, but without the antioxidant. Antioxidants tested were: hydroquinone, 2-4,6-tri-tert-butylphenol, diphenylamine, N-nitrosodiphenylamine, and 2,2-bis-(4-hydroxyphenyl) propane, all of which are known to have antioxidant action in other applications, and a commercial paraffin wax. None of these antioxidants gave significant protection to the coal. Of all the additives tested, wax most inhibited the absorption of oxygen, possibly because of the formation of a coating on the surfaces of the coal particles.

It is interesting to note that a process for treating lump coal to prevent weathering and consequent degradation has been patented (Marmaduke, 1939); it involves covering the surfaces with a waxy coating.

ESTIMATION OF THE EXTENT OF OXIDATION

It would be of value to many a user of coal to be able to determine the amount of weathering or oxidation his coal had undergone when he obtained or used it.

Numerous methods have been proposed for doing this (Kramers, 1946), but most of them are qualitative in nature and of practical value only if one is able to obtain similar data on a fresh sample of the same coal for comparison. It is well known, for example, that the plastic and coking properties of many coals are significantly changed by weathering which may be so slight as to defy detection by analytical methods (Schmidt, Elder, and Davis, 1940; Schmidt, 1945).

It has, therefore, been suggested that the evaluation of such plastic properties be used to determine the extent of weathering or oxidation. Actually such "determination" is in a qualitative sense, and is usually used to differentiate between a fresh coal which is known to give satisfactory results in the coke oven, for example, and a weathered shipment of the same coal which may have deteriorated to such an extent that it would cause trouble (for example, difficult pushing) in the coke oven, or produce an unsatisfactory coke.

A marked decrease in the agglutinating value is one of the most sensitive indications that the coal has been oxidized (Schmidt, 1941; Schmidt, Elder, and Davis, 1940; Rees and Wagner, 1943). Similarly the free swelling index (ASTM, 1951) falls off rapidly with oxidative deterioration (Rees and Wagner, 1943), and because of the convenience and rapidity with which this determination can be made, it is used in a number of coke plants to judge the freshness of their coals. The "fluidity" as measured by the Gieseler plastometer shows a similar trend with increasing oxidation (Rees et al., 1955). Use of the dilatometer (Casamassima and Meo, 1951) has also been suggested for estimating the degree of oxidation of coal.

Changes in the yields of by-products (Marshall and Draycott, 1954; Bastick, 1954), and a deterioration of the physical properties of the coke produced are also cited as sensitive measures of the extent of oxidation of coal (Schmidt, Elder, and Davis, 1940).

Brewer and coworkers (1948), after making a thorough study of the effects of oxidation on the coking properties of coals, stated: "Of the many properties studied, the best criteria for judging extent of oxidation of coal appear to be its agglutinating value, yield of tar, and strength index of its coke."

Onusaitis and Khrisanfova (1947) have indicated that measurements of electrical conductivity on coke samples can be used to indicate the degree of oxidation of the original coals.

Changes in the ability of coals to absorb gases or vapors have been correlated with the degree of oxidation of the coals. Lamba and Ettinger (1955) state that the original surface of coal is lyophobic toward water, and that it becomes lyophilic upon oxidation; then as the surface becomes hydrated, there is a marked reduction of its capacity to absorb methane. This effect may be related to the observation made by Zagrebel'naya (1946) in his studies of the effects of various factors on the bulk density of coal. He found that although the oxidation of coal increased its specific gravity (3.7 percent increase in "pour weight" after 3.5 months in the laboratory air at 20-28°; 8.5-10.6 percent increase after 72 hours at 130-40°), the effectiveness of treating the coal with kerosene diminished with progressive oxidation. Thus the volume weight ("bulk density") of a coal increased 10 percent after wetting it with kerosene, yet after oxidizing this coal for ten days, similar wetting resulted in an increase of volume weight of only 5.1 percent.

The effects noted by Sun (1954) in his studies of the flotation characteristics of coals also appear to be related to the change from lyophobic to lyophilic nature of the surface as oxidation proceeds. Using a light petroleum oil as collector, he found that although flotabilities were little affected (in fact occasionally benefited) by superficial oxidation at low temperatures, they were lowered gradually upon more extensive oxidation. The effect was attributed to the accumulation of water-insoluble oxidation products at the coal surfaces.

Gogitidze and Plaksin (1956) also reported that the flotability of coals is slightly but regularly impaired by storage in air, and that it can be removed completely with potassium permanganate. The flotability can be partially or completely restored, however, by boiling the coal with water, by heating in a vacuum to 40-60°, or by chemical reduction of the coal surface, as with benzidine, in a 1 percent sodium hydroxide solution.

Vologdin and Kamendrovskaya (1936) and Vologdin (1937) proposed a method for determining the degree of oxidation of coal based on its action on solutions of ferric ion. They stated that ferric ion was reduced but not adsorbed by unoxidized coal, whereas oxidized coal only adsorbed it. However, subsequent work by Grigor'ev and Plekhanova (1940) indicated that this method was not reliable, and that the degree of oxidation of Kuznetsk coals could not be determined by use of ferric chloride or ferric sulfate.

Thomas and coworkers (Thomas, 1953; Walton et al., 1953) found that the electrostatic charge acquired by a stream of fine coal particles after making contact with a metal surface was related to the degree of oxidation of the coal, and they used this effect as the basis of an instrument for quality control in plant operation.

Bangham and Dryden (1950), although not searching for a method to determine the degree of oxidation of coal, observed that oxidation caused an increase in the heat of wetting with methanol, and an increase in the difference in heat of wetting between methanol and ethylenediamine. They attributed the greater increase in heat of wetting with ethylenediamine to heat of reaction with carboxyl groups formed during oxidation. Podbel'skiĭ (1947) has described a method based on the absorption of pyridine vapors by coal samples which are exposed to an atmosphere of these vapors in a thermostat. A method based on the measurement of luminescence of alcohol-benzene extracts of coal has been published (Men'shchikov and Rozmanova, 1955). Oxidation causes such changes in the organic constituents of the coal that as the oxidation progresses, both the intensity and wave length of the luminescence change, the wave length being displaced toward the violet end of the spectrum.

Although it has received little application in the determination of the extent of oxidation, it would appear that the direct measurement of the acidic groups present in a coal should be of value in this connection. Methods which might be applicable are the sodium aminoethoxide titration as used by Brooks and Maher (1954, 1957) and the sodium hydroxide-sodium carbonate titrations proposed by Uporova and Rafikov (1956).

Kawana and Sato (1956) found that the air oxidation of a lignite increased its sorption of UO_2^{++} ion from a solution of $UO_2(NO_3)_2$ from 0.83 to12.12 milligrams per gram.

Determination of the changes in chemical composition may be of value in following extensive oxidation. Zabavin and coworkers (1956) have published analyses of various grades of Kuznetsk Basin coals which had been subjected to different degrees of natural weathering.

Several investigators have made use of the permanganate number in determining the degree of oxidation of coals. This is the number of cubic centimeters of *N* potassium permanganate solution reduced by 0.5 gram of ash-free, pyridine-extracted coal in one hour at 100°C. (Heathcoat, 1933). Khrisanfova (1949) says that oxygen acts as a polymerizing agent in the original oxidation of coal, and, in the case of agglomerating coals, lowers the permanganate number, which increases again only after additional oxidation.

Egorova (1942) considers that the permanganate numbers can be used to determine the degree of oxidation of coals, and to distinguish old, weathered deposits from unweathered ones. He reports that for some coals the permanganate number decreases in the first stage of oxidation, then increases rapidly in the second stage, whereas for other varieties there is almost no change in the first stage, but a rapid increase in the second.

Radspinner and Howard (1943) oxidized several typical bituminous coals at various temperatures up to 125°C. for varying periods of time, then determined the carboxyl groups present by reaction of the coals with calcium acetate and subsequent determination of the acetic acid liberated. They found a linear relationship between oxygen known to be present and the carboxyl found which permitted an estimation of the extent of surface oxidation. They also found a more sensitive determination which was based on a linear relation between fixed oxygen and oxides of carbon evolved by thermal decomposition of the oxidized coals at 350°C. in a vacuum.

Zabramnyi and Tadzhiev (1955) also utilized the analyses of gases evolved during low-temperature carbonization as a means of judging the extent of oxidation of coals. They found that the ratio of hydrocarbons plus hydrogen to oxides of carbon $(C_nH_m+CH_4+H_2)/(CO_2+CO)$ was 7.27-10.4 for nonoxidized bituminous coals, but dropped to 0.12-6.50 for oxidized bituminous coals. The ratio of oxygen evolved in water to that evolved in oxides of carbon was 3.78-4.25 for fresh coals, and 0.27-3.89 for oxidized coals.

The use of changes in "ignition temperature" of coal with atmospheric oxidation to estimate the extent of this oxidation has been suggested by a number of authors, but it brings to light some differences of opinion which may serve to emphasize the fact that coals are not all alike, and that it is dangerous to generalize on the assumption that what one investigator has learned in studying one coal must therefore be true of all other coals.

Budryk (1952) implies that unoxidized coals have ignition temperatures similar to those of oxidized coals; Rees and Wagner (1943), working with high-volatile bituminous C and A coals from Illinois, stated that ignition temperatures showed no significant change on storage and atmospheric oxidation. Schroeder (1954) reported that oxidized coal samples had higher ignition temperatures than the corresponding fresh samples.

A number of other authors, on the other hand, have reported that oxidation results in the lowering of the ignition temperature.

Orleanskaya (1952) says that spontaneous combustion of coal is preceded by an incubation period of low-temperature oxidation accompanied by a drop in ignition temperature. In further work on the determination of ignition temperatures by heating coal samples mixed with an oxidizing agent such as sodium nitrite, he concluded that initial oxidation (for example, during mining) lowered the ignition temperature (Orleanskaya, 1950).

Several investigators have reported that although the ignition temperature drops when coal undergoes oxidation, it may be restored to the original "fresh coal" value by admixture of benzidine with the oxidized coal (Zashkvara and Krym, 1953; Lamba and Ettinger, 1955; Veselovskii and Terpogosova, 1954; Veselovskii and Orleanskaya, 1954) thus making it possible to compare the ignition temperature of the oxidized coal with that of "fresh" coal when only the oxidized sample is at hand.

Zashkvara and Krym (1953), apparently basing their work on the findings of Veselovskii and Orleanskaya (1951), report the addition of benzidine in this manner to restore the coal to its highest ignition temperature, correpsonding to "0 percent oxidation," then treating a sample with perhydrol (hydrogen peroxide) which changes the ignition temperature to its lowest value, corresponding to "100 percent oxidation." The degree of oxidation of the specimen can then be expressed as a percentage oxidation stage.

Farenden and Spencer (1955) oxidized a Yorkshire weakly caking coal in a fluidized bed with air at 150°. Determinations on samples removed periodically showed a linear relationship between specific volume and the hydrogen content ($V=0.046H+0.527$), and indicated that such a relationship might be of general value in studying the extent of oxidation of a coal.

The occurrence of sulfate sulfur in coal is usually an indication that the coal has been exposed to an oxidizing environment. Rees and Kalinowski (1939) showed that coal samples stored 4.5 years at 30-32° gained on the average 330 percent in sulfate sulfur content while suffering a loss of only 2.29 percent in calorific value.

EFFECTS OF OXIDATION ON COKING PROPERTIES

The changes in coking properties of various coals upon oxidation have been studied by numerous investigators over many years, and the results have been summarized by Schmidt (1945).

It has been recognized that an appreciable falling off in coking power as detected by the quality of the coke (Davis et al., 1947), or by the laboratory measurements of such intimately related properties as Gieseler fluidity (Rees et al., 1955; Davis et al., 1947; Wildenstein, 1953), free swelling index (Yohe et al., 1955), or agglutinating value (Yohe et al., 1955; Schmidt, et al., 1943; Davis et al., 1947) may occur before the oxidation is detectable by analytical methods. In fact, Schmidt, Elder, and Davis (1940) have stated that "the majority of coals tested showed serious impairment of coking power before they are oxidized enough to decrease the heating value by one percent and before their ultimate and proximate analyses show changes definitely greater than the experimental error of analysis."

The effect of temperature on the rate of deterioration of coking coals may be seen in the results of experiments performed by Jackman et al. (1957). They stocked Illinois No. 5 and No. 6 seam coals (3″ x 1″ size) in out-of-doors piles at different times of year at Urbana, Illinois. They found that although six months of storage through the cold weather of fall, winter, and spring could be tolerated before appreciable deterioration in coking properties became evident, thirty days of storage in the summer was the approximate limit before undesirable changes in coke structure would occur. In both series of experiments they found a slight increase in the tumbler stability value of the coke during the earliest stages of the weathering.

Kamiya (1954) studied the air oxidation of coal, using a fluidized bed process. He found that the caking property of Miike coal (Japan), as measured by the button method, decreased to a constant value within the first twenty minutes above 240°, required more than an hour at 220°, but showed very little decrease of the button index at 180°.

It has been noted that the oxidation of coal increased the viscosity of the coal as measured in the plastic stage (Lambris and Gerdes, 1941; Inouye, 1953), presumably because of the increase in the forces of attraction between the molecules.

Sommers and Peters (1954) indicate that the oxidative aging of coal is a surface phenomenon, and that the changes produced in the nature of the surface prevent the caking of coal particles during carbonization.

Although it is generally recognized that lower rank coals are more susceptible to oxidation than those of higher rank, it must be pointed out that coals of a given rank are not equally susceptible. Such differences within rank have been shown in the effects of oxidation on coke strength. Schmidt et al. (1943) exposed coals to air at about 100°C. and recorded results in terms of the number of days of such oxidation required to reduce the coke strength by 15 percent. They found this value to be 3.4 and 6.5 days for two low-volatile bituminous coals tested; 9.7 to more than 15 days for four medium-volatile bituminous coals; 2.4 to 20.8 days for eight high-volatile A bituminous coals, and 1.3 days for the only high-volatile B bituminous coal tested.

Weber (1941) made tests on coals from four different mines, piling 300 tons of each coal separately in piles three meters deep, and leaving them up to 420 days during which time they were sampled ten times. During storage the coke yield increased at the expense of the tar and light-oil yields, but the amount of lump coke decreased, and its friability increased. The ammonia yield was substantially unchanged. The individual coals behaved differently in regard to both rate of change and coke properties.

Khrisanfova (1950) also reported a decrease in the yields of tar and volatile matter upon oxidation of younger coals, but reported that the oxidation of older coals increased the yield of volatile matter.

Macrae (1943) studied the carbonization of weathered outcrop coal. He found that the gases evolved up to 400° were principally carbon dioxide and water vapor, and attributed the low oil yields to the oxidative alteration of the aliphatic side-chain groups of the coal substance.

Industrial storage of a Kentucky coal (Smith et al., 1953) by approved methods (compacted layering) did not affect its coke making ability in 18 months, but reduced the tar yield by 15 percent; it was estimated that 32 months of storage would result in a decrease of 10 percent in coke strength and 30 percent in tar yield.

Brewer and coworkers (1948) in their studies of room temperature and accelerated air oxidation of a variety of coking coals reported that progressive oxidation resulted in a uniform reduction in the yield of dry tar, and that continued oxidation caused the coals to fuse poorly and yield a "pebbly" coke in which some of the original coal particles could be identified.

Gomez et al. (1956) reported that progressive oxidation of a Texas lignite decreased the tar yield and increased the gas yield, and showed that with extended oxidation the gas formed on carbonization was largely carbon dioxide, presumably derived from the humic acid-like structures in the oxidized coal.

Roy and Das (1942) worked with Indian coals, and reported that coking coals lose their coking properties on prolonged oxidation owing to oxidative damage to their vitrain and clarain constituents.

Although most of the work on the effect of oxidation on coking properties has been concerned with atmospheric oxidation, Tuturina and Kaigorodtseva (1953) have reported that nitric acid oxidation also reduces the cokeability of coal.

Higuchi and Shibuya (1954) have reported that as the oxidation of coal proceeds, the C/H ratio becomes larger. This is in accord with the observation made by Howard (1947), who found that the low-temperature oxidation of coal removes much larger amounts of hydrogen than of carbon on an atomic basis (that is, the atomic H/C ratios in volatile oxidation products are much higher than in the original coal), and suggested that as the hydrogen-rich parts of the coal are probably responsible for plasticizing action in the coking process, this may explain why a little oxidation has a large effect on the coking and swelling properties.

It has been noted that coals differ greatly in the rapidity and extent to which oxidation affects their coking properties. For example, Davis (1945) cites a comparison of a medium-volatile bituminous coal ("Hill") with a high-volatile A bituminous coal ("Pittsburgh"). The former heated only about half as fast as the latter in spontaneous heating tests, but lost its coking power with less than one-third the exposure required for a comparable effect on the latter.

Some coals, notably certain high-volatile B bituminous coals which are used in coking blends, should be used as fresh as possible, because their coking properties are such that very little loss can be tolerated. Others, such as some of the high-volatile A and medium-volatile bituminous coals which naturally possess strong coking properties, may be subjected to considerably longer exposure or greater oxidation without appreciable detrimental effect on the coke; a few even show slightly stronger coke after the early stages of mild oxidation (Kukharenko and Khrisanfova, 1947; Schmidt, 1945, p. 662-5). The latter, however, show a rapid drop in coke quality once the maximum is passed and oxidation is continued.

Under some circumstances coal is deliberately oxidized prior to utilization (Standard Oil Development Co., 1950) in order to decrease its coking, agglutinating, or swelling properties. This is true, for example, in the application of the Wisner low-temperature coking process to highly coking coals (Lesher, 1937, 1940, 1941), and in the preparation of coal for use in other specialized coking processes (Bénézech, 1939), and in making carbonized briquets (Boyer, 1956).

It has been reported that slight oxidation of "fatty" or "gas" coals of good fusibility and fluidity improves their coking properties (Khrisanfova and Soboleva, 1956).

The earlier work on the pretreatment of coal by oxidation prior to carbonization has been summarized by Lowry (1945).

Oreshko and Tislin (1952) have studied the relationship between heating of coal and its oxidation from the opposite point of view, that is, they investigated the effects of heating coal in an inert atmosphere upon its subsequent oxidation behavior. They found that pyrolysis at 270-340°C. resulted in an increase in the rate of formation of high-temperature oxygen complexes, but no significant change in ignition temperature, whereas heating to temperatures above about 400° increased the ignition temperature.

Agrawal and coworkers (1956) found that briquets made from weathered slack coal were not as strong as those made from fresh samples of the same coal, and attributed the difference in part to a weakening of the coal structure itself during weathering.

GASIFICATION AND COMBUSTION

Although a detailed discussion of gasification and combustion is beyond the scope of the present paper, it seems desirable to mention them because both involve oxidation of coal.

The process of gasification, perhaps most easily applied to coke, may be carried out with some coals. It is essentially a partial oxidation in which carbon monoxide is one of the products. Steam may be introduced with the oxygen (Newman and McGee, 1956; Donath, 1956), or the process may be operated intermittently with oxygen and steam cycles alternating; hydrogen and carbon monoxide result from this reaction.

Excellent summaries of the various modifications of these processes are available (Hoeven, 1945; Morgan, 1945). The gas produced may be used directly as a fuel, or, with a carefully adjusted CO/H_2 ratio the product ("synthesis gas") may be used for the synthesis of liquid hydrocarbon fuels (Storch, 1945; Herbert and Tramm, 1956), methanol (Hirst, 1945), or higher alcohols and various other oxygen-containing organic compounds (Herbert and Tramm, 1956). The literature contains many papers dealing with the production and use of synthesis gas and with gasification in general, and no attempt is made here to compile a bibliography on this topic.

The use of coal as a fuel is oxidation wherein (in the ideal case) all of the carbon is converted to carbon dioxide and all of the hydrogen to water. The goal, of course, is not to obtain knowledge about the coal, nor to produce chemical materials of value, but simply to get the maximum amount of useful energy. The many phases of combustion have received much attention from investigators in chemical and engineering laboratories, and have been summarized by Mayers (1945) and by Orning (1945).

Another phase of the oxidative utilization of coal is seen in the attempts, thus far unsuccessful, to devise a practical method of converting the chemical energy of coal directly to electrical energy by means of the so-called "fuel cell" (Howard, 1945b).

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