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Department of Fuel Technology
College of Mineral Industries
The Pennsylvania State University

THE IGNITIBILITY OF BITUMINOUS COAL
(A RESUME OF A LITERATURE SURVEY)

by

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and

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STATEMENT OF TRANSMITTAL

Special Report SR-9 transmitted herewith has been prepared by the Coal Research Section of the Mineral Industries Experiment Station. Each of the Special Reports presents the results of a phase of one of the research projects supported by the Pennsylvania Coal Research Board or a technical discussion of related research. It is intended to present all of the important results of the Coal Board research in Special Reports, although some of the results may already have been presented in progress reports. The following is a list of Special Research Reports issued previously.

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M.E. Bell, Director
M.I. Experiment Station
A thorough search of the literature was made and resulted in the study of thirty-six references pertaining to ignitibility. This work revealed that no standard ASTM test method for determining ignitibility exists in spite of a substantial research effort by numerous investigators. It appears that no single test will be suitable for calibrating the ignition temperature for both fuel bed and pulverized firing of coal.

Since the major consumer of bituminous coal is pulverized firing, attention will be given first to this phase. An "inflammability" test has been chosen which, although completely empirical in nature, seems to offer the best possibility of correlating laboratory results with field performance.

The test apparatus is shown in Figure 3 and was employed by Lambie (14) in his work on combustibility. A test somewhat similar to this has been explored by the Babcock and Wilcox Company Research Laboratory at Alliance, Ohio. Both techniques will be investigated simultaneously in an effort to learn which is the better all-around method.
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INTRODUCTION

Although a substantial amount of fundamental research has been devoted to the composition, characteristics and utilization of solid fuels, gaps still remain in our accumulated knowledge. The combustion of coal may therefore be considered more an art than a science. Frequently, successful combustion performance is obtained through a background of operating experience without benefit of assistance from scientific theories. This is not surprising when one is cognizant of the fact that coal is a complex, heterogeneous material and that much remains to be discovered about its exact physical and chemical composition. Moreover, so many beds and seams exist, each with its own peculiar characteristics, that the job of calibrating coal is a colossal undertaking.

As a rough generalization it can be said that the tests used to evaluate coal fall into two main groups. On the one hand there are those which attempt to ask basic questions about the nature of the material; on the other hand there are those empirical determinations which try to predict how it will behave in use. Needless to say, if there existed a complete understanding of what coal is, then its behavior under any given conditions of industrial use could be forecast with some certainty. The fact is, however, that even with such modern techniques as electron microscopy, x-ray diffraction, absorption spectroscopy and many other powerful analytical methods employed by the physical and organic chemist, a great deal remains to be discovered about the constitution of coal. Thus, the supplier, the user, and the designer of combustion equipment have had to rely to a great
extent upon information gained from a variety of empirical and hence carefully standardized tests. Over the years such information has been allied with actual plant operating results to provide a wealth of experience from which the present efficient methods of burning a wide range of coals have emerged. So far, however, industry has waited in vain for comparatively simple and speedy laboratory tests which will accurately predict combustion behavior and thus eliminate lengthy and expensive full-scale plant trials.

It is usual to regard the combustion of a solid fuel as occurring in two main stages, the ignition phase and the burning out phase. During the ignition of bituminous coal decomposition takes place by which a series of gases and vapors is evolved, a more or less reactive, solid, carbonaceous residue being left. Despite the fact that the changes which take place during ignition must greatly affect the following combustion process, much more is known about the burning out of the carbon residue than about the phenomena of ignition. Thus, although there is widespread agreement that a great need exists for a method by which industry could forecast the relative tendency of its fuels to ignite, no completely satisfactory test capable of being correlated with industrial operation has yet been developed. In the following report the more important techniques used to examine ignitibility in the past are reviewed, and recommendations are made for investigations into some important aspects of ignition which seem to have been relatively neglected.

OXIDATION, COMBUSTION AND EXPLOSION DEFINED

Oxidation may be regarded as the combination of oxygen with the combustible coal compounds of carbon, hydrogen, and to a lesser degree
the impurity sulfur. The term oxidation implies to most engineers a slow chemical combination, often unintentional, at low reaction rates and temperatures without the production of light while generating very small amounts of heat. Now compare this to combustion. The authors prefer to define combustion as the rapid, self-sustaining chemical combination between oxygen and fuels at relatively high temperatures with the production of light and heat. Combustion, for our purposes then, is an intentional controllable process with the primary goal the efficient production of heat by transforming the potential energy of a combustible material (coal in this case) to heat energy. Admittedly, unintentional, uncontrollable conflagrations such as forest fires are still combustion in the layman's interpretation.

The explosion of fuels is a special type of combustion. It may be defined as the instantaneous and violent combustion of fuels accompanied by a noisy production of pressure. Explosions are characterized by the ignition of fixed quantities of combustible material, in a highly reactive form, thoroughly mixed with the optimum quantities of oxygen necessary for an instantaneous chemical reaction. A useful example of this is the internal combustion engine where piston pressure (kinetic energy) rather than heat is the desired product.

From the above analysis it is apparent that (1) oxidation occurs in all cases; (2) oxidation, combustion and explosions are different in nature; and (3) oxidation and combustion are continuing reactions, as compared to explosions which are periodic. From these definitions it is apparent that there are three areas of interest, but for the purpose of this investigation the significance of ignitibility will be confined to combustion.
THE DEFINITION OF IGNITIBILITY

To the industrial user of bituminous coal the term "ignitibility" is normally taken to mean the ease with which the fuel may be brought to a state of visible, sustained combustion, and he is interested in this property only to the extent that its evaluation will enable him to predict just how a given coal will behave in storage or in the furnace. Now, to the practical engineer, the process of "visible, sustained combustion" is accompanied by flame or glow. However, cases have been quoted in the literature where visible, self-supporting combustion without flame or glow has occurred. Jenkins and Sinnatt, for instance, describe a type of slow "partial" combustion which occurred when a small gas flame was applied to the apex of a conical heap of finely powdered coal in the laboratory. Neither glow nor flame appeared, but small amounts of smoke were emitted and the travel of a combustion zone from apex to base could be followed by observing the color change from brown, powdered coal to the black, oxidation product.

It will be obvious, in the light of such phenomena, that any broad, general definition of ignitibility cannot be based on the appearance of flame or glow, since these are not necessarily concomitants of either ignition or even combustion. Thus the formal definition agreed upon by Subcommittee XVI on Ignitibility of Coal and Coke, of ASTM Committee D-5 on Coal and Coke (now inactive), states that: "The ignitibility of a fuel is that characteristic which determines the ease with which the fuel may be brought to a condition of self-supporting, active oxidation. The ignitibility is governed not only by the inherent chemical characteristics
of the fuel that determine its rate of oxidation at various temperatures, but also by the physical characteristics of the fuel and its surroundings that determine the rate at which it can be heated. Among these physical characteristics are (1) the size of the pieces of fuel, (2) the specific heat of the fuel, (3) the thermal conductivity of the pieces and of the aggregate, (4) the rate at which the oxygen or air is brought into contact with the fuel, and (5) the rate of heat loss to the surroundings. Chemical and physical changes, such as the melting and decomposition of bituminous coal, may occur as the fuel is heated."

This definition recognizes several important and fundamental features of ignitibility which have not always been appreciated in the past. However, by using as its criterion "the ease with which the fuel may be brought to a condition of self-supporting, active oxidation" it restricts consideration to the early stages of an oxidation process, as pointed out by Nelson and Pilcher. This limitation is in accord with the views expressed by C.R. Brown who, in a detailed review of the phenomena of ignition states that, although ignition must proceed continuously until active or visible combustion occurs to complete the process, ignition cannot be considered as synonymous with the appearance of flame or glow since these occur at the end rather than the beginning of the process. Rosim and Fehling, on the other hand, in their report upon the ignition of coal on grates, state that whilst at low temperatures ignition is initiated by the exothermic reactions of oxygen adsorption and auto-oxidation, these reactions do not occur with sufficient velocity to result in combustion except under such conditions as those of unsatisfactory coal storage where heat dissipation may be poor. The process of ignition of a bed of particles in their apparatus is
described as occurring in the following invariable sequence for all ranks of coal: (a) thermal decomposition; (b) development of glowing nuclei at the surface of the particles; (c) sudden ignition of the volatile matter, leading to the formation of a well developed gas flame. They consider that the slow oxidation reactions do not accelerate until gaseous constituents are evolved, and that the glowing nuclei are the result of surface activation caused by the formation of semi-coke. They picture ignition as a process in which thermal decomposition is of importance as the agency by which coal is split up into "a spontaneously igniting solid residue and an easily igniting volatile fraction". And they go on to state that: "The ignition reaction begins with the nascent semi-coke and ends with the inflammation of the volatiles."

The divergence between the concepts of Rosin and Fehling and those of Brown is typical of the literature on ignition, and can be explained by the different purpose of each investigation. The two former workers were concerned with the promotion of combustion, whilst Brown looked at ignition from the viewpoint of fire hazard. In studies where the main interest is in fire prevention the greatest emphasis must necessarily be upon phenomena occurring early in the process - in the slow reactions which give rise to spontaneous heating. Such emphasis may be greatly misplaced, however, if applied to the rapid, high temperature processes which go on in industrial furnaces.

In the light of previous paragraphs, the conclusion must be reached that, admirable as the formal A.S.T.M. definition may be for broad general purposes, it is too restrictive to be applied in the present investigations.
The definition which will be adopted, therefore, is as given by the A.S.T.M. with the exception that "combustion" will be substituted for "oxidation" as the last word of the first sentence. The latter will now read, "The ignitibility of a fuel is that characteristic which determines the ease with which the fuel may be brought to a condition of self-supporting, active combustion."

THE CONCEPT OF IGNITION TEMPERATURE

There is nothing in the A.S.T.M. definition to indicate just how the property of ignitibility should be determined, but many workers in the field have postulated the occurrence of a critical temperature in the ignition process beyond which autogenous combustion must certainly occur. This critical temperature has been variously defined and determined, but whether it does in fact wholly represent the ignition or combustibility characteristics of a fuel has been a matter of considerable controversy. Most workers seem now to be agreed, however, upon the following points:

(1) Coal and atmospheric oxygen combine at all temperatures, and there is thus no well defined ignition temperature below which combustion reactions do not occur. 3,7,8,9

(2) The concept of ignition temperature can best be expressed as that temperature in the fuel at which the heat produced by the reactions causing ignition is just greater than the heat dissipated to the surroundings. 4,7

(3) The ignition temperature thus defined is not an inherent property of the fuel, and any test by which it may be measured should be thought of as a purely empirical determination. 7,8,10

(4) Providing that test conditions are carefully chosen and rigidly
controlled, reproducible values for ignition temperature can be obtained which may be of value for classification purposes. 8, 10

It has already been stated that many doubts have been raised as to whether the ignition temperature does in fact characterize the ease with which a fuel will ignite and burn. Rosin and Fehling 7 point out that what matters in the case of combustion is not the magnitude of the ignition point but rather the time required to reach it. They cite the case of hydrogen which, having a comparatively high ignition temperature (572°C), should have relatively poor ignitibility. In actual fact, however, hydrogen ignites with great rapidity because it possesses a thermal conductivity some six or eight times higher than other fuel gases.

METHODS OF DETERMINING IGNITION TEMPERATURE

The methods used to determine ignition temperatures have been grouped into three main classes:

(a) Constant Temperature Methods

A series of runs is made, in each of which the furnace temperature is maintained at a set figure and the coal quickly introduced. If, after a short period of "ignition lag" the coal does not reach its ignition temperature - this being determined by the appearance of glow, flame, or accelerated temperature rise - the test is repeated with fresh specimens at progressively higher temperatures until, by a process of trial and error, the lowest "temperature of ignition" is obtained. Illustrative of this group are the methods used by Phillips 11 and Moore 13

(b) Rising Temperature Methods

The coal sample is placed in a furnace or apparatus the temperature of which is raised at a constant rate. Oxygen or air is passed through
the sample, or over the surface at a known rate, and the temperature of the coal and of the heating apparatus is measured. Various criteria of ignition have been used with this method. Brown\textsuperscript{15} took as the ignition temperature the point of inflection in the curve showing the difference between specimen and furnace temperature plotted against time. Swietoslawski, Roga and Chorazy\textsuperscript{16} used the intersection of the projections of the coal temperature curve before and after the rapid increase in temperature. Wheeler\textsuperscript{17}, Parr and Looms\textsuperscript{18}, Nelson et al.\textsuperscript{18}, Sebastian and Mayers\textsuperscript{19}, Sherman et al.\textsuperscript{10} took the point at which the coal sample and furnace temperature curves crossed when plotted against time. Kreulen's\textsuperscript{20} criterion was the intersection of the sample temperature-curve with a curve parallel to the apparatus temperature-curve but lying 6°C above it.

(c) Adiabatic Methods

In these methods the heat loss from sample to furnace is prevented, and thus all the heat produced during the oxidation process goes to raise the temperature of the reactants. The best known adiabatic method is perhaps that developed at the Coal Research Laboratory of the Carnegie Institute of Technology.\textsuperscript{21} A modification of the original Coal Research Laboratory test described by Sebastian and Mayers\textsuperscript{19}, the latter method enabled adiabatic conditions to be maintained in the system whilst self-heating rates between 3 and 25°C per minute were determined. Davis and Byrne in their work on spontaneous heating\textsuperscript{22} used what they termed an "adiabatic calorimeter" in which the temperature of a surrounding oil bath was automatically made to follow that of a sample, while oxygen preheated to the oil-bath temperature was passed through the coal. It was claimed that the temperature of the bath could be controlled to within 0.013°C of
the coal temperature.

**CRITICAL EXAMINATION OF IGNITIBILITY TESTS**

No standard A.S.T.M. method for determining ignitibility exists and it is doubtful whether any single, simple and reliable laboratory test can be developed which will allow an accurate forecast to be made of the ease with which a bituminous coal will ignite under the many conditions of industrial burning. As the A.S.T.M. definition makes clear, the property of ignitibility is not one which can be characterized solely by the chemical and physical properties of coal, different as these may well be. The physical environment in which the phenomena leading to ignition and combustion take place must necessarily have a profound influence upon any attempt to determine the property and to assign to it some precise numerical value. It seems, therefore, unrealistic to suppose that any meaningful index can be obtained which will correlate the behavior of a coal under laboratory conditions with its performance in both stoker and pulverized fuel firing.

In considering the various tests which have been carried out to determine ignitibility, it is necessary to bear in mind that many of them were done for purposes quite different from those which motivate the present investigation. It is therefore pertinent to examine in closer detail two of the most promising and widely known of the established techniques, and to attempt an assessment of their value in the work projected.

(a) The Coal Research Laboratory Test

As originally developed, the Coal Research Laboratory test gave values for the temperatures at which a coal sample in a stream of air or
oxygen under adiabatic conditions began to self-heat and attain a specified rate of temperature increase. The apparatus is shown in Figure 1. The test measures the sample temperature and the rate of temperature rise at the moment when sample and furnace temperature are equal, in other words, at the "crossing point", and it is presumed that under such conditions the rate of temperature rise is a measure of the reactivity of the coal. Reactivity indices T15 and T75 are reported, these being the crossing points or ignition temperatures when the self-heating rates are 15°C and 75°C per minute, respectively. The values of the reactivity indices are critically dependent upon the determination of the instant when the readings of the sample and furnace thermocouples are identical - that is, when there is zero heat flow between the coal sample and its environment.

In the original procedure it was necessary to use both air and oxygen because information could only be obtained over a restricted range of temperature when working with a single oxygen partial pressure. Furthermore, the effect of this partial pressure on the self-heating rates required a simplifying assumption in calculating the reactivity indices. A modified apparatus was therefore developed, whereby adiabatic conditions could be maintained in the system and self-heating rates from 3°C to 25°C per minute determined at any oxygen partial pressure from 0 to 1 atmosphere. This made it possible to obtain reactivity indices without any assumptions regarding the effect of the partial pressure of oxygen.

It was found that the Coal Research Laboratory test yielded indices which correlated well with the dry ash free (d.a.f.) volatile content of the coal. Figure 2 shows T15 and T75 plotted against the percentage of
DIAGRAM OF C. R. L. IGNITION APPARATUS
(SHERMAN, PILCHER AND OSTBORG\textsuperscript{10})

Figure 1
Reactivity indices $T_{15}$ and $T_{75}$ for coals as a function of volatile matter contents on dry ash-free basis (Orning\textsuperscript{24})

Figure 2
volatile matter (d.a.f. basis) for 68 coals ranging in volatile content from 3.5% to 48.2%. The equations for the curves are:

\[ T_{15} \pm 8.0^\circ C = 229.7 - 0.01041 (V - 27.5)^3 \]
\[ T_{75} \pm 11.4^\circ C = 272.1 - 0.01338 (V - 27.5)^3 \]

The adiabatic method gave equations as below:

\[ T_{15} \pm 8.1^\circ C = 229.7 - 0.01022 (V - 27.5)^3 \]
\[ T_{75} \pm 11.2^\circ C = 285.9 - 0.01282 (V - 27.5)^3 \]

Unfortunately, over the range of volatile contents associated with bituminous coals, e.g. 17-37% (d.a.f.), it can be seen that there is little variation of reactivity with volatile content, whereas it is a matter of everyday plant experience that higher volatile coals are easier to ignite and burn than low volatile materials. Furthermore, the fact that the equations for T15 and T75 give the reactivities to within about \( \pm 8^\circ C \) and \( \pm 11^\circ C \) respectively, while the accuracy of the test itself is \( \pm 2^\circ C \), indicates that factors other than volatile content are responsible for the variation in the reactivity indices.

(b) Inflammability Tests

The term "inflammability" has been used because here the criterion of ignitibility is the appearance of flame. The method belongs to the constant temperature class and is exemplified by the tests described by Phillips and Lambie. In the case of the former, approximately 0.2 gm of -325 mesh coal is blown through a heated, vertical electrical furnace and past a hot, copper coil by a puff of 2 psig air. The furnace temperature is progressively increased until a flame results, when the ignition temperature is reported to the nearest 10\( ^\circ C \).
In the work by Lambie, whose apparatus is shown in Figure 3, a vertical ignition tube is heated by an electric furnace to a temperature of 700°C. Varying proportions of -200 B.S. mesh coal and calcined fullers' earth are then used to form mixtures, 1 gram samples from which are blown by oxygen at a pressure of 12" Hg through the ignition tube. The minimum amount of fullers' earth necessary to prevent good ignition is determined, and the inflammability of the fuel is reported as the ratio by weight of the fullers' earth to fuel in this limiting mixture. The ratio is termed the Godbert number. The criterion which best defined "good ignition" was the appearance of a white flame which just reached the open end of the ignition tube. Both of the foregoing tests are basically similar to that used by Godbert and Greenwald, and in all three cases it was concluded that the inflammability as determined in the laboratory agreed fairly well with the behavior of pulverized coal in practice, and that the index of ignitibility obtained in each could be fairly well correlated with the d.a.f. volatile content of the fuel.

(c) Discussion

Although it has been stated that the Coal Research Laboratory reactivity indices express a basic and inherent property of the fuel, the fact remains that the behavior of a sample in this test has not yet yielded information of much value to the user of coal or the designer of combustion equipment. On the other hand the much more empirical "inflammability" tests seem to have been of more use. Lambie discusses work by the Fuel Research Station in Britain which showed a general relationship between the performance of pulverized fuels in a Lancashire boiler and their inflammability.
GODBERT INFLAMMABILITY APPARATUS. (LAMBIE\textsuperscript{(14)})

Figure 3
in the Godbert type apparatus. He also states: "It would appear that the combustibility of pulverized peat in a given combustion chamber can be roughly correlated with the combustibility as indicated by the Godbert apparatus." Of the ignition temperatures obtained by the test which Phillips describes, he writes that they have been found to agree reasonably well with actual results in operation.

It is, perhaps, not surprising that, despite its excellent theoretical basis, the C.R.L. test yields indices which have not yet been correlated with industrial practice. The test is, after all, carried out under conditions far remote from those to which lump or pulverized coal is subjected during burning. It is difficult to avoid the conclusion that admirable as the C.R.L. test may be for studying the gradual processes of initial oxidation, it will not be at all useful in predicting the ignition behavior of powdered coal projected into the flame from a pulverized fuel burner. Consider the behavior of coal dust which is shock-heated to the extent that the periods of pre-ignition, volatiles expulsion and combustion, and combustion of solid carbonized residue are all compressed into an interval of time which can be measured in fractions of a second. How is this behavior to be assessed in terms of a test in which the coal temperature rises for instance to 325°C over a period of say, 25 minutes? The rate of volatile release from a cloud of airborne particles, the ignition properties of this volatile matter and of the partially carbonized coal surface must surely be of real importance in pulverized fuel firing. Yet they are phenomena of which the C.R.L. test takes no account. The inflammability tests on the other hand do attempt to simulate practical conditions, and at the present stage of knowledge must
be preferred as a measure of the propensity of powdered fuel to ignite. It is recommended that an inflammability test be chosen as the starting point in the investigations contemplated, but it should be kept in mind that fairly elaborate methods (using, for example, high speed photography) over a considerable period of time will have to be employed if the ignition of pulverized fuel is to be thoroughly investigated from a more basic standpoint.*

THE IMPORTANCE OF THERMAL DECOMPOSITION IN THE IGNITION PROCESS

It is somewhat surprising that more attention has not been paid to the important aspects of thermal decomposition in connection with ignitibility. It has long been known that high volatile coals ignite and burn in lump and powdered form more easily than do low volatile materials. Indeed the C.R.L. ignitibility test has probably not been more widely used partly because the reactivity indices can be calculated with reasonable accuracy from the easy-to-determine d.a.f. volatile contents. However, Ceely and Wheater concluded that the composition of the volatile matter was important and that the ignition and combustion characteristics of coal cannot be closely correlated with the quantity of volatile matter alone. They also stated that the C.R.L. reactivity index, T15, does not of itself accurately predict the ignition characteristics of all solid fuels, and came to the tentative conclusion that it will adequately forecast the ignition behavior of only those fuels which do not evolve appreciable combustible volatile matter at low temperatures. The fact that T15 does not adequately predict the ignition characteristics of all fuels can be deduced from the graphs published.

*Project CR-20 - "Factors Affecting the Flames of Powdered Fuels, in particular, Pennsylvania Bituminous Coal", will undoubtedly devote time to this phase.
by Orning (see Fig. 2), which show little variation of either T15 or T75 within the range 17 - 37% V.M. (d.a.f.). Orning himself pointed out that, since the precision of the test was much higher than the accuracy of the equations correlating relativity indices with simple volatile content, there must be other factors responsible for variations in the indices. From laboratory observations made when igniting lump coal on small grates by means of radiation from above, it would seem that the reactivity of the partially coked or charred surfaces must be important. Carman, Graf and Corey state that under such conditions the exposed surfaces of bituminous coals are devolatilized and coked or charred, and that the surfaces of the coke or char begin to glow before ignition of the volatile matter occurs. Ignition and flaming of the volatile matter usually follow quickly and result in rapid spread of ignition and burning across the entire bed top. It may be noted that the sequence described by Carman et al, viz. thermal decomposition, appearance of glowing nuclei on the particle surfaces, and sudden ignition of the volatile matter, is identical with the order of events described by Rosin and Fehling and discussed previously in the present report. Carman et al also state, in discussing the mode of ignition of a solid fuel particle, that although the temperature range of thermal decomposition of bituminous coals overlaps that of ignition of the coke formed, immediate ignition of the volatiles at the surface does not necessarily follow even at that point on the surface where ignition of the solid particle has occurred, since the ignition temperatures of the decomposition products are, in general, higher than those of the highly reactive coke surface. The evolved gases will be quickly ignited, however, by the rapid temperature increase at the coal surface after the onset of initial
glowing. In discussing the influence of the ignition of volatile matter on the ignition of bituminous coal, Seyler and Jenkins\textsuperscript{26} noted that their tests showed no indication of breaks when the rate of heat evolution was plotted against the reciprocal of the absolute temperature. They point out that if ignition of the coal were caused by inflammation of the volatile matter, a change of slope of the Arrhenius Line would occur. However, they warn that their particular tests may not have been taken to sufficiently high temperatures, since in the case of anthracite a distinct break in the Arrhenius Line occurred at a temperature near to the ignition point.

It should be noted that the results of the three investigations discussed in the previous paragraph were obtained on small scale equipment, or with laboratory apparatus, where conditions of ignition are very different from those of industrial fuel beds. In the case of chain grate or spreader stoker firing, for example, flames from the actively burning bed would doubtless ignite the gases from the freshly charged, decomposing coal. It is therefore likely in practice that general ignition of the bed results not only from ignition of volatile matter by the glowing surface of the charred or coked particles, but also from ignition of these volatiles by established flames. If this be so, then the ignition properties of the newly formed char or semi-coke surfaces, the temperature at which volatile evolution commences, the temperature of maximum volatile emission, and the ignition properties of the volatile matter must be of importance. In the case of pulverized fuel firing it is probable that the phases of pre-ignition, volatiles expulsion, ignition and combustion of volatile matter and of solid residue occur simultaneously at different points in the furnace.
according to the size of the coal particles and the environmental conditions.

It has been seen that the d.a.f. volatile content of a coal is a valuable index of its ignitibility behavior, and perhaps as good an index as has yet been developed. On the other hand, the total volatile content is not of itself an infallible criterion, and it has been suggested that the ignition properties of the surface of the decomposing coal and of the decomposition products must be important, as must the temperature at which volatile evolution commences. A search of the literature, however, indicates that extremely little appears to be known about the combustibility of volatile matter, for example. Obviously there are difficulties in studying the release and ignition of volatiles, especially in the case of pulverized coal where the time periods involved are exceptionally small. Such difficulties may account for the fact that, although the changes which occur during the ignition and combustion of volatile matter considerably influence the succeeding stages of pulverized fuel combustion, much more is known about the combustion of the residual coke particles than about the phenomena associated with the primary ignition process. In connection with the latter, an apparatus has been described by Finch which gives a controllable supply of volatile matter for more than one hour. The volatiles were ignited by an electrically heated spiral to give a diffusion flame in air, and the ignition temperatures of the volatile matter from both coal and char were measured. Differing results were obtained according to the material from which the igniting spiral was made. Platinum gave ignition temperatures considerably lower than tungsten and nichrome, for example. Results with nichrome were reproducible to within 10°C, and
the ignition temperatures of volatiles from two chars were lower than those of the volatile matter from the parent coals.

Undoubtedly much remains to be learned about the manner in which the phenomena accompanying decomposition affect the ignition process, and this might well be a fruitful field in which to carry out a long-term program of investigations.

THE APPLICATION OF DIFFERENTIAL THERMAL ANALYSIS IN IGNITIBILITY TESTING

This survey of the ignitibility problem cannot be concluded without reference to a technique which, although applied in other researches upon coal, has so far been little used to examine the influence of heat on coal under oxidizing conditions. The technique in question is that of "differential thermal analysis", and it is possible that it might prove of value in ignitibility studies.

The methods of thermal analysis can be applied to any material which when heated or cooled undergoes physical or chemical changes with the liberation or absorption of heat. The heat developed or absorbed can be measured, and changes in the structure of metals upon heating have been studied for many years in this way. Le Chatelier, as long ago as 1887, used the method to examine clays, and attempted to classify alumino-silicates according to their thermal characteristics.

It was Houldsworth and Cobb who, more than forty years ago, first applied the differential thermal analysis method to coal, by measuring the temperature of the test material relative to that of an adjoining inert material. Thermocouples embedded in the coal sample and the inert material were connected in opposition, so that the E.M.F. developed during heating resulted from the absorption or generation of heat. In modern
methods, quite small quantities of material are used (1 gram or less), and are packed side by side with an inert material in a refractory or metal block (see Fig. 4). This is placed in an automatically controlled electric furnace so that a constant rate of temperature increase is obtained. The temperature of the block and the temperature difference between the coal and inert are both recorded automatically. If the temperature difference is plotted on the ordinate scale against the block temperature on the abscissa, a graph is obtained on which a release of heat is indicated by an upward deflection of the curve, whilst an absorption is shown by a downwards break. Typical curves are shown in Figure 5. If good reproducibility is to be obtained, strict standardization with respect to packing of coal and inert, positioning of thermocouples, and so on, is essential.

Most of the work on the differential thermal analysis of coal has been carried out in connection with classification and carbonization studies. Apart from the pioneer work by Houldsworth and Cobb, the recent studies by King and Whitehead and by Glass in such fields may be cited. Stott and Baker, however, have used the technique to evaluate the behavior of coal on heating in a stream of air. Because they considered the accepted experimental methods for measuring ignition temperatures to be unsatisfactory, their studies were concerned chiefly with the problem of how best to follow the heat release rate of coal as its temperature was increased. They considered the method of differential thermal analysis to be a useful means of studying the heat release as a function of temperature and oxygen concentration, and stated that it could be applied to the investigation, control and separation of the reactions occurring when coal is heated.
DIFFERENTIAL THERMAL ANALYSIS APPARATUS.
RECRYSTALLISED ALUMINA SPECIMEN BLOCK AND HOLDER
WITH THERMOCOUPLIES IN PLACE, (GRIMSHAW, HEATON AND ROBERTS (36))

Figure 4
Figure 5

Differential thermal analysis plots for three New Zealand bituminous coals. (Stott and Baker (35))
CONCLUSIONS

(1) The definition of ignitibility agreed upon by Subcommittee XVI of A.S.T.M. Committee D-5 on Coal and Coke is an excellent basis from which to investigate and discuss the initial stages of the reactions between coal and oxidizing gases. By restricting consideration to the early stages of an oxidation process, however, it is felt that it is too rigid to meet the requirements of a definition which can be of value in investigating the practical problems of the ignition of lump or powdered fuel in industrial furnaces.

(2) The purposes of the present investigation would be better served if "combustion" were substituted for "oxidation" as the last word in the first sentence of the ASTM definition. Ignitibility would thus be defined as "the ease with which the fuel may be brought to a condition of self-supporting, active combustion . . . ." Combustion is used here to define a reaction in which light as well as heat is produced, i.e. a reaction accompanied by flame or glow.

(3) A criterion widely used to assess ignitibility has been that of "ignition temperature". This has been defined as that temperature in the fuel at which the heat produced by the reactions causing ignition is just greater than the heat loss to the surroundings.

(4) Ignition temperature thus defined is certainly not an inherent property of the fuel itself. The experimental value obtained is greatly influenced by the method and apparatus used, and the determination must be recognized as completely empirical in character.

(5) While the ignition temperature of a coal is possibly a factor
in its ignitibility, it is doubtful whether it can wholly characterize the
tendency of a fuel to ignite under conditions of industrial burning. No
fully satisfactory test for ignitibility yet exists.

(6) It is doubtful whether a single, simple laboratory test can be
developed which will be of value in predicting the ignitibility of coal
when fired in both pulverized and lump form.

(7) Of the techniques used in the past, the "crossing point" methods
and the "inflammability" methods appear to have been most widely favored.
Of the former group, the test developed in the Coal Research Laboratory of
the Carnegie Institute of Technology has undoubtedly a sound theoretical
basis, but the reactivity indices which it yields have not yet been correla-
ted with industrial practice. Although the C.R.L. test is a valuable method
of studying the early phases of the reactions between coal and air or oxygen,
the inflammability tests while much more empirical in nature, seem to offer
a better possibility of correlating ignitibility behavior in the laboratory
with that of pulverized fuel in practice.

(8) The property of coal most useful in forecasting the ease with
which a coal will ignite and burn is the volatile content. Despite the
fact that volatile content alone is not wholly satisfactory in this connec-
tion, little attention has been given to those aspects of thermal decomposi-
tion which must surely be of importance in the ignition process. Thus,
little seems to be known about the comparative importance of the reactivity
of the newly formed char or semi-coke surfaces, of the ignition properties
of the gaseous decomposition products, or of the temperature range and rate
of release of volatile matter from the decomposing coal. There are
experimental difficulties in studying such phenomena, especially in the case of pulverized coal ignition where stable suspensions are not easy to achieve and the time periods of the events leading to ignition are exceedingly brief. Nevertheless, it would seem that this should be a fertile field in which to carry out a long-term program of investigation.

(9) The differential thermal method of analysis might possibly be a useful research tool with which to investigate ignitibility. Most of the D.T.A. work on coal has been done in connection with carbonization or classification studies, and the application of this method to coal heated under oxidizing conditions has been relatively unexplored.

RECOMMENDATIONS

(1) The investigation should be commenced by attempting to obtain consistent values for the ignitibility of pulverized coal by means of an inflammability test. The apparatus required is relatively simple and inexpensive, the method attempts to simulate practical conditions, and the results have been said to correlate reasonably well with those obtained in practice. The results may be expressed as an "ignition temperature", as in the work reported by Phillips or in terms of the amount of inert required just to prevent good ignition of a coal inert mixture as in the work by Lambie. Both techniques should be carried out and compared.

(2) Since the inflammability method of testing is admittedly empirical, it is scarcely likely to provide a basic understanding of the factors which control ignition in the pulverized fuel furnace. High speed photography would seem to be one of the few suitable methods by which the transient phenomena leading to the ignition of pulverized coal may be studied.
(3) None of the tests so far employed can be recommended for studying the ease of ignition of lump fuel in beds. However, little attention has been given in the past to those aspects of thermal decomposition which it is felt must be of importance in the study of ignitibility. This literature survey indicates the many possible areas of ignitibility that may be investigated. Due to the uncertainty of the amounts of money that may become available, the ignition temperature of pulverized coal will be studied first. The reason for this choice is based upon the fact that pulverized coal firing leads all other combustion techniques in the quantity of bituminous coal consumed.

(4) The possibilities of the differential thermal analysis method should be explored. In this connection it may be possible to call upon the resources of the Department of Ceramics where considerable experience in the use of D.T.A. apparatus should be available.
LIST OF REFERENCES


(5) Brown, C.R., ibid, 16-18, 57-59.

(6) Brown, C.R., ibid, 56-57.


(20) Kreulen, D.J.W., Brennstoff-Chemie, 12, 107 (1931).


