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Reaction of Lignite and Oxygen at Low Temperature: Heat of Reaction and Rate of Oxygen Consumption

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REACTION OF LIGHTS AND OXYGEN AT LOW TEMPERATURES:

HEAT OF REACTION AND RATE OF OXYGEN CONSUMPTION

By

Duane M. Sanderson

B.S. in Chemical Engineering, University of North Dakota, 1962

A Thesis

Submitted to the Faculty

of the

University of North Dakota

in partial fulfillment of the requirements

for the Degree of

Master of Science

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This thesis submitted by Duane M. Sanderson in partial fulfillment of the requirements for the degree of Master of Science in the University of North Dakota is hereby approved by the committee under whom the work has been done.

Wayne R. Kube

Chairman

A. M. Cooley

John C. Elson

James L. Elder

Woodrow H. McBride

Christopher J. Horne

Dean of the Graduate School

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ABSTRACT

The rate and heat of oxidation for lignite in oxygen below 90° C were studied as functions of temperature, particle size, moisture content and prior oxidation. The experimental procedures involved passing oxygen through a prepared sample in an adiabatic calorimeter and measuring the temperature rise and oxygen consumed for a given time.

The heat of oxidation appeared to increase with increasing temperature. At 20° C, values were sporadic and ranged down to 23,550 calories per gram mole oxygen as compared to values of 85,000 \pm 9,600 and 89,000 \pm 9,600 at 60° and 90° respectively. The low values at 20° C are attributed to the occurrence of increased physical adsorption relative to chemical reaction.

At 20° C the smallest particle size of 0.125 to 0.036 inches gave low values for the heat of reaction (23,500 and 24,800 calories per gram mole oxygen), while larger sizes produced values greater than 70,840. The low values are attributed to greater physical adsorption in the smaller sizes corresponding to increased surface area.

Moisture content and prior oxidation produced no significant difference in heat of oxidation.

The rate of oxidation increased with increasing temperature and with decreasing particle size. Moisture content and prior oxidation also affected the rate of oxidation.

INTRODUCTION

The trend to large thermal electric power generating stations burning lignite increases the need for storing large quantities of this fuel at the plant. Successful storage requires precautions against spontaneous ignition in the stockpiles. Large-scale storage of lignite has been demonstrated to be feasible with 2.4 million tons stored for 13 years at the Garrison Dam site. However, there is a need for adequate data to determine safe storage conditions at minimum cost.

The primary objective of this investigation was to determine the heat of reaction of lignite at low temperatures, 20° to 90° C. This data is needed as part of the total program on spontaneous heating and storage of lignite which is being conducted at the Bureau of Mines Coal Research Laboratory, Grand Forks, N. Dak.

The scope of this investigation was to reassemble, modify, and calibrate existing equipment to determine the heat produced per gram mole of oxygen consumed and rate of oxygen consumption as a function of temperature, particle size, moisture content, and history of prior oxidation. The data obtained were to be used in an attempt to correlate the heat of reaction with the parameters studied.

The determination of the heat of reaction of lignite is of mutual interest to the Coal Research Laboratory and Chemical Engineering Department, University of North Dakota which prompted this investigation as the subject of a jointly sponsored research fellowship in chemical engineering at the University of North Dakota.

CHAPTER I

STUDIES ON THE SPONTANEOUS HEATING OF COAL

Effect of Spontaneous Heating

Spontaneous heating of coal has been a problem ever since coal has been stored in large quantities (1).^{1/} The problem is twofold in that not only does the coal lose heating value during storage, but the probability is high that a stockpile which is heating will ignite.

Spontaneous heating occurs when atmospheric oxygen reacts with the coal carbon and heat is produced at a faster rate than it can be dissipated. Basically, the solution of the storage problem is either to prevent contact of atmospheric oxygen with the coal or to dissipate the heat generated from the oxidation.

Considerable literature has accumulated from studies on spontaneous heating of coal. The literature, for the most part, can be classified under three main headings:

1. The mechanism of the oxidation of coal at various temperatures.
2. The relative spontaneous heating tendencies of coal.
3. The development of suitable storage parameters.

^{1/} Numbers in parenthesis refer to items in List of References.

Mechanism of Coal Oxidation

V. F. Oreshko (2) studied the change in weight of eleven coal samples ranging from brown coal to high-rank bituminous coal. The temperature of the coal was increased at a rate of 1.4° to 1.6° C per minute while a stream of oxygen passed through the sample. The change in weight in milligrams of a 1 gram sample of the coal was recorded graphically on a gravimetric balance (Figure 1). The pattern of variations in weight observed by Oreshko was similar for all coals. The only difference between coals existed in the extent of the weight change and the exact temperature intervals at which the weight change occurred. Oreshko concluded from his data that oxidation occurred in four stages associated with four distinct changes in weight:

1. There is an increase in weight due to chemisorption at temperatures up to about 70° C.
2. A decrease in weight associated with a decomposition of the adsorption complex occurs at temperatures between 70° and 150° C.
3. In the interval of about 150° to 230° C, there is an increase in weight accompanied by formation of stable oxygen complexes. Excessive heat evolution is observed.
4. Above 230° C there is a sharp loss in weight and rise in temperature as combustion occurs.

The net results of each of the stages of oxidation was exothermic even though the evolution of chemisorbed gases was endothermic. The evolved gases contained carbon monoxide and carbon dioxide which were formed by the decomposition of peroxides and oxyc coal complexes. Oreshko also concluded that humic acids were formed in all stages of oxidation (3).

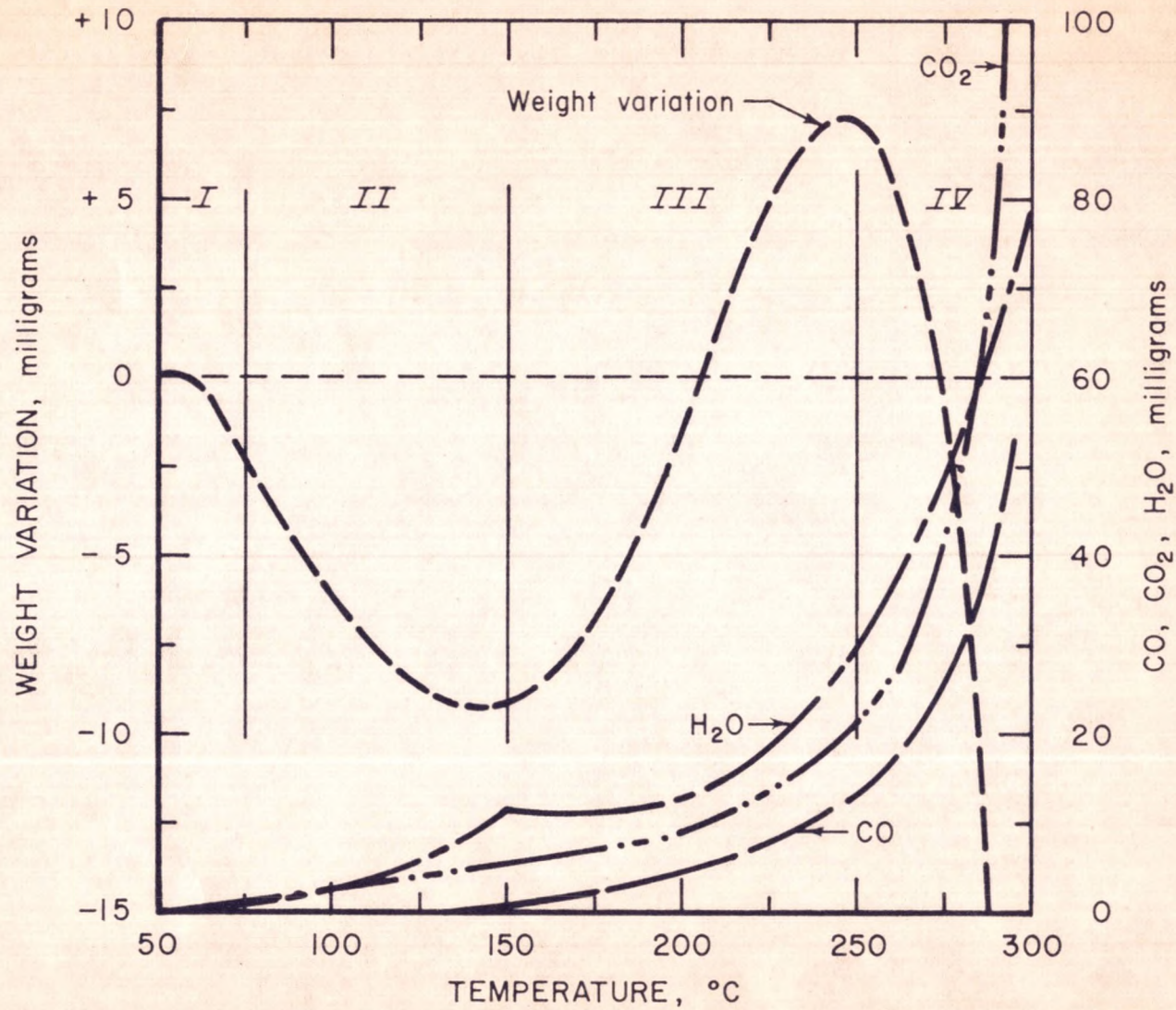


Fig 1 Weight variation of coal during oxidation.

Similar conclusions derived by others in the field of coal oxidation tend to strengthen the work done by Oreshko. B. V. Tronov (4) in a study on the phenolic theory of coal oxidation concluded that there are four primary stages of oxidation of coal associated with compounds of varying reactivity. The most vulnerable of the structures subject to oxidation was found by C. Yokokawa and associates (5) to be the alicyclic compounds in an investigation which he conducted on the stepwise oxidation degradation of coal. Siberyskova and Azerbaev (6), and Jones and Townend (7) reported in independent studies that freshly-ground coal accumulates peroxygen when exposed to the atmosphere at temperatures below 80° C. Above 80° C the amount of peroxygen complexes decreases with continuing oxidation and the reactivity of the coal is increased. This corresponds to the first and second stages of Oreshko's model. Jones and Townend also concluded that the rate of oxidation was a function of the surface area of the coal samples.

Relative Spontaneous Heating Tendencies of Coal

J. L. Elder and associates (8) examined samples of coal varying in rank from low-volatile bituminous to lignite. These studies indicate that the relative tendency of coals to heat spontaneously decreases as the rank of the coal increases. The variables investigated included temperature, oxygen concentration, decreased reactivity with aging, particle size, and moisture content.

As a result of studies on the determination of spontaneous ignition of coal, W. Olpinski (9) found that an increase in moisture content is accompanied by an increase in the tendency for spontaneous ignition.

Establishment of Suitable Storage Parameters

A satisfactory prediction of the behavior of coal in storage is presented by Van Doornum (1). His approach was to group the variables thought to affect spontaneous heating in storage into dimensionless groups. These groups were used to correlate experimental data on the heat generated by low-temperature oxidation of coal with factors affecting the reactivity of the coal. By this method, parameters were established for the safe storage of coal. However, since his tests were conducted on a limited variety of coals and on a small-scale, further testing on other coals is needed to apply his work to the storage of lignite. The method used by Van Doornum will probably be followed in principle for correlation of data obtained in the overall investigation on the project of spontaneous heating of lignite in storage.

Heat of Reaction of Low Temperature

Radsacher and Hooverath (10) used a value for the heat of reaction obtained by Scott (11) during a study on the effects of oxidation of bituminous coal in storage. The results of their study enabled them to predict safe storage conditions for bituminous coal.

Scott determined the heat of reaction of three types of coal by measuring the loss in heating value after various stages of oxidation. His data indicated a range in heat of reaction from 63,550 to 98,560 calories per gram mole of oxygen consumed. The variables investigated were the rank of coal, temperature, particle size and prior oxidation. Scott was unable to correlate the variation in heat of reaction with any of the variables studied so he recommended that a value of 90,000 calories per gram mole oxygen consumed be used as the heat of reaction for bituminous coal.

CHAPTER II

ASSEMBLY AND CALIBRATION OF EQUIPMENT

Basic components were available from previous work, and major effort was directed towards assembly and modifications of these components into a working assembly for the present tests. Equipment necessary was:

1. A container for preoxidation of samples.
2. An adiabatic calorimeter.
3. An oxygen supply.
4. Column for collection of evolved gases.
5. Temperature recording and controlling instruments.

Container for Preoxidation

A gas-tight container (Figure 2) was constructed within which a sample of lignite could be oxidized at room temperatures. By periodically measuring the amount of oxygen in the container during the course of oxidation, a continuing record of the rate of oxidation and of the total oxygen adsorbed was obtained. The decrease in reactivity of the lignite during oxidation was calculated from the rates and oxygen concentrations.

Adiabatic Calorimeter

The calorimeter (Figure 3) is an 8-inch length of 6-inch aluminum stock into which thirteen 1-inch diameter cylindrical holes had been drilled. The top and bottom of the block were recessed 1 inch to create an inlet

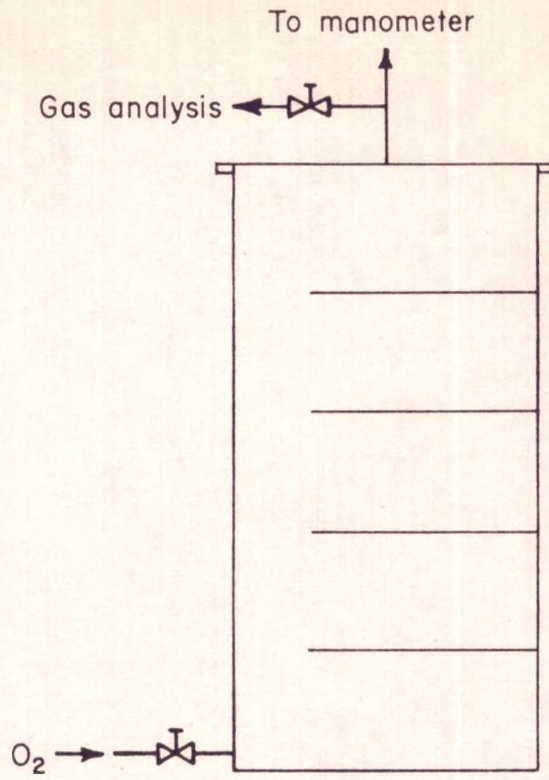


Fig 2 Preoxidation container.

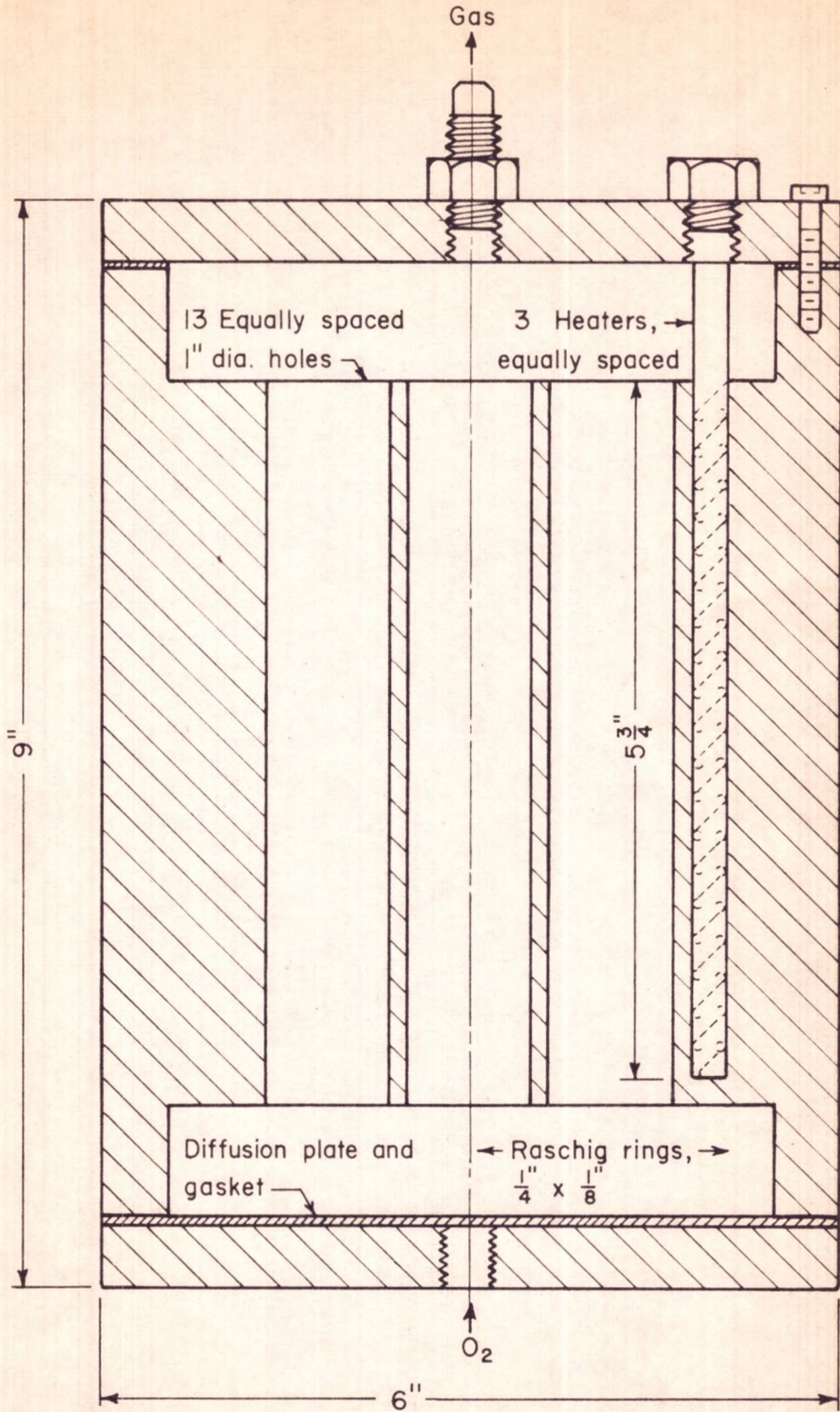


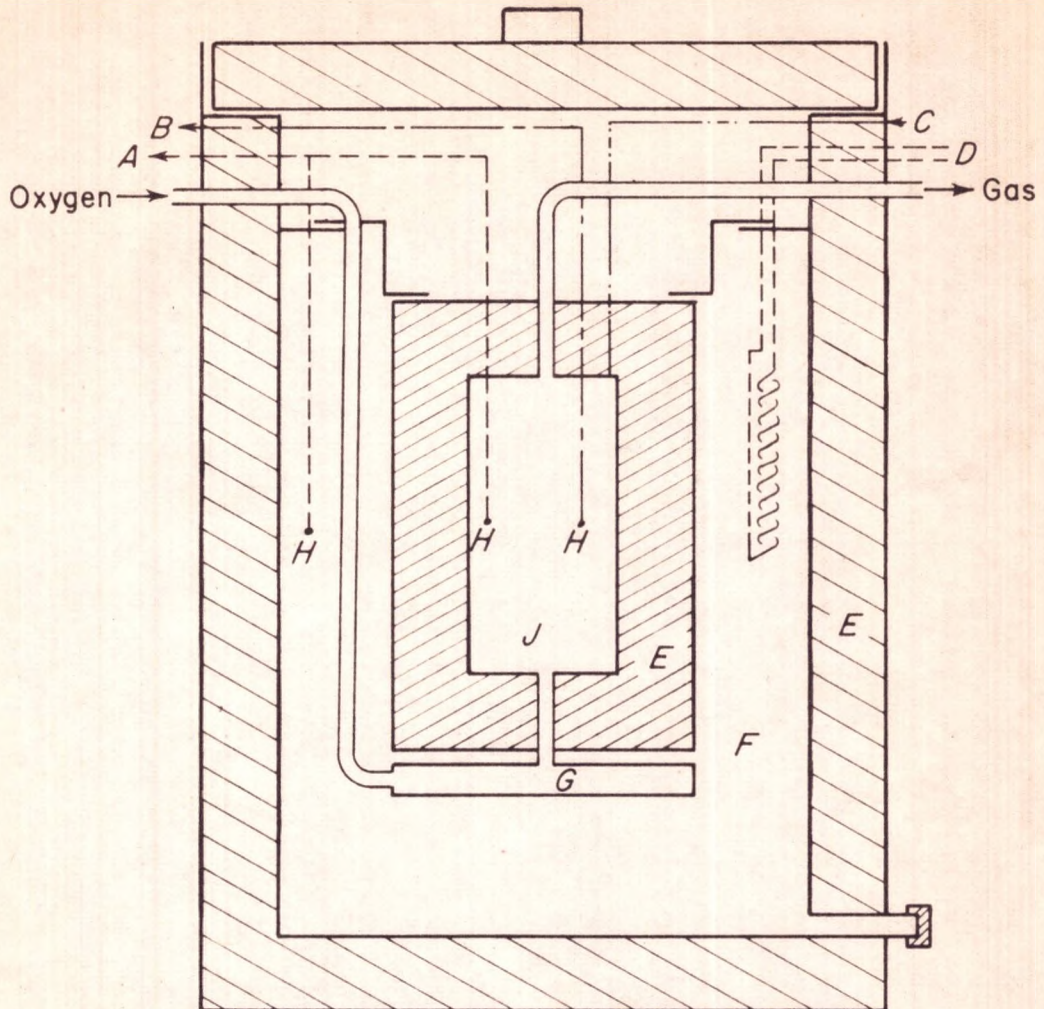
Fig 3 Calorimeter.

and discharge plenums. Three internal electrical heaters were installed in the calorimeter so that the calorimeter and charge could be raised to the desired starting temperature. These heaters had a maximum heating rate of 40°C per hour. The calorimeter had a maximum capacity of 700 grams of $1/2$ -inch maximum size charge. Division of this charge into slender cylinders separated by a material of high-thermal conductivity prevented the formation of appreciable temperature gradients within the charge.

In preliminary tests it was noted that channeling of oxygen flow occurred. To overcome this difficulty, the bottom plenum was filled with $1/4$ - by $1/8$ -inch raschig rings and a diffusion plate was installed just inside the bottom end plate. The arrangement provided the necessary uniform distribution of oxygen flow.

The calorimeter was enclosed in water-tight, insulated containers to which connections for the thermocouples and heaters were fitted. This assembly was in turn immersed in the water bath (Figure 4). Heaters in the water bath maintained the water temperature the same as that of the calorimeter within $\pm 0.1^{\circ}\text{C}$, resulting in the desired adiabatic condition.

Total capacity of the heaters in the water bath was 2,300 watts, sufficient to raise water temperature at 30°C per hour. To obtain uniform water temperature with no significant gradients, air was bubbled through the water. This method was suggested by Perry (12) in a discussion on mixing of liquids.



- A* To controller
- B* To recorder
- C* Powerstat to internal heaters
- D* Controller to external heaters
- E* Insulation
- F* Water bath
- G* Oxygen preheater
- H* Thermocouples
- J* Calorimeter

Fig 4 Adiabatic calorimeter assembly.

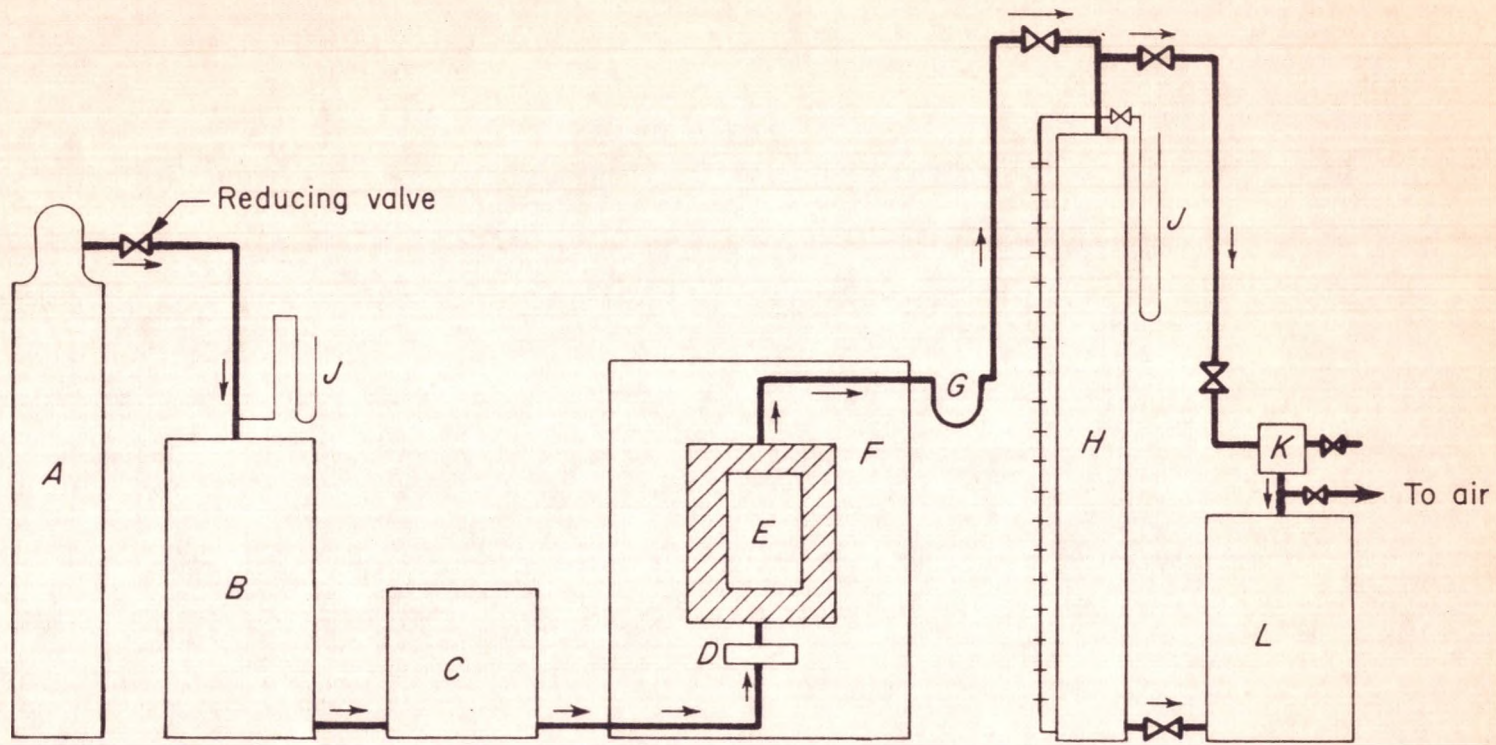
Gas Flow System

The flow system (Figure 5) consisted of an oxygen supply, metering unit and a gas collection column. An oxygen bottle (A) was connected through two pressure reducing valves to an air-tight container (B). Oxygen pressure in (B) was maintained constant during each test. Container (B) was connected to a constant displacement pump (C) used as a metering device. The pump (Figure 6) consisted of a synchronous motor driving a 30 milliliter syringe. Prior to entering the calorimeter, the metered oxygen passed through a preheater in the water bath (D Figure 5), consisting of a 15-foot coil of 1/4-inch copper tubing, to heat the oxygen to the temperature of the bath.

Moisture was removed from the effluent gas by condensation in a U-tube (G) inserted in an ice-water bath. The dry gas was collected over a saturated brine solution in a column constructed of 4-inch steel pipe (H Figure 5). Gas pressure was measured with a water manometer (J) and a brine level indicator was fitted to the column to measure the volume of gas. The temperature of the gas was assumed ambient.

A brine reservoir (L) was connected to the gas column. This reservoir was fitted to an air pressure line through an automatic pressure relief valve (K). Air pressure in the brine reservoir maintained the brine level in the gas column. Once the pressure relief valve was properly adjusted, the gas in the column was maintained at atmospheric pressure, \pm 0.1 inch of water.

A sample of the collected gas was removed from the column and analyzed for carbon dioxide and oxygen using an Orsat gas analyzer.



A Oxygen bottle
B Low pressure oxygen supply
C Constant displacement pump
D Preheater
E Calorimeter

F Water bath
G Drying tube
H Brine column
J Manometer
K Automatic relief valve
L Brine reservoir

Fig 5 Oxygen flow diagram.

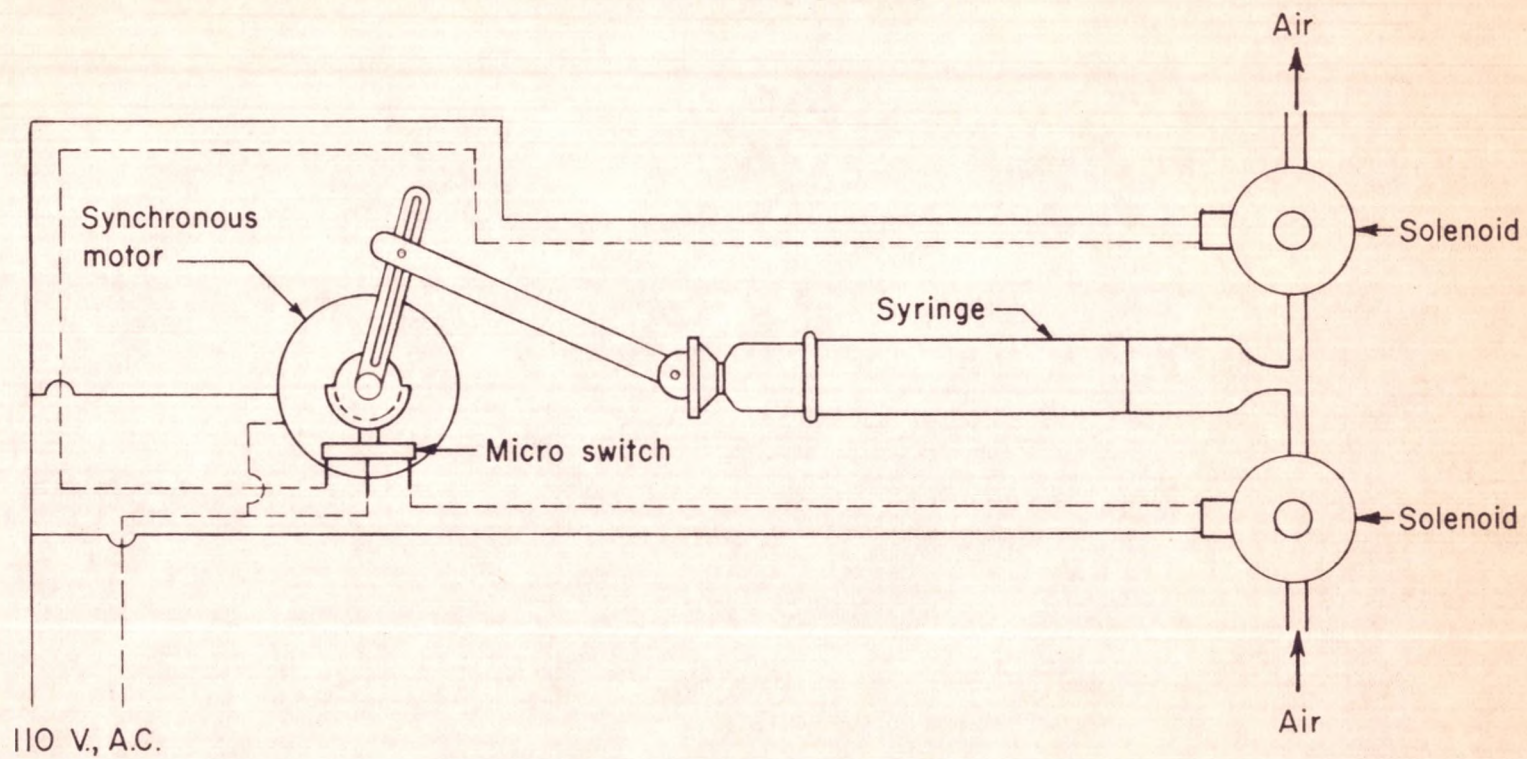


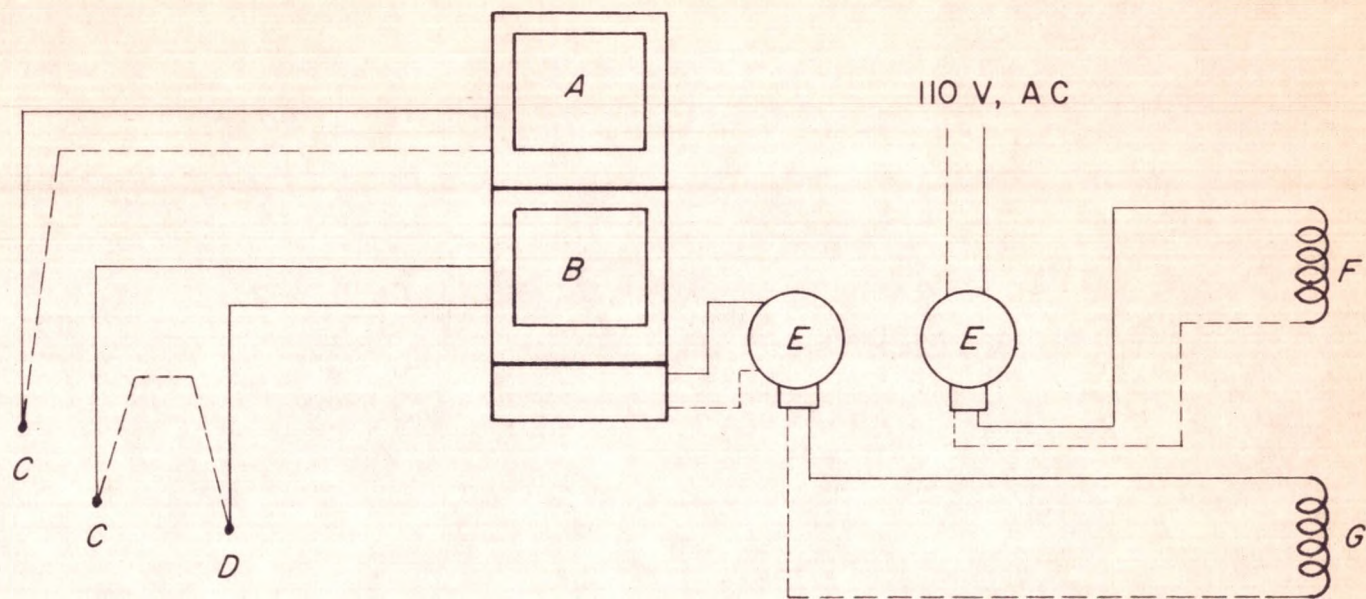
Fig 6 Constant displacement pump.

Initially, a Burrell Haldane analyzer was used. However, because of the high concentration of oxygen in the collected gas, a Burrell portable Orsat analyzer was found to be more satisfactory in operation and was of sufficient accuracy for the present work.

Temperature Measurement

Iron-constantan thermocouples were used as temperature sensing devices in all instances. Initially, two thermocouples were employed, one in the calorimeter and one in the water bath. The thermocouple in the calorimeter was connected to all points of a Honeywell multipoint EMF recorder to continuously record the coal temperature. Both thermocouples were connected to a Honeywell-Lycan potentiometer-controller so that the difference in EMF could be regulated. However, feedback from the potentiometer affected readings of the recorder. To eliminate this feedback, another thermocouple was installed in the calorimeter and connected to the recorder. The original two thermocouples were connected only to the controller used to regulate the difference in EMF (Figure 7).

The recorder registering the coal temperature (A Figure 7) had a scale of -0.1 to 1.0 millivolts. Since a range of +0.0 to +5.0 millivolts was required for the temperature range, an external variable voltage unit was added so that readings could be adjusted to zero after full-scale deflection was reached. This adjustment could be repeated four times giving the required range and retaining the sensitivity of 0.01 millivolt per scale division.



- A* Temperature recorder
- B* Temperature controller
- C* Thermocouples in calorimeter
- D* Thermocouple in water bath
- E* Powerstat
- F* Internal heaters, three
- G* Control heaters, two, 600 watt

Fig 7 Wiring diagram for heaters and thermocouples.

The Honeywell-Brown potentiometer (B Figure 7) had a range of ± 0.5 millivolts with the control point, 0 millivolts, centered on the chart. This instrument was connected to the two opposing thermocouples to read differential EMF between the water bath and calorimeter. Whenever the water bath was cooler than the calorimeter, the potentiometer energized the water bath heaters (9) through powerstat (E). The heaters remained energized until the water bath temperature was the same as that of the calorimeter.

Two manually-controlled electrical circuits included the internal heaters in the calorimeters and the auxiliary heaters in the water bath. The heaters in the calorimeter consisted of three resistance wire coils connected in series to a 110-volt power supply through a powerstat. Maximum voltage setting for these heaters was 50 volts.

The auxiliary heaters in the water bath were added to increase the rate of heating of the bath for tests at higher temperatures. The heaters were connected to a 110-volt power supply through a powerstat. At the maximum setting of 110 volts, the heaters were rated at 1,700 watts.

Calibration of Equipment

The multipoint recorder was calibrated using a Leeds and Northrup portable potentiometer. By applying an EMF to the recorder from the potentiometer, settings were obtained for the external variable voltage unit to give the desired scale readings. The 0 reading of the recorder was checked at ice bath temperatures.

The Brown potentiometer was calibrated in a similar fashion as the recorder. Drift, experienced in preliminary trials, was reduced

by shielding the thermocouples in a grounded copper tube. The iron-constantan thermocouples corroded rapidly, especially during trials at 90° C, making it necessary to replace the thermocouples several times during the investigation.

The constant displacement pump which was used to meter oxygen was calibrated at the rates of 10 and 30 milliliters per minute, (Figure 8) which were the flow rates used in the tests. Oxygen was pumped from the low pressure oxygen supply (B Figure 5) into the gas collection column (H). Each calibration was conducted for 2 hours while holding the pressure in the oxygen supply constant and maintaining atmospheric pressure in the brine column. Calibration at each flow rate was conducted at six pressure levels of the oxygen supply. The flow rate that was used for most of the tests was 10 milliliters per minute.

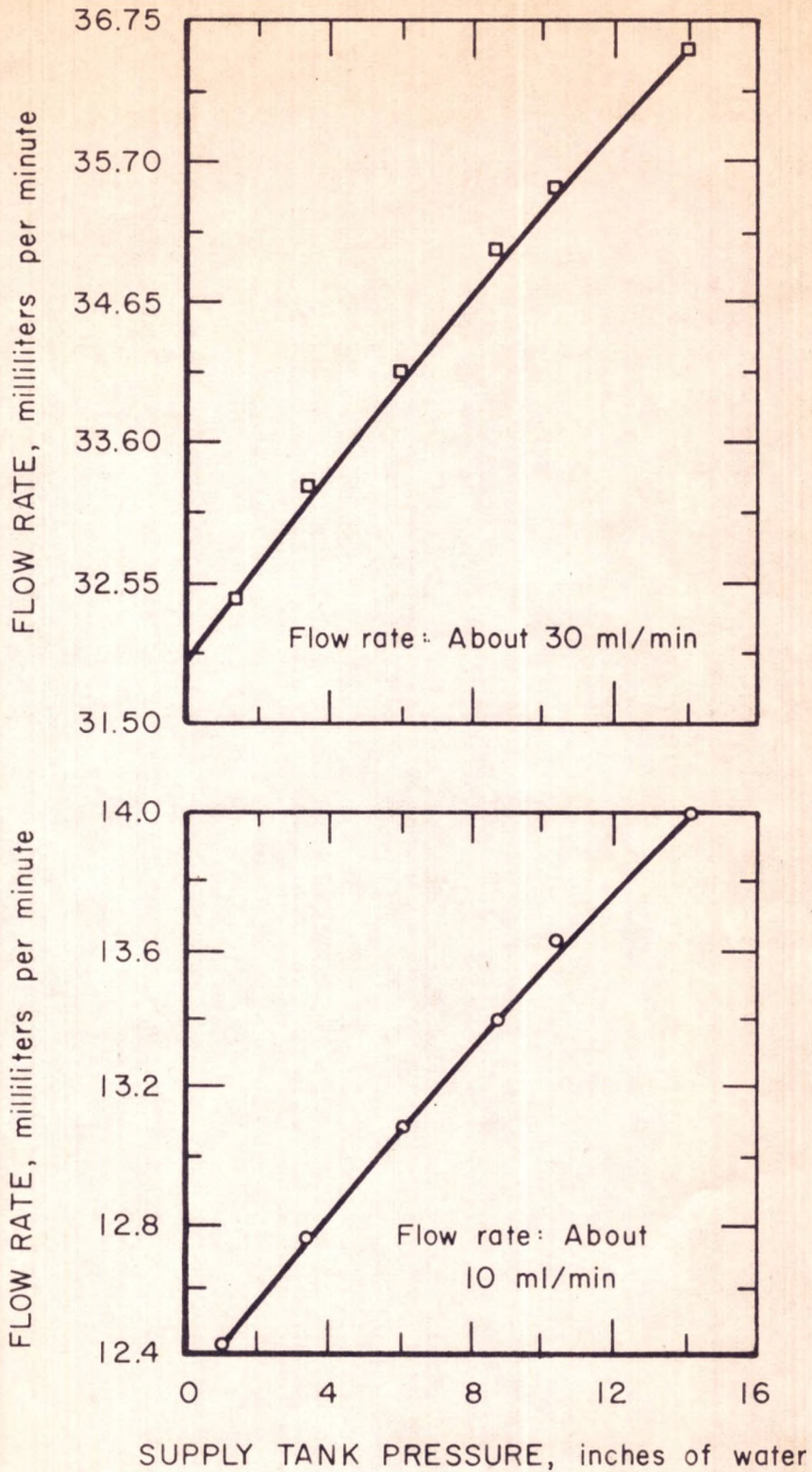


Fig 8 Calibration curves for oxygen admission.

CHAPTER III

EXPERIMENTAL PROCEDURES

Sample Preparation

Raw lignite for this investigation was obtained from a shipment that had been mined at the Leukel-Noonan mine, Noonan, N. Dak., approximately 1 week prior to the preparation of samples. The average proximate analysis was: moisture 34.8 percent, volatile matter 26.7 percent, fixed carbon 32.5 percent, and ash 6.0 percent.

Three particle size ranges 0.50 x 0.25 inch, 0.25 x 0.125 inch, and 0.125 x 0.036 inch, were prepared from +1 inch raw lignite by crushing and screening to the desired size ranges. Sized samples were stored under nitrogen in air-tight containers.

Using the 0.25 x 0.125 inch freshly crushed raw lignite, five 4,000 gram samples were prepared having different histories of preoxidation and associated levels of reactivity toward further oxidation. Reactivity was measured by an oxygen depletion rate constant (k) defined by the expression:

$$\ln P_1/P_2 = kt$$

where P_1 and P_2 are the initial and final partial pressures of oxygen over the time interval t .

The five oxidation history levels studied were:

1. Freshly crushed.
2. Partially deactivated by adsorption of oxygen.

3. Completely deactivated^{2/} by adsorption of oxygen.
4. Partially reactivated by desorption of carbon dioxide.
5. Completely reactivated^{3/} by desorption of carbon dioxide.

(Appendix A).

Sample 1 was stored under nitrogen immediately after crushing and screening. The depletion rate constant was 0.14 hr^{-1} . Sample 2, to prepare a partially deactivated sample, was placed in the preoxidation container for 2 days. The rate of oxygen adsorbed gave a value for (k) of 0.0105 hr^{-1} . Sample 3 was oxidized for 3 weeks, reducing (k) to 0.0024 hr^{-1} . Samples 4 and 5 were first deactivated to a (k) of 0.004 hr^{-1} , and then reactivated by heating in the absence of oxygen to drive off adsorbed gases. Sample 4 was reactivated at 80° C for 1/2 hour to increase (k) to 0.016 hr^{-1} . Sample 5 was reactivated to a (k) of 0.163 hr^{-1} , about 1.2 times that of freshly-crushed lignite, by heating at 90° C for 1 hour. All depletion rate constants were evaluated at 20° C .

Dry lignite was prepared by drying +1 inch particles in nitrogen to a moisture content of 1.6 percent. The dry sample was then crushed and screened to 0.125×0.036 inch and stored under nitrogen.

Experimental Procedure

Tests were run at three temperatures, 20° , 60° , and 90° C , two moisture contents, raw (34.8 percent) and dry (1.6 percent), five oxidation histories and three particle sizes for a total of 24 experiments.

^{2/} The oxygen depletion rate constant (k) was reduced to about 1/60 that of freshly-crushed lignite.

^{3/} The reactivity was greater than that of freshly-crushed lignite.

Test conditions were selected at random to reduce the probability of any bias affecting the correlations. Preliminary calibration checks were conducted and required adjustments were made prior to each test.

The calorimeter was first charged with a weighed sample of from 650 to 700 grams of lignite. The calorimeter was sealed and placed in the insulated, water-tight container. The assembly was immersed in the water bath and all electrical, thermocouple, and gas connections were secured. The calorimeter and water bath were heated to the desired initial temperature at a rate of 30° C per hour. While the calorimeter assembly was being heated, the drying tube (G Figure 5) was weighed and the gas column (H) was filled with brine by applying air pressure to the brine reservoir.

As soon as the desired initial temperature was reached, the calorimeter was purged with oxygen at a high flow rate for 5 minutes. Some oxidation occurred during this period, however, it was necessary as a measure to remove most of the residual nitrogen from the lignite sample, permitting a more accurate oxygen balance through the system. The test was conducted at the desired temperature while oxygen was metered into the calorimeter and desorbed gases and excess oxygen were collected by displacement in the brine column. The tests were run for 2 to 6 hours depending on the rate of oxygen adsorption.

When the test was completed, a record was made of the ambient temperature, barometric pressure, volume of gas collected, weight of water collected, oxidation tank pressure and calorimeter temperature rise. The oxidizing and collected gases were analyzed and the analysis recorded. From the observed data and the heat capacity of the

calorimeter and lignite sample, the heat of reaction of lignite in calories per gram mole of oxygen consumed and the average rate of oxygen consumption per kilogram of moisture ash free lignite charge was calculated. See Appendix C for calculation methods.

CHAPTER IV

RESULTS AND DISCUSSION

There appears to be a trend of increasing heat of reaction and increasing rate of oxygen consumption with increasing temperature (Figure 9). This phenomena would indicate that the higher the temperature of a given sample of lignite exposed to oxygen, the more heat would have to be removed to prevent spontaneous heating and subsequent combustion.

The average value for the heat of reaction from all of the data at 20° C is 55,894 calories per gram mole of oxygen consumed with a standard deviation of 29,300 while the average rate of oxygen consumption is 0.01145 ± 0.00966 gram moles per hour-killogram of moisture ash free lignite. At 60° C the heat of reaction is 85,000 calories per gram mole of oxygen with a standard deviation of 5,350. The average oxygen consumption rate is increased over that at 20° C to 0.02612 ± 0.00700 gram moles of oxygen per hour-killogram moisture ash free lignite. The heat of reaction at 90° C was 89,000 calories per gram mole oxygen with a standard deviation of 5,570. Rate of oxygen consumed was increased still further to 0.04870 ± 0.02140 gram moles oxygen per hour-killogram of moisture ash free lignite.

The values for the heat of reaction at 60° and 90° C had standard deviations of 5,350 and 5,570, which includes experimental error and

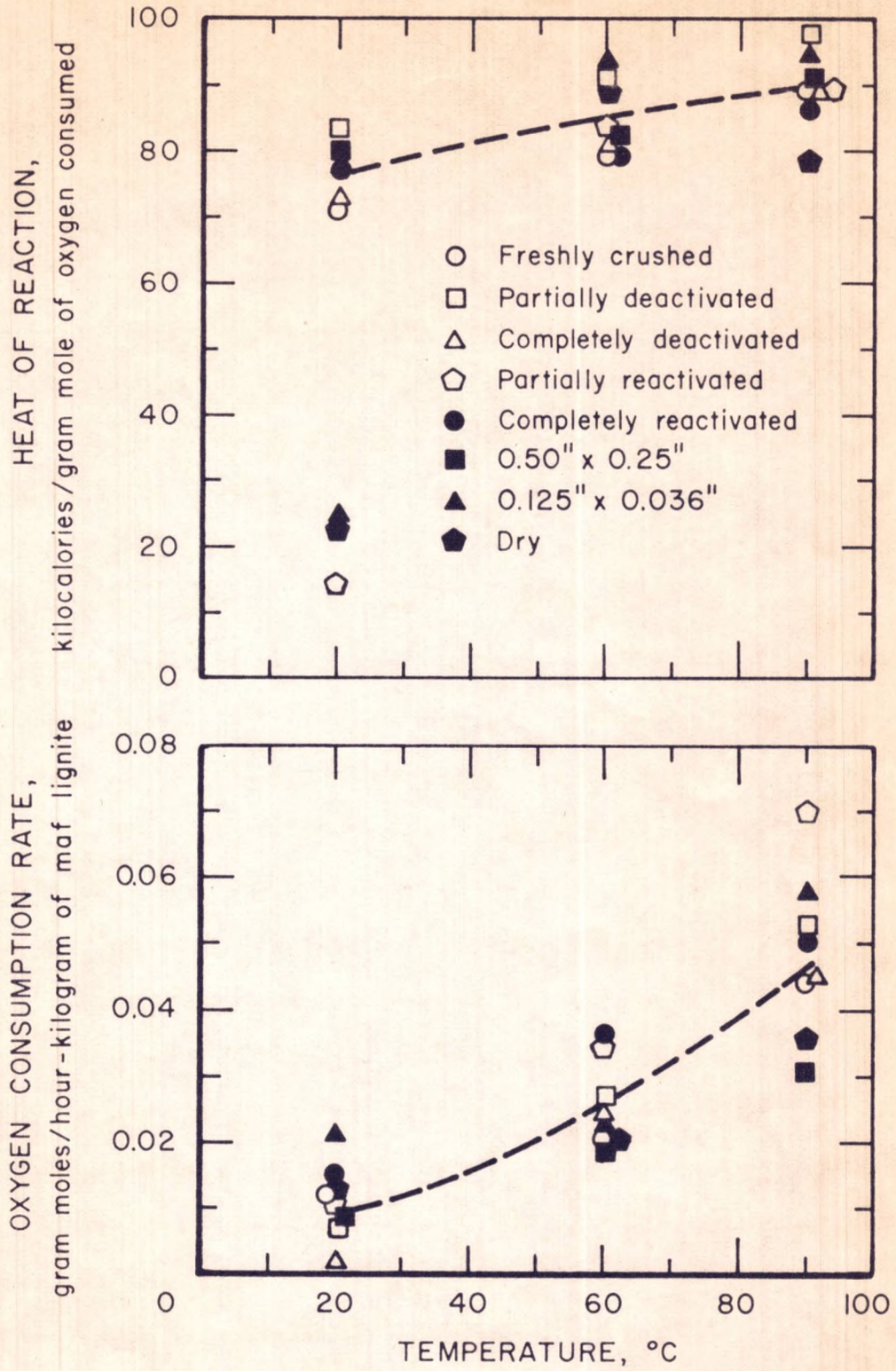


Fig 9 Heat of reaction and rate of oxygen consumption versus temperature.

effects of the other variables studied. The standard deviation at 20° C was 29,300, over five times that of the deviation at the higher temperatures. This larger variation in the data at 20° C is caused in part by physical adsorption without chemical reaction at the low temperature, resulting in a very low rate of heat generation. At the higher temperatures of 60° and 90° C, a larger fraction of the total oxygen adsorbed reacts with the coal substance to form a chemical bond. Values for the heat of oxidation at these temperatures approximates the heat of oxidation for converting carbon to carbon dioxide (94,052 calories per gram mole of oxygen reacted) (13).

Two of the three low values at 20° C were for the smaller size fraction, 0.125 x 0.036 inches (Table 1). This would indicate that the physical adsorption at 20° C was occurring more predominantly on the smaller particle sizes than on the larger sizes. One value of 14,600 calories per gram mole oxygen is believed to be in error due to inadequate control of temperature.

The relatively large spread in rate of oxygen consumption is due to the other three parameters studied as well as temperature.

Particle size (Table 1), as already discussed, significantly influenced the heat of reaction at 20° C in the small size range. In all cases using smaller particle sizes increased the rate of oxygen consumption indicating that size reduction increased the effective surface area exposed to oxygen and hence increased the rate of consumption.

Moisture content had no apparent effect on the heat of reaction. However, the rate of oxygen consumption of the dry lignite was decreased in all instances over that of raw lignite.

TABLE 1

EFFECT OF PARTICLE SIZE AND MOISTURE CONTENT ON HEAT
OF REACTION AND OXYGEN ADSORPTION RATE

Particle size, inches (moisture, percent)	Rate of oxygen consumption g moles/hr-kilogram naf lignite, temperature °C			Heat of reaction calories/g mole oxygen temperature °C		
	20	60	90	20	60	90
0.50 x 0.25 (34.8)	0.00926	0.01902	0.03191	80,223	82,642	88,896
0.25 x 0.125 (34.8)	0.01194	0.02076	0.04406	70,842	79,750	89,300
0.125 x 0.036 (34.8)	0.02141	0.02392	0.05899	24,800	93,200	95,018
0.125 x 0.036 (1.6)	0.01320	0.02087	0.03686	23,550	89,904	78,846

Oxidation history (Table 2) produced a marked effect on the rate of oxygen adsorption. This was expected, as the activity of four of the five levels studied was altered by prior oxidation. This change in activity, however, did not significantly alter the heat of reaction as the amount of oxygen consumed liberated a proportional amount of heat, indicating that the mechanisms of the reactions occurring were independent of the oxidation history. Only the value for the heat of reaction of partially reactivated lignite at 20° C is much different and that is believed to represent an error due to inadequate control of temperature.

All but three of the values for the heat of reaction fall within the interval derived by Scott (11) of 68,550 to 98,560 calories per gram mole of oxygen adsorbed. The values not included in this interval are at 20° C whereas Scott's tests were conducted above 100° C. Most of the values for heat of reaction of lignite are lower than the standard state heat of oxidation of carbon to form carbon dioxide, suggesting that physical adsorption without chemical reaction and other reactions forming CO, H₂O, and various oxygen complexes within the coal occurred. Values above 94,052 could result when oxygen which is already adsorbed into the lignite reacts with the coal substance and additional thermal energy in excess of measured oxygen consumption is released.

TABLE 2

EFFECT OF OXIDATION HISTORY ON HEAT OF
REACTION AND OXYGEN CONSUMPTION RATE

Oxidation history	Rate of oxygen consumption g moles/hr-kilogram maf lignite, temperature °C			Heat of reaction calories/g mole oxygen temperature °C		
	20	60	90	20	60	90
Freshly crushed	0.01194	0.02078	0.04406	70,842	79,750	89,300
Partially deactivated	0.00692	0.02711	0.05239	83,200	90,225	97,427
Completely deactivated	0.00179	0.02251	0.04525	72,600	81,238	89,040
Partially reactivated	0.01157	0.03490	0.07010	14,600	84,700	88,261
Completely reactivated	0.01552	0.03685	0.05008	77,313	79,116	86,403

CHAPTER V

SUMMARY AND CONCLUSIONS

All of the parameters; temperatures, particle size, moisture content and oxidation history; affected the rate at which oxygen was consumed by lignite. At low temperatures, the consumption appeared to be at least partially a physical adsorption rather than a chemical reaction, particularly in the smaller particle size range where a low heat release per gram mole of oxygen consumed was observed. This physical adsorption is believed to be the greatest cause for the significantly greater variation in the data at 20° C. At the higher temperatures of 60° and 90° C, a larger fraction of consumed oxygen reacted with the coal substance producing higher heats of reaction than that at 20° C. The values obtained at 60° and 90° are $85,000 \pm 9,600$ and $89,000 \pm 9,600$ calories per gram mole of oxygen consumed.

The rate of oxygen consumption increased with decreasing particle size and increasing moisture content. However, the heat of reaction was significantly low due to physical adsorption, only in the small particle sizes at 20° C, and was unaffected by moisture content.

History of prior oxidation affected the rate of oxidation in proportion to the relative reactivity of the prepared samples. However, prior oxidation did not significantly affect the heat of reaction.

Values for the heat of reaction and the rate of adsorption will permit calculation of the amount of heat that must be removed from lignite to prevent spontaneous heating in storage. It is recommended that the appropriate rate constant (reactivity) be used together with an average heat of oxidation of $85,000 \pm 9,600$ calories per gram mole of oxygen for this purpose. While physical adsorption occurring at low temperatures may lower this value, the average value represents an estimate which would be on the safe side for temperatures below 60°C . For temperatures above 60°C , a value of $89,000 \pm 9,600$ calories per gram mole oxygen should be used.

For example, if 1 ton of the raw Baukol-Noonan lignite used in these tests was freshly crushed and screened to 0.25×0.125 inches and stored so that sufficient oxygen was available, then the lignite would initially consume oxygen at a rate of about 0.01194 gram moles per hour-kilogram of lignite, or 6.40 gram moles of oxygen would be consumed per hour by the pile. Since below 60°C heat is generated at an average rate of 85,000 calories per gram mole of oxygen, 543 kilocalories will have to be removed per hour to prevent heating at a rate of 1.15°C/hr . If the heat is not removed and the temperature is allowed to rise to 60°C , the rate of oxygen consumption nearly doubles and 11.3 gram moles of oxygen will be consumed per hour generating 946 kilocalories which would increase the heating rate to 2.01°C/hr . Still further, if the temperature reaches 90°C , 24.8 gram moles of oxygen will be consumed per hour generating 2207.2 kilocalories, or a temperature rise of 4.68°C/hr as the heat of oxidation at 90°C will have increased to an average of 89 kilocalories per gram mole oxygen.

If the sample was raw lignite with 34.8 percent moisture, a portion of the generated heat would go to supply the latent heat for vaporization of moisture up to a temperature of about 100° C. The temperature would remain fairly constant at 100° C until the moisture was removed; then nearly all of the heat of reaction would be available to increase the temperature within the stockpile. This example shows how data obtained in this investigation may be used to predict the amount of heat generated and associated temperature rise when a given amount of lignite is exposed to sufficient oxygen under adiabatic conditions. This data together with information on the appropriate rate constant (reactivity) of lignite, the availability of oxygen and the thermal conductivity of lignite will be used to calculate heat balances on stored lignite and will help to establish suitable conditions for storage of large quantities of this fuel.

Recommendations

Due to variations in the data reported at 20° C it is recommended that additional work be done at this temperature, both on the heat of reaction and on gas adsorption (including oxygen and inert gases).

It is further recommended that thermocouples other than iron-constantan be used. Iron-constantan couples are sensitive, however, the rate of corrosion in the presence of oxygen makes them unusable after very few tests.

Further work would be enhanced by improving the accuracy of the adiabatic temperature control system and measurement of the amount of oxygen consumed.

APPENDIX A

DATA ON OXIDATION HISTORY PREPARATION

History	Sample weight (grams)	Oxygen absorbed (grams)	Gases desorbed (grams)		Oxygen depletion rate constant (k) (hr ⁻¹)
			oxygen	carbon dioxide	
1. Freshly crushed	---	---	---	---	0.1400
2. Partially deactivated	4,477	22.7	---	---	0.0105
3. Completely deactivated	4,677	139.5	---	---	0.0024
4. Partially reactivated	4,409	58.0	3.33	0.332	0.0160
5. Completely reactivated	4,481	48.5	3.22	0.498	0.1680

APPENDIX B

DATA ON HEAT OF REACTION AND RATE OF OXYGEN CONSUMPTION

Temp. °C	Sample condition		Moisture percent	Charge grams	Time hours	Oxygen consumed g/moles	Temp. rise °C	Water evaporated grams	Heat of reaction cal/g mole O ₂
	Size inches	Oxidation history							
20	0.250 x	freshly							
	0.500	crushed	34.8	576	3.08	0.00977	1.100	0.0000	80,223
60	0.250 x	freshly							
	0.500	crushed	34.8	608	3.42	0.0234	1.032	0.6387	82,642
90	0.250 x	freshly							
	0.500	crushed	34.8	615	4.52	0.0525	0.717	1.7894	86,896
20	0.125 x	freshly							
	0.250	crushed	34.8	673	2.50	0.05960	2.350	0.0000	70,842
60	0.125 x	freshly							
	0.250	crushed	34.8	689	2.92	0.02470	1.033	0.0298	79,750
90	0.125 x	freshly							
	0.250	crushed	34.8	623	3.10	0.0503	1.720	0.7693	89,300
20	0.125 x	partially							
	0.250	deactivated	34.8	664	2.67	0.00726	0.319	0.0000	83,200
60	0.125 x	partially							
	0.250	deactivated	34.8	648	4.00	0.04153	4.133	0.3962	90,225
90	0.125 x	partially							
	0.250	deactivated	34.8	643	5.33	0.01062	5.500	2.0693	97,427
20	0.125 x	completely							
	0.250	deactivated	34.8	639	2.00	0.00135	1.082	0.0000	72,600
60	0.125 x	completely							
	0.250	deactivated	34.8	639	4.92	0.04744	3.000	0.7269	81,238
90	0.125 x	completely							
	0.250	deactivated	34.8	672	5.17	0.09310	3.900	2.4847	89,040

APPENDIX B Continued

DATA ON HEAT OF REACTION AND RATE OF OXYGEN CONSUMPTION

Temp. °C	Size inches	Sample condition		Charge grams	Time hours	Oxygen consumed g./moles	Temp. rise °C	Water evaporated grams	Heat of reaction cal/g mole O ₂
		Oxidation history	Moisture percent						
20	0.125 x	partially		689	6.00	0.02829	0.219	0.0000	14,600
	0.250	reactivated	34.8						
60	0.125 x	partially		668	6.00	0.07839	3.512	0.5626	84,700
	0.250	reactivated	34.8						
90	0.125 x	partially		660	2.33	0.0638	2.767	1.1482	88,261
	0.250	reactivated	34.8						
20	0.125 x	completely		676	2.00	0.01242	0.504	0.0000	77,313
	0.250	reactivated	34.8						
60	0.125 x	completely		684	5.00	0.07453	3.102	0.0198	79,116
	0.250	reactivated	34.8						
90	0.125 x	completely		688	4.00	0.08155	3.563	0.1888	86,403
	0.250	reactivated	34.8						
20	0.036 x	freshly		639	3.08	0.02490	0.326	0.0000	24,800
	0.125	crushed	34.8						
60	0.036 x	freshly		702	4.00	0.03970	1.912	0.1247	93,200
	0.125	crushed	34.8						
90	0.036 x	freshly		683	5.00	0.11294	5.643	1.3675	95,018
	0.125	crushed	34.8						
20	0.036 x	freshly		705	3.42	0.0294	0.400	0.0000	23,550
	0.125	crushed	1.6						
60	0.036 x	freshly		771	4.50	0.06679	3.433	0.0000	89,904
	0.125	crushed	1.6						
90	0.036 x	freshly		866	5.00	0.14738	6.124	0.0000	78,846
	0.125	crushed	1.6						

APPENDIX C

SAMPLE CALCULATIONS

1. Calculation of the oxygen depletion rate constant (k) was performed by repeatedly evaluating initial and final partial pressure over time intervals using the relation:

$$\ln P_1/P_2 = kt$$

which defines k.

Data from preparation of the completely deactivated samples are:

$$P_1 = 34.20 \text{ in H}_g$$

$$P_2 = 23.30 \text{ in H}_g$$

$$t = 168 \text{ hours}$$

$$\ln P_1/P_2 = 0.336 = k(t) = 168 k$$

$$k = 2.4 \times 10^{-3} \text{ hr}^{-1}$$

2. Oxygen consumption rate per hour-kilogram moisture and ash free lignite:

$$\text{Oxygen consumption rate} = \frac{\text{Oxygen consumed (gram moles)}}{\text{time(hr) wt of charge (kilograms maf)}}$$

$$\text{Weight of charge (maf)} = [\text{weight of charge (kilogram)}] \left(1.0 - \frac{\%M}{100} - \frac{\%A}{100} \right)$$

where %M = percent moisture

%A = percent ash

$$\text{Oxygen consumed} = \frac{\text{Volume admitted (ml at STP)} - \text{Volume collected (ml at STP)}}{22,400 \text{ ml/gram mole}}$$

Example: For the completely deactivated sample at 90° C:

$$\begin{aligned} \text{Weight of charge (maf)} &= (.672 \text{ kilograms})(1.0 - 0.348 - 0.06) \\ &= 0.3978 \text{ kilograms maf} \end{aligned}$$

$$\begin{aligned} \text{Oxygen consumption rate} &= \frac{(0.09310 \text{ gram moles})}{(5.17 \text{ hr})(0.3978 \text{ kilograms maf})(\text{lignite})} \\ &= 0.04525 \text{ gram moles oxygen/hr-kilogram lignite} \end{aligned}$$

3. Heat of reaction is calculated by dividing the heat generated by the amount of oxygen consumed:

$$\text{Heat generated} = (\Delta T)(C_c + C_1) + (\text{water evaporated grams})(H)$$

where C_c = heat capacity of calorimeter

C_1 = heat capacity of lignite charge

ΔT = temperature rise

H = heat of vaporization

$$\text{Heat of reaction} = \frac{\text{Heat generated (calories)}}{\text{oxygen consumed (gram moles)}}$$

Example: Partially deactivated sample at 20° C:

$$\text{Heat generated} = (.319^\circ \text{ C})(1,924 \text{ calories}/^\circ \text{ C}) = 614 \text{ calories}$$

$$\text{Heat of reaction} = \frac{614}{0.00726} = 83,200 \text{ calories/gram mole oxygen}$$

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