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AN ABSTRACT OF THE THESIS OF Salvador Leon Arredondo for the Master of Science in Chemistry presented June 16, 1980.

Title: Surface Area of Coal as Influenced by Low Temperature Oxidation Processes.

APPROVED BY MEMBERS OF THE THESIS COMMITTEE:

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Robert J. O'Brien

Production of liquid fuels or of a synthetic high B.T.U. pipeline gas from coal is a means of meeting our energy needs. However, most of the American coals become plastic and agglomerate (cake) when they are heated to the gasification temperature.

Several pretreatments have been carried out in order to convert caking coal to non-caking coals. All of them are based upon the results found by Channabasappa and Linden. The caking tendency of coals is destroyed by oxidizing the surface of coal particles. Although the effects of preoxida-

tion on fluidity, dilation upon heating and surface area and reactivity of the chars have been studied the effect of preoxidation on the surface area of the treated coal is not known.

The possibility of increasing the amount of readily accessible surface area by enlarging the 5 Å pore was examined via pretreating the PSOC-371 coal with gases such as nitrogen, nitrogen-oxygen, and ozone-oxygen and hydrogen peroxide solutions. Surface areas were obtained from nitrogen adsorption at 77 K and carbon dioxide adsorption at either 298 or 195 K for each sample before and after treatment.

The surface area was established first for coal heated to 400°, 450°, 500°, 600°, and 1000°C in a stream of nitrogen. Second, the surface of coal was determined after it was pretreated at 400°, 450°, and 500°C in a stream of oxygen-nitrogen (5% by volume of oxygen). Third, the surface of coal was determined after extraction at 85°C using a hydrogen peroxide solution at three different concentrations. Finally, the surface area of coal was determined after pretreatment at -78°, 25°, and 100°C in a stream of ozone-oxygen (2.7% by volume of ozone).

This research has shown that the surface area of chars increases up to 600°C and then decreases. At temperatures of 250°C and below, coal picked up oxygen and became non-caking. Nitrogen penetration was increased by a factor of 100 after

oxygen pretreatment at 400°C. Neither treatment with hydrogen peroxide at 85°C nor treatment with ozone at -78 to 100°C seemed to alter the pore size. It is believed that controlled oxidation with oxygen at temperatures in the range 300° to 400°C may be a promising approach for further work on other coals.

A sample of Pittsburgh coal pretreated with oxygen by the Bureau of Mines to make it non-caking showed negligible surface area as measured by nitrogen at 77 K; however, treatment with 5% oxygen-95% nitrogen gas at 450°C, increases the surface area by a factor of about 150 as measured by nitrogen at 77 K.

SURFACE AREA OF COAL AS INFLUENCED BY
LOW TEMPERATURE OXIDATION PROCESSES

by

SALVADOR LEON ARREDONDO

A thesis submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE
in
CHEMISTRY

Portland State University

1980

TO THE OFFICE OF GRADUATE STUDIES AND RESEARCH:

The members of the Committee approve the thesis of
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CHAPTER I

INTRODUCTION

Background

Coal is composed of organic and inorganic substances that form a heterogeneous multicomponent mixture with a complex composition. It has a variable physical structure with a highly complex interior system. Each coal is different from another one on the macro, micro and molecular levels; hence it is one of the more difficult substances to study.

As is pointed out by Van Krevelen (1), and Chakrabartty (2, 3), the organic structure of coal is composed of aromatic and heterocyclic structures tied together in various configurations by groups such as alkyl, ether, thioether, and others with some functional groups distributed over these structures. The inorganic structure of coal consists of clays (mainly $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$), pyrite, calcite and quartz.

Some elements that are found include As, Cu, Ti, Zn, Pb, Mg, Ba, V, Ge and P. Ions such as chlorides, sulfates and nitrates are also found.

The physical and chemical properties of the organic compounds found in coal account for the overall properties

of coal and are influenced by the mineral matter acting as catalysts (4).

For a long time it has been known that coals are porous materials, neither fluid nor rigid; Bangham (5), has called them "visco elastic colloids" possessing an empty volume formed by pores which are not cylindrical in shape but thin slits containing even more narrow portions which accept only a monolayer of adsorbate without suffering a change.

According to Gan, Nandi, and Walker (6), coal can have three pore systems: (a) macropore system, (b) a transitional pore system, and (c) a micropore system. Pores in the size range above 300 Å are described as macropores, those below 12 Å as micropores, and those pores in the size ranges 12-300 Å as transitional pores. They studied the pore structure for a number of American coals which they characterized by such properties as total pore volume (from helium and mercury densities), pore surface area (from adsorption of nitrogen at 77 K and carbon dioxide at 298 K), macropore size distribution (from mercury porosimetry), and size distribution of pores below 300 Å (from nitrogen isotherm measured at 77 K). They found that the internal surface of coal is mainly due to a micropore system and that the majority of American coals had surface areas less than $1 \text{ m}^2/\text{g}$, as measured by nitrogen at 77 K, and surface areas between 100 and 420 m^2/g as measured by carbon dioxide at room temperature.

Important questions needing to be answered are those referring to the surface physics and chemistry of coal; that is, data about the change of pore volume, pore size distribution, and surface area when coal is treated with heat or chemicals. Answers to these questions are needed because both surface physics and chemistry of coal can control the processing of entering reactants as well as exiting products in certain catalytic reactions and they can influence the rates of mass transfer as well as affecting the rate of gas adsorption. These processes are important steps in the chemical processing and use of coal. Of particular interest is the change in surface area when coal is treated with heat or chemicals. It is known that when coal is heated, volatile matter is liberated. Fuller (7), has shown that at 150°C, hydrocarbons are released and that at 180°C aromatics and sulfur-containing species appear. Above 350°C, gases, liquids and semi-solid tars are produced. Van Krevelen (1) has pointed out that hydrogen and methane are the main products at 600-800°C and also observed that when some coals are heated they proceed through a transitory plastic phase in which they soften, expand, and resolidify. In general, the plastic property, when present, is a function of volatile matter content and porosity. The former is directly related and the latter is inversely related; that is, the higher the volatile matter content the more pronounced the plastic behavior, and the smaller the porosity the higher the plasticity. It should be noted that some exceptions have been

found (8) and that the observable facts can be affected by composition, by heating and by changes in pressure and atmospheric conditions. In fact, Dulhunty and Harrison (9) found that the expansion phenomenon does not occur if the heating rate is reduced. Loisen (8) found that reduced pressure reduces the plastic property of coal. We have found in our laboratory that plasticity appears to be drastically diminished by using a nitrogen-oxygen atmosphere at temperatures up to 500°C. It has also been shown (10) that porosity becomes greater and the accessibility of the pores to longer molecules become smaller when the carbonization temperature is increased; that is, above 600°C the accessibility decreases markedly so that only atoms or molecules like helium, neon and hydrogen can penetrate the internal surface area. Chiche and coworkers (11) found that a considerable fraction of porosity disappeared at carbonization temperatures above 1500°C.

Some additional work has been done by using other suitable reagents in different atmospheres at different temperatures. The effect of preoxidation, of two highly caking coals, has been examined by several workers. The weight loss during pyrolysis in a nitrogen atmosphere up to 1000°C and the reactivity of the resultant chars in air at 470°C, was studied by Mahajan, Konatsu and Walker (12). They found that preoxidation increases the surface area of the chars. This investigation was restricted to the chars and was not applied to the original coal samples.

Purpose and Significance

As already mentioned, most American coals have negligible nitrogen surface area and high carbon dioxide surface area. This observation enables one to conclude that the pores of American coals are usually only about 5 Å in size and therefore are not readily accessible to large solvent molecules and to many gaseous reactants.

The purpose of this research is to examine the possibility of increasing the amount of readily accessible surface by enlarging the 5 Å pores via treating coal with gases and liquids at different temperatures. Such enlargement of the pores should increase the rate of and lower the temperature of the reaction of coal with various gases or solvent and should thereby speed up and simplify the conversion of coal to useful products. According to a recent literature update (1977-80), there are several papers that relate to the field of this research; however, out of 25 papers that were examined, only a few have surface area measurement with nitrogen at 77 K and carbon dioxide at either -78°C or room temperature. Three papers are related to the effect of extraction of coal with liquid ammonia or with various solvents. The remainder related to pore size measurements on chars or to treatment and extractions that did not include surface area measurements. Table I shows some results of pretreatment.

There are two main reasons for the present study on coal:

TABLE I
SURFACE AREAS OF COALS

Coal	Surface Area (m ² /g) (Raw Coal)			Treat- ment	Surface Area (m ² /g) (After Treatment)			Ref.
	N ₂ (77K)	CO ₂ (298K)	CO ₂ (195K)		N ₂ (77K)	CO ₂ (298K)	CO ₂ (195K)	
PSOC-87	1.0	268		A	93	260		27
87				A AW	11	610		
87				A DEM	1	600		
PSOC-138	2.2	225		A	120	560		
138				A AW	4	680		
138				A DEM	47	115		
PSOC-127	4.0	253		A	2	12		
127				A DEM	4	37		
Roland Seam	1.0		99					
				B PYR	10	247	247	28
				B DPA	5	170	170	
				B TPA	4	172	172	
				B EDA	44	195	195	
				B QUI	8	209	209	
				B PIP	8	144	144	
				B B		158	158	29
				B T		95	95	
				B PH		115	115	
				B D		108	108	
902	55		200	B PYR	5		270	30
702	16		155	B PYR	3		240	
601	6		130	B PRY	3		220	
Leopold		160		C		160		31
Shin-Yubori		100		C		110		
PSOC-127	1	253		D		45		12
Illinois No. 6	2.8		~160	E	3.1		~160	
Wyodak	2.6		200	E	0.7		1.6	34

TABLE I Legend

A. The treatment was in H_2 atmosphere at $980^\circ C$ over chars which were obtained when raw as well as acid-washed (AW) and demineralized (DEM) U.S. coals were charred to $1000^\circ C$ in N_2 atmosphere.

B. The treatment was a progressive extraction at temperatures between $200-300^\circ C$, by using solvents such as pyridine (PYR); dipropylamine (DPA); tripropylamine (TPA); ethylenediamine (EDA); quinoline (QUI); piperidine (PIP); benzene (B); tetralin (T); phenol (PH); and decalin (D).

C. The treatment was over the coal using liquid ammonia at 373 K.

D. The treatment was over the char, which was obtained when the raw coal was preoxidized, pyrolyzed, and treated in an air atmosphere.

E. Alkaline treatment involved slurring portions of these powders with known amounts of 1 N NaOH solutions.

First, coal constitutes one of the alternatives for an available energy source. In fact, according to Keller (25), coal represents 90% of the recoverable fossil energy resource of the United States which would last hundreds of years at present consumption rates.

Second, in order to efficiently use coal we need to know more about its surface properties. In some of the government research proposals for work to be done, high priority is given to measuring the surface area and pore size as a function of pretreatment or processing conditions. For example, a recent report on Coal Chemistry (26) makes the following statement:

Many questions that could be expected to be answered by basic researches on the physical structure of coal and solid coal products are still incompletely answered. The most important of these, for long-term support of developing coal technologies are those involving the surface physics and chemistry (the internal surface and the pore distribution) of coal that control reagent ingress and product egress during processing or use.

And again,

A basic understanding of the internal surface of coals and of the changes in the internal surface and pore volume upon treatment with heat and with chemical reagents is an urgent need.

It seems to be that the present work may be an effective part of the overall goal to learn how to beneficiate coal by adjusting the pore distribution in such a manner as to increase the reactivity of the coal for various processes that may be involved in converting it to useful gaseous or liquid products.

Specifically, oxygen-nitrogen and ozone-oxygen atmospheres at different temperatures were used in the present study in an attempt to enlarge the internal pore structure of coal. The time of coal treatment as well as the flow of gases were kept constant. As a comparison, the surface area data on the coal for treatment in an inert gas up to 1000°C were obtained. Finally, hydrogen peroxide was used at different concentrations at constant temperature.

CHAPTER II

EXPERIMENTAL

Surface Area Measurements

All the methods for determining surface area of coal can be related to the method of Brunauer, Emmett, and Teller (13, 14, 15). It is one of the best methods for determining surface areas of porous materials. The principle of the method is simple. It is based on the assumption that it is possible to determine, from an experimental adsorption isotherm, the volume and therefore the number of molecules of gas which fully cover a solid with a monomolecular layer when the gas is adsorbed on the surface of the solid. From this value, a simple multiplication by the average cross-sectional area of each molecule yields directly the absolute surface area of the adsorbent. A discussion of the selection of the point on the adsorption isotherm corresponding to a monolayer adsorbed gas may be found in the paper by Emmett (15). The data required for the adsorption isotherms of gases which are obtained close to their condensation pressure, may be determined by either a volumetric or gravimetric apparatus.

Using the BET equation, the isotherm can be plotted to yield a straight line whose slope and intercept give

directly the volume of the gas needed to form a monolayer.

The equation is:

$$\frac{P}{V_{\text{ads}}(P_0 - P)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C} \cdot \frac{P}{P_0} \quad (1)^*$$

Where:

V_{ads} = Volume of gas adsorbed (referred to S T P)

V_m = Volume of gas in cubic centimeters required to form a monolayer (referred to S T P)

P = Equilibrium pressure of the adsorbate

P_0 = Vapor pressure of the adsorbate at the temperature of adsorption

C = a constant given as:

$$C = c \exp \frac{(E_A - E_L)}{RT}$$

Where E_A and E_L are the heat of adsorption and liquefaction of the adsorbate respectively and c is a constant generally regarded as unity.

As is pointed out by Emmett (15)

. . . the linearity of the isotherms plotted according to equation (1) extends up to a relative pressure of about 0.35. . . only a few experimental points are needed in the range from 0.05 to 0.35 relative pressure of about 0.3 will, when connected with the origin on such a plot, differ by less than 5 per cent from that drawn with the help of a number of adsorption points. In practice it has become customary to determine only three or four experimental points in the relative pressure range below 0.35, since the slope of the straight line so obtained is indistinguishable from that resulting from a larger number of points . . .

* For derivation, see reference (14).

The surface areas are calculated from the following equation:

$$S = \frac{sV_m}{W}$$

Where:

S = Surface area in square meters per gram

W = Weight of the sample in grams

s = Constant given by:

$$s = \frac{NL}{22,400 \times 10^4}$$

Where:

N = Avogadro's number

L = Area occupied by each adsorbed molecule in square centimeters.

As may be seen, the constant s is a function of L. The value of 4.38* for s was reported by Emmett (15), when nitrogen was used as adsorbate and a liquid nitrogen bath as cold bath, was utilized. Values of 4.56 and 6.8 were used when carbon dioxide was used as adsorbate at 195 K and 298 K respectively. These two values for the constant s were obtained by using $17 \text{ \AA}^2$ (16) and $25.3 \text{ \AA}^{2**}$ as the molecular

*This figure was obtained when Avogadro's number was determined to be 6.061×10^{23} molecules/mole.

**This value was calculated using the equation given by Emmett and Brunauer (13):

$$\text{Area (L)} = (4)^{-1} (0.866) (M/4/2AD)^{2/3}$$

Where M is the molecular weight of the gas, D is the density of the liquefied gas and A is Avogadro's number.

area (L) of the carbon dioxide at 195 K and 298 K respectively.

Recently, carbon dioxide has been utilized in order to obtain the internal area of coal (17, 18, 19, 20). Walker and Kini (21) obtained the surface area of coal from carbon dioxide adsorption isotherms at 298 K using the BET equation. They concluded that these surface areas more nearly describe the total surface area than any other attempt now utilized. Gan, Nandi and Walker (6) examined nitrogen adsorption at 77 K and carbon dioxide adsorption at 298 K on several American coals. They found that the surface areas obtained from the nitrogen isotherms were much lower than those from carbon dioxide isotherms.

Inasmuch as the vapor pressure of carbon dioxide at 298 K is 63.5 atmospheres, a high pressure apparatus is needed to obtain the relative pressure range (0.05-0.35) that is required when the BET equation is used.

Since adsorption data can be obtained below one atmosphere of pressure using an ordinary vacuum apparatus, Marsh and Siemieniowska (22) have proposed the use of the Dubinin-Polanyi equation (for an extended discussion about this equation see reference 19) to attain the surface area of coal from carbon dioxide at 298 K. The complete equation is:

$$\text{Log } V_{\text{ads}} = \text{log } V_{\text{O}} - \frac{BT^2}{\beta} \text{log}^2 (P_{\text{O}}/P)$$

Where:

V_{ads} = Volume of gas adsorbed at equilibrium pressure

P = Equilibrium pressure

V_O = Micropore capacity

P_O = Saturation vapor pressure of adsorbate at temperature T K.

β = Affinity coefficient of adsorbate relative to nitrogen

B = A constant

It is evident that from the intercept of a plot of $\log V_{ads}$ against $\log^2 P_O/P$, V_O can be evaluated and because the adsorption of carbon dioxide is limited to a monolayer, the intercept $\log V_O$ should be equal to $\log V_m$.

Walker and Patel (23) compared surface areas calculated by the BET equation (high pressure data) and the Dubinin-Polanyi equation (low pressure data) from adsorption data measured in two distinct apparatus. They found good agreement between the areas calculated from the BET and the Dubinin-Polanyi equations in all coal samples used. They concluded that it is not required to use a high pressure apparatus to measure the surface area and recommended the use of the Dubinin-Polanyi equation for calculating surface areas using a conventional vacuum apparatus, at a temperature of 298 K and pressure below one atmosphere.

Apparatus

Adsorption Apparatus. The adsorption apparatus used was designed according to Constabaris (32) and Emmett (15). It is shown in Figure 1 and consists of:

Figure 1. Diagram of B.E.T. Apparatus

- an adsorption bulb A
- a calibrated gas buret B
- a manometer M
- a Cenco high vacuum mechanical pump
- an oil diffusion pump
- a Televac vacuum gauge

Basically, the method of operation has been discussed in detail by Quale (24). It is not complicated and will be clear from the following brief description:

The adsorption bulb containing a certain amount of coal is joined to the apparatus below stopcock A-1 by a slip joint and evacuated until the pressure is less than one micron. It should be checked by closing the stopcock D for at least 15 minutes in order to see if the required vacuum is obtained. If it is not, evacuation should continue for a period of time that permits the total removal of liquid water, water vapor, and other physically adsorbed gases. In the event that additional evacuation is needed for a short time it is possible to evacuate at a temperature of about 110-120°C. The same procedure should be made if the sample has been previously exposed to an adsorbed gas.

After the proper vacuum is obtained the "dead space" around the adsorbent sample and up to stopcock A-1 is then determined with pure helium. To make this dead space determination a volume of purified helium is admitted into the buret B, the stopcock A-1 being closed. The volume of this helium is measured in the following manner:

The level of mercury in the buret is adjusted to the appropriate calibrating mark (number six is ordinarily used) by the use of stopcock (B - 1). The level of mercury in the reference leg of the manometer is set by the use of stopcock (M - 2). Stopcock (M - 1) must be open to the vacuum pump during any run to insure a vacuum over the column of mercury. The pressure on the manometer and the temperature of the buret are recorded. Continuing on the higher mercury levels in the buret (three or four levels are ordinarily used) and recording their corresponding pressures, it is possible to determine accurately the volume of gas at standard temperature and pressure by using the following equation:

$$V_t = \frac{V_f P}{T_b + T_o}$$

Where:

V_t = Total volume of helium admitted in cubic centimeters

V_f = Volume factor of each bulb in the buret in cubic centimeters multiplied by 273/760.

T_b = Temperature of the buret in °C.

T_o = Standard temperature (273.15 K).

P = Pressure for each corresponding calibration mark in mm of Hg.

It is recommended that the volume factor of each bulb in the buret should be obtained for each person who is going to use the apparatus.

After placing the desired bath around the sample bulb (liquid nitrogen at 77 K, water at 25°C and methanol-dry ice at -78°C are baths used), one opens stopcock A-1 and determines the volume of helium left in the buret at equilibrium. The difference between the original volume of helium and that left in the buret is the volume required to fill the dead space to the observed pressure. Dividing this value by the observed pressure the bulb factor, (F_B), which is a constant, is obtained. Such calibration assumes, of course, that helium is not adsorbed but merely fills the space surrounding the adsorbent.

After the dead space and hence the bulb factor is determined, one again evacuates the apparatus to remove the helium and then, after closing stopcock A-1, admits to the buret the adsorbate to be used (nitrogen or carbon dioxide) and measures the quantity taken. The procedure is similar to that which has been described for helium. The stopcock A-1 is then opened and the sample permitted to stand long enough to effect equilibration (a period of time of 30 minutes was kept constant).

In a similar manner as described for helium the level of mercury in the buret is varied and the corresponding pressure, buret and bath temperature are recorded. Three of four points were used for the adsorption branch of the isotherm and only one point for the desorption branch of the isotherm.

The volume of gas adsorbed (referred to S T P) is given by the equation:

$$V_{ads} = V_t - V_r - \left[\frac{\alpha p}{760} + 1 \right] f_B p$$

Where:

V_{ads} = Volume of gas adsorbed

V_t = Total volume of adsorbate that has been admitted to the system

V_r = Volume of adsorbate remaining in the buret at the time of measurement

α = Correction factor required to take into account the gas imperfection of the adsorbate at the temperature of the bath

P = Pressure of the experiment

760 = Standard pressure in mm of Hg

f_B = Bulb factor

Ozonizer. The oxygen-ozone treatments on coal were carried out using a Chemiluminescent NO_x Analyzer made by Thermo Electron Corp., Waltham, Massachusetts. An oxygen-ozone flow of 24 cc/min. was measured using a bubble type flowmeter. The concentration of ozone (2.731% by volume) was determined by passing it through a potassium iodide solution, acidifying the resulting solution with sulfuric acid, and titrating the liberated iodine with standardized sodium thiosulfate.

Furnaces. Two types of furnaces were used: (a) A horizontal quartz tube furnace model HST-112 made by Lucifer Furnaces, Inc., Warrington, PA, having a maximum heating temperature

of 1000°C, and (b) a vertical furnace, Model 119A made by Telrus Technical Products Corp. having a maximum heating temperature of 2,200°F.

Auxiliary Equipment. Steel and quartz boats whose dimensions are 15.5 cm long by 1.6 cm wide and 14.5 cm long by 1.8 cm wide were used. The first one was used for heat treatment up to 450°C. The quartz boat was used for heat treatment at 500°C. A quartz reactor with 48 cm³ of volume was used for treatment up to 1000°C. RGI compact flowmeters plain ends, size no. 1, made by Roger Gilmont Instruments, Inc., were calibrated for nitrogen and oxygen, using a bubble type flowmeter. Two types of thermocouples were used: copper constantan thermocouple for room temperature and low temperature, and a chromel-alumel thermocouple for high temperatures. A Digital Multimeter model 8810A manufactured by The John Fluke Mfg. Co., was used.

Coal Studied. One coal, PSOC-371* was used in the present study. The approximate and ultimate analyses are given in Table II. The original sample was sieved. The -20 to +40 US mesh fraction was selected for pretreatment and the -200 to +250 US mesh fraction was used for the weight gain during preoxidation study.

Gases. Helium, nitrogen and oxygen were obtained from Airco, chemically pure grade. Carbon dioxide was obtained from Industrial Air Products Co., research grade.

*Coal sample and the proximate and ultimate analysis were kindly donated by Pennsylvania State University.

TABLE II

PROXIMATE AND ULTIMATE ANALYSIS OF PSOC-371 COAL SAMPLE

Proximate Analysis	As Rec'd	Dry	DAF†
% Moisture	1.14		
% Ash	16.54	16.73	
% Volatile	30.39	30.74	36.92
% Fixed Carbon	51.93	52.53	63.08

Ultimate Analysis	As Rec'd	Dry	DAF†
% Ash	16.54	16.73	
% Carbon	69.82	70.63	84.82
% Hydrogen	4.53(*)	4.58	5.50
% Nitrogen	1.18	1.19	1.43
% Total sulfur	1.02	1.03	1.24
% Oxygen (Diff)	5.77(*)	5.84	7.01

* Excludes Moisture

† DAF = Dry Ash Free

Hydrogen Peroxide Solutions. A.R. hydrogen peroxide solution was titrated using the techniques given by Kolthoff (33). A concentration of 28.47% (by weight) was obtained. Two diluted solutions were prepared and titrated in a similar manner giving 15.03% and 3.01% by weight. All three concentrations were used.

Pretreatments

Nitrogen Atmosphere, Heating up to 500°C. About 5 grams of coal was spread uniformly into a quartz boat which in turn was placed in the horizontal tube furnace. A flow of nitrogen was passed through at a rate of 100 cc/min. Heating was carried out to the following temperatures: 400, 450 and 500 degrees centigrade at a rate approximately 10°C/min. to the desired temperature. The temperature rise was monitored by the chromel-alumel thermocouple connected in series with the 8810A Digital multimeter. When the desired temperature (500°C) was reached, the system was permitted to stay for a period of time of 4 hours. Then, the system was allowed to cool while continuing to pass nitrogen through the horizontal tube. Finally, the coal was weighed and kept in a small bottle.

Heating up to 600° or 1000°C. About 3 g of coal was placed into the quartz reactor. Nitrogen was passed over the coal at a rate of 100 cc/minute. Heating was carried out at a rate of approximately 20°C/min. to a desired temperature of 600° or 1000°C. The temperature rise was monitored by a chromel-alumel thermocouple (connected in series with the

8810A Digital multimeter) inserted directly into the mass of coal. The system was permitted to stay at the desired temperature of 600°C or 1000°C for a period of 4 hours. Then, the system was permitted to cool while continuing to pass nitrogen through the reactor. Finally, the coal was weighed and kept in a small bottle.

Nitrogen-Oxygen Atmosphere, Heating up to 500°C. About 5 g of coal was spread uniformly into a quartz boat which in turn was placed in the horizontal tube furnace. A flow of nitrogen-oxygen at a ratio of 95%:5% (by volume) was passed through at a rate of 100 cc/min. Heating was carried out at a rate of 10°C/min. to final temperatures of 300, 400, 450 and 500 degrees centigrade. The temperature rise was monitored by the chromel-alumel thermocouple connected in series with the 8810A Digital multimeter. At the desired temperature, the system was permitted to stay for 4 hours. Then, the system was allowed to cool while continuing to pass only nitrogen through the horizontal tube. Finally, the coal was weighed and kept in small bottles.

Oxygen-Ozone Atmosphere. About 1 g of coal was introduced into a U-shaped tube which in turn was placed in a constant temperature bath; a water bath at 298 K and a dry ice-methanol bath at 195 K were used. A flow of oxygen-ozone, at a concentration of 2.731% by volume of ozone, was passed through the coal at a rate of 24 cc/min. During this treatment, the temperature of baths were monitored continuously in order to

see if an abrupt change in temperature occurred. The copper-constantan thermocouple connected in series with the 8810A Digital multimeter was used. The system was permitted to stay in both cases, for a period of 1.5 hours. The exit flow was titrated in order to determine the amount of unreacted ozone. The coal was weighed and then out-gassed using a water pump and stored in a small bottle.

About 4 g of coal was spread uniformly in the quartz boat which in turn was placed in the horizontal tube furnace. A flow of oxygen-ozone was passed through at a rate of 23 cc/min. Temperature was raised to 100°C by heating at a rate approximately 10°C/min. The temperature rise was monitored by the chromel-alumel thermocouple connected in series with the 8810A Digital multimeter. When the desired temperature was reached (100°C), the system was allowed to stay for a period of 1.5 hours. After that the system was permitted to cool while nitrogen was passed through the horizontal tube. The coal was weighed and out-gassed using a water pump and stored in a small bottle.

Hydrogen Peroxide. The soaking vessel was an Erlenmeyer flask of 500 cm³ volume with a condenser. In a typical procedure, 1.5 g of coal and about 150 cc of hydrogen peroxide (3% by weight) were charged into the vessel and this was heated to 85°C while being stirred gently. The coal was kept in contact with the solution until the solution did not give the characteristic color to a KI solution test; then the vessel was cooled and the remaining solution was

removed by filtering. The sample left in the filter was washed with water and dried at 80°C in an oven for 1 hour.

Gas adsorption. Adsorption of nitrogen at 77 K and carbon dioxide at 298 K and 195 K were conducted on every sample pretreated. The equipment and operation have already been described. An arbitrary adsorption time of 30 minutes was allowed for each adsorption point on the isotherm.

CHAPTER III

RESULTS AND DISCUSSION

It is known that most coals go through a plastic stage at about 350 to 450°C and that this change can alter the surface area. Therefore in establishing the influence of oxidation by oxygen-nitrogen mixtures on pore size, it was necessary in every case to run a blank in a stream of an inert gas such as nitrogen. Accordingly, to match the oxygen experiments, blank runs with nitrogen were made at 300, 400, 450 and 500°C. To supplement these observations on the behavior of the coal to 500°C, runs were also made in nitrogen at 600 and 1000°C. The results obtained by heating the sample in nitrogen to 1000°C, and attempts to open the pore structure by oxidation with oxygen, hydrogen peroxide or ozone will now be presented.

Effect of Heat Treatment in Nitrogen on Surface Area. The coal (PSOC-371) was heated in an electric furnace, under an atmosphere of pure nitrogen gas, at 400, 450, 500, 600 and 1000°C. The N₂ flow rate at atmospheric pressure was 100 cc per minute. Qualitatively, agglomeration was observed to occur at 450, 500 and 600°C. Figures 2 and 3 show the BET and the Dubinin-Polanyi (D.P.) plots while Figure 4 shows the variation of surface area and weight loss with temperature

Figure 2. BET nitrogen isotherms at 77 K ($\odot$) and carbon dioxide isotherms at 195 K (Δ). Temperature treatment in nitrogen (PSOC-371).

Figure 3. Dubinin-Polanyi carbon dioxide isotherms at 298 K (O) and 195 K (Δ). Temperature treatment in nitrogen (PSOC-371).

Table III contains the values of surface areas obtained after the above treatment. As may be seen in Figure 4, the surface area increased to a maximum at 600°C and decreased at 1000°C. On the other hand, as the temperature of treatment increased, the weight loss increased as more of the volatile materials were removed.

These results are in good agreement with conclusions drawn by other workers for different coals. For example, it has been found that when coal is exposed to an atmosphere of hydrogen or nitrogen at high temperature, either atmospheric pressure or some higher pressure, rapid and severe fusion of the coal particles cause caking and agglomeration, accompanied by changes in porosity. In fact, Franklin (10) showed from true and apparent density determinations, that the porosity of the char increases when the temperature of carbonization increases above 500°C but that accessibility to larger molecules decreases. Bond and Spencer (37) found that caking coals differ from other coals, the non-caking coals, in that they soften and become plastic within a narrow temperature range (~400°C) and that at higher temperatures a coherent solid mass is produced.

Similar results were found by Chiche and co-workers (11) when they studied the effect of temperature on surface areas of coals during carbonization. They found that a sealing-up of the pores at high temperatures was a general feature for all the coals studied and that a maxima in nitrogen surface areas corresponded to about 750°C. Above 750°C a sharp

Figure 4. Effect of temperature treatment in nitrogen on weight loss (W.L.) and on nitrogen and carbon dioxide surface area. (PSOC-371).

TABLE III
TEMPERATURE TREATMENT IN NITROGEN (PSOC-371)

Weight loss % as Rec'd.	Temperature of treatment °C	Surface Area (m ² /g)*				
		N ₂		CO ₂		
		77K		298K	195K	
		BET	D.P.	D.P.	BET	D.P.
2.00 [‡]	130	1.76	--	90.04	12.5	16.06
8.00 [‡]	300	0.25	--	98.7	19.5	25.4
14.65	400	0.35	0.63	117.9	48.8	63.7
20.60	450	0.46	0.77	247.4	161.2	230.8
22.54	500	0.61	0.81	271.0	271.0	337.0
26.63	600	16.77	20.78	537.2	217.2	272.0
48.33	1000	138.35	186.50	216.8	137.0	178.2

Conditions: Time of the treatment: 4 hours flow of gas
100 cc/min., amount of coal ~5 grams.

* After treatment.

[‡] These values obtained at the start of this
work by Dr. Myrna Klotzkin.

decrease in the nitrogen surface areas occurred and continued up to 1100°C.

From the experimental results, the changes of surface area of heat-treated coal with temperature may be interpreted as follows:

1) The decrease of carbon dioxide surface area, measured either at 298 K or 197 K, at 1000°C probably results from sintering of the carbon structure and closing of some of the pores (11).

2) The increase in either the nitrogen surface area (at 77 K) or the carbon dioxide surface area (at 298 K and 197 K) up to 600°C can be attributed to the removal of volatile materials including processes of demethanation, decarboxylation, and dehydration.

It is of interest to point out that in a nitrogen stream at 600°C, but not at 450°C, a significant increase in the surface area by nitrogen occurred (an increase in the number of pores whose size is 5 Å or greater).

Absorption of Oxygen on Coal. The amount of oxygen absorbed at 250°C was measured by the weight gain during a treatment of the coal sample (PSOC-371) using a 95% N₂-5% O₂ flow at a flow rate of 100 cc/min. for 270 minutes. The results are given in Figure 5. The maximum weight gain was obtained in about 3.5 hours after which a marked decrease in weight was observed.

This result qualitatively agrees with measurements recently reported by Walker and co-workers (12) for different bituminous coals. As pointed out in their paper (12), when

Figure 5. Effect of temperature treatment in nitrogen-oxygen on weight gain (PSOC-371).

coal is exposed to nitrogen-oxygen mixtures "there are broadly two processes which can take place: (1) addition of oxygen to the coal leading to a weight gain and (2) removal of carbon and heteroatoms from coal as volatile oxides, leading to a weight loss." These two processes may be noted in the present work as can be seen in Figure 5.

Effect of nitrogen-oxygen treatment on surface area. The coal (PSOC-371) was heated in an electrical horizontal tube furnace in a stream of 95% nitrogen and 5% oxygen (by volume) at 300, 400, 450 and 500°C. Figures 6 and 7 contain the BET and Dubinin-Polanyi plots and Figure 8 shows the variation of surface area and weight loss with temperature. Table IV gives the calculated values for the surface areas.

Results given in Table IV show that the surface area of the coal, after treatment at 400°C, increased by a factor of 100 when measured by nitrogen at 77 K and by a factor of two when measured by carbon dioxide at 298 K. Therefore, it is reasonable to assume this increase in nitrogen surface area is due to an enlargement of existing pores and to the creation of new pores.

As already mentioned, most of the American coals are highly caking, becoming viscous and plastic when they are heated to a given temperature range which is characteristic for each coal. Much work has been done on the destruction of the caking properties of coal. All methods are based upon the results found by Channabasappa and Linden (35). They found that the caking tendency is destroyed by oxidizing the surface of coal particles. Accordingly, Gasior and co-workers (36)

Figure 6. BET nitrogen isotherms at 77 K (○) and carbon dioxide isotherms at 195 K (Δ). Temperature treatment in nitrogen-oxygen (PSOC-371).

Figure 7. Dubinin-Polanyi carbon dioxide isotherms at 298 K (O) and 195 K (Δ). Temperature treatment in nitrogen-oxygen (PSOC-371).

Figure 8. Effect of temperature treatment in nitrogen-oxygen on weight loss (W.L.) and on nitrogen and carbon dioxide surface areas (PSOC-371).

TABLE IV

TEMPERATURE TREATMENT IN NITROGEN-OXYGEN (PSOC-371)

Weight loss % as Rec'd	Temperature of treatment °C	Surface Area (m ² /g) *				
		N ₂		CO ₂		
		77K		298K	195K	
		BET	D.P.	D.P.	BET	D.P.
11.0	300	0.25	0.37	133.3	58.31	75.7
11.70	400	51.38	71.47	236.7	135.6	169.6
21.00	450	41.62	66.66	261.7	207.8	284.6
28.54	500	46.17	59.0	345.7	274.7	291.5

Conditions: Same as show in Table III

*After treatment

found that when six different samples of coal were heated with steam containing 1% oxygen: (1) expansion of coal during pretreatment was related to the flow of gas (low flow produces less expansion), pressure (high pressure produces less expansion), and volatile matter content (high volatile matter produces more expansion), (2) volatile matter content decreases in treated coal, and (3) the loss in weight is the same as the loss in volatile matter content. Nevertheless, they pointed out that:

The role of oxygen in helping to destroy the caking property of coal is not precisely known. However, it is theorized that the 'sticky' matter normally formed when coal is heated through its softening and plastic range is oxidized to a 'nonsticky' material.

The Bureau of Mines developed a combined thermal and mild oxidation treatment to destroy, in a fluidized bed, the caking properties of typical coals found in the Eastern United States. They kindly supplied us with two samples (Pittsburgh Coal); one untreated and the other treated. We carried out with these samples the same treatment as for the coal (PSOC-371) used in this study. The surface areas obtained for the Pittsburgh coal are given in Table V. It is to be noted the sample as treated by the Bureau of Mines showed no increase in the surface area as measured by nitrogen, whereas those measured by carbon dioxide showed rather large increases. Furthermore, our treatment of their sample at 450°C showed a 150 fold increase in the area as measured by nitrogen at 77 K.

The most recent work published by Walker and co-workers (12), deals with the effect which preoxidation of the caking

TABLE V
SURFACE AREAS OF PITTSBURGH COAL

Weight loss % as Rec'd	Temperature of treatment °C	Surface Area (m ² /g)				
		N ₂		CO ₂		
		77K		298K	195K	
		BET	D.P.	D.P.	BET	D.P.
	*	0.678	0.998	172.78	71.53	92.91
	**	0.692	1.116	284.32	126.41	159.25
27.19	450***	110.37	128.20	384.37	225.60	286.27

* Determination of surface areas for coal sample without treatment

** Determination of surface area for coal treated by Bureau of Mines

*** Determination of surface area after nitrogen-oxygen treatment at a temperature of 450°C.

coal has on the gasification rate of the resultant chars. They pointed out that "preoxidation of caking coals reduces their subsequent fluidity upon heat treatment and leads to the production of chars of higher surface areas. The greater the extent of preoxidation, the greater is the surface area in the char produced." In fact, they found that "the surface area of the char produced following pyrolysis in N_2 increases sharply with increase in the extent of preoxidation given to the coal precursor. Surface area of chars produced from the PSOC-337 and 127 coals oxidized to a weight gain of about 4% are about 12 and 8 times larger than those of the chars produced from the as received coals."

These studies were oriented to obtain treated coals without caking properties as well as to study the effect of any pretreatment on the char; however, no work heretofore has been reported on the surface area of the resulting coal after the pretreatment.

The possible factors that could have affected the degree of the change on coal studied may be: (1) the structure of coal, (2) temperature pretreatment, (3) gas used and (4) impurities present.

From the structure of American coals it can be concluded that almost all the reactive sites are located in the micropore system. Opening of closed pores or enlarging of existing ones can result from the change in concentration of the reactive sites. As heating proceeds, diffusion of the gases to reactive sites increases as well as the diffusion

products formed. Obviously, that diffusion depends also on the kind of reactive gas. As already mentioned inorganic impurities can act as catalysts. Their activity can change depending upon the atmospheric conditions as well as their chemical and physical state.

Finally, a heat-controlled oxidation at temperatures in the range 300-400°C may be a promising approach for further work on other coal.

Effect of Ozone-Oxygen Treatment on Surface Area. Nobody, to our knowledge, has reported the use of ozone-oxygen mixtures as a reactive gas. We have carried out this pretreatment in order to determine whether pore enlargement can take place. At low temperature, we were expecting that ozone would attack the 5 Å pores or bottlenecks thereby creating a more accessible and reactive pore structure than possessed by the original coal.

As already mentioned the treatment was carried out at -78°, 25° and 100°C using the flow of ozone-oxygen mixture produced by the ozonizer. Figures 9 and 10 show the BET and Dubinin-Polanyi plots and Table VI gives the values of the surface areas as well as the variation in weight. It is interesting to point out that the weight gain rather than a weight loss was obtained both in the ozone-oxygen pretreatment at 25°C and also in the pretreatment at 250°C. In the ozone experiments no pore change as measured by nitrogen at 77 K was obtained although a small increase in the carbon dioxide surface area was observed.

Figure 9. BET nitrogen isotherms at 77 K (○) and carbon dioxide isotherms at 195 K (Δ). Temperature treatment in ozone-oxygen (PSOC-371).

Figure 10. Dubinin-Polanyi carbon dioxide isotherms at 298 K (●) and 195 K (▲). Temperature treatment in ozone-oxygen (PSOC -371).

TABLE VI

TEMPERATURE TREATMENT IN OZONE-OXYGEN (PSOC-371)

Weight % Gain/Loss as Rec'd	Temperature of treatment °C	Time (hr)	Surface Area (m ² /g)				
			N ₂		CO ₂		
			77K		298K		195K
			BET	D.P.	D.P.	BET	D.P.
0.35(gain)	-78	1.5	0.63	0.93	112.60	17.05	21.64
0.16(gain)	25	1.5	0.68	0.96	147.36	2.62	3.58
0.98(loss)	100	1.5	0.76	0.98	191.34	8.17	10.96

Conditions: Time of treatment 1.5 hours
 Flow of gas 24 cc/min
 Amount of coal 1.5 grams

Effect of Hydrogen Peroxide Solutions on Surface Area. A

great deal of work has been done in recent years on the use of various solvent and liquid treatments of coal to help in liquefaction or beneficiation processes. Only a few, however, have reported the change in surface area induced by these liquids (28, 29, 30, 31, 34).

Among the many solvents examined in coal extraction work, hydrogen peroxide has been used to extract the organic portion of coal and leave a residue of quartz, clay minerals and other insoluble species (38).

We initiated a study of hydrogen peroxide as a reactive solvent in order to modify the pore structure of coal particularly with respect to enlargement of narrow pores. The selection of hydrogen peroxide as a solvent was based upon the amount of oxygen liberated when extraction is carried out at a temperature of about 85°C. Treatments were carried out using three different concentrations (about 3, 15 and 30% by weight), and at a constant temperature of $85 \pm 3^\circ\text{C}$. The time of extraction was 7, 3.5 and 4 hours for the above solution respectively. Figures 11 and 12 show the BET and Dubinin-Polanyi plots. Table VII gives the values of the surface areas obtained. From these results it was concluded that no significant change in surface area was attained.

Conclusions

1. Surface areas of chars obtained by heat treatment temperature first increase, then decrease somewhere above 600°C.

Figure 11. BET nitrogen isotherms at 77 K (○) and carbon dioxide isotherms at 195 K (△). Hydrogen Peroxide treatment (PSOC-371).

Figure 12. Dubinski-Polanyi carbon dioxide isotherms at 298 K (○) and 195 K (△). Hydrogen peroxide treatment (PSOC-371).

TABLE VII
HYDROGEN PEROXIDE TREATMENT

Extraction Conditions			Surface Area (m^2/g)				
Time (hr)	Temp. ($^{\circ}\text{C}$)	Concentration (% by weight)	N_2		CO_2		
			77K	298K	197K		
			BET	D.P.	D.P.	BET	D.P.
7	85	3.01	2.61	3.32	115.51	23.08	33.54
3.5	85	15.03	1.06	3.56	123.87	21.00	26.0
4	85	28.47	0.88	1.40	193.48	27.53	36.0

2. At temperatures of 250°C and below, coal picks up oxygen and presumably becomes non-caking.
3. Treatment temperatures of 300°C in an oxygen-nitrogen mixture develops no new surface area capable of being measured by nitrogen at 77 K although the carbon dioxide surface areas do increase.
4. Treatment at a temperature of 400°C in an oxygen-nitrogen mixture results in a nitrogen penetration at 77 K being increased by a factor of 100.
5. Bureau of Mines pretreatment with oxygen does not appear to increase the nitrogen surface area.
6. Neither treatment with 3 to 30% by weight of hydrogen peroxide at 85°C nor treatment with ozone-oxygen at -78°C to 100°C seemed to alter pore size or cause much attack on coal.

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