THE EFFECT OF PREOXIDATION ON THE COKING PROPERTIES OF PENN-LEE COAL

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INTRODUCTION

Coal is one of the world's largest remaining mineral resources. The supply of this rich source of fuel and chemicals is sufficient to serve the world for several thousand years. Coal is used directly and is also heat treated at high and low temperatures to produce fuel and by-products. Of the several methods of treatment that can be used, low-temperature carbonization is one of the most promising.

Nearly all of the coke and coal chemicals produced today come from the production of high temperature coke. However, there are many lower rank coals not suited for metallurgical purposes that will produce an excellent char and high yields of by-products. One of the disadvantages of many lower rank coals is their tendency to swell and become plastic when heated to carbonization temperatures, and this property has to a great extent made the operation of the retorts difficult.

In an effort to reduce or circumvent this undesirable property, several methods of pretreating the raw coal have been tried including preoxidation, dilution with non-coking coal, preheating, and weathering. The type and severity of the pretreatments vary in their effects on the coking properties of different coals.

The purpose of this investigation was to study the effect of preoxidation on the coking properties and the quantities and composition of the by-products and char obtained from the low-temperature carbonization of Penn-Lee coal.

II. LITERATURE REVIEW

In this section will be found a survey of the literature to obtain information concerning the pretreatment of coal for carbonization. Included in this section also is information pertinent to preoxidation and its effect on the quantities and compositions of the products resulting when the pretreated coal is carbonized at low temperatures.

The Evolution of Low-Temperature Carbonization

This section contains a summary of the evolution of low-temperature carbonization, its inherent problems and its advantages over other types of carbonizing processes.

The Beginnings of Carbonization. England was the scene of the first historically recorded account of the destructive distillation of coal. Clayton (17) dug coal from beneath a dammed-up creek bed and distilled some of it in a retort over an open fire obtaining a black oil and non-condensable gas. In the year 1619, mention was made of the fact that certain coals after "charking" would outperform charcoal; however, there was no mention of any tars or gases being collected.

From 1700 on, the carbonization industry grew until in the year 1895, in the United States, the first oven for the production of carbonization products was reported. It soon became apparent that the gaseous and liquid products of coking were valuable. It was also known that the lower the temperature of carbonization the greater the yield of liquid and smaller the yield of gaseous products. These facts led to the development of the modern low-temperature carbonization processes that operate at temperatures from 700 to 1500 °F.

One of the many problems confronting designers was the fact that many of the high volatile coals most suitable for low-temperature carbonization became soft and plastic when heated to about 750 °F. These coals, in many cases, also tended to swell considerably, sometimes to as much as nine times their original volume if unrestricted.

Types of Pretreatment.

Of the many ways that coals have been pretreated, preheating, preoxidation, solvent extraction, and dilution are the more important methods and each will be discussed briefly below.

Preheating. An investigation was conducted by Parr (37) and his associates wherein samples of an Illinois coal were preheated at temperatures ranging up to 566 °F and then charged into a retort maintained at a temperature of 1293 to 1383 °F. The results of this investigation purported to show that the coking properties were reduced due to a rapid carbonizing reaction which was aided by the exothermal reactions of carbonization. It is quite possible, however, that this conclusion could lead to false assumptions since many coals have some endothermic heats of carbonization (14).

Even though the reasons are not clear, it is known (10) that preheating of the coal in an inert atmosphere will, to some extent, reduce the coking properties of most coking coals. Warren (42) suggests that the existance of a majority of large molecules formed during preheating could reduce the coking properties of the coal in question.

Pretreatment by Solvent Extraction. The treatment of coal with solvents for extracting certain constituents has been studied (9). Polar solvents such as phenol, and aniline gave greater yields than non-polar solvents such as benzene and tetralin. Berl and Koerber (27) found that certain solvents were preferential for certain coal constituents. Phenolics, for example, are preferentially removed from coal by ketones. The removal of these phenolic compounds lowered the coking properties of the coal and suggest the possibility that solvent extraction might be an efficient method of pretreating coal.

Dilution with Non-Coking Materials. In an effort to minimize the effects of a strongly coking coal, attempts have been made to operate carbonizing retorts in which the coking coal was diluted with a non-coking coal, a char or coke, and anthracite. The success of these attempts have been questionalbe since it was impossible to obtain a uniform char or coke.

Pretreatment with Oxygen. Treating the coal to be carbonized with air or oxygen is another way of altering the coking properties of a coal. The pretreatment is carried out at temperatures up to the ignition point of the coal, therefore, the change in coking properties is also partly due to the preheating effect. The act of preoxidizing the coal also alters the quantities and composition of the products obtained from carbonization (18).

The English investigators, Barrett and Reilly (11), studied a Durham coal by heating it for two hours at 572 °F and at the end of this time it had not lost all of its coking powers. In another part of this investigation, samples of coal were heated to 374 °F in a current of oxygen which was analyzed for carbon monoxide, carbon dioxide, and water. The oxygen content of the gas used in the test ranged from 1.18 to 47.15 per cent, and the duration of the tests ranged from 0.5 to 115 hours. These pretreated samples were than carbonized at 1112 °F and the products analyzed to determine the pretreatment effects. It was found that the gas yield increased linearly with the amount of oxygen added to the coal. The hydrocarbons and hydrogen evolved decreased and the carbon monoxide and carbon dioxide evolved increased as the preoxidation became more severe. The increased used of oxygen caused the tar yields to decrease from 17.2 to 3.3 per cent while the coke yields remained essentially constant.

In general, the coking properties of a coal can be modified by preoxidation with the result that there will be a decrease in the tar yields and an increase in the gas yields.

The Oxygenation of Coal

The oxygenation of coal will be discussed in this section. Included in this discussion will be topics concerning the effect of the severity of oxygenation on the coal and carbonization products, the mechanisms by which oxygenation is accomplished, the kinetics of the reaction, how oxygenation affects the properties of coal.

The Composition and Structure of Coal. It is necessary to understand something of the physical makeup of coal before attempting to study its reactions with oxygen. Coal is essentially a mineral rock composed of organic matter whose chronological evolution is shown in Figure 1, page 9. There are many theories concerning the manner in which coal was formed but that problem will not be considered here.

Kreulen(27) and his coworkers have outlined their theses about the structure of coal. These theses are (1) an organosol is the name applied to that part of coal that can be extracted with an organic solvent and is usually called coal bitumin; (2) this bitumin or organosol consists of two phases, an oily phase acting as the dispersing medium and a dispersed (micelle) phase; (3) the micelle phase consists of two parts, an oleophilic (protective) part and an oleophobic (nucleus) part.

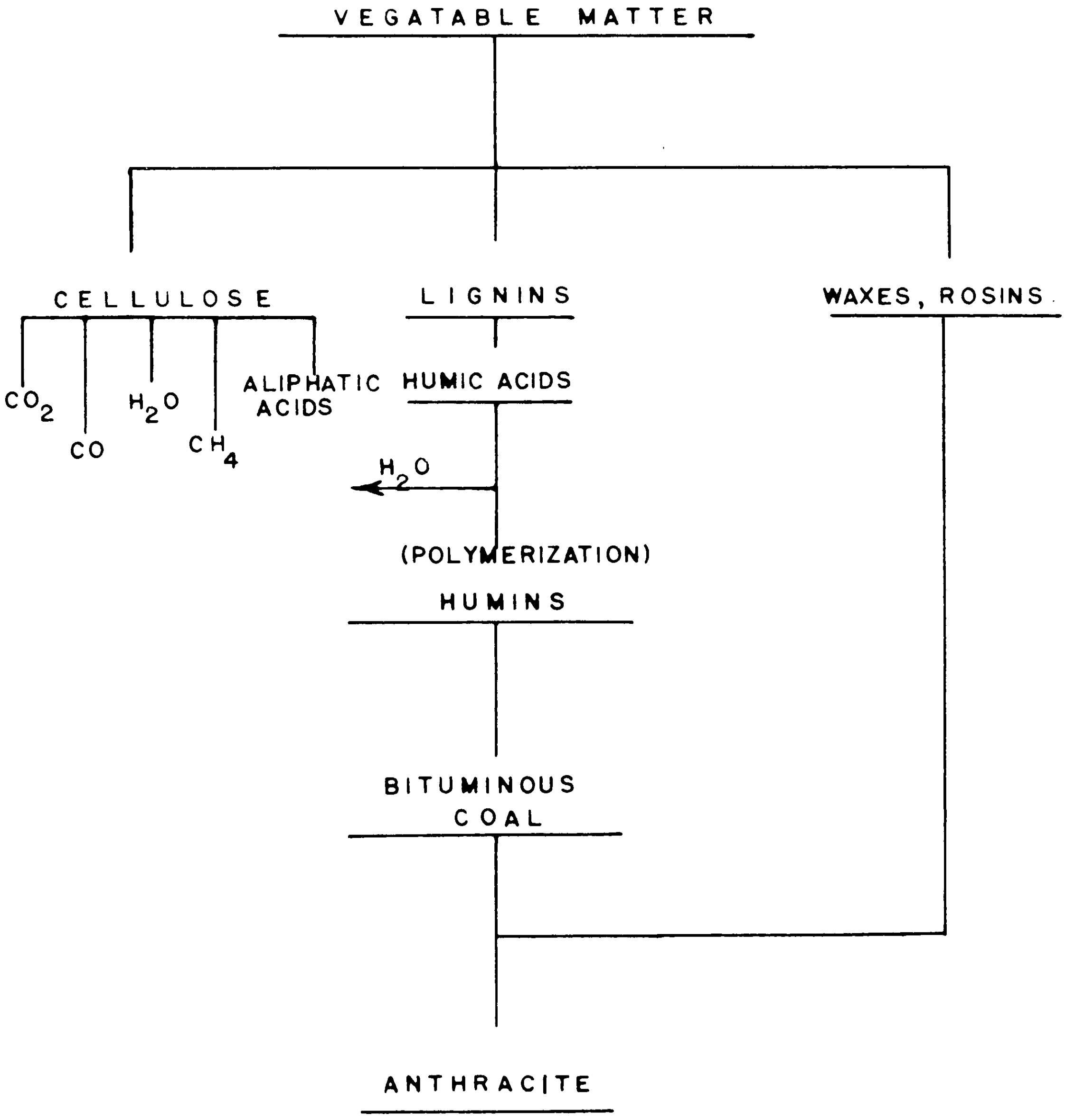

FIGURE NO. 1 **HUMIC COAL FORMATION**

KREULEN, D.J.W., "ELEMENTS OF COAL CHEMISTRY" P 67.
NIJGH & VAN DITMAR N.V. ROTTERDAM, 1948.

The micelle phase consists of a nucleus surrounded by an oily protective layer; (4) the oily layer consists of bitumins and the nucleus of humins; (5) bitumins are mixtures of organic compounds that are soluble in organic solvents and they are derived from humic acids; (6) the structure of the bitumins is highly similar to that of the humic acids and the humins but they lack most of the OH and COOH groups found in the parent compounds and there is evidence of cyclic-bound oxygen; (7) the protective coating on the micelle nucleus is held so tightly that it is apparently impossible to separate it with an organic solvent. It is suggested that the micelle nucleus is difficult to separate because the humin complexes are locally oleophilic causing them to unite with the bitumins to give one apparent complex masking the properties of the humins. A proposed model of the humic acid molecule and how it is formed is shown in Figure 2, page 11. This model as presented is based on certain experimental evidence by Fuchs(28) showing that the average humic acid molecule has a molecular weight of about 1400 with four COOH groups, four OH groups, two cyclic oxygens. Kreulen,(29) however, does not entirely agree with this model saying that there are probably more oxygenated rings in the molecule. The results of this investigation indicate

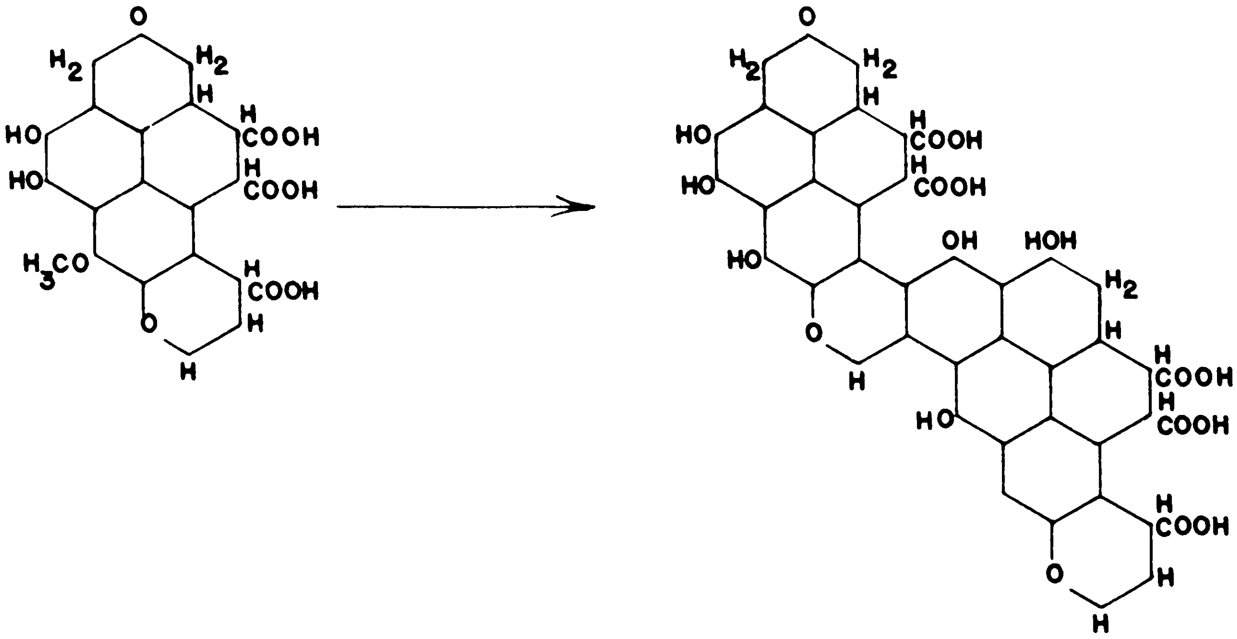

FIGURE NO. 2 STRUCTURE OF A TYPICAL COAL MOLECULE

KREULEN, D. J. W., "ELEMENTS OF COAL CHEMISTRY." P 54. NIJGH & VAN DITMAR N.V. ROTTERDAM, 1948.

that there are approximately 2.75 rings per molecule, 40 per cent by weight napthenic rings, 60 per cent by weight paraffinic side chains, and 5 tertiary carbon atoms per molecule.

Orchin (36) states that the available evidence seems to indicate that coal is a "polydisperse" system containing molecules varying over a wide range of molecular weight. This statement is in general agreement with Kreulen; however, Orchin presents his conception of what the average coal molecule might look like in Figure 3, page 13. This molecule is based on the indene structure which is present in many of the compounds found in coal tar.

It is interesting to note that many of the investigators think of the coal molecule as a polymer. The term "polymer" may be somewhat misleading; although many of the mechanisms of coal chemistry can be explained on this basis, the mechanism that usually takes place is more nearly a condensation or fusing of two or more molecules with the formation of by-products.

Higuchi and Shibuya (22) attempted to arrive at the formula for humic acid through a series os methylation studies using a Na^+/H^+ exchange reaction. Their results

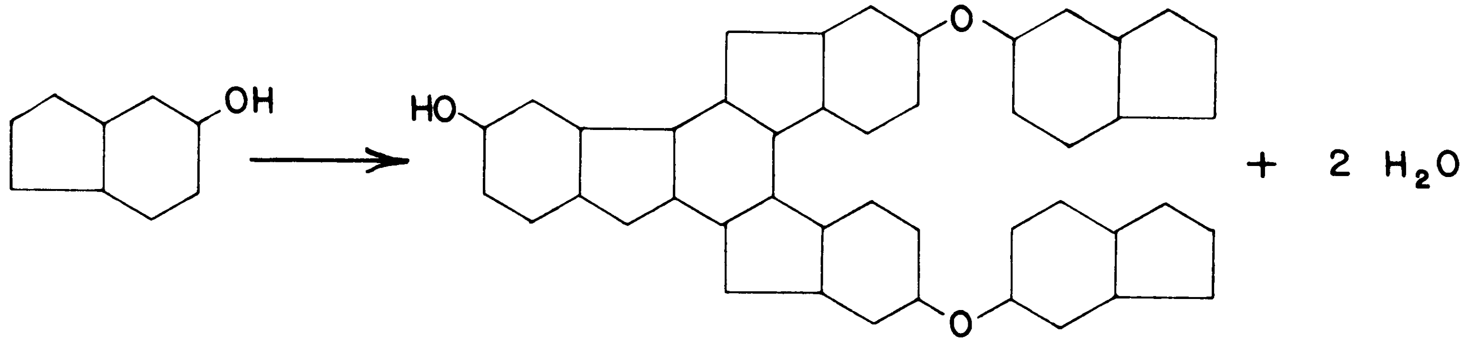

FIGURE NO. 3 STRUCTURE OF A TYPICAL COAL MOLECULE

ORCHIN, MILTON. THE CHEMICAL STRUCTURE OF COAL, OHIO STATE UNIVERSITY ENGINEERING EXPERIMENT STATION NEWS. 25 NO. 5, P 25–31. (1953).

give the methylated humic acid the formula, $C_{204}H_{161}O_{16}N_3(COOH)_8(OH)_{11}(CO)_6(OMe)_3$. They say that if it can be assumed that each of the COOH, OH, CO, and OMe groups replaced a H atom and a lactone ring replaced 2 (H) atoms, then the molecular formula for humic acid would be $C_{204}H_{211}O_{16}$, if any nitrogen is neglected.

Other Japanese investigators, Sakabe, Inoue, Ouchi, and Honda (40), studied the structure of bitumins and pseudo-bitumins by extracting the bitumins from coal with benzene and studying their structure. These men reached the conclusions that (1) all of the bitumins extracted from the coal had essentially the same structure as the humins remaining in the coal; (2) the bitumins are of aromatic structure with condensed rings varying from one to several with an average of three to four, these rings contained alkylic peripheries as well as partially hydrogenated rings; (3) several of these units composed a stable state "polymer" whose average molecular weight was in excess of 1000; and (4) there was oxygen present which would bridge the units forming apparent coal molecules.

Labari (35) writes that the structure of coal is believed to consist of three phases, α,β,γ, of a mixed isogel of the nonhardening type having a definite gel temperature; the relation between the dispersing and dispersed phase is governed by surface active forces.

A Russian investigator, Aronov, (8) states that the basic structural unit of coal is a macromolecule which is a combination of many smaller molecules all of a similar structure but which have been "polymerized" to different degrees. The whole structure consists mainly of six-membered rings forming a condensed polycyclic structure surrounded by a layer of side groups. It was stated that the nucleus had a much higher resistance to chemical attack and heat than the fringe groups which were easily broken or removed by heat.

The literature on the structure of the coal molecule can be summarized as (1) most coals, except those of waxy origin or the boghead coals, are of humic origin; (2) most investigators based their theories on the premise that humic acid is the parent compound; (3) the properties of the humic acids are determined chiefly by the number and placement of the <u>COOH</u> and <u>OH</u> groups and the humic acids are characterized by the presence of a large number of these groups. At the opposite end of the scale (see Figure 1, page 9) lie the bitumins which, although structurally similar to the humic acids, do not have nearly as many of the <u>COOH</u> and <u>OH</u> groups. The bitumins are characterized by the fact that they are the only humic acid derivatives soluble in organic solvents. In the center of the scale lie the humins which contain fewer COOH and OH groups than the humic acids but more than the bitumins. They are similar to the humic acids in that they are soluble in aqueous alkali solutions but not in organic solvents. The coal molecule is probably a complex molecule composed of many fused or condensed rings. These rings are probably condensed using oxygen in the majority of cases to effect the linkage. It is probable that coal is colloidal in nature with the oleophilic bitumins being the dispersing phase, and the oleophobic micelle structure being the dispersed phase.

The Mechanisms of Oxygenating Coal. If coal is subjected to a stream of air or oxygen, it will begin to absorb oxygen. The purpose of this section is to review the literature with regard to this phenomenon.

Higuchi, and Shibuya (23) investigated the oxidation of humic substances using wet air. Analysis of the non-volatile coal after the tests showed that various peroxides appeared as unstable intermediates during the oxidation. Furthermore, they concluded that most of the active groups containing oxygen, which were formed by the decomposition of the peroxides, are immediately decomposed to form water. The C/H ratio increases with temperature. The oxygen added increased and reached a saturation value as the reaction proceeded; and the saturation value was higher, the greater the temperature. The increase in oxygen in the coal was always greater than the increase of acidic groups in the coal. In the coals studied in this investigation, there was no appreciable decrease in weight observed at temperatures below 338 °F and the humic acid content of the coal could reach 80 per cent at any temperature between 302 and 392 °F.

Yamasaki(48) studied the reaction of coal with oxygen. In his investigation, various types of coal were crushed and treated with oxygen, in varying amounts. The results of this study were that oxygen is taken up by the coal in two ways, one being very rapid and becoming nearly complete in a few hours, and the other being very slow to complete, taking nearly a month. Bituminous coal is typical of the first reaction and lignite of the second. The rate at which the reaction proceeds is dependent on the temperature and is given by:

$$\log (x) = b\, t + c$$

where:

x = cc of oxygen consumed/gm of fresh coal

b = constant

c = constant

This equation is good only between 86 and 212 °F. The failure of this equation to apply outside of this temperature range is explained by the adsorption of oxygen by Van der Waal's forces below 86 °F and by decomposition, with the evolution of carbon dioxide, above 212 °F.

Kamiya (24) studied the air oxidation of coal, its reaction velocity and mechanisms in a fluidized bed and came to the conclusions that (1) the properties of the products differed considerably over the temperature range; (2) the formation of humic acid reaches a maximum within 60 minutes at a definite temperature. The investigation was carried out over a temperature range of 392 to 572 °F.

Georgiadis and Gailliard (20) made studies of the air oxidation of coal at temperatures ranging from 302 to 482 °F and concluded that (1) the oxidation of coal is a heterogeneous process being affected by the duration of exposure, the temperature at which the reaction is carried out, diffusion, and the nature and fineness of the fuel; (2) no matter what the conditions of oxidation, the CO_2/CO ratio of the gaseous decomposition products remains nearly constant throughout the reaction; (3) after varying times, the coal molecule reaches a state of saturation characterized by a limited content of fixed oxygen; (4) the velocity of the addition of oxygen is dependent on two consecutive reactions, (a) a reaction of zero order for which the velocity coefficient depends on the nature of the coal, and diffusion, and follows Arrhenius's law between 302 and 482 °F, (This reaction represents the formation of intermediate complexes of carbon and oxygen.), and (b) a reaction of the first order in which the velocity coefficient is independent of diffusion and the nature of the coal but depends on the oxygen content of the coal and to a lesser extent on the temperature (This reaction represents the decomposition of the carbon-oxygen complexes.); (5) the apparent continuous variation of the activation energy and the progressive modification of the ratio $(CO + CO_2)/H_2O$ are the indexes of the continuous variation of the oxidation process as the reaction progresses. The mechanisms of the oxidation of coal have been studied rather extensively by Kreulen and others. Kreulen(30) has reached the conclusion that coals of low rank are oxidized directly to humic acids, but that coals of high rank are oxidized through an intermediate stage. Through studies of the activation energies required for these reactions, it seems probable that, for coals of intermediate rank, both mechanisms are present and the relative degree to which each mechanisms present depends on the rank of the coal. For a middle rank bituminous coal such as Penn-Lee coal, it is likely that both mechanisms play a large part in the oxidation of the coal.

Kreulen (29) uses the following method to determine the oxidizing mechanism. Data were collected giving the amount of humic acids formed when the oxidation reaction had been allowed to proceed for as long as three hours, at constant temperatures up to 500 °F. In order to determine the number of stages in the reaction, the data are plotted on logarithmic paper with the amount of humic acids formed plotted versus the time required for their formation. These plots resulted in straight lines, their slopes indicated the number of stages through which the reaction progressed. The equations for these lines when using consistent units, are:

$$\log C_H = b + 2 \log(t) \text{ or } C_H = k' C_A t^2$$

where:

C = concentration,

H refers to humic acid,

A refers to oxidizable humins.

The plots of this data indicated a two stage mechanism for high rank coals and a single stage mechanism for low rank coals.

Although Kreulen does not mention the fact it is obvious from studying Corrigan's (13) work that Kreulen must have assumed that the reactions which he studied were either of the first or zero order, otherwise his method for determining the number of stages would be erroneous. This assumption may have been correct since Georgiadis and Gailliard report the first step to be zero order and the second step first order.

The conclusion is that for a mid-rank coal, that both mechanisms proceed simultaneously in the following manner:

(1) oxygen + humins → intermediates
intermediates + oxygen → humic acids.

(2) oxygen + humins → humic acids

It is possible to infer from the preceding discussion that coalification of humic acids represents two separate processes, a continual reduction of the humic acids, and a continual degradation of the reduced acids. It is also possible to reason that the oxygen preferentially attacks the bitumin, (dispersing phase) in the coal causing these molecules to become heat sensitive. Further, it can be argued that the evolved gases during oxygenation are due primarily to the destruction of the more heat sensitive side chains. These observations now lead to a discussion of the coking and agglutinating properties of coal and how these properties may be modified.

The Effect of Oxygen on the Coking Properties of Coal. From the preceding discussion it appears that the addition of oxygen will considerably change the chemical properties of the coal molecules. With these chemical changes in mind, the review of the literature will turn to the effects of oxygen on the physical properties of the coal molecule. It has been generally agreed that coal is colloidal in nature, and it is probable that the fluid properties of the coal will be largely determined by the fluid properties of the dispersing phase.

To summarize briefly, these general statements can be made for most coals (1) the agglomerating properties of most coals tend to decrease as coalification, or rank increases(5); (2) the C/H ratio for most coals increases with rank; and (3) the volatile content of coal decreases with increasing rank(5). These generalities will help to explain the plastic behavior of coal.

Kreulen(33) studied coals in various stages of coalification and observed that the average molecular weight, the softening point, the melting point, and the viscosity of the bitumins decreased as coalification progressed. He attributes this to a simplification of the molecule caused by the splitting off of the paraffinic side chains. He also postulates that many of the side chains result from the degradation of oxygen-containing heterocyclic rings which in addition liberates the large quantities of carbon monoxide and carbon dioxide that have been detected.

A possible explanation for the reduced agglomerating properties of coals of high rank would be that the higher C/H ratio results in a coal molecule more crystalline in nature and hence less susceptible to melting. Aranov(8) explains the caking of coal as chemical changes taking place inside the macromolecule. These changes result in the tearing away of the side groups that are changed into a liquid phase which undergoes thermal condensation simultaneously with the nuclei of the macromolecules, with one another, and with the hydrocarbons of other side groups. Volatile matter is formed by thermal action on the broken side groups. It follows that the caking properties and the formation of liquids and gases are dependent on the quantity and type of the side groups present on the molecule.

Kamiya (25) studied the effect of air oxidation on the caking power of certain coals. The reactions were studied over a temperature range of 392 to 572 °F. He found that the caking property of Miike coal decreases to a constant value (as determined by the button test) within the first twenty minutes above 464 °F, but more than one hour was required at 428 °F, and very little decrease in button index was observed at a temperature of 365 °F. Kamiya also reports that the amount of humic acid formed within one hour reacted a maximum at any definite temperature. This investigator also studied the kinetics of oxygenation and concluded that the rate equation (assuming that the rate controlling step is the reaction itself) for the caking reaction was given by:

$$R-r = kt$$

where: All units are consistent, and

R=the original radius of an unreacted sphere of coal,

r=the radius of the sphere of the unreacted part at time (t)

t = time

k = a constant.

This rate equation is said to be substantiated by the relation:

$$\frac{t_1}{t_2} = \frac{R_1}{R_2}$$

The activation energy for this reaction is reported to be 18 kilocalories per mol, for the Miike coal.

Takeya and Kugo (41) report that the condensation (polymerization) reaction was predominant at temperatures up to 572 °F and the dispersed humic substances appeared increasingly only above temperatures of 622 °F with the evolution of gases. It was observed that this increase did not occur in a non-coking coal.

Kugo (34) investigated the chemical changes occuring in coal at temperatures below the plastic state and concluded that condensation has very active below 572 °F. Since water was the only gas evolved, condensation must represent the reaction due to dehydration occuring among molecules with oxygen-containing outer groups. Kugo further states that, since most of the oxygen was removed by heating the coal to the plastic state, the resulting reduction in coking ability must have been the result of condensation brought about by deoxygenation.

The review of the literature concerning the effect of oxygen on the coking properties indicates that following situation exists. The addition of oxygen to the coal causes the following things to happen: (1) the oxygen enters the bitumins and forms additional acidic groups on the side chains; (2) the presence of the oxygen renders the side groups more unstable to heat, and since heat is usually applied to effect the oxidation, there is a simulatneous oxidation and degradation of the side chains to form gases and liquid products. Not all of the oxidized groups are completely decomposed, however, for the oxygen remaining on the coal molecule apparently undergoes a condensation with other similar molecules to form a sort of polymer. It is the formation of these polymers that destroys the ability of the coal to become plastic at elevated temperatures.

One investigator (33) separated the bitumin and humin parts of the micelle structure and studied their properties. It was found that the humins were extremely active relative to their swelling characteristics. It was found that the humin content of the micelle structure would swell to twenty-five times its original volume when heated.

The Carbonization of Coal. Several Japanese investigators (26) studied the thermal decomposition of coal in an atmosphere of nitrogen. They reported that their best yields of tars and liquids were obtained at temperatures of 752 to 842 °F. The primary gas yields up to 662 °F were carbon monoxide and carbon dioxide which indicated that at temperatures below 662 °F a recarboxylation was taking place with the desorption of oxygen. At temperatures above 662 °F considerable amounts of paraffins appeared in the gas with a maximum occuring at about 842 °F.

Yoshikawa and Hirota (49) attempted to determine the source of the hydrocarbon gases evolved during carbonization.

They heated samples of coal in a vacuum and identified the following gases as shown in Table I, page 28. These workers concluded that these hydrocarbons were not formed by heating but were occluded when the coal was formed. The argument is that the amount of gas evolved decreases with an increase in temperature up to the temperature at which tar is given off.

TABLE I

An Analysis of Gases Occluded in Coal (1)

Gas	Quantity Volume Per Cent at 342 °F	Quantity Volume Per Cent at 525-662 °F
CH_4	0.5	32.8
C_2H_6	1.8	18.0
C_3H_8	5.7	4.8
C_4H_{10} and isomers	21.0	5.0
C_2H_4	0.0	0.9
C_3H_6	2.6	1.2
C_4H_8 and isomers	5.5	4.5
C_5H_{12} and isomers	3.1	2.8
C_6H_6	8.5	0.2
CO	2.5	6.0
CO_2	36.0	9.0
H_2S	0.0	2.0
O_2	0.0	0.0

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(1) Yoshikawa, Y and H. Hirota. Gases Evolved by Heating Coal in Vacuo at Low Temperatures. Bulletin of the Applied Research Institute, 5, p. 123 (1953); C.A., 48, 14,160 (1954).

Applications of Statistics

Statistics can be used to aid an engineer in several ways. First, he can design his experiments so that the maximum amount of information may be obtained from them and secondly, he can use statistical techniques to analyze and correlate his results.

Factorial Experiment. An experiment can be designed so that several variables can be studied in the same experiment. For each variable, a number of categories or levels may be chosen for study. If observations are made for all possible combinations of levels selected, the experiment is called a complete factorial experiment (15).

The "F" Ratio (18b). The "F" ratio is defined by the equation

$$F = S_1^2/S_2^2$$

where S_1^2 and S_2^2 are the variances of random samples one and two, respectively. There are also two sets of degrees of freedom, $N_1 - 1$, and $N_2 - 1$, where N_1 and N_2 are the number of observations in the first and second samples.

In making use of the "F" ratio, the availability of tabulated "F" distributions (16) is implied. Three values are needed to enter the table, namely, the appropriate percentage level, the number of degrees of freedom in the numerator, and the number of degrees of freedom in the denominator. A complete explanation of the use of the "F" statistic can be found in many standard statistics testbooks (17).

Analysis of Variance. The analysis of variance is a procedure for testing for significant differences among two or more means. The analysis of differences in means is based upon the fact that if the apparent difference in two variances being compared is large, the apparent differences in the means will be declared to be real (16). For a more thorough introduction into the mechanics and basic theory of analysis of variance, the author would suggest any available statistics textbook (17).

Vapor-Phase Chromotography

Vapor-phase chromotography is a promising new method for analyzing gases and liquids boiling up to approximately 572 °F. The principles of vapor-phase chromotography and applications will be discussed in the following paragraphs.

Chromotography. Chromotography is a descriptive word for the process of separation, by differential sorption of solution, of the components of a flowing mixture, with respect to a stationary solid or liquid medium. Various forms of chromotography exist: (1) liquid chromotography in which the mobile phase is solid and the stationary phase is either solid, or an immiscible liquid supported by an inert solid, and (2) vapor-phase chromotography, in which the mobile phase is gaseous and the stationary phase is either solid or a non-volatile liquid supported by an inert solid. This discussion will be limited to vapor-phase chromotography.

Means of Separation. The two general mechanisms used to separate the components of a sample in a vapor-phase chromotographic column are (1) differential absorption and (2) differential solution or "partition". The apparatus and techniques are essentially identical, differing only in the choice of materials used in the chromotographic column. Activated forms of charcoal, molecular seives, alumina, or silica gel are commonly used in absorption columns, while an inert solid coated with a non-volatile liquid is used in partition columns.

Apparatus and Techniques for Vapor-Phase Chromotography. A simplified diagram of an elution analysis apparatus (38) is shown in Figure 4, page 31A. The essential items in the apparatus are the carrier gas, the pressure controller, the chromotographic column, and the detector.

Carrier Gases. Three gases have been most often used by the researchers in this field: namely, nitrogen, helium, and hydrogen. The fact that all the eluted

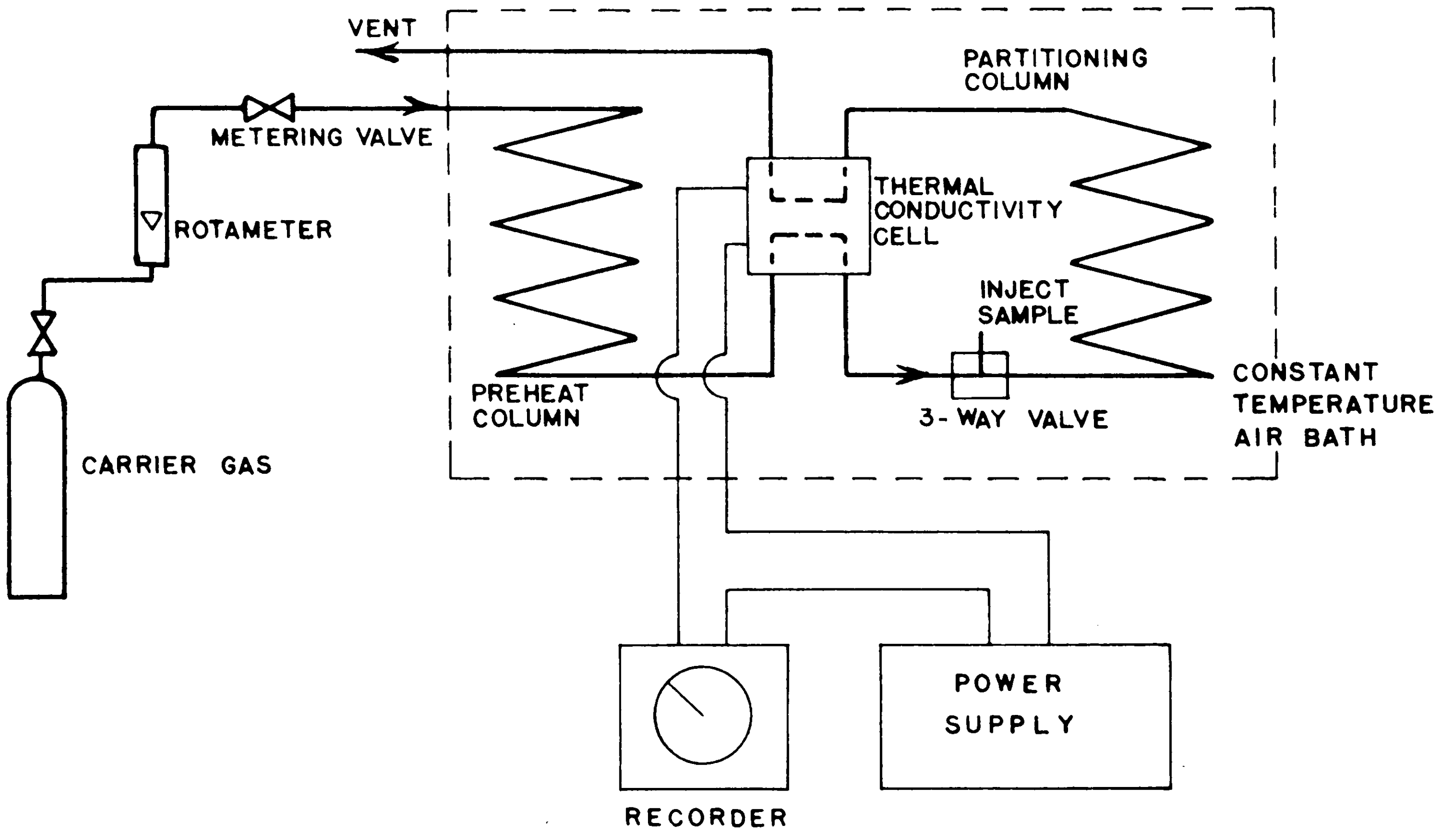


FIGURE NO. 4 SIMPLIFIED FLOW DIAGRAM FOR A LIQUID-VAPOUR CHROMATOGRAPH components have lower thermal conductivities is an advantage as all peaks will appear on the same side of the base line.(38)

Chromotographic Column. The columns in general use vary from three to fourteen feet in length, and are made from copper, stainless steel, or glass. The solid material used as packing is usually 40-mesh or finer.

Partition Agents. Previous investigators have used a number of liquids(36) such as normal dodecane, dinonyl phthalate, benzyl diphenyl, hexatriacontane, tri-isobutylene, silicones, glycerol, liquid paraffin, and others. The main criteria for a liquid to partition high boiling liquids is a low vapor pressure. Higher column temperatures are required to analyze high boiling components, however, the column temperature may be 50 to 100 °C below the boiling point of the component.

Detectors. Various methods of detecting the concentration of components in the gas leaving the column have been used including thermal conductivity, measurements, gas density (flow impedance bridge)(38) surface potential(21), infra-red spectrometer, and titration where eluted substances exhibit acidic or basic reactions. Typical designs are described by Ray and Patton(38).

Analysis of Non-Hydrocarbon and Light Hydrocarbon Gases. The separation and analysis of the non-hydrocarbon and light hydrocarbon gases(42) has been accomplished in columns packed with charcoal, alumina, silca gel, zeolites, and stationary phase liquids, and others.

III. EXPERIMENTAL

In this section will be found experimental information pertaining to the effect of preoxidation on coking properties of Penn-Lee coal. This information includes the purpose, method of investigation, materials and apparatus, data and results, and sample calculations.

Purpose of Investigation

The purpose of this investigation was to study the effect of preoxidation on the coking properties and the quantities and composition of the by-products and char obtained from the low-temperature carbonization of Penn-Lee coal.

Plan of Investigation

The plan of investigation consisted of the following: A survey of the literature pertinent to this investigation was made. Bench-scale experiments were conducted to determine the effect of reaction with oxygen, below the ignition point of the coal, on the physical properties of the coal and coke. Pilot-scale studies were conducted to determine the effect of preoxidation on the properties and yields of products of the low-temperature carbonization of Penn-Lee coal.

Literature Survey. A literature search was made to determine the effect of various pretreatments on the low-temperature carbonization of bituminous coal, to select the most feasible pretreatment for this investigation, and to study the chemistry of the pretreatment selected and its effect on the properties and yields of products obtained when the pretreated coal is carbonized at low temperatures (850 to 1200 °F).

Bench-Scale Investigations. A bench-scale investigation was conducted to study the effect of oxygen on coal at low temperature. A factorial experiment was designed. The coal samples were treated at temperatures of 400, 500, and 600 °F at timed periods of one, two, and three hours. Three replicates of each test were made to aid in reducing the sampling error. The treated samples were analyzed to determine the effect of the oxygen on the weight loss, the volatile matter in the coal, and the free swelling index of the coal. In addition, the action of the coal was observed during pretreatment and carbonization in an effort to predict the behavior of the coal in the pilot-scale retort.

Pilot-Scale Investigation. Pilot-scale studies were conducted in an apparatus suitable for supplying the retort with gas heated to temperatures up to approximately 1000 °F and which had facilities for collecting the extracted tars and gases, and for sampling the gas stream. Twelve tests were made on samples which had been treated with oxygen for two and four hours at 600 °F. These pretreated samples were carbonized at temperatures of 830 and 930 °F for one-half, one, and two hours. The pilot-scale unit to be used in these studies is shown in Figure 6, rear pocket.

Yield and Property Determinations. The weight of tar and coke obtained from each test was recorded. The gas evolved during the carbonization was metered. The gas was analyzed with the Fisher-Gulf chromograph to determine the qualitative and quantitative yields of the various components. The volatile matter in the coke was determined. American Society for Testing Materials tests were used throughout the investigation to determine the volatile matter, free swelling index, and apparent density of the coke, and to determine distillation curves, viscosity and specific gravity of the tar.

Materials

The materials used in this investigation are contained in this section.

Carbon Dioxide. Commercial grade. Obtained in cylinders from Southern Oxygen Company, Roanoke, Virginia. Used as the inert atmosphere for carbonizing studies.

Coal, Penn-Lee. Washed, run-of-mine coal. Obtained from Seams No. 1 and No. 4 of the Penn-Lee Coal Corporation, Maness, Virginia. The proximate analysis of Penn-Lee Coal is 37 per cent volatile matter, 54 per cent fixed carbon, 5.6 per cent ash, and 2.7 per cent moisture.

Dibutyl Phthalate. Normal, purified. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used as a manometer fluid.

Helium. U. S. Bureau of Mines, standard grade. Obtained in cylinders from Southern Oxygen Company, Roanoke, Virginia. Used as a carrier gas in the chromatograph.

Molecular Seives. No. 5A, 1/16 inch pellets. Obtained from Linde Air Products Company, Tonawanda Park, New York. Used as a column packing in the chromatograph.

Oil. S.A.E. 30. Obtained from Esso Standard Oil Company, Radford, Virginia. Used to lubricate gas pump.

Oxygen, Compressed. Commercial grade. Obtained in cylinders from Air Reduction Sales Company, Charlotte, North Carolina. Used in Parr oxygen bomb.

Plastiseal. Expanding joint compound. Obtained from Tidewater Supply Corporation, Roanoke, Virginia. Used in sealing joints in carbonizing column.

Silica Gel. 6-16 mesh, lot No. 753462. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used as column packing in chromatograph.

Sodium Chloride. Granulated. Obtained from Blacksburg, Feed and Seed Store, Blacksburg, Virginia. Used to prepare brine for refrigeration.

Apparatus

The following list of apparatus was used in this investigation.

Apparatus, Free Swelling. Built (39) in the Chemical Engineering Department, Virginia Polytechnic Institute. Used to determine the effect of pretreatment on the free-swelling index of Penn-Lee coal.

Balance, Analytical. Serial No. 7Y2056. Capacity, 1500 grams, five-milligram sensitivity. Manufactured by Seeder-Kohlbusch. Fisher Catalog No. 1-919. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to weigh tar samples.

Balance, Analytical. Chainomatic type, capacity 500 grams, model 220-0, serial No. N-13860, Fisher Catalog No. 1-967. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to weigh coal samples for pretreatment studies.

Balls, Ceramic. Three-eighths inch average diameter. Used as packing in the tube heater for bench-scale pre-oxidation studies. Obtained from the Department of Chemical Engineering, Virginia Polytechnic Institute.

Bath, Constant Temperature. Fisher unitized, Catalog No. 15-445-5. Manufactured by Fisher Scientific Company, Silver Spring, Maryland. Used to maintain tar samples at constant temperature for specific gravity measurement.

Crucibles Free Swelling. ASTM, Vitreosil. Fisher Catalog No. 6-710. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to determine the effect of pretreatment on the free-swelling index of Penn-Lee coal.

Crucibles Vitreosil. Capacity 10, milliliters. Fisher Catalog No. 6-712. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to determine the volatile content of coal and char samples.

Desiccator Pyrex. One each 6, 10 and 12-inch diameter. Fisher Catalog No. 8-595. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to store bench-scale samples.

Distillation Apparatus. Creosote and Road Oil. ASTM. Fisher Catalog No. 1-729. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to obtain distillation curves of Penn-Lee coal tar.

Distillation Apparatus. Gasoline and Light Oil. ASTM. Fisher Catalog No. B-459. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to purify coal tar distillation fractions for analysis.

Furnace, Combustion. Type 70, Serial No. 4882. Manufactured by Hevi-Duti Electric Company, Milwaukee, Wisconsin. Obtained from Esso Standard Oil Company, New Jersey. Used to heat gas in bench-scale studies.

Furnace. Meeker Type. ASTM. Type FA 120. Serial No. 11577, Fisher Catalog No. 6-645. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to determine the volatile content of coal and char samples.

Glassware. Miscellaneous, such as beakers, pipets, gas sampling bulbs. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used for storage and handling of the tar, gas, and char samples.

Meter. Precision Wet Test. Capacity 10,000 cubic feet. Fisher Catalog No. 11-167. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to measure the gas evolved from the pilot-scale carbonization unit.

Potentiometer. Millivolt Meter. Model 73P021. Manufactured by the Lewis Manufacturing Company, Naugatuck, Connecticut. Used to measure the EMF generated by thermocouple.

Partitioner. Liquid-Vapor, chromotagraphic, Fisher-Gulf type, model FIS-IPH560-51-T24-T4-T82, serial No. 622279. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to analyze liquid and gaseous products of carbonization.

Pipe, Stainless. Type 18-8. 3/4 inch nominal diameter, Obtained from Union Carbide and Carbon Company, Belle, West Virginia. Used for shell of gas heater in pretreatment studies.

Sampling Bulbs, Gas. Pyrex, with stopcocks. Capacity 250 milliliters. Fisher Catalog No. 10-920. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to collect gas samples from pilot-scale carbonizing tests.

Scale Platform. Capacity, 115 pounds. One ounce graduations. Model 31-0851. Serial No. 1788. Obtained from Toledo Scale Company, Toledo, Ohio. Used to weigh coal charge for pilot-scale studies.

Screens, Sizing. 3/8, 1/2, 3/4, 1; 2 inch openings. Built in the Department of Chemical Engineering, Virginia Polytechnic Institute. Used to size the coal samples for experimental studies.

Timer, Electric. Graduated in hundredths of a minute. Range 0-10,000 minutes. Fisher Catalog No. 14-653-5. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used for timing the duration of tests.

Viscosimeter. Saybolt Furol. Fisher Catalog No. 13-571. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to determine the viscosities of coal tar and coal tar fractions.

Wire, Constantan. No. 20 B&S gauge. Enamel insulation. Obtained from Leeds and Northrup Company, Philadelphia, Pennsylvania. Used to make iron-constantan thermocouples.

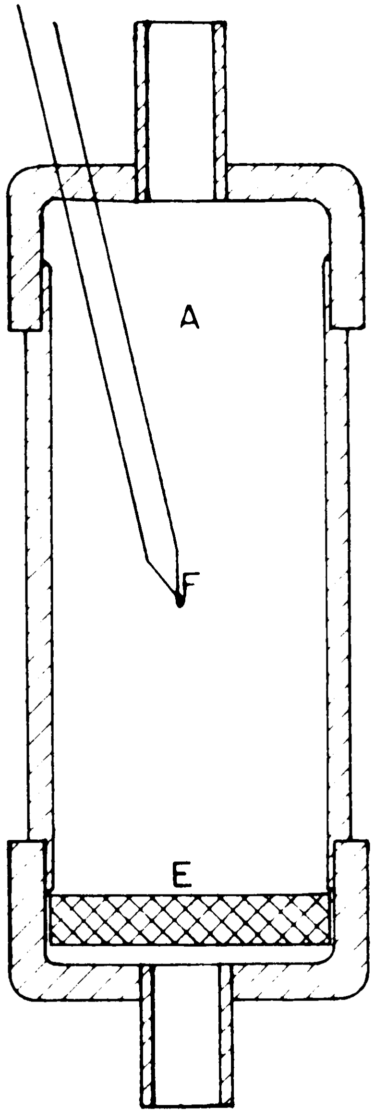
Wire, Iron. No. 20 B&S Gauge. Enamel insulation. Obtained from Leeds and Northrup Company, Philadelphia, Pennsylvania. Used to make iron-constantan thermocouples that were used to measure the temperatures in the condensers in the pilot-scale carbonization unit.

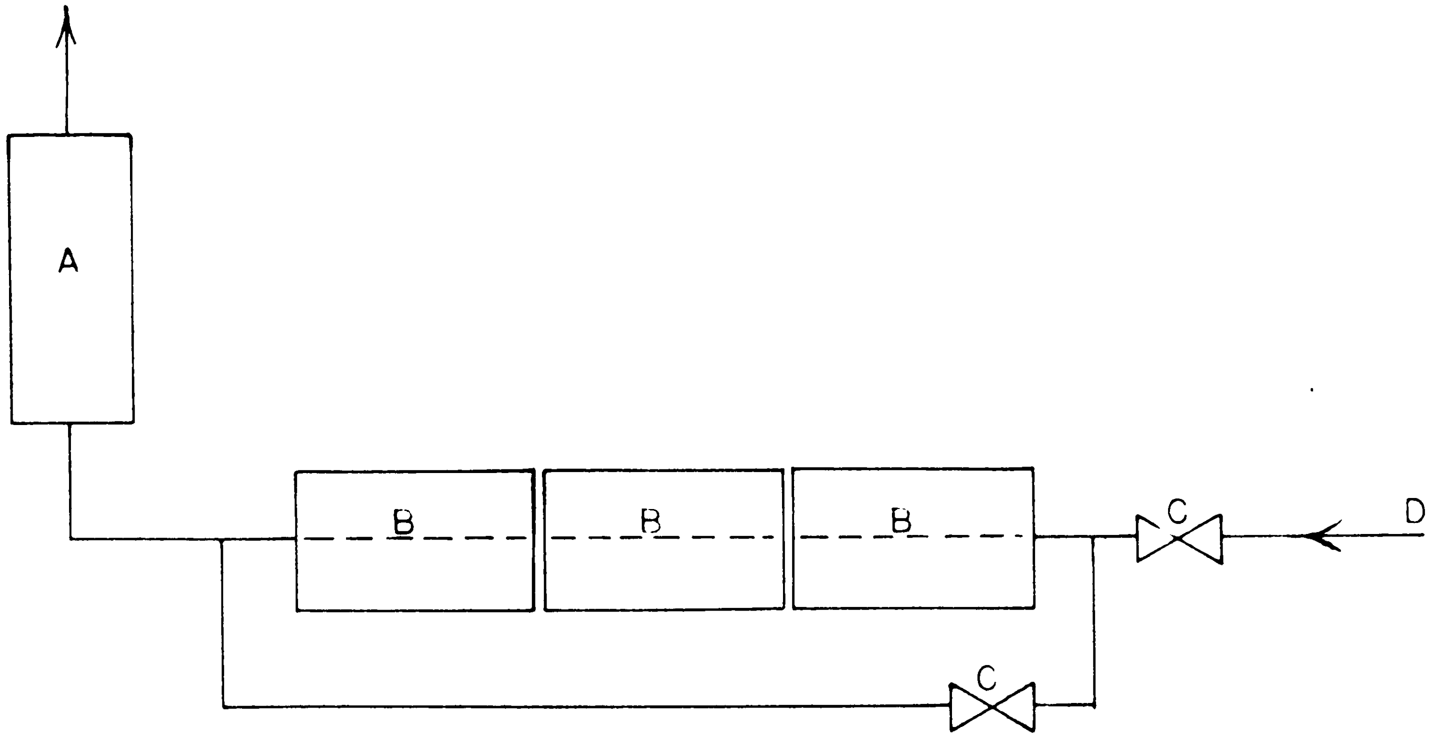
Method of Procedure

The procedure following in this investigation consisted of two phases, a bench-scale investigation, and a larger pilot-scale investigation. The experimental method is outlined below.

Bench Scale Preoxidation. Bench scale preoxidation tests were performed at temperature levels of 400, 500 and 600 °F for time periods of one, two and three hours. Three replications of these experiments were made. These tests were performed on fifty-gram samples of coal sized to minus 3/4, plus 1/2 inch. The apparatus used is shown in Figure 5, page 44. The samples were weighed on an analytical balance and then placed in the retort. The cap was screwed on, and the thermocouple connected. The pump was then started and the coal bed brought up to the desired temperature. At the end of the test, the sample was removed and weighed, and the volatile matter remaining in the sample determined.

Combustion Tests. The temperature at which combustion occurs was determined in a manner similar to that used in the preoxidation studies. The apparatus used was that shown in Figure 5, page 44. A fifty-gram coal sample, sized to minus 3/4, plus 1/2 inch, was placed in the retort, the cap screwed on, and the thermocouple connected. The pump was then started and the inlet air was heated to temperatures of 600, 625, and 650 °F. The flow rate of air





LEGEND:

- A- RETORT
- B- ELECTRIC COMBUSTION HEATERS
- C- THROTTLING VALVES
- D- AIR FROM PUMP
- E- FILTROS DIFFUSING PLATE
- F- THERMOCOUPLE

DEPARTMENT OF CHEMICAL ENGINEERING
VIRGINIA POLYTECHNIC INSTITUTE
BLACKSBURG, VIRGINIA

BENCH-SCALE PRETREATMENT APPARATUS

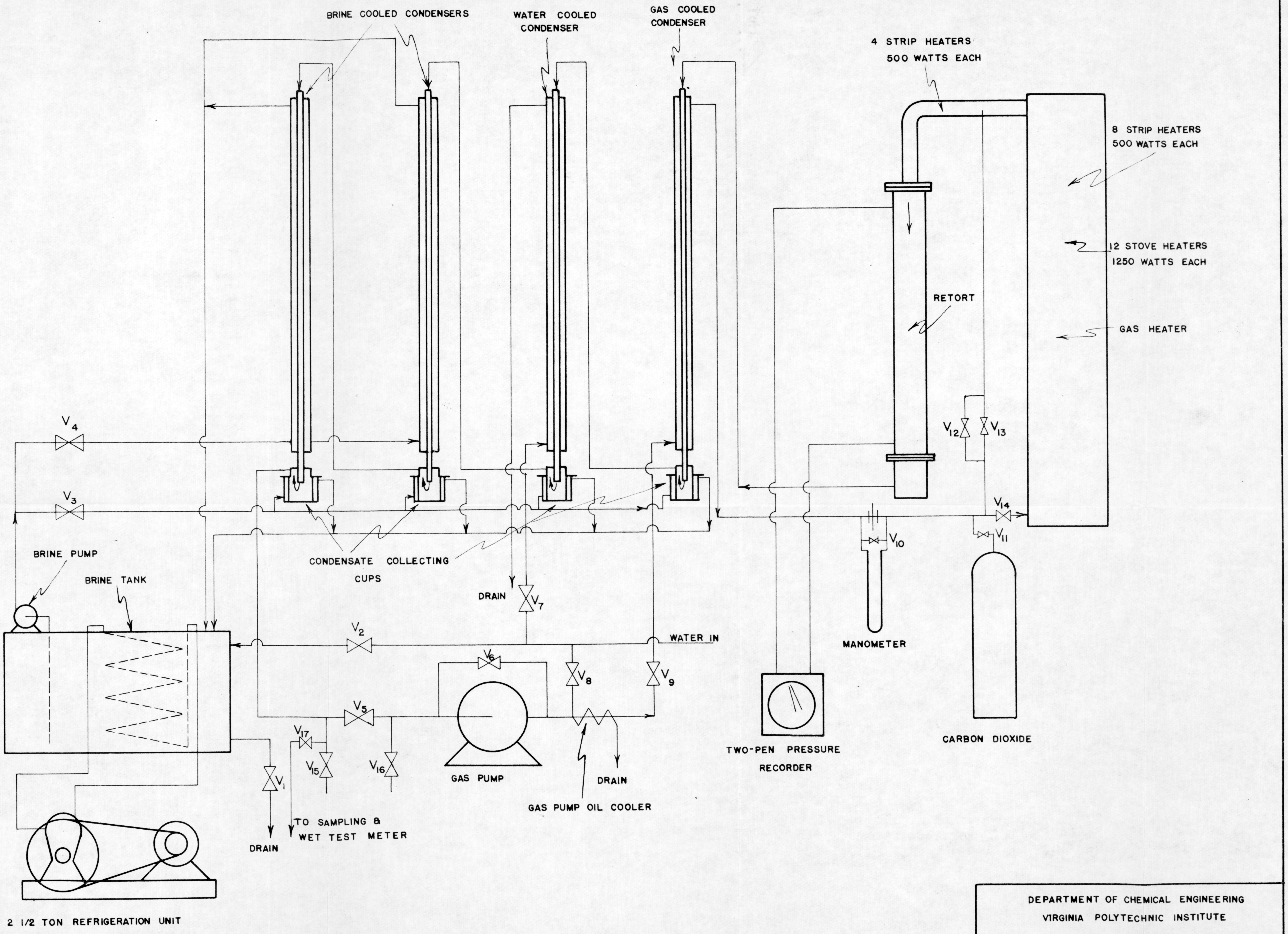
SCALE: NONE
DATE 1/4/57
CASE NO:
DRAWN BY: HLR
FILE NO:
CHECKED BY: G.F.Q
FIGURE NO: 8
APPROVED BY: FvB 4/4/57
SHEET NO

was maintained at 12±0.1 cubic feet per minute. The combustion temperature was taken as the inlet air temperature which resulted in bed ignition. Ignition was noted when the temperature in the bed rose rapidly without any change in conditions.

Pilot-Scale Preoxidation. Preoxidation tests were performed at a maximum bed temperature of 630± 20 °F. The coal was preoxidized for time intervals of two and four hours. The bed temperatures were measured with the retort thermocouples in positions as shown in Figure 6, rear pocket. Samples of the exit gases were taken and analyzed. The maximum bed temperatures were maintained by recycling the exit bed gases and adding air to just sustain the exothermal reaction. The amount of air added is critical in so far as ignition may occur if the concentration of oxygen in the retorting gas becomes too high at this temperature. The oxygen content in the gas was not determined quantitatively.

Pilot-Scale Carbonization. The pretreated samples were then subjected to carbonization for time intervals of one, one and one-half, and two hours at temperatures of 830 and 950 °F. The system was purged with carbon dioxide until the retorting atmosphere contained less than two per cent oxygen. The carbonizing interval was begun from the time at which the first pressure increase in the system occurred, indicating that the initial decomposition of the coal

Figure 6. Schematic Diagram of Pilot-Scale Carbonizing Unit



DEPARTMENT OF CHEMICAL ENGINEERING
VIRGINIA POLYTECHNIC INSTITUTE
BLACKSBURG, VIRGINIA

FLOW DIAGRAM FOR LOW-TEMPERATURE CARBONIZATION UNIT

SCALE: NONE DATE 7/4/56 CASE NO:
DRAWN BY: H L Rhinehart FILE NO:
CHECKED BY: J. L. Q. FIGURE NO: 6
APPROVED BY: F.W.B. 4/16/56 SHEET NO:

had taken place. The retorting temperature was taken as the maximum temperature in the bed. Gas samples were taken at the end of each test. The condensers were allowed to drain overnight and the liquid products were then collected. The retort was allowed to cool, the charge removed, weighed, and stored.

Detailed Pilot Plant Procedure. The detailed procedure for the operation of the pilot plant shown schematically in Figure 6, rear pocket, is as follows:

1. Load weighed charge (5.5-10 pounds) into a retort, bolt retort in place with corrugated iron-asbestos gaskets coated with "plastiseal" between the flange faces, and insulate the retort with glass wool.
2. Connect thermocouple leads.
3. Turn on refrigerating unit for brine tank.
4. Close relay supply switch, heater switches, and potentiometer switch, and turn on strip heaters on "ell" section.
5. Turn on pump cooling water, using valve V_8.
6. Adjust flow rate to one inch of di-butyl-phthalate measured on gas-flow manometer with valve V_6, (see Figure 6, rear pocket). Allow gas heater to heat for two hours to allow the packing in the heater to come to a uniform heat.

After two hours, adjust the gas flow to five and one-half inches di-butyl-phthalate measured on gas-flow manometer and allow bed to come up to retorting control temperature.

8. Control temperature as desired by adjusting valves V_5, V_{15}, V_{12}, V_{13}, and V_{14}.
9. Sample bed exhaust gases by turning V_{17}.
10. After pretreatment is complete, purge the system with carbon dioxide by opening valve V_{11}, with valves V_{15} and V_{16} closed, and then bleed system down. Repeat until the oxygen content of the retorting atmosphere is less than one per cent.
11. With system purged and at 15 pounds per square inch gage, turn on the gas pump and adjust the flow rate to eight inches of di-butyl phthalate, measured on gas-flow manometer, with valve V_6.
12. Turn on pressure recorded, close brine pump switch.
13. Turn on water to water-cooled condenser using Valve V_7 and adjust so that the temperature drop of the gas being cooled is not less than 100 °F.

14. Hold the pressure in the system at the desired point, not to exceed 10 pounds per square inch gage by bleeding down through wet test meter, using valve V_{17}.
15. Control the retort temperature by manipulating valves V_{13} and V_{14}.
16. Collect gas samples by turning valve V_{17}.
17. At the end of the carbonizing test, turn off the relay switch, heater switch, gas pump switch, brine pump switch, potentiometer switch and pressure recorder switch. Turn off the water to water-cooled condenser with valve V_1, and the pump cooling water with valve V_8.
18. Allow the condensers to drain before removing the cups and trap to collect condensate.
19. Measure gas evolved by reading the wet test meter.
20. Remove the insulation on the retort. Allow the retort to cool, and then remove and weigh the remaining charge of product char.

PRECAUTION! Turn off the main power switch before working on any part of carbonizing equipment.

Volatile Matter Determination. The determination of the volatile matter in a sample was made in the standard manner described by the American Society for Testing Materials (7).

Bulk Density Determination. The bulk density of the char product was determined by the American Society for Testing Materials method (1).

Calorific Value Determination. The calorific value of the char samples was determined by the standard method suggested by the American Society for Testing Materials (2).

Free Swelling Index Test. The free swelling index determinations were performed in accordance with the method proposed by the American Society for Testing Materials (4) with one modification. A length of four-inch steel pipe was used for the draft shield.

Specific Gravity of Liquid Product. The specific gravity of the liquid product was determined in the following manner. A tared, 10-milliliter sample bottle was filled with distilled water and weighed. The volume of the bottle was then calculated from a knowledge of the weight of the water and its density. The bottle was then filled with tar, and the weight of the known volume of tar was obtained by weighing the tar in the bottle and subtracting the weight of the bottle. Then the specific gravity of the tar was calculated.

Viscosity of Liquid Product. The viscosity of the liquid product was determined in the manner suggested by the American Society for Testing Materials, using the Saybolt viscosimeter (6). The Saybolt Furol visconsimeter was used rather than the Universal because of the extreme outflow times involved.

Distillation of Liquid Products. The distillation curves of the tar products were obtained by the method proposed by the American Society for Testing Materials for tars and creosote (3). The tar sample was distilled until 60 per cent of its water-free volume had been collected. The water phase which had been distilled as a separate phase, was then separated from the distilled tar by means of a separatory funnel. The distillation was then repeated using the dry 60 per cent of the original distillate and distilling this to an end point of 662 °F as prescribed by the American Society for Testing Materials.

Gas Sample Analysis. The gas samples were analyzed in the Fisher-Gulf chromotographic partitioner. The carrier gas for the analysis was helium. The columns used for the analysis were filled, one with 5A molecular sieves, and the other with silica gel.

The gas sampling bulb with the sample to be analyzed was fitted with a leveling bulb filled with water and a short length (about 6 inches) of tygon tubing. The water in the leveling bulb was allowed to flow by gravity into the sampling bulb thus slowly expelling the sample through the piece of tygon tubing flushing it with the sample gas. A one cubic centimeter hypodermic syringe which had been previously flushed with helium was then used to withdraw a sample of one cubic centimeter from the piece of tygon tubing. Three extractions were made in every case to insure that the syringe had been throughly flushed with the sample gas.

At least two determinations were made of every analysis to insure the precision of the results.

The gases were first analyzed using the silica gel column, this column would resolve all the components of the samples except air. All of the tests were then repeated using the molecular sieve column to analyze the air component of the samples. Through the use of two columns, a complete analysis of sampled gases was effected.

Data and Results

The data collected during this investigation and the results obtained from these data are presented in the tables and figures shown in the following pages.

Bench-Scale Pretreatment. The data and results obtained from the bench-scale study of the effect of the pretreatment of Penn-Lee coal with oxygen are given in this section. Dependent variables studied in this phase of the investigation were the effect of oxygen on the sample weight loss, the volatile matter retained in the char, and the free swelling index. These data and results are shown in Table II, page 55, and are plotted in Figures 7, 8, and 9 on pages 56, 57, and 58.

Pilot-Scale Carbonization. The second phase of this investigation consisted of a series of carbonization tests which were conducted in a batch-type, pilot-scale unit. The data and results obtained from this phase of the investigation are given in Table III, page 59, and plotted in Figures 10, 11, and 12 on pages 60, 61, and 62.

Distillation of Tar Samples. The tar samples collected during the pilot-scale carbonization tests were distilled using a modified ASTM procedure and the data to plot curves were obtained. This data, from which the curves can be plotted, is shown in Table IV, page 63.

Analysis of Variance Tables. Many of the dependent variables studied in this investigation were studied statistically to determine the effect of changing the independent variables. Dependent variables that were studied statistically are sample weight loss, free-swelling index volatile matter, tar yield, gas yield, specific gravity of the tar, viscosity of the tar, the 20 per cent distillation point of the tar, and the bulk density of the char. The results of the analysis of variance of these data are shown in Table V, rear pocket.

TABLE II

The Effect of Preoxidation Time and Temperature on the Weight Loss, Volatile Matter, and Free Swelling Index of Penn-Lee Coal

Test No [a]	Temperature °F	Time hr	Replicate No	Weight Loss %	Volatile Matter %	Free Swelling Index
1	400	1	1	2.42	37.4	2.0
2			2	2.31	36.5	2.5
3			3	2.43	36.3	2.0
4		2	1	2.36	35.0	2.0
5			2	2.63	34.8	2.0
6			3	2.23	35.6	1.5
7		3	1	2.45	31.0	1.5
8			2	2.16	33.2	2.0
9			3	2.14	31.4	1.5
10	500	1	1	2.53	34.2	2.0
11			2	2.26	35.1	1.5
12			3	2.67	35.6	3.0
13		2	1	3.17	34.6	1.5
14			2	3.48	33.6	1.5
15			3	2.16	34.0	1.5
16		3	1	2.25	35.7	1.5
17			2	2.19	34.8	1.0
18			3	2.01	35.7	1.5
19	600	1	1	3.71	34.6	1.5
20			2	4.50	35.2	1.5
21			3	3.92	32.6	1.5
22		2	1	3.26	33.8	1.0
23			2	3.80	33.9	1.5
24			3	3.38	33.1	2.0
25		3	1	4.05	34.7	1.0
26			2	4.13	34.0	1.0
27			3	4.39	33.6	1.0

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[a] The test numbers were selected from a table of random numbers and the experiments were run in that order.

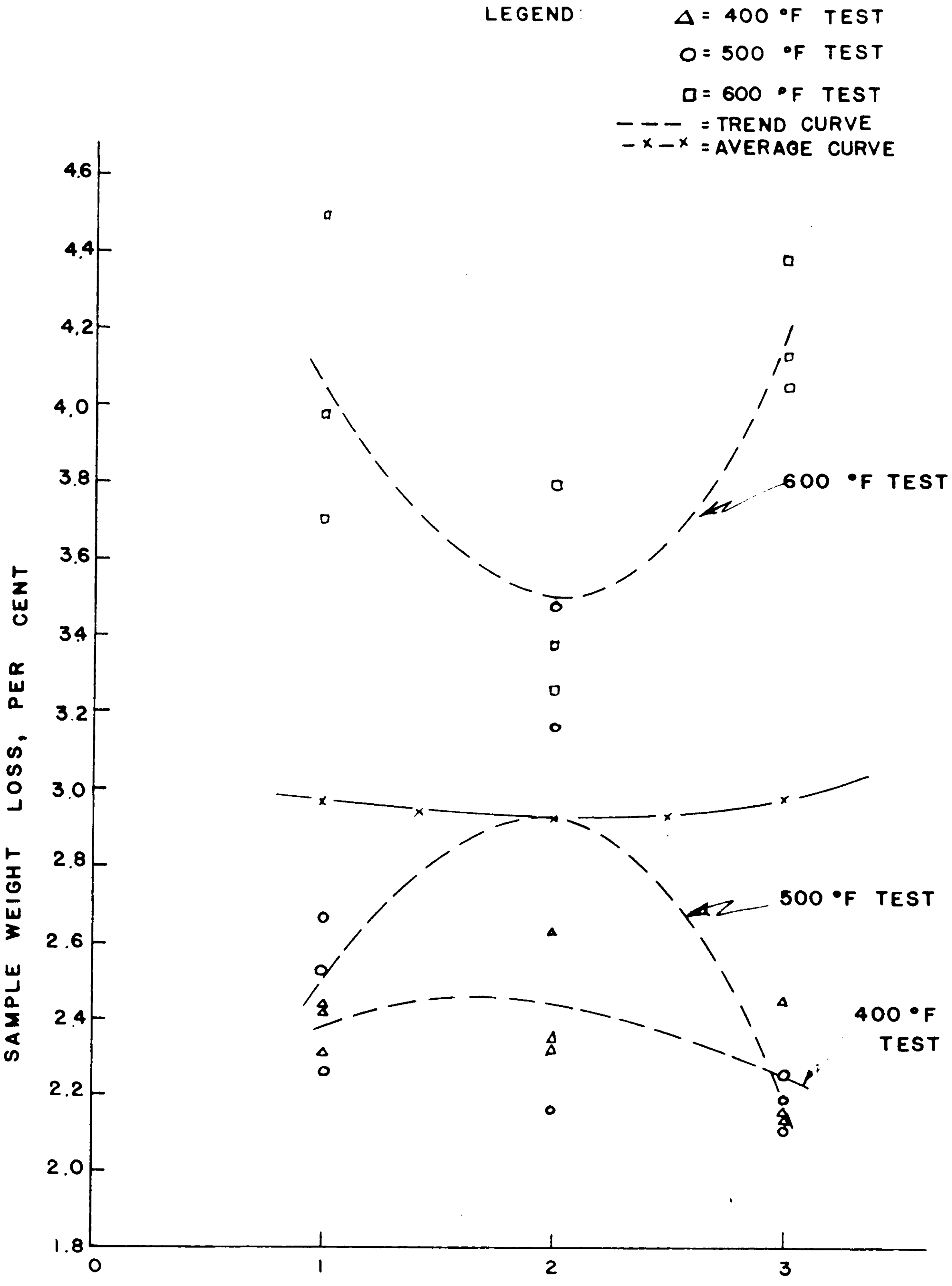

FIGURE 7. THE EFFECT OF PRETREATMENT TIME ON THE SAMPLE WEIGHT LOSS OF PENN-LEE COAL.

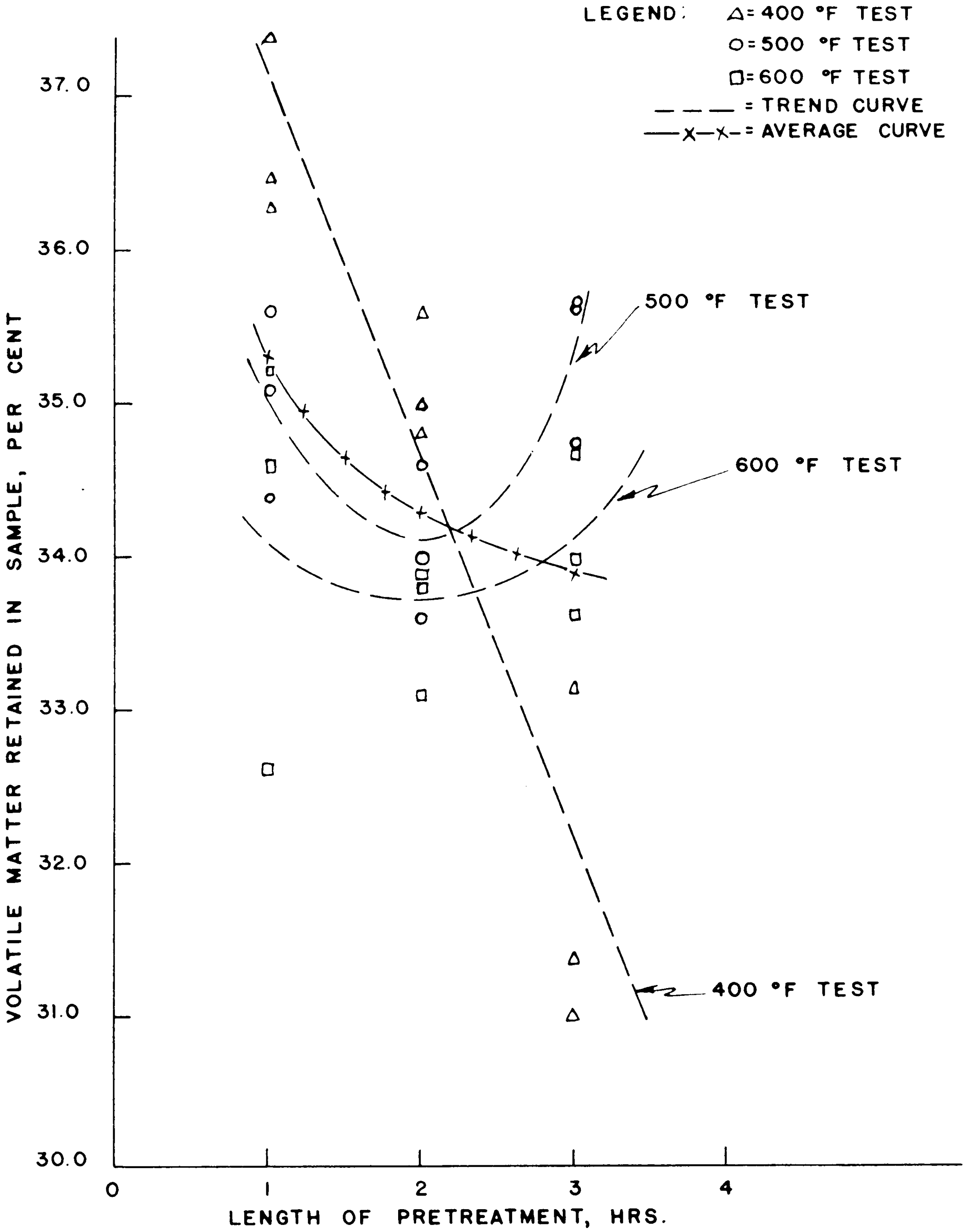

FIGURE 8. THE EFFECT OF THE LENGTH OF PRETREATMENT ON THE VOLATILE MATTER RETAINED IN SAMPLES OF PENN—LEE COAL

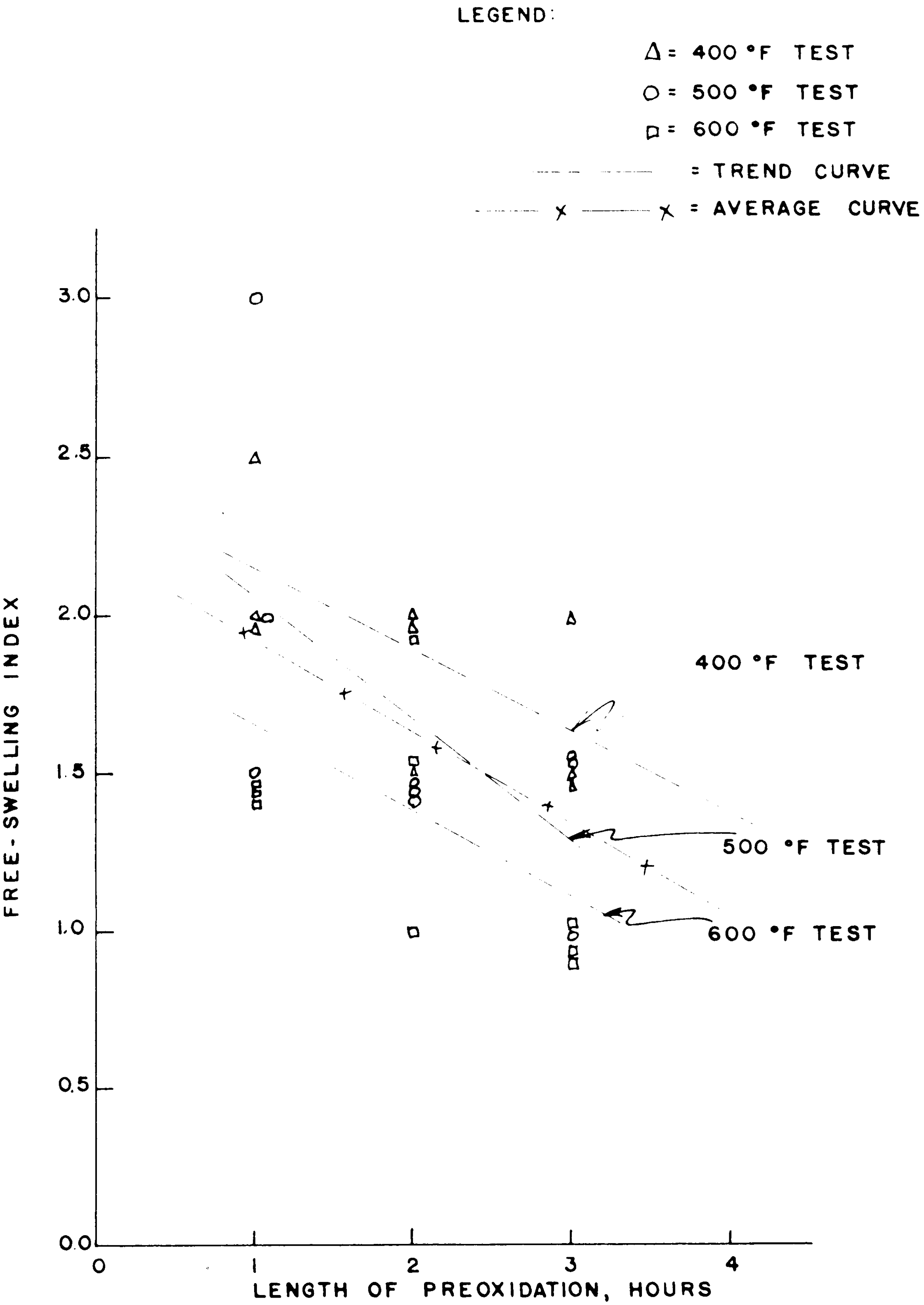

FIGURE 9 . THE EFFECT OF THE LENGTH OF PRETREATMENT ON THE FREE - SWELLING INDEX OF PENN-LEE COAL

TABLE III

Pilot Plant Data

Test[a] No	Preoxidation Time	Preoxidation Temperature	Maximum Carbonization Temperature	Length of Carbonization	Weight of Charge	Char Yield	Crude Water Yield	Total Crude Condensate Yield	Drained Tar Yield	Dry Tar Yield	Coded Dry Tar Yield	Water in Decanted Tar	Total Water Yield	Decanted Tar Viscosity at 180 °F	Decanted Tar Specific Gravity	20 Per Cent Distillation Temperature	Bulk Density of Char	Calorific Value of Char	Volatile Matter in Char	Calorific Value of Gas	Gas Evolved During Carbonization	Gas Composition, Volume Per Cent					
	hr	°F	°F	hr	lb	%	%	%	%	%		wt %	wt %	Furol sec		°F	lb/ft^3	Btu/lb	wt %	Btu/mol	ft^3	CO	CH_4	C_2H_6	C_3H_8	CO_2	N_2
1	2.0	480	750	0.2	8.0	93.4	--	5.0	--	--	--	--	--	--	--	--	--	--	--	--	0.08	--	--	--	--	--	--
2	6.0	500	770	0.3	8.0	94.5	--	4.2	--	--	--	--	--	--	--	--	--	--	--	--	0.08	--	--	--	--	--	--
3	6.0	525	765	0.25	6.0	93.0	--	5.0	--	--	--	--	--	--	--	--	--	--	--	--	0.09	--	--	--	--	--	--
4	2.0	590	758	0.25	6.0	92.1	--	5.6	--	--	--	--	--	--	--	--	--	--	--	--	0.11	--	--	--	--	--	--
5	2.7	600	830	0.5	6.0	93.0	--	5.9	--	--	--	--	--	--	--	--	--	--	--	--	0.15	--	--	--	--	--	--
6	2.0	630	830	1.0	5.5	83.5	3.3	12.5	9.2	5.5	0.237	40	7.0	85.1	1.025	257	17.2	13.936	8.34	164,764	0.32	19.3	31.8	2.9	--	45.2	0.8
7	2.0	630	950	1.0	5.5	85.9	2.4	14.1	11.7	7.4	0.276	37	5.1	77.1	1.022	258	15.5	13.497	8.36	168,389	0.57	18.2	34.1	1.9	0.3	44.8	0.7
8	2.0	630	830	1.5	5.5	80.9	2.4	15.0	12.6	8.1	0.289	36	6.9	83.5	1.026	256	16.6	13.571	8.14	308,266	0.96	12.2	68.3	3.6	0.8	14.8	0.3
9	2.0	630	950	1.5	5.5	80.9	2.2	15.2	13.0	7.8	0.283	40	7.4	77.3	1.028	253	16.0	13,914	8.01	297,905	1.01	13.6	63.6	4.2	1.0	17.6	--
10	2.0	630	950	1.5	5.5	78.0	2.6	17.9	15.3	9.2	0.308	40	8.7	77.2	1.031	253	17.4	13,574	7.91	339,206	1.54	6.7	80.1	2.9	0.5	9.7	0.1
11	2.0	630	950	2.0	5.5	74.3	2.5	21.5	19.0	11.8	0.351	38	9.7	67.2	1.026	251	17.7	14,040	8.08	332,009	1.96	5.8	75.6	2.5	0.9	15.2	--
12	4.0	630	830	1.0	5.5	84.5	4.4	11.5	7.1	4.3	0.209	39	7.2	144.1	1.041	350	15.5	13,649	8.05	169,401	0.62	24.0	28.1	3.0	1.3	42.8	0.7
13	4.0	630	950	1.0	5.5	84.3	4.2	11.4	7.2	4.2	0.207	42	7.2	125.6	1.041	339	19.1	13,908	7.95	179,706	0.98	24.9	33.2	2.6	0.5	38.2	0.6
14	4.0	630	830	1.5	5.5	83.7	4.3	12.1	7.8	4.8	0.221	38	7.3	133.2	1.039	345	16.0	13,656	7.50	313,251	1.04	12.1	69.0	5.1	--	13.4	0.5
15	4.0	630	950	1.5	5.5	83.8	4.5	11.9	7.4	4.3	0.209	42	7.6	116.4	1.041	299	17.2	13,793	7.52	321,616	1.66	15.2	71.6	4.3	--	8.7	0.2
16	4.0	630	830	2.0	5.5	79.1	4.5	16.8	12.3	6.9	0.266	44	9.9	118.2	1.042	302	18.2	14,117	7.36	335,945	1.78	8.1	72.2	6.1	0.9	12.7	--
17	4.0	630	950	2.0	5.5	82.0	4.3	13.8	9.5	5.6	0.239	41	8.2	121.2	1.044	315	15.1	13,632	7.25	361,959	2.12	10.1	78.1	7.1	0.3	4.4	--

[a] The test numbers were selected from a table of random numbers and the experiments were run in that order.

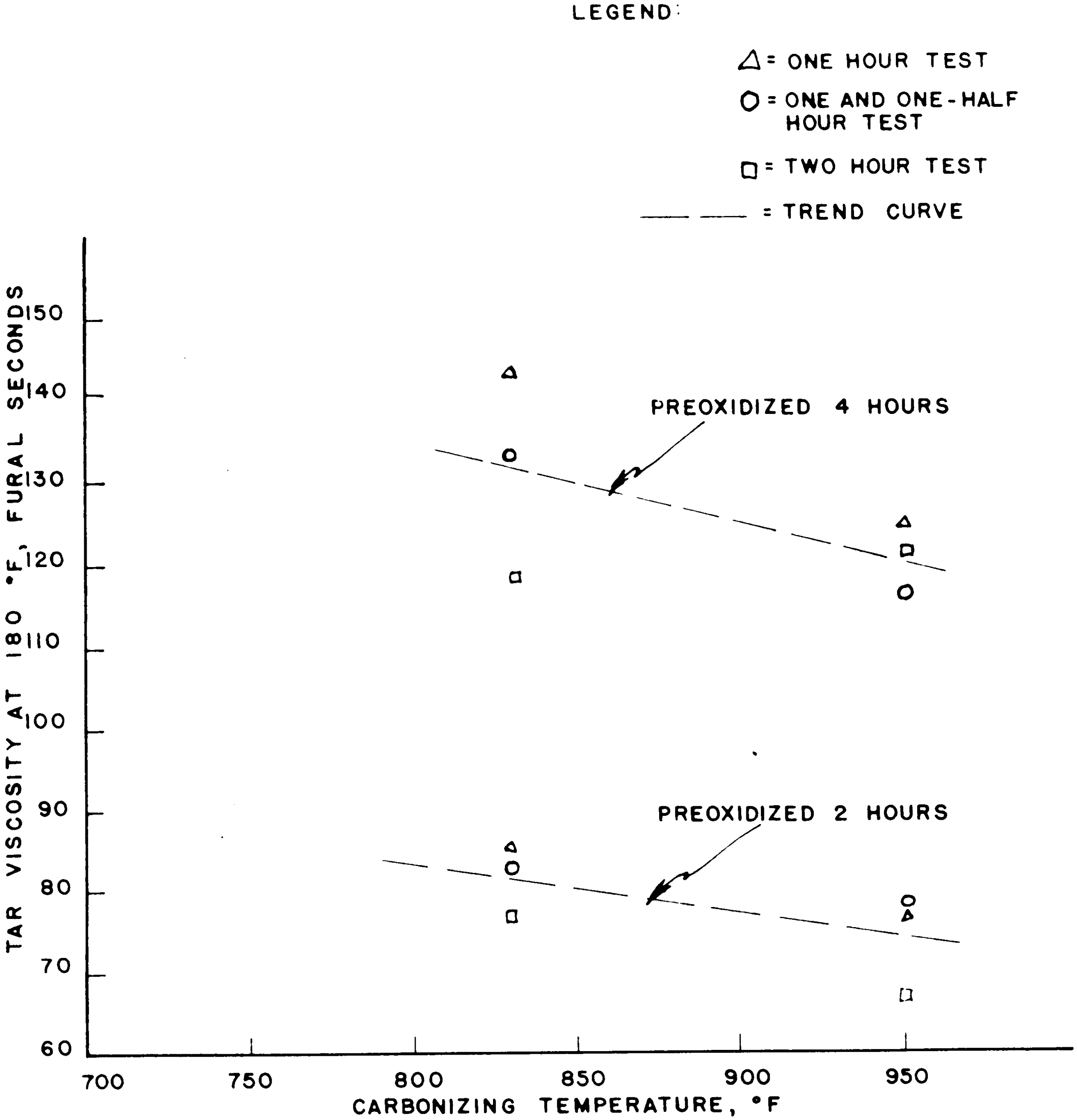

FIGURE 10. THE EFFECT OF CARBONIZING TEMPERATURE ON THE VISCOSITY OF TAR OBTAINED FROM PENN-LEE COAL.

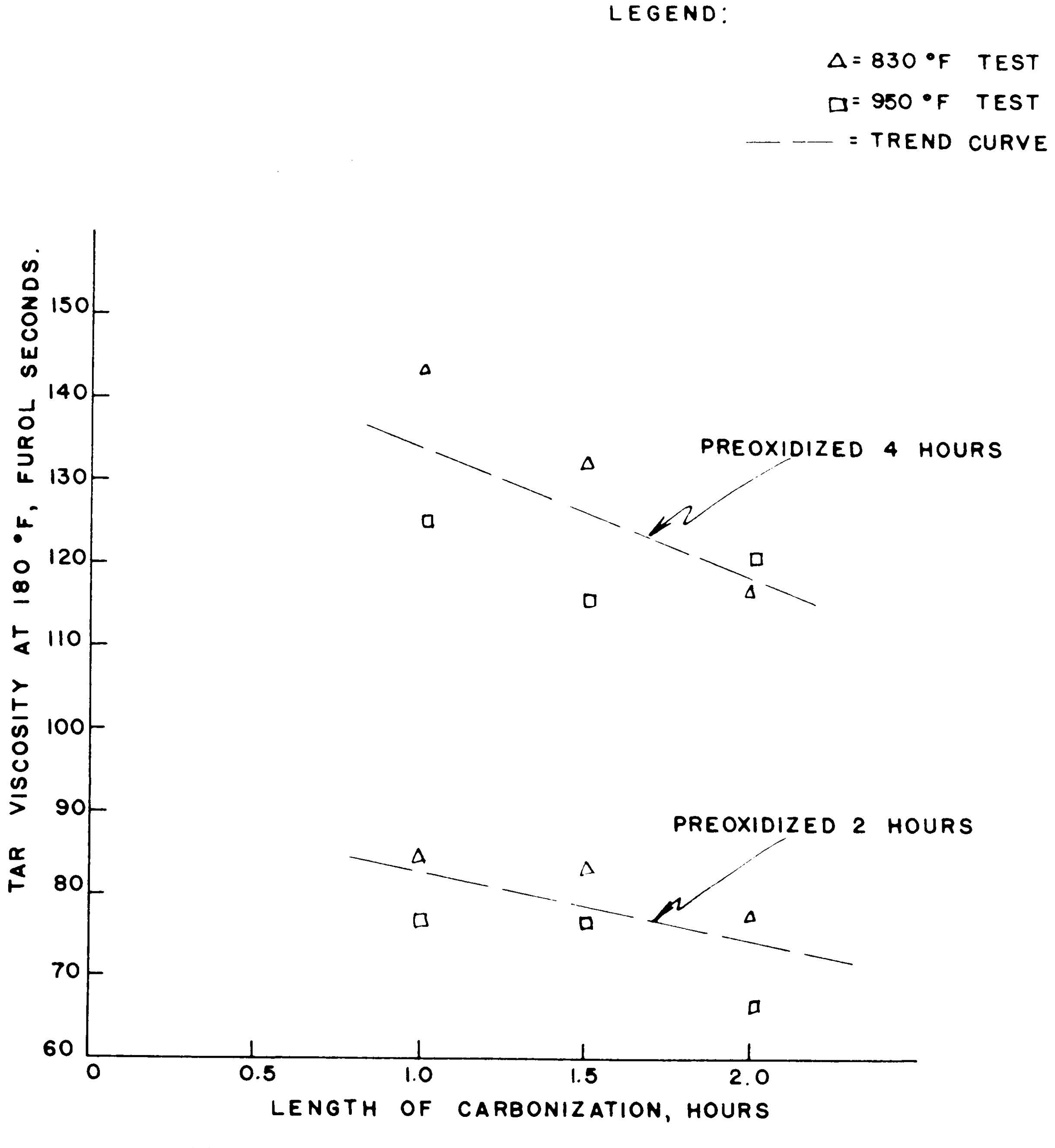

FIGURE 11. THE EFFECT OF THE LENGTH OF CARBONIZATION ON TAR VISCOSITY

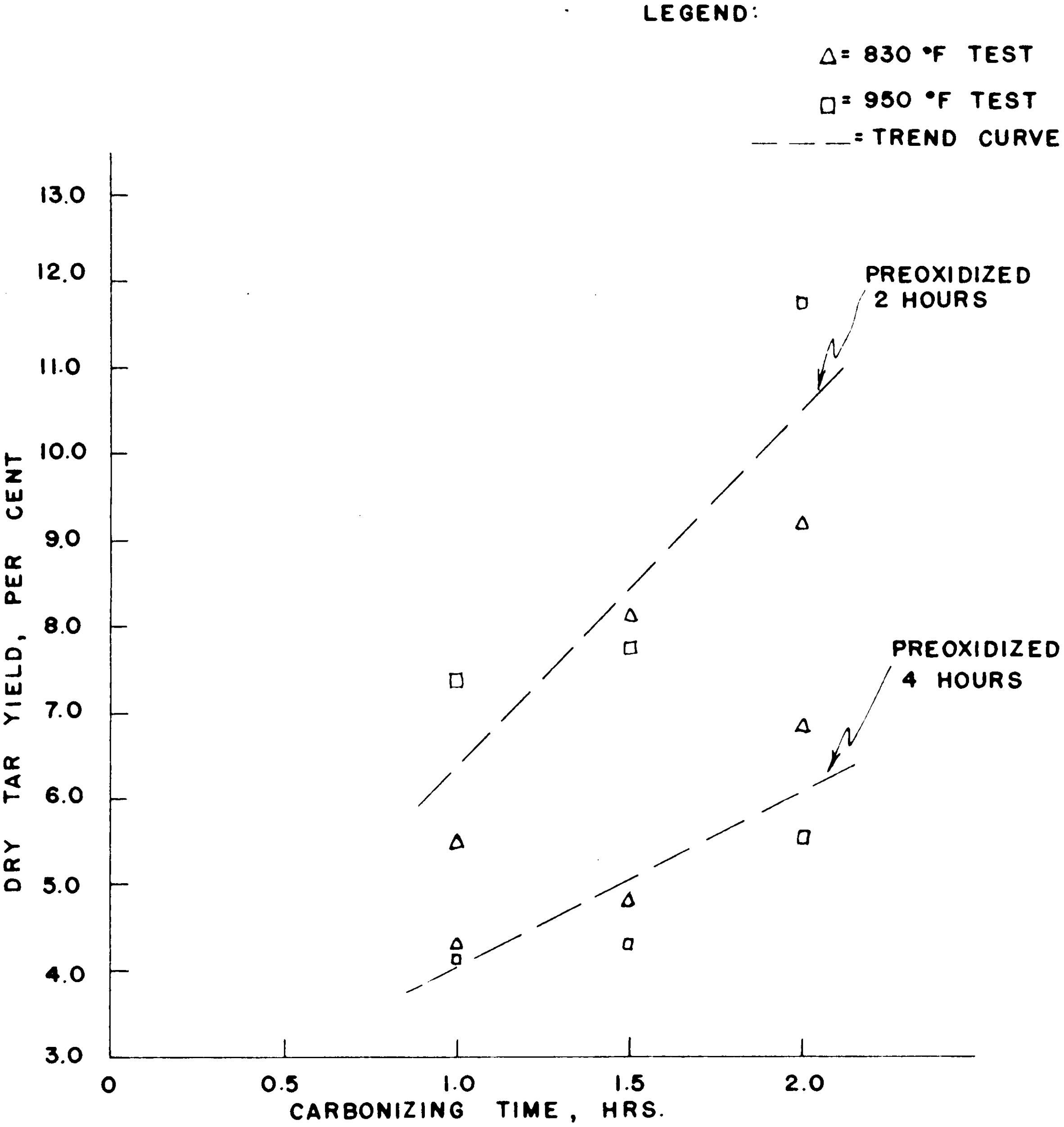

FIGURE 12. THE EFFECT OF CARBONIZING TIME ON THE DRY TAR YIELD OBTAINED FROM PENN-LEE COAL

TABLE IV

Results of the Distillation of Coal Tar Samples

Test No	Preoxidation Time	Carbonization Time	Carbonization Temperature	20 Per Cent Distillation Temperature	Volume Per Cent Distilled at the Centigrade Temperatures Shown Below																					
	hr	hr	°F	°C	100	120	130	160	180	200	210	220	230	240	250	260	270	280	290	300	310	320	330	340	350
6	2	1	830	257	1.3	1.7	2.7	3.2	3.3	3.7	6.3	8.3	10.8	13.7	17.7	21.0	23.4	25.2	26.7	29.0	30.9	32.0	34.2	35.0	36.7
7	2	1	950	258	1.3	1.6	2.9	3.2	3.8	4.4	6.7	8.7	11.6	14.4	17.5	21.6	24.8	26.8	28.6	31.7	34.0	35.0	36.8	38.1	39.7
8	2	1.5	830	256	1.3	1.6	2.8	3.0	3.6	3.9	6.4	8.4	11.7	15.1	18.1	21.3	24.4	26.3	27.5	30.3	32.2	33.2	35.2	36.0	37.5
9	2	1.5	950	253	1.3	1.5	1.7	3.3	4.7	4.7	7.0	9.0	12.6	16.3	19.2	22.7	26.0	28.2	29.5	32.7	34.9	36.0	38.0	39.2	41.0
10	2	2	830	253	1.2	1.5	1.7	3.3	4.2	4.7	7.0	9.2	12.8	16.2	19.3	22.6	26.0	27.8	29.9	33.0	34.8	36.2	38.5	39.5	41.3
11	2	2	950	251	1.1	1.6	2.1	3.4	4.0	4.5	6.9	9.5	12.7	16.1	19.7	24.2	28.7	30.9	33.0	35.7	37.2	39.6	42.3	43.5	46.2
12	4	1	830	335	—	1.1	1.3	1.6	2.6	3.0	3.4	4.1	5.7	7.4	9.0	10.5	12.0	12.6	13.4	14.9	15.9	17.1	18.2	18.9	19.9
13	4	1	950	339	—	1.4	1.5	1.7	2.9	3.6	4.1	4.5	6.6	8.6	10.5	12.0	13.8	14.8	15.5	16.9	17.6	18.7	19.7	20.4	22.1
14	4	1.5	830	349	--	1.1	1.3	1.6	2.7	3.4	3.7	4.2	6.0	7.6	9.0	10.5	12.1	13.1	13.7	15.1	15.6	16.3	17.4	18.4	20.2
15	4	1.5	950	299	--	1.2	1.5	1.7	2.9	3.8	4.3	4.8	7.2	9.8	12.9	14.8	16.7	17.6	18.5	20.2	21.0	23.0	24.9	25.7	27.4
16	4	2	830	302	--	1.4	1.6	1.8	2.9	3.7	4.1	4.5	7.3	9.8	11.8	13.4	15.9	16.6	17.8	19.8	20.9	22.7	24.5	25.3	27.1
17	4	2	950	315	—	1.4	1.7	2.7	3.1	3.7	4.1	4.4	6.8	9.3	11.0	12.7	14.4	15.6	16.5	18.3	19.0	20.7	22.6	23.6	25.1

TABLE V. Results of the Analysis of Variance of the Bench and Pilot-Scale Data

TABLE V

Results of Analysis of Variance Tests

Dependent Variable	Effect	Sum of Squares	Degrees of Freedom	Mean Sum of Squares	Calculated F Statistic	Tabulated $F_{0.95}$ Statistic
Weight loss (bench scale)	Preoxidation time	0.000260	2	0.000130	1.37	3.55
	Preoxidation temperature	0.010206	2	0.005103	53.72	3.55
	Temperature-time interaction	0.001465	4	0.000366	3.85	2.95
	Error	0.001708	18	0.000095		
	Total	0.013639	26			
Free swelling index (bench scale)	Preoxidation time	1.68518	2	0.84259	8.27	3.55
	Preoxidation temperature	1.40741	2	0.70371	6.91	3.55
	Temperature-time interaction	0.37037	4	0.09259	0.91	2.95
	Error	1.833334	18			
	Total	5.29630	26			
Volatile matter (bench scale)	Preoxidation time	0.00110	2	0.00055	8.25	3.55
	Preoxidation temperature	0.00040	2	0.00020	3.00	3.55
	Temperature-time interaction	0.00340	4	0.00085	12.75	2.95
	Error	0.00120	18	0.00007		
	Total	0.00610	26			
Tar yield (dry basis)	Carbonizing time	0.007233	2	0.003617	13.50	19.0
	Carbonizing temperature	0.000104	1	0.000104	0.39	18.5
	Preoxidizing time	0.012872	1	0.012872	47.90	18.5
	Carbonizing time-temperature interaction	0.000383	2	0.000191	0.71	19.0
	Carbonizing time-preoxidation time interaction	0.000450	2	0.000225	0.84	19.0
	Preoxidation time-carbonization temperature interaction	0.001137	1	0.00137	4.23	18.5
	Three-way interaction	0.000518	2	0.000269		
	Total	0.022699	11			
Gas yield	Preoxidation time	0.3072	1	0.3072	10.78	18.5
	Carbonization temperature	0.3468	1	0.3468	12.17	18.5
	Carbonization time	3.1400	2	1.5700	55.09	19.0
	Preoxidation time-temperature interaction	0.0280	1	0.0280	0.98	18.5
	Preoxidation time-carbonization time interaction	0.0126	2	0.0063	0.22	19.0
	Carbonization time-temperature interaction	0.0182	2	0.0091	0.32	19.0
	Three-way interaction	0.0569	2	0.0285		
	Total	3.9097	11			
Specific gravity of tar	Preoxidizing time	0.000685	1	0.000685	114.17	18.5
	Carbonization time	0.000001	1	0.000001	0.17	18.5
	Carbonization temperature	0.000025	2	0.000012	2.00	19.0
	Preoxidation time-temperature interaction	0.000001	1	0.000001	0.17	18.5
	Preoxidation time-carbonization time interaction	0.000001	2	0.0000005	0.08	19.0
	Carbonization time-temperature interaction	0.000008	2	0.000004	0.67	19.0
	Three-way interaction	0.000013	2	0.000006		
Bulk density of char	Carbonization temperature	0.00753	1	0.00753	0.0017	18.5
	Carbonization time	0.84920	2	0.42460	0.0886	19.0
	Preoxidation time	0.04000	1	0.04000	0.0083	18.5
	Carbonization time-temperature interaction	2.95000	2	1.47000	0.3070	19.0
	Preoxidation time-temperature interaction	1.77000	2	0.85000	0.1770	19.0
	Preoxidation time-temperature interaction	1.14300	1	1.14300	0.2390	19.0
	Three-way interaction	9.58000	2	4.79000		
Tar viscosity	Preoxidation time	7071.31	1	7071.31	151.36	18.5
	Carbonization time	290.20	2	145.10	5.25	19.0
	Carbonization temperature	266.03	1	266.03	5.69	18.5
	Preoxidation time-carbonization time interaction	45.37	2	22.78	0.49	19.0
	Preoxidation time-temperature interaction	5.46	1	5.46	0.16	18.5
	Carbonization time-temperature interaction	54.03	2	27.01	0.58	19.0
	Three-way interaction	92.44	2	46.72		
	Total	7824.93	11			
20 Per Cent Distillation temperature of tar product	Preoxidation time	15,052.09	1	15,052.09	64.16	18.5
	Carbonization	216.75	1	216.75	0.92	18.5
	Carbonization time	868.17	2	434.09	1.85	19.0
	Preoxidation time	470.16	2	235.08	1.00	19.0
	Preoxidation temperature	154.08	1	154.08	0.66	18.5
	Time-temperature interaction	514.50	2	257.25	1.10	19.0
	Three-way interaction	467.17	2	234.59		

Sample Calculations

Samples of the calculations neccessary to obtain the results shown in the preceding sections are given in the following paragraphs.

Distillate Yields. The manner by which the various distillate yields were calculated is presented below. The calculation is shown for the yield of total condensate in test number eleven.

$$y = W_d / W_c$$

where:

y = distillate yield, per cent
W_d = weight of condensate, pounds
W_c = weight of charge, pounds

$$y = 1.18/5.5$$
$$y = 21.5\%$$

Determination of Volatile Matter. The calculation for the amount of volatile matter contained in sample is shown below. The calculation is shown for T_{111}, Table VI, page 74.

$$x = W_1 / W_s$$

where:

x = volatile matter, per cent

W_1 = weight low of sample upon heating, gm

W_s = sample weight, gm

$$x = 0.3766/1.007$$

$$x = 37.4\%$$

Gas Analysis. The percentage of a given component in a gas sample was determined by the following calculation. The calculation is shown for the carbon dioxide in the retorting gas in test number twelve, Table III, page 59.

$$x_c = A_c(1/T_o - T_c)/\Sigma A^*$$

where:

x_c = amount of component in gas, per cent

A_c = area under peak on chromatographic curve, area units

T_c = thermal conductivity of component, cal/gm-sec x 10^5

T_o = thermal conductivity of carrier gas, cal/gm-sec x 10^5

A^* = sum of all the corrected areas under the peaks on the chromatographic curve, area units

$$x_c = 15.3(\ 1/36.7 - 4.3\ )/1.11$$

$$x_c = 42.8\%$$

Determination of Tar Specific Gravity. The specific gravity of the various tar samples was calculated as shown below. The calculation is shown for test number nine, Table III, page 59.

$$s = (W_t - W)/(W_w - W)$$

where:

s = specific gravity of sample

W_t = weight of bottle plus tar, gm

W_w = weight of bottle plus water, gm

W = weight of bottle, gm

$$s = (53.7960 - 27.6438)/(53.0734 - 27.6438)$$

$$s = 1.028$$

Determination of Bulk Density of Coke. The equation for determining the bulk density of the coke is

$$D_b = \frac{W_t - W_b}{V_b}$$

where:

D_b = bulk density of the coke, lb/cu ft

W_t = weight of coke plus density box, lb

W_b = tare weight of density box, lb

V_b = volume of density box, cu ft.

Substituting data from Sample number 7, Table III, page 59.

$$D_b = \frac{3.156-1.406}{0.113} = 15.5 \text{ lb/cu ft.}$$

<u>Determination of Calorific Value of Coke</u>. The equation for determining the calorific value of the coke is

$$H = \frac{t\ (Cwe) - 5(L)\ \ 23\ (w_s \times S)\ \ V}{w_s}$$

where:

H = calorific value of coke, Btu/lb

t = corrected temperature rise in calorimeter, ^{o}F

C_{we} = water equivalent of calorimeter, Btu/^{o}F

L = length of fuse wire burned, cm

w_s = weight of coke sample, gm (all samples were 1.0 gm)

S = per cent of sulfur in coke sample, %

V = volume of sodium carbonate used in acid titration, ml.

Substituting data from sample number 6, Table III, page 59.

$$H = (5.755)(2444) - 5(6.2)\ 23$$
$$(1.0 \times 0.8)\ 23 = 13{,}992 \text{ Btu/lb.}$$

Determination of Calorific Value of Gas. The equation for determining the calorific value of the gas is

$$H_g = [(N_{CO})(H_{CO}) + (N_{CH_4})(H_{CH_4}) + (N_{C_2H_6})(H_{C_2H_6}) + (N_{C_3H_8})(H_{C_3H_3})]\ 1.8$$

where:

H_g = calorific value of gas Btu/mol

N_{CO} = mol fraction of carbon monoxide in sample, dimensionless

H_{CO} = heat of combustion[a] of carbon monoxide, cal/gm mol

N_{CH_4} = mol fraction of methane in sample, dimensionless

H_{CH_4} = heat of combustion[a] of methane, cal/gm mol

$N_{C_2H_6}$ = mol fraction of ethane in sample, dimensionless

$H_{C_2H_6}$ = heat of combustion[a] of ethane cal/gm mol

$N_{C_3H_8}$ = mol fraction of propane in sample, dimensionless

$H_{C_3H_3}$ = heat of combustion[a] of propane, cal/gm mol

1.8 = conversion factor, gm mol-Btu/lb mol-cal.

Substituting data from sample number 6, Table III, page 59,

$$\begin{aligned} H_g &= [(0.193)(67{,}636.1)+(0.318)(212{,}798) \\ &\quad +(0.029)(372{,}870)+(0.0)(530.605)] \times 1.8 \\ &= 164{,}764 \text{ Btu/mol.} \end{aligned}$$

[a] The heats of combustion are for the formation of liquid water and gaseous carbon dioxide at 25 °C and constant pressure.

<u>Coding Percentages</u>. In the analysis-of-variance method, percentages have to be coded before they can be subjected to analysis. The percentages, p, are converted to the scores, x, which approximate a normally distributed variable, as shown below.

$$x = \arcsin \sqrt{p}$$

where:

x = score, radians

p = percentage

$$x = \arcsin \sqrt{0.0231}$$

$$x = 0.153 \text{ radians}$$

Analysis of Variance Technique. The statistical methods used in this investigation for the analysis of the data were the analysis-of-variance tests suggested by Dixon and Massey. This method of statistical analysis entailed the calculation of the sums of squares, degrees of freedom, and means sums of squares for the effects of the various independent variables studied in the investigation, and the interactions between these variables. With these calculations completed, it was necessary to determine the value of the "F" statistic for each variable and for the various interactions between these variables.

As a sample of the calculations employed in the analysis of variance method, the analysis-of-variance of the data showing the effect of time and temperature of preoxidation upon the volatile matter in the treated coal is presented in detail in the paragraphs that follow.

Before proceeding with this explanation, the author wishes to clarify the coding and terminology used hereafter. In this phase of the investigation, twenty-seven tests were performed, at three levels of preoxidation time, three levels of preoxidation temperature, and with three replications at each combination. The twenty-seven tests were each assigned a number; these numbers were selected randomly and the tests were then performed in that order. To best explain the calculations, a coding system was used. Each individual test was designated by a "T" followed by a three digit subscript; in general T_{abc}. Numbers (1, 2, or 3) in an a, b, or c position of the three digit subscript indicate the various levels of temperature, replication, or time, respectively.

In computing the sums of squares for the variables it is necessary to determine various totals as sums of the dependent variable values. Reference is made to the symbols presented in Table VI, page 74. A symbol such as $T_{.11}$ designates the sum of T_{111}, T_{112}, and T_{113}. Further, $T_{.1.}$ designates the sum of $T_{11.}$, $T_{21.}$, and $T_{31.}$. Finally, $T_{...}$ represents the sum of all of the twenty-seven individual test values. The twenty-seven tests (three replicates) were performed in order to increase the number of degrees of freedom for the residual term thus making a more sensitive "F" test.

Calculation of the Sums of Squares. To conduct an analysis-of-variance test it was necessary to compute the sum of squares for the length of preoxidation time, the temperature of preoxidation, the interaction between these variables, and the error sum of squares. The totals employed in the sum of squares calculations are presented in Table VI, page 74, for example.

TABLE VI

Symbols Involved in the Application of the Analysis of Variance Techniques to the Data of This Investigation

Code for Volatile Matter				Volatile Matter in Sample After Preoxidation, Weight Per Cent			
T_{111}	T_{211}	T_{311}		0.658	0.625	0.629	
T_{112}	T_{212}	T_{312}	$T_{.1.}$	0.634	0.628	0.621	
T_{113}	T_{213}	T_{312}		0.590	0.641	0.630	
T_{121}	T_{221}	T_{321}		0.649	0.634	0.635	
T_{122}	T_{222}	T_{322}	$T_{.2.}$	0.631	0.618	0.621	
T_{123}	T_{223}	T_{323}		0.614	0.631	0.623	
T_{131}	T_{231}	T_{331}		0.647	0.639	0.606	
T_{132}	T_{232}	T_{332}	$T_{.3.}$	0.639	0.623	0.613	
T_{133}	T_{233}	T_{333}		0.595	0.640	0.618	
$T_{1...}$	$T_{2...}$	$T_{3...}$	$T_{...}$	5.657	5.679	5.596	16.932
T_{111}	T_{211}	T_{311}		0.658	0.625	0.629	
T_{121}	T_{221}	T_{321}	$T_{..1}$	0.649	0.634	0.635	5.722
T_{131}	T_{231}	T_{331}		0.647	0.639	0.606	
T_{112}	T_{212}	T_{312}		0.634	0.628	0.621	
T_{122}	T_{222}	T_{322}	$T_{..2}$	0.631	0.618	0.621	5.628
T_{132}	T_{232}	T_{332}		0.639	0.623	0.613	
T_{113}	T_{213}	T_{313}		0.590	0.641	0.630	
T_{123}	T_{223}	T_{323}	$T_{..3}$	0.614	0.631	0.623	5.582
T_{133}	T_{233}	T_{333}		0.595	0.640	0.618	
$T_{1..}$	$T_{2..}$	$T_{3..}$	$T_{...}$	5.657	5.679	5.596	16.932

Sum of Squares for Temperature. The sum of squares for temperature was calculated as shown below:

$$SSA = \frac{(T_{1..})^2}{n} \quad \frac{(T_{2..})^2}{n} \quad \frac{(T_{3..})^2}{n} - \frac{(T_{...})^2}{N}$$

where:

SSA = sum of squares for temperature effect

T's = previously defined

n = number of observations in each total

N = total number of observations

$$SSA = \frac{(5.657)^2}{9} \quad \frac{(5.679)^2}{9} \quad \frac{(5.596)^2}{9} - \frac{(16.932)^2}{27}$$

$$SSA = 0.0004$$

Sum of Squares for Time Effect. The sum of squares for the time effect was calculated as shown below:

$$SSB = \frac{(T_{..1})^2}{n} + \frac{(T_{..2})^2}{n} + \frac{(T_{..3})^2}{n} - \frac{(T_{...})^2}{N}$$

where:

SSB = sum of squares for time effect

T's = previously defined

N = total number of observations

n = number of observations in each total

$$SSB = \frac{(5.722)^2}{9} + \frac{(5.628)^2}{9} + \frac{(5.582)^2}{9} - \frac{(16.932)^2}{27}$$

$$SSB = 0.0011$$

<u>Sum of Squares for Interaction Between Time and Temperature of Preoxidation</u>. The sum of squares for the interaction between the time and temperature of preoxidation was calculated as shown below.

$$\begin{aligned} SSAB = {} & \frac{(T_{1.1})^2}{n} + \frac{(T_{1.2})^2}{n} + \frac{(T_{1.3})^2}{n} + \frac{(T_{2.1})^2}{n} \\ & + \frac{(T_{2.2})^2}{n} + \frac{(T_{2.3})^2}{n} + \frac{(T_{3.1})^2}{n} + \frac{(T_{3.2})^2}{n} \\ & + \frac{(T_{3.3})^2}{n} - \frac{(T_{...})^2}{N} - SSA - SSB \end{aligned}$$

where:

SSAB = sum of squares for the time-temperature interaction

SSA = sum of squares for the temperature effect

SSB = sum of squares for the time effect

T's = previously defined

n = number of observations in each total

N = total number of observations

$$\begin{aligned} SSAB = {} & \frac{(1.954)^2}{3} + \frac{(1.898)^2}{3} + \frac{(1.870)^2}{3} + \frac{(1.904)^2}{3} \\ & + \frac{(1.869)^2}{3} + \frac{(1.855)^2}{3} + \frac{(1.799)^2}{3} + \frac{(1.912)^2}{3} \\ & + \frac{(1.871)^2}{3} - \frac{(16.932)^2}{27} - 0.0004 - 0.0011 \\ = {} & 0.0034 \end{aligned}$$

<u>Calculation of Error Sum of Squares</u>. The error sum of squares in calculation as shown below.

$$SSE = \Sigma(T_{abc})^2 - \frac{(T_{\cdots})^2}{N} - SSA - SSB - SSAB$$

where:

SSE = error sum of squares

SSA = temperature sum of squares

SSB = time sum of squares

SSAB = time-temperature interaction sum of squares

$\Sigma(T_{abc})2$ = sum of squares of all individual values

$T_{\cdots}$ = Previously defined

N = total number of observations

$$SSE = 10.6244 - \frac{(16.932)^2}{27} - 0.0004 - 0.0011 - 0.0034$$

$$SSE = 0.0012$$

Degrees of Freedom. The number of terms, in a sum of squares, which can be arbitrarily assigned (56). For example, the sum of squares of deviations from the mean in a sample of (n) observations has (n-1) degrees of freedom, because when any (n-1) deviations are known the (n)th is also known.

Mean Sum of Squares. The mean sum of squares was calculated as shown below:

$$\mathrm{MSSA} = \frac{\mathrm{SSA}}{\mathrm{df}}$$

where:

MSSA = mean sum of squares for temperature

SSA = sum of squares for temperature

df = degrees of freedom for temperature

$$\mathrm{MSSA} = \frac{0.0011}{2}$$

$$\mathrm{MSSA} = 0.00055$$

<u>Calculation of "F" Statistic</u>. The "F" statistic was calculated as shown below.

$$F = \frac{MSSA}{MSSE}$$

where:

F = "F" statistic

MSSA = mean sum of squares for temperature

MSSE = mean sum of squares for error

$$F = \frac{0.000550}{0.000067}$$

$$F = 8.25$$

Determination of the "$F_{0.95}$" Value. The value of the "F" statistic can be found in tabular form in Dixon and Massey (26). The two significance levels most commonly used are the 0.95 and the 0.99. The significance level used in this investigation was 0.95.

IV. DISCUSSION

The following section contains a discussion of the phases of this investigation. The phases to be discussed are (1) why the experimentation was divided into two phases; (2) how the levels for the independent variables were chosen; (3) the operating characteristics of the experimental equipment; and (4) a discussion of the results of the experimentation. Also included in this discussion are the recommendations for further study and the limitations under which the experimental work was conducted.

Discussion of the Two Phases of Experimentation

In the following paragraphs is a discussion of why it was believed necessary to conduct the experimental work in this investigation in two phases.

Sampling and Replication. The whole investigation concerning the low-temperature carbonization of Penn-Lee coal, of which this thesis is a part, was restricted to a study of lump coal. Hence, it was decided to use lump coal in the bench-scale studies in an attempt to scale up the operating variables to a pilot-scale retort. The coal, as received, was in lump form varying in size from 1/2 to 6 inches. These lumps were crushed until all of the coal to be used in the tests was minus two inches. The lumps for the bench-scale studies were screened to minus 3/4, plus 1/2 inch. All samples used in the investigation were taken by the generally accepted method of coning and quartering. In an effort to reduce the sampling error to a minimum, three replicates were made of all bench-scale tests.

Bench-Scale Experimental Tests. Except for the proximate and ultimate analyses, there was virtually no information available in the literature concerning the properties of Penn-Lee coal such as ignition point, decomposition point, etc. In order to gain as much information as possible about Penn-Lee coal, before attempting to use the pilot-scale carbonization unit, it was decided to conduct a series of bench-scale experiments. This was done in order to determine the unknown properties and to gain a general idea as to the range of operating variables that should be used on the pilot-scale unit. The bench-scale equipment used was not an exact model of the larger equipment but an attempt was made to keep the superficial mass flow rate of the gas approximately the same for both units.

Pilot-Scale Experimental Tests. The pilot-scale experimentation was conducted to obtain the maximum amount of information from the least possible number of tests. This experimental design was necessary because of the expense and the length of time required for a test. The pilot-scale equipment was designed so that all of the independent variables could be adjusted during the course of each test. In addition, provision was made for collecting gas samples, measuring the gas evolved, and collecting the coal distillate. It was believed that the apparatus used would allow a thorough examination of all the dependent variables studied in this investigation.

Discussion of the Independent Variables Studied

The paragraphs that follow contain a discussion of the independent variables and why the operating levels were chosen.

Bench-Scale Investigation. The three independent variables chosen for the bench-scale study were the temperature, the length of pretreatment, and the pretreating atmosphere.

Air was chosen as the pretreating medium since the survey of the literature indicated that the addition of oxygen to the coal could modify its carbonizing properties. Air was chosen because of its availability, ease of handling, and because large quantities of the pretreating medium were needed.

The temperature levels were chosen at 400, 500 and 600 °F. The lower level was set at 400 °F because various authors (22, 24, 34, 41) had pointed out that the addition of oxygen to coal at temperatures lower than 400 °F had relatively little effect on the carbonizing properties of the coal. The upper limit for the pretreatment of coal was set at 600 °F when it was determined that the coal used in this investigation would ignite spontaneously when exposed to air at temperatures of approximately 625 °F. The 100 °F-interval was selected because it was believed that this interval would disclose any trends due to the effect of temperature without requiring an unnecessarily large number of experiments in the statistical design.

The time levels for the pretreatment were chosen at 1, 2, and 3 hours. The one-hour level was chosen based on information found in the literature (25). The three-hour level was decided upon after making some preliminary tests in order to determine approximately how long pretreatment should be carried on to destroy the caking power of the coal. Ground samples of the coal (minus 100-mesh) pretreated and then carbonized. The coke button was then examined to ascertain the extent of caking. The results were deduced entirely by qualitative means. From the results it was decided that three hours of pretreatment at a temperature of 600 °F was sufficient to destroy the caking powers of Penn-Lee coal.

Pilot-Scale Investigation. The pretreating medium was previously chosen to be air, hence there were four independent variables to be studied in the pilot-scale investigation, namely, the length and the temperature of pretreatment, the length and the temperature of carbonization.

It soon became apparent that the results and conditions thought to be suitable for the pretreatment in the bench-scale tests were not necessarily suitable for the pilot-scale tests. The first five tests as shown in Table III, rear pocket, indicated that the pretreatment conditions of 600 °F for 3 hours (bench-scale tests) were insufficient to enable the completion of a test without plugging of the coal in the retort. The first tests indicated that the minimum temperature of pretreatment that would give a non-caking bed was 600 °F. The temperature finally selected was 620 ± 20 °F. This temperature resulted in a bed that was continually on the verge of combustion; the tendency of the bed to ignite spontaneously was controlled as explained in the procedure on page 48. The tests also indicated that a minimum of two hours at 620 °F would be required to produce a bed of coal that would not fuse and plug the retort. The four-hour pretreatment was selected arbitrarily to give another level so that any trend resulting from the increased time could be detected.

The carbonizing temperatures were selected at 830 °F and 950 °F. A temperature of 830 °F was selected as being just above the decomposition point of the coal (approximately

750 °F) and 950 °F was selected as the upper limit because this temperature was just below the upper operating limit of the carbonizing unit.

The carbonizing times were selected at 1, 1-1/2, and 2 hours. The one-hour limit was chosen in order to have a portion of the tests stopped before the carbonization was complete, and the two-hour tests were chosen so as to have a portion of the tests stopped after carbonization had been completed.

Discussion of Operating Characteristics

In the following paragraphs will be found a discussion of the operating characteristics of both the bench-scale and the pilot-scale experimental apparatus.

Bench-Scale Unit. Operation of the bench-scale equipment proved to be fairly simple. The major difficulty that had to be overcome was that of heating the air to the proper temperature. This problem was primarily one of heater design. It was necessary to pack the heater tube with crushed fire brick in order to obtain high enough local velocities in the heater to get the necessary heat transfer. No other difficulties were encountered in the operation of the bench-scale equipment.

Pilot-Scale Unit. The same heater characteristics were observed in the operation of the pilot-scale unit as in the operation of the bench-scale heater. During the pretreatment of the coal charge in the retort, it was found that manual operation of the valves admitting air into the system and controlling the amount of recycle gas was unsatisfactory. Coal is heterogeneous by nature and in this investigation where lump studies were being made, the coal in the retort tended to develop "hot" spots where a local reaction was taking place. Since there were only three thermocouples in the retort, spaced at one-foot intervals, Figure VI, rear pocket, there were times when the localized reaction would take place between the thermocouples and it would not be known to the operators until the reaction was beyond control. It would be desirable in a study of this sort to have closely spaced sensing elements in the retort that controlled automatic valves to change the amount of air admitted into the system so that the reaction could be maintained at the rate desired.

Discussion of Results

In the following sections is a discussion of the results of the experimentation performed during the course of this investigation.

Effect of Bench-Scale Pretreatment on the Free-Swelling Index. The free-swelling index of the raw coal was 3.0. An increase in the length of pretreatment from one to three hours was found to decrease the average free-swelling index of the treated coal from 1.94 to 1.33. An increase in the temperature of pretreatment from 400 to 600 °F was found to decrease the average free-swelling index of the treated coal from 1.89 to 1.33. An analysis of variance of the data gave "F" values of 6.91 and 8.27 for the temperature and time effects respectively. An "F" value of 3.55 was required at the 95 per cent level for significance.

It is probable that, on the basis of this data, the same effect can be achieved by treating the coal for a longer time at a lower temperature, that is to say that the coal could be treated for one hour at 600 °F and the same result could be achieved by treating the coal for two hours at 500 °F. This argument is reasonable since other investigators(55) have shown that heat causes the coal molecules to polymerize, and if some substance such as oxygen is present to react with the coal an increase in the temperature will increase the reaction rate. The polymerization theory is based on the fact that the tar removed from the pretreated samples was less in quantity and of a more viscous nature when obtained from strongly pretreated samples.

Effect of the Bench-Scale Pretreatment on the Volatile Matter Retained in the Coal. An increase in the length of pretreatment from one to three hours caused a decrease in the average in the volatile matter retained in the samples from 35.3 to 33.8 per cent. An analysis of variance of the data gave an "F" value of 8.25 where a value of 3.55 was necessary for significance at the 95 per cent level.

The reduction in the volatile matter in the samples can be explained in two ways. The effect of temperature on the coal could have resulted in driving off the natural moisture in the coal with a subsequent loss in the volatiles in the coal. On the other hand, the effect of temperature could have been that the coal molecules were polymerized to the point that when the coal was carbonized, the polymers were non-volatile.

The effect of the temperature on the volatile matter retained in the coal samples was found to be statistically insignificant. An "F" value of 3.00 was calculated by an analysis of variance, and a value of 3.55 was required at the 95 per cent level for significance.

The time-temperature interaction was found to be significant as an "F" value of 12.75 was calculated from the data where a value of 2.93 was required for significance at the 95 per cent level. This interaction is clearly shown by the trend in Figure 8, page 57. It can be seen that at a pretreatment temperature of 400 °F an increase in pretreatment time causes a sharp decrease in the retained volatile matter. At 600 °F, however, an increase in pretreatment time has little effect on the retained volatiles. This would indicate that the loss of moisture is of only minor importance on the loss of volatile matter in pretreated coal. The greatest decrease in volatiles with increasing pretreatment time occurred at the lowest temperature studied, 400 °F. Apparently, pretreatment at higher temperatures must lead to some actual cracking-type reactions or oxidation reactions in which relatively volatile reaction products are formed. Other reactions such as the simple addition of oxygen should be of the opposing type. In this sense it would tend to "tie up" the volatile matter, while the cracking or degradation type of reaction would tend to create more volatile material in the coal. Figure 8, page 57 would indicate this type of reaction.

The Effect of Pretreatment on the Sample Weight Loss in Bench-Scale Tests. An increase in the length of pretreatment caused an increase in the weight loss for the tests at 400 and 500 °F for the first two hours of treatment. This loss is probably due to the loss of moisture from the coal; opposing this loss is the addition of oxygen. It is possible that the weight gained due to the addition of the oxygen eventually exceeds that lost due to the loss of moisture. The maximums in the weight loss curves at approximately two hours can probably be explained by this phenomenon. The opposite effect is found for the 600 °F isotherm. One possible explanation for this apparent anomaly is that the loss of moisture is complete in less than one hour and that the polymerization and oxygen addition reactions cause a decrease in the weight loss for times up to two hours. Continuing the pretreatment longer than two hours apparently results in the degradation of some of the fringe groups on the coal molecules, and as the products of this degradation are largely gaseous, this could explain the increase in weight loss at three hours.

An analysis of variance of the data resulted in an "F" value of 1.37 where a value of 3.55 is required for significance at the 95 per cent level. The effect of time at various levels of preoxidation temperature is significant. This significance is shown by the time-temperature interaction "F" value of 3.85 where a value of 2.93 is required at the 95 per cent level for significance. The fact that this interaction is significant lends support to the attempt in explaining the apparent reversal of the trend in the weight loss curves from 500 to 600 °F.

The effect of increasing the preoxidation temperature resulted in a rapid increase in the sample weight loss above 500 °F. From 400 °F to 500 °F the weight loss of the sample increased from an average of 2.35 to 2.63 per cent when going from the lower to the higher temperature. From 500 °F to 600 °F, however, the average weight loss increased from 2.63 to 3.90 per cent. The total temperature effect was significant having a "F" value calculated from the data of 53.72, where a value of 3.55 was necessary for significance at the 95 per cent level.

Gas Evolved During Carbonization in Pilot-Scale Tests. The effects of pretreatment on the quantity of gas evolved during carbonization were found to be statistically insignificant. Increasing the level of preoxidation from two to four hours caused an increase in the quantity of gas evolved from 1.05 to 1.37 cubic feet. During the carbonization of the charge, the average quantity of gas evolved at the end of one hour was 0.615 cubic feet and at the end of two hours was 1.87 cubic feet. This increase was to be expected (49).

The Effect of Pretreatment Conditions on the Composition of the Gas Evolved During Carbonization in Pilot-Scale Tests. An increase in the length of pretreatment from two to four hours resulted in an increase in the carbon monoxide content of gas from 12.6 to 15.7 per cent.

According to Hurd (52) an increase in the degree of oxidation of the coal prior to carbonization will increase the formation of oxidized compounds such as hydroxy-ketones, keto-acids, aldehydes, hydroxy-acids, and ketones. Many of these compounds decompose upon pyrolysis to form carbon monoxide or carbon dioxide. Hickenbottom (51) states that keto-acids decompose on heating to form carbon monoxide and water. Hurd (52) states that benzaldehyde and dibenzyl-ketone decompose upon heating to form carbon monoxide as on of the products.

An examination of Table III, page 59, shows that the maximum concentration of carbon monoxide in the retorting gas is found at the end of the one hour tests. This indicates that most of the carbon monoxide if formed during the first hour of carbonization, thereafter, the concentration of methane in the retorting gas increased steadily as the carbonization proceeded, averaging 31.8 per cent at the end of one hour and 76.5 per cent at the end of two hours. An explanation for this continuous increase in the methane concentration is that the heavier coal molecules that are vaporized from the coal are cracked as they pass through the gas heater. No trace of hydrogen was found in the retorting gas as would have been expected (50) since the temperatures on the surfaces of the heater were 1200 °F. There are two reasons why hydrogen would be removed from the retorting gas stream. The most feasible reason is that the oxygen, which had been absorbed on the surface of the coal, is driven off when the coal is heated to carbonizing temperature and is free to react with any hydrogen that may be present to form water. This reaction also partially explains the large quantities of water that appear in the condensate collecting cups. Since the carbonizing unit was of the recycle type, all of the noncondensable gases were recycled through the gas heater. In passing through the gas heater the light hydrocarbon gases might have been cracked. This cracking process would undoubtedly produce two lighter molecules, one saturated and one unsaturated. The conditions in the retort were such that any hydrogen present would have combined with the unsaturated molecules. The possibility of the latter mechanism accounting for any large reduction in any hydrogen present is small because the concentration of ethane in the retorting gases at the end of a test was less than 5 per cent.

The Effect of Pretreatment on the Dry Tar Yield. An increase in the length of pretreatment had a definite effect on the dry tar yield. It was found that an increase from two to four hours of pretreatment caused the dry tar yield to decrease from an average of 8.3 to 5.0 per cent. There may be several reasons why this occurred. The addition of oxygen to the coal molecules resulted in a heavier molecule both because of the addition and because of the polymerization caused by the oxygen. These heavier molecules are less volatile than the lighter ones and they may not have been vaporized at the carbonization temperatures studied. The conditions under which the coal was pretreated could have produced a film or dense layer on the surface of the lumps that would resist the diffusion of the vapers to the surface. The probability is that all of these phenomenon occurred to some degree but it was not possible, during the course of this investigation, to determine the degree to which each was present.

An analysis of variance of the data resulted in an "F" value of 47.9 when a value of 18.5 was needed for significance at the 95 per cent level. Since these experiments were replicated only once, the mean square for the preoxidation time effect was compared with the (three way interaction) residual mean square.

<u>The Effect of Pretreatment on the Dry Tar Yield at Different Carbonizing Time Levels</u>. An increase in the length of pretreatment had the same effect on the dry tar yield when the coal was carbonized for times of one, one and one-half, and two hours. Increasing the pretreatment time from two to fours hours reduced the dry tar yields by 41, 42, and 36 per cent respectively. The reasons for this decrease

in dry tar yield are tha same as those discussed in the preceding paragraph. The fact that the effect is similar at different time levels of carbonization helps to substantiate the results obtained concerning the effect of pretreatment time on the dry tar yields.

The Effect of Pretreatment on Tar Viscosity. Increasing the length of pretreatment from two to four hours resulted in a 62.5 per cent increase in the viscosity of the tar obtained during the carbonization. "Drained tar," as used in this investigation, refers to the crude tar condensate after the water had been decanted. The drained tar still contained about 40 per cent water which could be removed by distillation at 572 °F, if the two distilled phases were carefully separated.

The reasons for the increase in the viscosity of the tar are probably similar to those given for the effect of pretreatment on the tar yields. It is known that the addition of oxygen to the molecules causes an increase in molecular weight and increases the degree of polymerization of the molecules (53). It has also been shown (54) that heating the coal in the absence of oxygen will also cause some degree of polymerization. It is probably that a combination of these three effects caused the observed increase in viscosity of the tar.

An analysis of variance of the data gave an "F" value of 151.36 where a value of 18.5 was required for significance at the 95 per cent level. This very large "F" value clearly substantiates the strong effect of pretreatment on the viscosity of the coal tar.

The Effect of Pretreatment on the Tar Distillation Characteristics. An increase in the length of pretreatment from two to four hours caused an increase in the average 20 per cent-point distillation temperature from 491 to 628 °F. It would be normal to expect the distillation curves to be higher on the temperature scale if the average molecular weight of the molecules were increased. It is believed that this is the case and the presence of the heavier molecules in the tar obtained from more strongly preoxidized coal is explained by the reasons given in the preceding paragaphs. Since the tar yields were considerably reduced by the more severe treatment, it is also possible that the stronger treatment reduced the quantity of low boiling compounds in the coal, thereby increasing the apparent viscosity and the boiling range of the tar.

The analysis of variance of the data resulted in an "F" value of 64.16 for the effect of pretreatment time on the 20 per cent distillation point of the tar. A value of 18.5 was required at the 95 per cent levle for significance.

The Effect of Pretreatment on the Viscosity of the Tar. An increase in the length of pretreatment of the coal from two to four hours resulted in an average increase in the average specific gravity of the tar from 1.026 to 1.040. This effect is to be expected since the preoxidation of the coal results in products with a higher carbon to hydrogen ratio (22) and with fewer of the side chains that would cause spatial effects where the density of the tar is concerned.

The analysis of variance of the data gave an "F" value of 114.17 where a value of 18.5 was required for significance at the 95 per cent level.

The Effect of Pretreatment on the Bulk Density Yield, Calorific Value, and Volatile Matter of the Char. The average bulk density of the char was 16.58 pounds per cubic feet. This average was not affected by the conditions of pretreatment. This is compared with a bulk density of 38.7 pounds per cubic feet for the raw coal.

The conditions of pretreatment had little or no effect on the yields of char, although the carbonizing conditions do have a marked effect. The average char yield expressed as a per cent of the weight of the raw coal charge was 81.0, the loss being due to the tars and gases that were evolved during carbonization and preoxidation.

The average calorific value of the char was 13,860 Btu/lb compared to a value of 13,550 Btu/lb for the raw coal. This increase over that of the raw coal can be explained in part by the fact that the char is dry and it is not necessary for part of the heat of combustion to be used to vaporize the moisture that is found in the raw coal.

The average volatile matter contained in the char was 7.9 per cent. The char was found to burn cleanly with no noticeable amount of smoke or soot.

Statistically, the effect of pretreatment conditions was found to be insignificant.

Water Formed During Carbonization. The total amount of water collected during the carbonization of the coal charge was an average of 7.8 weight per cent of the raw coal charge, while the moisture content of the raw coal was known to be 2.7 per cent. The appearance of this additional water can be explained in two ways. The hydrogen that is formed during the carbonization could react with the oxygen that is desorbed from the coal surface to form the water. Orchin (36) states that certain condensation reactions occur on the fringe groups on the coal molecule with water as a by-product. It is also possible that some of the oxygen evolved from the coal surface reacted with the hydrocarbons to form completely oxidized products such as carbon dioxide and water.

Recommendations

In the following sections will be found the recommendations that are offered for continuing this or similar investigations. These recommendations are based on the results of the experimentation and the operating characteristics of the experimental equipment.

Redesign of the Carbonizing Unit. The paragraphs below contain suggestions for changes in the low-temperature carbonization unit.

Redesign of the Gas Heater. A more versatile unit for heating the gas medium for the carbonizing process would enable the system to be operated as either a recycle or a single-pass "non-closed" system.

The recycle type of heater has advantages in that it allows the effects of pressure and various types of gaseous mediums to be studied. This heater should be designed so that a "clean" type of heat such as electrical heating can be used. This heater does not have to be of the packed-tube type, but it is necessary that the design be sophisticated enough so that the gas flowing through the heater is well into the turbulent range.

The single pass or "non-closed" type of heater has certain advantages in that it is possible to pass a hot gas of known composition through the bed of coal without having the carbonizing gases diluted with the gas and liquid components that are evolved from the coal. This heater can be designed so that the hot flue gases from the combustion of fuel oil or gas can be passed through the coal bed, or some other gas such as superheated steam might be employed. One advantage of the single-pass system is that any industrial application of this type of carbonization would probably be of the single-pass type and thus the experimental equipment would be more easily scaled-up to full size.

Modification of the Retort. Certain changes should be made in the method by which the retort is placed in the carbonizing unit. A hoist should be devised so that it would not be necessary for the operators to handle the entire weight of the retort when it is hot. Clamps of a type similar to those used on the Pfaudler type "P" reactor should be used to hold the retort in place. These changes will expedite the procedure for re-changing the retort and will shorten considerably the time required for a complete test.

Gas Pump. The sliding vane type of pump available for use in carbonizing system was unsuited to this application. Two of the major disadvantages of this type of pump are (1) the tendency of the pump to "freeze" when any entrained coal tar liquids are passed through it and (2) vaporization and entrainment of the oil used as the seal in the pump, to contaminate the gas stream. It is recommended that a pump of the rotary-lobe type be used as it will not tend to stick if entrained liquids are carried into it and is externally lubricated.

High Temperature Insulation. A high temperature insulation of the "Pink Kaylo" type sold by the Owens-Corning Fiberglass Corporation is recommended for insulating the gas heater. White Kaylo was used in the original design but it failed to withstand temperatures in excess of 1200 °F. The recommended insulation can withstand skin temperatures of 1800 °F. When it is used in conjunction with a four-inch layer of fiberglass the total heat loss can be reduced to approximately ten Btu/hr ft^2 when the skin temperature of the heater is 1800 °F.

Condensate Recovery. It is recommended that the condensers be so modified that either steam or hot gas of some type can be passed through the annular spaces. Reheating the condensers at the end of a test will enable the experimenters to collect the tar quantitatively in a much shorter time than would be required if the condensers were allowed to drain as they warmed to ambient temperature (normal operating temperatures for the condensers were 28 to 32 °F). It is also recommended that the volume of the collecting cups be tripled.

Gas Transmission Lines. In order to prevent the tars that are evolved during the carbonization process from condensing in the pipes between the retort and the condensers, it is recommended that these pipes be heated with electrical strip heaters. These heaters will require insulation of the type described for the gas heater. It was found that the 3/4 inch pipe used for the gas transmission lines in the carbonizing unit caused excess pressure drop in the system so it is recommended that piping no smaller than one and one-half inches be used in nay future investigation.

Metering the Pretreatment Air. A thin-plate orifice should be installed in the air intake line so that a quantitative determination of the amount of air added to the system can be obtained. If the exhaust gases are analyzed, it would then be possible to write a material balance around the system and determine the quantity of oxygen actually consumed during the pretreatment operation.

Controlling the Pretreatment Reaction. Manual operation of the valves used to control the amount of air entering the system during the pretreatment period, is unsatisfactory as the temperature of the reaction cannot be easily controlled. It is recommended that fast response thermocouples be installed in the retort as sensing elements for automatic valves in the recycle and air intake lines. Any rise in the retort temperature would result in the reduction of air added into the system resulting in a greater amount of the gas in the system being recycled.

Pilot-Scale Investigation. Recommendations for further pilot-scale studies on the low-temperature carbonization of Penn-Lee coal are listed in the following paragraphs.

Effect of Carbonizing Temperature. The effect of carbonizing temperatures should be studied over the range of 800 to 1200 °F at 50 °F intervals. This study would make possible the investigation of the effect of carbonizing temperature on the quantities and properties of the gases and liquids obtained. From the study of the temperature effect, it would be possible to determine the amount of cracking and degradation of the products.

Gas and Condensate Evolution. The evolution of tars and gases during carbonization should be studied as a function of time to determine the decomposition rate of the coal so that carbonizing conditions can be optimized. Information of this type is of great value in the preliminary design of a full scale unit. It is recommended that the amount of tar and gas evolved be measured at fifteen-minute intervals during the carbonization period and that this period be extended to at least four hours.

The Effect of Carbonizing Pressure. The effect of the pressure in the system during carbonization should be studied from partial vacuum to ten atmospheres. Since the coke formed during the carbonization is porous in nature, it is likely that the pressure in the system would have an effect on the rate at which the tars and gases diffuse through the coke and hence the rate at which the coal can be carbonized.

Other Pretreatments. It is recommended that other types of pretreatment prior to carbonization be studied. Some of the pretreatments that should be tried are oxidation with nitric acid or permanganates, and solvent extraction. The effects of the different types of pretreatment should be compared to determine the value of each from the standpoint of effectiveness and economics.

Bench-Scale Investigation. Recommendations for further bench-scale studies on the low-temperature carbonization of Penn-Lee coal are listed in the following paragraphs.

Rate and Mechanisms of Oxidation. The rate at which oxygen reacts with coal should be studied to obtain fundamental thermodynamic and kinetic data concerning the reaction. The mechanisms of oxidation should be studied on coals of different rank to obtain fundamental information concerning the structure of these coals. A correlation of the results of these studies would give a more complete and accurate picture of coal and its chemistry than is now available.

The Use of Dry Coal for Experimentation. It is recommended that coal dried at temperatures up to 400 °F be used in any future investigations. It is probable that the removal of water during the pretreatment tends to mask the loss of volatiles and the sample weight loss.

Pretreatment with Inert Gases. It is recommended that the coal samples be pretreated with various inert gases such as nitrogen and carbon dioxide in order to separate the effects of heat from those of oxidation. It should be possible to determine from these studies just how much of the polymerization is due to oxygen linking.

Products of Pretreatment. Condensers and gas sampling apparatus should be provided so that an analysis of the products of pretreatment can be collected and analyzed. It has not been reported in the literature just what were the products of oxygenation or at what point during the pretreatment they were evolved.

Analysis of the Products of Pretreatment and Carbonization. The vapor-liquid chromatograph is potentially a very valuable instrument for the analysis of gases and liquids. The instrument currently available is limited in that it cannot analyze liquids boiling at temperatures above about 450 °F. It is recommended that a chromatographic partitioner be constructed that uses a vapor bath and is capable of analyzing liquids boiling up to about 675 °F.

Limitations

This investigation was conducted under the limitations outlined below.

Coal. The coal used throughout the investigation was seam No. one, Penn-Lee coal from Maness, Virginia. The analysis of this coal is 37 per cent volatile matter, 54 per cent fixed carbon, 5.6 per cent ash, and 2.7 per cent moisture.

Charge Weight. The weight of the coal charge used for the bench-scale tests was 50 grams and the weight of the charge used for the pilot-scale tests was 5.5 pounds.

Gas Flow Rate. The gas flow rate used in both the bench and the pilot-scale tests was 12±0.1 cubic feet per minute.

Bench-Scale Investigation. The bench-scale investigation was conducted under the following limitations.

Temperature of Pretreatment. The coal samples were treated at temperatures of 400, 500, and 600 °F.

Time of Pretreatment. The coal samples were treated for times of one, two, and three hours.

Pilot-Scale Investigation. The pilot-scale investigation was conducted under the following limitations.

Temperature of Pretreatment. The samples of coal were pretreated at a temperature of 630±20 °F.

Time of Pretreatment. The coal samples were pretreated for times of two and four hours.

Time of Carbonization. The coal samples were carbonized for times of one, one and one-half, and two hours.

Pretreatment Medium. The medium used for the pretreatment of the coal samples in this investigation was air.

Carbonizing Medium. The medium used for the pretreatment of the coal samples in this investigation was carbon dioxide.

Coal Particle Size. In the bench-scale tests, the coal particle size was minus 3/4, plus 1/2 inch; in the pilot-scale tests the coal particle size was minus 2, plus 1 inch.

Type of Carbonizing Unit. The carbonizing unit used in all the pilot-scale tests was of the recycle, closed circuit type and was designed to operate at retort temperatures of 1000 °F and pressures of 20 pounds per square inch, gage.

Carbonizing Pressure. The pressure maintained in the retort during all carbonizing tests was 10 pounds per square inch, gage.

Condenser Temperature. The brine used to cool the condensers in the carbonizing unit was maintained at 28 to 32 °F, and water was fed to the water cooled condenser at 60±5 °F.

Vapor-Liquid Chromatograph. The gas samples obtained from the pilot-scale tests were analyzed in the Fisher-Gulf vapor-liquid chromatograph. Silica gel and 5A molecular sieves were used as column packings. The carrier gas flow rate was maintained at 30 milliliters per minute. The column temperature was maintained at 122 °F. The sample size used in the tests varied from 0.1 to 0.4 milliliter. The carrier gas used was helium.

V. CONCLUSIONS

Pretreatment and carbonization studies were made on Penn-Lee coal using standard techniques developed during the course of the investigation. The bench-scale studies were performed on 50-gram samples of Penn-Lee coal at temperatures of 400, 500, and 600 °F. The time levels studied were one, two, and three hours. Three replications of the data were made. The pilot-scale studies were performed on 5.5-pound samples of Penn-Lee coal. The samples were pretreated at 630±20 °F for times of two and four hours. The samples were carbonized at temperatures of 830 and 950 °F for times of one, one and one-half, and two hours. The gas flow rate for all tests was 12±0.1 cubic feet per minute, and the pressure in the retorting system was 10 pounds per square inch, gage. The particle size of the coal was minus 2, plus one inch. The pilot-scale unit was of the recycle, closed circuit type. All gas samples were analyzed in the Fisher-Gulf chromatographic partitioner and the properties of the gas samples were determined by ASTM methods.

The results of this study led to the following conclusion.

1. In the bench-scale tests, both time and temperature had significant effect on the free-swelling index of the coal. "F" values of 6.91 and 8.29 were calculated for the effects of time and temperature respectively,

where a value of 3.55 was required for significance at the 95 per cent level. Three hours at 600 °F were found to be sufficient to completely destroy the swelling properties of minus 3/4, plus 1/2 inch Penn-Lee coal.

2. In the bench-scale tests, increasing the temperature of pretreatment from 400 to 600 °F resulted in an increase in the sample weight loss from 2.32 to 3.89 per cent. A statistical analysis of the data showed that the effect of the temperature of pretreatment was significant. An "F" value of 53.72 was calculated where a value of 3.55 was required for significance at the 95 per cent level.

3. In the bench-scale studies, increasing the length of pretreatment from one to three hours resulted in decreasing the volatile matter remaining in the samples from 35.5 to 33.8 per cent. The "F" value calculated for these tests was 8.25 where a value of 3.55 was required for significance at the 95 per cent level.

4. In the pilot-scale studies, increasing the length of pretreatment from two to four hours resulted in (1) reducing the dry tar yield from 8.4 to 5.2 per cent, (2) increasing the tar viscosity from 78.1 to 126.3 Furol seconds, (3) increasing the specific gravity from 1.026 to 1.041, and (4) increasing the twenty per cent distillation point of the tar from 473 to 610 °F. The "F" values that were calculated for these tests were 47.90, 151.36,

114.17, and 64.16 respectively where a value of 18.5 was required for significance at the 95 per cent level.

5. None of the variables studied had a significant effect on the quantity of volatile matter in the char product, the bulk density or the calorific value of the char product.

Note: In all of the conclusions stated above, if the effect of a variable is not stated, that effect was found to be insignificant.

VI. SUMMARY

Coal is one of the world's largest remaining mineral resources. The supply of this rich source of fuel and chemicals is sufficient to serve the world for several thousand years. Coal is used directly and is also heat treated at high and low temperatures to produce fuel and by-products. Of the several methods of treatment that can be used, low-temperature carbonization is one of the most promising.

There are many low rank coals that are not suited for metallurgical purposes that will produce an excellent char and high yields of gaseous and liquid by-products. One of the disadvantages of many of the low rank coals is that they have the tendency to swell and become plastic when heated to carbonization temperatures, and this property has to a great extent made the operation of retorts difficult.

The purpose of this investigation was to study the effect of preoxidation on the coking properties and the quantities and composition of the by-products and char obtained from the low-temperature carbonization of Penn-Lee coal.

A bench-scale investigation was conducted to study the effect of oxygen on coal at low temperature. A factorial experiment was designed. The coal samples were treated at temperatures of 400, 500, and 600 °F at time levels of one, two, and three hours. Three replicates of each test were made to aid in reducing the sampling error. The treated samples were analyzed to determine the effect of the oxygen on the weight loss, the volatile matter in the coal, and the free swelling index of the coal. In addition, the action of the coal was observed during pretreatment and carbonization in an effort to predict the behavior of the coal in the pilot-scale retort.

Time and temperature had a significant effect upon the free-swelling index. Temperature of pretreatment was found to show a significant effect upon the weight loss during pretreatment. Time of pretreatment and the time-temperature effect were found to show a significant effect upon the volatile matter remaining in the coal after pretreatment.

Pilot-scale studies were conducted in an apparatus suitable for supplying the retort with gas heated to temperatures up to approximately 1000 °F and which had facilities for collecting the extracted tars and gases, and for sampling the gas stream. Twelve tests were made on samples which had been treated with oxygen for two and four hours at 600 °F. These pretreated samples were carbonized at temperatures of 830 and 950 °F for one-half, one, and two hours.

The pretreatment time had a significant effect on the dry tar yield, the tar viscosity, the tar specific gravity, and the twenty per cent tar distillation temperature. The time of carbonization was found to show a significant effect upon the gas yield.

None of the variables studied showed a significant effect with the range studied, upon the volatile matter in the char products, the bulk density of the char, or the calorific value of the char.

VII. BIBLIOGRAPHY

1. American Society for Testing Materials, Bulk Density Determination of Coal and Coke; Designation D 292-29.

2. American Society for Testing Materials, Calorific Determination by Means of a Paar Bomb; Designation D 271-48.

3. American Society for Testing Materials, Distillation of Tars and Creosote; Designation D 20-56.

4. American Society for Testing Materials, Determination of the Free Swelling Index of Coal; Designation D 720-46.

5. American Society for Testing Materials, Rank of Coals; Designation D 338-86.

6. American Society for Testing Materials, Viscosity by Means of the Saybolt Viscosimeter; Designation D 88-53.

7. American Society for Testing Materials, Determination of Volatile Matter in Coke; Designation D 291-29.

8. Aronov, S.G.: The Caking of Coal and the Formation of Coke, Zhur. Priklad. Khim., 25, pp. 927-935 (1952); C.A., 48, 3008 (1954)

9. Asbury, R.S.: Action of Solvents on Coal, Ind. Eng. Chem. 26, 1301 (1934).

10. Audebert, E. and L. Delmus: Plastic Properties of Coal, Rev. Ind. Minerale, 32, pp. 115-136 (1925); C.A., 20, 2238 (1926).

11. Barrett, W.J., C. Hamilton Foote, and J. Reilly: The Effect of Preoxidation on the Primary Distillation Products of Coal, J. Soc. Chem. Ind., 47, pp. 142-143 (1928).

12. Berl, E., and W. Koerber: Extraction of Natural and Artificial Coals with Solvents, Ind. Eng. Chem., 32, 1605 (1940).

13. Corrigan, Thomas E.: Chemical Engineering Fundamentals, Kinetics of Homogeneous Reactions-I, Chem. Eng., 61, 8 --208 (1954).

14. Davis, J.D., and Palmer B. Place: Thermal Reactions of Coal During Carbonization, Ind. Eng. Chem., 16, 589-592 (1924).

15. Dixon, Wilfred, and Frank J. Massey, Jr.: "Introduction to Statistical Analysis," pp. 1-5 McGraw-Hill Book Co., Inc., New York, N.Y., 1951

16. ibid, p. 127

17. ibid, p. 310

18. Fieldner, A.C., and J.D. Davis: Carbonizing Properties and Petrographic Composition of Pittsburgh-Bed Coal from Bur. of Mines Experimental mine, Bruceton, Allegheny County, Pennsylvania, U.S. Bur. Mines Tech. Paper No. 594 (1939).

19. Gentry, R. M; "The Technology of Low-Temperature Carbonization," pp. 1-6. The Williams and Wilkins Co., Baltimore, Maryland, 1928.

20. Georgiadis, Constantile, and Gilbert Gaillard, Sur L'emination de L'oxygene au cours de la pyrolyse des houilles, Comptes Rend., 238, 225-257 (1954).

21. Griffiths, J.H. and C.S.G. Phillips. The Chromatography of Gases and Vapours, Part IV, Applications of the Surface-Potential Detector, J. Chem. Soc., 3446 (1954).

22. Higuchi, Kugo and Yutaka Shibuya: The Air Oxidation of Lignite Humic Substances, and Analysis of Oxidized Coal, J. Fuel Soc., Japan, 33, 366-73 (1954); C.A., 48, 11,029i (1954).

23. ibid.

24. Kamiya, Yoshiu: Air Oxidation of Coal, Reaction Velocity, Oxidation Products, and Reaction Mechanisms Influidized Bed Reaction Coal, J. Fuel. Soc., Japan, 33, 412-23 (1954); 48, 14,158b (1954).

25. ibid.

26. Khalturin, A.I., Izvest Akad, Nauk Kazakh: Thermal Decomposition of Coal, S.S.R. No. 123 Ser. Khim. No. 7, 118-24 (1953); 48, 5,462i (1954).

27. Kreulen, D.J.: "Elements of Coal Chemistry," p.27. Nijgh and Van Ditmar Co., Rotterdam, 1948.

28. ibid, p. 67.

29. ibid, p. 120-131.

30. ibid, p. 142.

31. ibid, p. 170-171.

32. ibid, p. 185.

33. ibid, p. 193.

34. Kugo, Masao, Changes in the Coal Constituents below the Plastic State, Mem. Fac. Eng., Hokkaido Univ., 9, 383-427 (1953); C.A. 48, 6098 (1954).

35. Labari, A.: Colloidal Structure of Coal and Mechanism of Coke Formation, Fuel, 30, 241-247 (1951); C.A., 46, 235 (1952).

36. Orchin, Milton: Chemical Structure of Coal, Ohio State Univ. Eng. Exp. Sta. News, 25, 25-31 (1953).

37. Parr, W., and T.E. Laying: Low-Temperature Carbonization and its Application to High Oxygen Fuels, Ind. Eng. Chem., 13, 14-17 (1921).

38. Patton, H.W., J.S. Lewis, and W.J. Kay: Separation and Analysis of Gases and Volatile Liquids by Gas Chromatography, Anal. Chem., 21, No. 2, 170-174 (1955).

39. Pusey, Robert: The Physical Properties of the Products of the Low-Temperature Carbonization of Penn-Lee Coal. Unpublished B.S. Thesis, Library Virginia Polytechnic Institute, Blacksburg, Virginia (1957).

40. Sakabe, Tsutomu, Katsuya Inoue, Koji Ouch, and Hidemasa Honda: The Structure of a Bituminous Coal from the Properties of Bitumens and Pseudo-Bitumens, J. Fuel Soc., Japan, 32, 610-26 (1953); 48, 14,163g (1954).

41. Takeya, Gen and Masao Kugo: The Caking Property of Coal with Special Reference to the Plastic State, J. Fuel Soc., Japan, 32, 337-69 (1953); 48, 14,163g (1954).

42. Warren, William B.: Carbonization of Coal, Ind. and Eng. Chem. 27 1350-1354 (1935).

43. Winterstein, A., K. Schon, and H. Vetter: Fractionation and Purification of Organic Substances by the Principle of Chromatographic Adsorption Analysis, V Anthracene, Chrysens, Pyrene, Z. Phy. Chem., 230, 158 (1934); C.A. 29 1411 (1935).

44. ibid.

45. ibid.

46. ibid.

47. ibid.

48. Yamasaki, Tayohito: "The Adsorption of Oxygen on Coal," J. Mining Inst. Japan, 69, 253-258 (1953); C.A. 48, 11027 (1954).

49. Yoshikawa, Yosaburo, Kozo Hirota, and Yasushikobayashi: Gases Evolved by Heating Coal in Vacuo at Low Temperature, Bulletin Reasearch Inst. Allp. Elec., 5, 123 (1953); C.A., 48, 14,160h (1954).

Addenda

50. Farkas, Adalbert: "The Physical Chemistry of the Hydrocarbons, pp. 245-247, Vol. II. Academic Press, Inc., New York, N.Y., 1953.

51. Hickenbottom, Wilfred J.: "Reactions of Organic Compounds," p. 246. Longmaus, Green and Co., Ltd., London, (1948).

52. Hurd, Charles Dewitt: "The Pyrolysis of Carbon Compounds," pp. 93-97. The Chemical Catolog Co, New York, N.Y., 1929.

53. Kreulen, D.J.: "Elements of Coal Chemistry," p.27. Nijgh and Van Ditmar Co., Rotterdam, 1948.

54. Kruber, Otto: Biphenylensulfid in Steinkohlenteer, Ber., 53B, 1566-67 (1920).

55. Nelson, W.L. : "Petroleum Refinery Engineering," p. 316. McGraw-Hill Book Co., Inc., New York, N.Y., 1941.

56. Davies, Owen L.: Statistical Methods in Research and Production, p. 246. Hafner Publishing Company, New York, N.Y. (1949).

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