

FACTORS AFFECTING THE YIELDS AND PROPERTIES OF THE
PRODUCTS OF THE LOW-TEMPERATURE CARBONIZATION OF
PENN-LEE COALS FROM SOUTHWESTERN VIRGINIA

by

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Thesis submitted to the Graduate Faculty of the
Virginia Polytechnic Institute
in candidacy for the degree of

DOCTOR OF PHILOSOPHY

in

Chemical Engineering

APPROVED:

Chairman, Advisory Committee

June, 1957

Blacksburg, Virginia

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I. INTRODUCTION

At present, the coal industry in this country is faced with a crisis. The most lucrative coal markets have been taken away by more efficient and convenient fuel-oil and natural gas for heating; diesel fuels for ship and railroads. Now the coal industry is faced with the rapid emergence of atomic power and solar energy as additional competitors.

Coal, however, can be a rich source of valuable chemicals. Benzene, phenol, toluene, xylene, naphthalene, and anthracene are but a few of the aromatic compounds that can be derived from coal. Many aliphatic hydrocarbons and inorganic compounds, such as nitrogen and sulphur, can also be derived from coal. There are five methods of extracting this hidden wealth of chemical material from coal: carbonization, partial combustion, the Fisher-Tropsch reaction, hydrogenation, and solvent extraction.

Carbonization is the oldest of these processes, in which bituminous coals are roasted at high temperatures in a controlled atmosphere, to provide

coke, coal tar, and gases. The low-or medium-temperature carbonization processes, under closely controlled conditions, could yield more of the desired chemicals without lowering the quality of the coke, thereby providing a sound solution to the economical problem of the coal industry.

The purpose of this investigation was to study the factors affecting the low-temperature carbonization of seam number one, Penn-Lee coal from southwestern Virginia, by determining the effect of pretreatment of the charge, temperature of the retorting gas, and time of retorting on the yields and properties of the products of carbonization.

II. LITERATURE REVIEW

In the following section, the general topics involved in the carbonization of a high-volatile bituminous coking coal are considered. A brief discussion of the history of carbonization and the origin of coal is also included.

Historical

This section contains a historical review of the origin of coal, its place in our economy, and the development of the coking industry.

The Origin of Coal. While nearly all authorities agree that coal is a rock composed of organic matter, there is some disagreement as to the manner in which coal was originally formed. Gentry⁽⁴²⁾ advanced the theory that coal is formed from decaying matter. Today it is well established that the carbonaceous deposits, ranging from peat to anthracite, represent progressive changes which have taken place in the structure of decayed vegetable matter. Evidence is furnished by fossil remains that among the early

geologic ages, the dead vegetation, which was so abundant at that time, accumulated in damp lowlands and bogs⁽⁷³⁾. There, with the exclusion of air by the water, a slow process of disintegration took place. As the bottom lands sank below the surface of the water, and sedimentary deposits built up, a pressure developed which rendered the peat deposits more compact and consolidated, thus forming the lignites and sub-bituminous coal. Additional pressure and the generation of heat led to the transformation of these low-rank coals into bituminous coals. The remaining change into anthracite is said to have been brought about by further excessive pressure and by the cracking of the rock folds to permit the escape of entrapped hydrocarbons evolved from the carbonaceous material. This theory, however, does not account for all known coal deposits. There is the "Transportation Theory"⁽⁷⁴⁾ which was popular during the nineteenth century that theorized that the parent material of coal was not formed by degradation of plant material in place in peat swamps but rather resulted from the deposition of transported plant material in lakes, seas, and estuaries. One of the early theories was

that particles of soot from smoke, soluble organic matter carried by streams, and the remains of plants and animals native to the sea and transported from land were deposited in the sea, buried by inorganic debris, and later converted into coal. Perhaps the most imaginative of the theories concerning the origin of coal is presented by Armstrong⁽²⁾. It is his theory that much of the earth's coal deposits result from astral bodies which have bombarded the earth during its history. Support for his theory is based upon the fact that a bombardment of this type presents the only means by which thick layers of sedimentation could be quickly formed over layers of vegetation and animal life before they could be decomposed by the atmosphere. In the formation of coal there is unmistakable evidence of a sudden entombment of animal life. This entombment was not only immediate but also complete, shutting out the atmosphere and preserving the bodies until they became petrified.

Coal in Our Economy. Coal is one of our most abundant natural resources. It supplies as much of the energy used in the United States as the combined

total of gas, petroleum, and water power, amounting to 51.3 per cent of the total in 1945⁽⁵¹⁾.

The Origin of Carbonization. The first historically recorded account of the destructive distillation of coal was in England. Upon damming the water and digging beneath a creek bed, Clayton⁽⁴²⁾ discovered a coal deposit and distilled some of the coal in a retort over an open fire, obtaining a black oil and non-condensable gas. In the year 1619, it was found⁽⁴²⁾ that certain coals after "charking" would outperform charcoal, but no mention is made of any gas or tars being collected. By the year 1709, the coke industry was becoming important, for in that year coke was first used in the production of iron. This was to be the forerunner of today's modern steel industry. Coke was first prepared by the partial combustion of bituminous coal in conical piles covered with loose earth. Later, walls of brick were built around the piles and from this the beehive oven was evolved.

Development of Carbonization in the United States.

The first commercial application of the products of the carbonization of coal was begun in the United

States during the American Revolution. The American navy was the major user of the tars and pitch made in this manner, and Murdoch⁽⁴²⁾ produced illuminating gas in 1792 from the gaseous products. The first coke oven in the United States built specifically for obtaining carbonization by-products was built in Rochester, New York, in 1895. The coke industry continued to expand until about 1900 when petroleum began to compete for the market. In 1946 there were 27,358 coke ovens in operation in the United States of which 31 were medium and low-temperature ovens. The combined total of the industry was 58,000,000 tons of coke; of this total 190,100 tons were produced in medium and low-temperature ovens⁽⁵³⁾.

Carbonization Processes

This section contains a review of the carbonization processes of importance in use today, with particular emphasis on the low-temperature processes.

High-Temperature Processes. The high-temperature processes are generally in use where a high grade of metallurgical coke is required. The volatile and liquid products obtained from high-temperature coke ovens are quite different from those obtained from low-temperature ovens. The temperature at which these products escape is high enough so that considerable thermal cracking and molecular rearrangement occur. The result of this cracking and rearrangement is that a hard, shiny coke is formed containing very little volatile matter. The products that are driven off contain relatively more gas with a lower heating value and less tar with more aromatic and pure paraffinic compounds⁽⁵⁴⁾.

Almost the entire American coke production since 1935 has been carried on in the horizontal chamber by-product coke oven. The production of beehive coke has been so small during the greater part of the period 1930 to 1940, as to be almost negligible.

Beehive coke ovens are now considered standby carbonization equipment of low capital cost to take up excess demand that might arise during periods of extraordinary industrial activity caused by short boom times or by war. Only a few remaining continuous and intermittent vertical retorts are in operation. These retorts, as well as the old horizontal and inclined retorts, have been almost entirely displaced by the large central by-product coke plants for gas and coke making purposes.

In by-product coking, the production of the heat necessary for coking is in flues adjacent to the chamber holding the coal, the heat passing through the wall that separates the coal-containing chamber and the flues. No air is permitted to enter the by-product oven, and all volatile by-products are withdrawn from the chamber and collected within a collecting main for transmission to the by-product house where they are separated from the gas in either the gaseous, liquid, or solid phase by scrubbing, cooling, chemical reactions, or other methods. The by-product oven is usually a narrow, high, and relatively long chamber. Groups of chambers built

adjacent to one another, are known as batteries. The ovens hold from 5 to 30 tons of coal, the average American oven holding from 12 to 13 tons of coal, depending upon its dimensions. Such ovens are charged from their tops, and are provided with end doors, which are removed when coking is complete and the coke is pushed out horizontally with a ram on a machine called a pusher.

Low-Temperature Carbonization. Low-temperature carbonization is defined⁽¹⁰⁸⁾ as that carbonization process which is carried on at final coke temperatures between 427 and 703 °C (800 and 1300 °F). It is characterized by a higher yield of tar and a poorer quality coke than that produced by the high-temperature process. The principal products are a semicoke or char, equivalent to about 70 to 80 per cent of the coal and 15 to 30 gallons of tar per ton of coal. In addition, several thousand cubic feet of gas and 2.5 to 3.0 gallons of light oil are usually produced per ton of coal.

Hayes Process. The Hayes process⁽¹⁰⁹⁾, controlled by the Allis-Chalmers Manufacturing Company, was operated on fine coal in

Moundsville, West Virginia. A steel retort, 17 inches in diameter and 20 feet long, was supported in a horizontal furnace by rollers located at both ends. Stationary coal feed and coke discharge connections were made at opposite ends of the tube. The tube was rotated at 1.5 revolutions per minute. A screw conveyor, 16 inches outside diameter, was rotated inside the tube by a gear drive. The screw had an oscillating motion, agitating the coal and thoroughly contacting it with the hot retort wall during the 20-minute period within the retort.

The retorts were heated by burning gas in combustion chambers. The temperature at the feed end was maintained in the range of 600 to 706 °C (1105 to 1303 °F) by automatic regulation. The heat required for carbonization has been reported at 1100 Btu per pound of coal charged.

Krupp-Lurgi Process. Coal is coked in narrow cells within steel walls in the Krupp-Lurgi⁽¹¹⁰⁾ process. The walls are heated by

hot gases. The process was used in Germany and produced 0.84 ton of coke per ton of coal.

Each oven consisted of six cells. Each cell was 10.5 feet long by 6.9 feet high by three inches wide at the top and four inches at the bottom. The cells were heated by hot gases circulated through seven sets of heating flues with all-welded steel walls nearly one inch thick. The ovens were closed at the top with water-sealed cover plates, and at the bottom with water-sealed doors. Coal was charged through the top and coke was dropped out of the bottom of the oven at the completion of carbonization. The temperature of the entering gas at the bottom of the flue was held at 622 °C (1150 °F). The heat requirements were reported to be 900 to 1000 Btu per pound of coal charged. The total carbonizing time averaged between 5.3 and 6.0 hours.

Disco Process. The Disco process⁽⁵³⁾ is the only process operating on a large scale in the United States at the present time. This appears to be the only process that can handle

any kind of coal and it can produce any size of coke up to eight inches in diameter.

The plant now in operation uses coal that is smaller than three-eighths of an inch in diameter. The products of the carbonization are low-temperature coke, tar, and tar products. The gas produced is all used for heating purposes in the process. The coke is produced in sizes from one to six inches in diameter.

In the process, the raw coal is fed to roasters where it is stirred until it reaches 317 °C (600 °F). If the coal being used is a strongly coking coal, some air is admitted to partially oxidize the coal and prevent it from plasticizing. The roasted coal is then fed into an inclined, concentric twin-shell, rotating cylinder where the actual carbonization takes place. The coal is tumbled and turned as it travels the length of the retort. The heating medium is flue gas at 560 °C (1040 °F) that enters the annular space between the shells and flows countercurrently to the coal. The

exhausted flue gas at 317 °C (600 °F) is fed to the roasters to supply part of the heat. By rotating the retort at the proper speed and using a system of baffle and grates and by admitting the correct amount of air to the retort, the coke can be made to the desired degree of hardness and friability.

KSG Process. One of the largest plants in the United States for the low-temperature carbonization of coal utilized the German KSG (Kohlenscheidungs-Gesellschaft) process⁽¹¹¹⁾ and was designed to carbonize 650 tons of coal per day in eight rotary, double-drum retorts. Each retort was 85 feet long by 5.5 feet in diameter. The carbonization was carried out in two stages. The first stage, the drying of the crushed coal and preheating to a temperature just below the softening point, took place in the inner cylinder of the retort. The heated coal was then dropped through open ports into the outer shell in which carbonization was completed. The final coke was discharged in spherical lumps.

The cylinder was inclined slightly and rotated at three-fourths revolution per minute. The heat required for carbonization was reported to be 800 Btu per pound of coal charged. Due to the difficulty in obtaining a consistent size of coke, the operation of the process in the United States was abandoned.

Pretreatment of Coal for Carbonization

Methods in use for pretreatment of coals for carbonization include preheating, oxidation at temperatures above normal atmospheric temperatures, washing, and solvent extraction.

Preheating. Parr⁽⁸⁷⁾ and co-workers investigated the preheating of an Illinois coal up to temperatures of 300 °C (566 °F), subsequently charging the preheated coal to a retort maintained at a temperature of 700 to 750 °C (1293 to 1383 °F). It was claimed that the exothermic reactions that occur above the decomposition point maintained rapid coking throughout the mass, and led to the production of a coke of superior density and strength. However, as many

coals have both exothermic and endothermic heats of carbonization⁽²¹⁾, this theory must be excluded from the causes for the rapid carbonization of preheated coal.

A second explanation has been sought in the removal of moisture from coal in the preheating step⁽⁵⁵⁾, and it seems apparent⁽⁷⁷⁾ that a decrease in moisture will decrease the time necessary for carbonizing a coal.

The data of Litterscheidt⁽⁷¹⁾, showing the rise in temperature at the center of an oven charged with coal preheated at various temperatures, indicate that the time of carbonization of a coal preheated at 300 °C (572 °F) is slightly less than half that for a coal preheated at 100 °C (212 °F). The data for untreated coal were not given.

Effect of Preheating on the Physical Properties of Coal. It has been reported that a Saar coal of 34.5 per cent volatile matter, preheated in nitrogen for two hours at 400 °C (750 °F) lost its coking power completely⁽⁵⁾.

Other results indicate that the effects of preheating on swelling and coking properties of coal

vary extensively with the type and nature of the coal used.

Warren⁽¹⁰³⁾ suggests that the preponderance of large molecules formed in preheating could reduce the plasticity of the coal in question.

Pretreating with Oxygen. Pretreatment of coal with oxygen at elevated temperatures is, of necessity, a combination of both preheating and oxidizing treatments. This preoxidation not only changes the agglutinating properties of coals but also affects the yields and quantities of the products obtained upon subsequent carbonization⁽³⁴⁾. The studies of Barrett and Reilly⁽¹¹⁾ were on a Durham coal. This coal did not completely lose its coking power after heating for two hours at 300 °C (572 °F). In this study coal was also heated at 185 °C (374 °F) in a current of oxygen from which the carbon monoxide, carbon dioxide, and water were removed and determined. The oxygen content of the gas used ranged from 1.18 to 47.15 per cent for a time range of 0.5 to 115.0 hours. The pre-oxidized coal was then carbonized at 600 °C (1112 °F) and the products examined.

The yield of gas was a linear function of the quantity of oxygen used. The concentration of carbon monoxide and carbon dioxide increased greatly, while hydrogen and hydrocarbons decreased. The coke yields remained essentially constant. The yield of tar decreased continually from 17.2 to 3.3 per cent, as the oxygen content of the heating gas increased. In general⁽⁷⁸⁾, thermal preoxidation may be used to modify the coking properties of coal and, under controlled conditions, an improvement in coke quality may be achieved.

Solvent Extraction. The depolymerization of coal by solvent extraction⁽⁴⁾ has been studied, and a correlation between the polarity of the solvent and the yield of dissolved coal has been observed. Polar solvents, such as phenol and aniline, gave greater yields than benzene and tetralin. Work by Kiebler⁽⁵²⁾ correlated the internal pressure of the solvent and the yield. Berl and Koerber⁽¹³⁾, however, found that certain solvents were selective for certain components in the coal. For example, polar solvents remove the phenolics from coal. This phenolic removal lowered the coking properties of

the coal, and suggested the possibility of solvent extraction as a pretreating agent for a coking coal. Other solvents used for the extraction of coal include pyridine, quinoline, and cyclohexane⁽⁶⁰⁾.

Plastic and Swelling Properties of Coal

In this section the pertinent literature concerning the plastic, swelling, and agglutinating properties of various coals is reviewed.

Plastic Properties. Kreulen states that plasticity in a coal is a "complex phenomenon which appears to be induced primarily by the pressure of gases causing surface flow at the moment when, under the action of heat, the molecules at the surface have attained a degree of freedom comparable with that obtained in a liquid"⁽⁵⁹⁾. Proof that surface flow of heated coal exists during the formation of coke has been demonstrated by numerous investigators. Two such investigations will serve to illustrate the evidence of plasticity in both the lump and in a briquetted sample of coal particles.

Davies and Mott⁽²⁰⁾ found that Parkgate seam coal, when heated to a temperature of 360 °C

(680 °F) could be compressed losing 38 per cent of its expanded volume. Also, Mott⁽⁸³⁾ demonstrated surface flow in a South Wales coal. First, the surface of the coal sample, which was prepared by briquetting particles of 60-mesh size under a pressure of three tons per square inch, was polished with carborundum powder. Identifying scratches were then made on the polished surface. The sample was subjected to a series of temperatures and it was found that at 445 °C (832 °F) the identifying scratches disappeared completely. In other words, the new surface continuity was due to a liquid-like flow on the coal surface.

Swelling Properties. Two terms are used to describe the characteristic expansion that coal undergoes during heating⁽⁷⁶⁾. The first is true swelling, signifying a volume change that takes place in such a way that the softened coal can expand freely in the direction perpendicular to the heating surface. The second is swelling pressure, which describes the pressure exerted by the softened mass when obstructed from free expansion.

The problem of investigating the plastic swelling properties of various coals has been complicated by the total lack of test standards and specifications. Detailed descriptions of test procedures have been compiled in the United States Bureau of Mines Bulletin⁽¹⁴⁾ entitled "Plastic and Swelling Properties of Bituminous Coking Coals."

Agglutinating Value. The agglutinating value is defined by Brewer⁽¹⁴⁾ as a measure of the binding qualities of a coke and is an indication of its coking and caking properties. In general, as the agglutinating value of various coals increases, the strength of the cokes prepared from them will also increase. The agglutinating values have also been found to decrease⁽³⁵⁾ with increasing oxygen content of the coal.

Colloidal Nature of Coal. Within the past 20 years, it has become generally accepted that coal is a colloid. Kruelen⁽⁶¹⁾ has summarized the fundamental ideas that have developed from the new theory of the colloidal nature of coal. These fundamental principles of Kruelen are presented below.

1. The product obtained from coal by extraction and termed coal bitumen is an organosol.

2. The organosol consists of two phases, an oily phase, acting as a dispersion medium, and a dispersed phase (micelle phase).

3. A micelle consists of an oleophilic (protective body) and an oleophobic part (micelle nucleus).

4. The oily medium and the protective bodies consist of bitumens. The micelle nucleus consists of humins.

5. Bitumens are mixtures of organic compounds which are soluble in organic solvents. They originate from humic acids. As a consequence of their origin, they show a certain conformity in structure with humic acids and humins. Aromatic nuclei are present; the side chains, especially the COOH groups, are mostly split off. Hydroxyl groups are still present. Cyclic-bound oxygen is present; the lower the rank of the coal, the more cyclic-bound oxygen.

6. Intimate coherence exists between the protective bodies and the micelle nucleus. It appears impossible to separate them by extraction. Due to this intimacy the bitumen properties of the protective bodies mask the humin properties of the micelle nucleus.

Colloidal Structure of Coal and Mechanism of Coke Formation. The colloidal structure of coal is likened⁽⁶⁸⁾ to a mixed isogel of the non-hardening type, having a definite gel-point temperature. The relation between dispersed and dispersing phases is governed by surface-active forces. The mechanism of coke formation is believed to be a phenomenon of coagulation of the surface-active micelles in the dispersed state due to loss of or change in the nature of the dispersing medium during heating, followed by a strengthening of the primary bonds at the expense of the secondary bonds.

Chemical Nature of Coal. Aronov⁽³⁾ states that the basic unit of coal structure is a macromolecule which is an aggregate of many molecules of similar structure, but of different degree of polymerization. The structure consists basically of hexagonal carbon rings forming condensed polycyclic structures surrounded by a fringe of side groups. The nucleus has stronger chemical bonds and greater resistance to heat than the side groups. Coking of coal is attributed to chemical changes inside the macromolecule that result in tearing away the hydrocarbon side groups and

their conversion into a liquid phase which undergoes thermal condensation simultaneously with an interaction of the nuclei of the macromolecules with one another and with the hydrocarbons of the side groups. Volatile matter is simultaneously formed from the side groups of the macromolecules, which are thermally transformed during the coking of the coal. The coking, and the formation of coal chemicals and gas are determined by the quantity and quality of the side chains. Orchin⁽⁸⁶⁾ and coworkers found that phenanthrene disperses 95 per cent of the organic matter of Pittsburgh-bed coal. Solvent fractionation by means of extraction with benzene and cyclohexane separates coal into fractions having different degrees of aromatization and coking properties. The benzene-insoluble fraction is agglomerating but non-swelling and the benzene-soluble fraction has swelling properties only. Probably, phenanthrene has a selective solvent action on those constituents of coal that act as binding agents for the micellar portion of the coal. Removal of the binder leads to complete disintegration of the colloidal structure of the coal.

Changes in the Coal Constituents at Temperatures Below the Plastic State. Kogo⁽⁵⁴⁾ reported that condensation reactions were very active below 300 °C (572 °F). Water was the only product; therefore, condensation must represent the reaction due to dehydration occurring among the coal molecules with oxygen-containing outer groups. As most of the oxygen was disengaged by heating to the plastic range, the resulting decrease in fluidity must have been due to condensation brought about by deoxygenation.

Preoxidation

The literature dealing with the reactions of various coals with oxygen or oxidizing agents is reviewed in this section.

The Chemistry of Preoxidation. The chemistry involved in the oxidation of coal at moderate temperatures is very complex and to a great extent unknown. The action of oxygen on coal at these temperatures gives a large number of products corresponding to various degrees of degradation of the coal. The nature of the products formed ranges from slightly

oxidized highly complex tars and acids, to highly oxidized products such as carbon dioxide and water. The relative amounts of the different products formed are determined by the method and degree of oxidation and it is not possible to obtain yields of any one product to the exclusion of all others.

Kramers⁽⁷⁾ has presented an arbitrary division of the oxidation products of coal into four groups. The division was made in this manner because of the ease with which these groups can be separated analytically. The groups are: (1) products with peroxidic properties and believed to consist of coal-oxygen-water surface complexes; (2) products characterized by solubility in alkali and insolubility in water, i. e., humic acids; (3) products characterized by solubility in water, i. e., the fulvic acids; and (4) gaseous end products.

Preoxidation Mechanism. Under the preoxidation conditions to be studied in this investigation, the group of so-called humic acids will probably predominate because of the low temperature of the reaction and, therefore, they will be discussed in some detail. Kreulen⁽⁶⁾ has demonstrated experimentally

that the mechanism of the oxidation is dependent on the rank of the coal. The oxidation of high rank coal takes place through an intermediate to form humic acids but the oxidation of low rank coals results in the direct formation of the humic acids.

An extensive investigation has been conducted to determine the chemical and physical properties of the humic acids and investigators are now in general agreement as to the molecular weight, substituents, and composition of the molecule.

Two independent investigators, Odenn and Fuchs⁽³⁹⁾, agree that the molecular weight of humic acid is approximately 1400 and that there are four COOH groups on the molecule.

Information is given by Kramers⁽⁹⁾ to the effect that surface complexes with peroxidic properties are formed via a chain reaction in which the peroxide radical is the chain carrier, thus:



This reaction takes place in the presence of water vapor and can be initiated and promoted by the decomposition of the peroxide itself to produce additional chain carriers.

Fuchs⁽³⁹⁾ attempts to describe the structure of the humic acid molecule by condensing two molecules of I to form one molecule of II, as shown in Figure 1, page 29. During the condensation, some of the side chains may be detached from the molecule.

The soluble or fulvic acids are formed in quantity under conditions more extreme than those required for the formation of humic acids. The fulvic acids constitute a mixture ranging from highly complex colored molecules to some of the definitely crystalline acids such as oxalic and succinic, and some of the benzene carboxylic types. The average equivalent weight of the fulvic acids is lower than the humic acids and they are more soluble in water and certain organic solvents such as ether, alcohol, or acetone⁽⁶⁾. The constitution of the fulvic acids is largely unknown, but some of their methyl esters have been separated in the molecular still. Some of these acids are thought to be five or six-membered heterocyclic compounds with active double bonds.

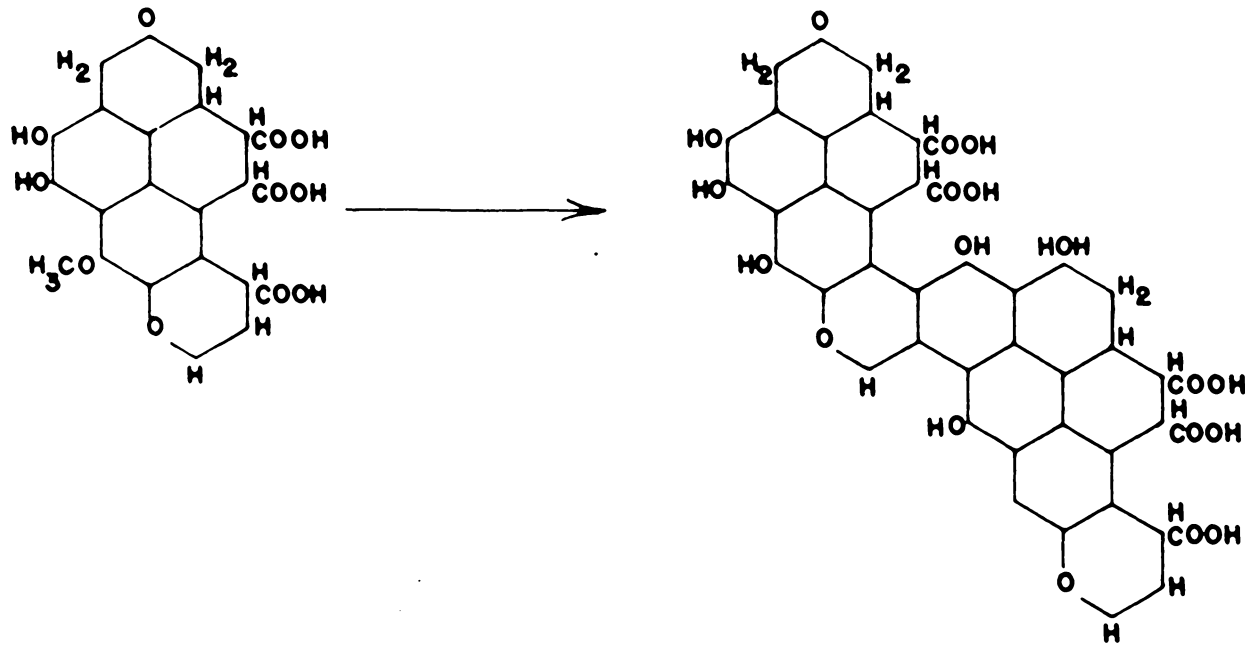


FIGURE NO. 1. STRUCTURE OF A TYPICAL COAL MOLECULE

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

Factors Affecting the Coal Oxidation Rate. The rate of oxidation of coal by air is affected by several factors⁽⁶⁾. These include the nature of the coal and the mineral impurities contained in it, particle size, temperature, and moisture content. In general, ease of oxidation decreases with an increase in the rank of the coal employed. These differences are in part due to variations in physical structure, the more accessible and greater inner surface of the lower rank coals rendering them more sensitive to attack. Particle size has been found to exert only a slight effect on the oxidation rate⁽³²⁾. The rate of oxidation has been found to increase with an increase in the amount of moisture content⁽¹⁰²⁾. Oxidation is retarded by a high pyrites content and a high ash content in conjunction with a small proportion of iron oxide and finely divided impurities, while a high iron oxide content is found to accelerate the oxidation rate.

The Adsorption of Oxygen on Coal. Yamasaki⁽¹¹³⁾ reports that oxygen is adsorbed upon coal in two different ways. The first type of adsorption is rapid, being nearly complete in a few hours. The second type takes place very slowly. Bituminous coals show

adsorptive characteristics of the first type, and lignites of the second. It is suggested that Vanderwaal forces cause adsorption below 30 °C (86 °F), chemical sorption occurring between 30 and 100 °C (86 and 212 °F), and oxidation with the evolution of carbon dioxide occurring above 100 °C (212 °F).

Also, Swieloslowski⁽⁹⁸⁾ reports that in general sub-bituminous and high volatile coals possess an exceedingly high adsorption capacity, being very similar to activated carbon in their adsorptive properties.

Preparation of Organic Acids by the Oxidation of Coal. The oxidation of various coals leads to quantities of benzyl carboxylic acids, prominent among which is mellitic or benzene hexacarboxylic acid. The isolation of this acid is an argument in favor of the presence of a polynuclear structure in coal in which one ring is surrounded by three other fused rings. Orchin's conception of a typical coal molecule is shown in Figure 2, page 32. The reaction of coal with oxygen at low temperatures has been suggested⁽³⁸⁾ as a possible source of inexpensive organic acids.

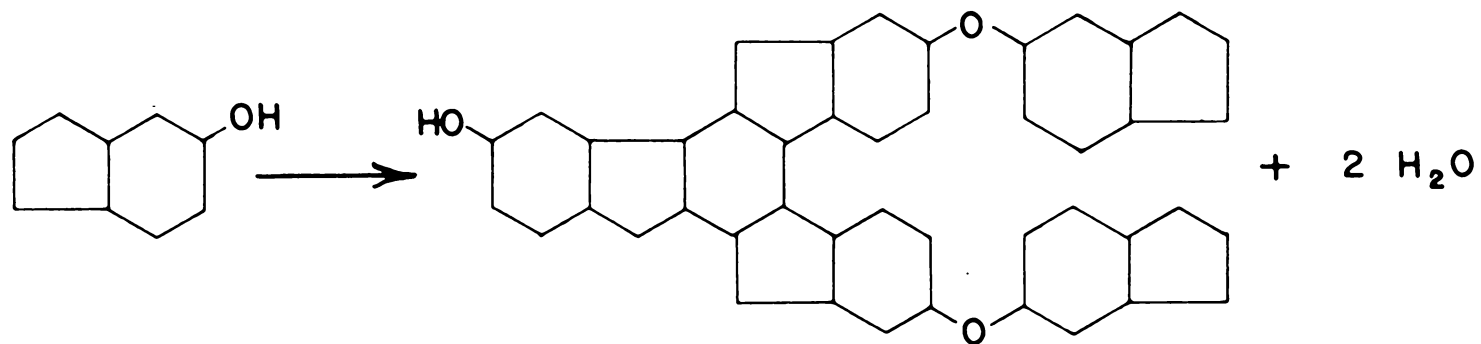


FIGURE NO. 2 STRUCTURE OF A TYPICAL COAL MOLECULE

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

The operating range in a pilot plant producing five to ten pounds of product per day is 200 to 300 °C (392 to 571 °F) at 500 to 1200 pounds per square inch pressure. The oxidation takes two to three hours and the conversion of coal to mixed aromatic acids is over 60 per cent of the coal used. The acids are largely tri- and tetracarboxylic with an average molecular weight of 250.

Reactions with Other Oxidizing Agents. The oxidation of coal can be affected by alkaline permanganate⁽³⁶⁾, nitric acid⁽⁴⁶⁾, hydrogen peroxide and ozone⁽³⁷⁾, and atmospheric oxygen.

Effect of Carbonization, Temperature, and
Heating Rates on Yields of Products

The temperature of carbonization and the heating rates through the plastic and preplastic zone in carbonization have been found to affect the yields of the products obtained. In this section the literature pertaining to this subject is reviewed.

Rate of Heating in Coke Oven. Ryan⁽⁹⁶⁾, in studying the rate of travel of the fusion zone in a 20-inch, rectangular coke oven, observed that the temperature gradient across that zone is the steepest throughout the bed. He reported a temperature range for the plastic zone of from 400 to 483 °C (750 to 900 °F).

Mott and Wheeler⁽⁸⁴⁾ state that the most important period in carbonization is the period in which plasticity of the coal occurs. They have observed that the temperature range during which the coal first fuses and then sets to form coke is fixed within narrow limits for all coals. Therefore, if the rate of heating or the time of exposure to the plastic range are varied, the yields of products should vary.

Juettner and Howard⁽²⁾, working with a molecular still at extremely low pressures, report that rapid

heating resulted in a greater yield of condensate than stepwise heating at the same temperature. Also, they found that larger condensate yields were obtained at atmospheric pressures than at high vacuum. In the Bureau of Mines survey of carbonizing properties of American coals⁽³⁵⁾, the Fisher assay, with 50 grams of coal, and BM-AGA retort with 80 to 90 pounds of coal were used to determine the yields of carbonization products at 500 °C (930 °F). The carbonizing time in the Fisher retort was 2.5 hours, compared with 30 hours in the BM-AGA report. This increase in carbonization time caused a 30 per cent decrease in tar yield, and a 20 per cent increase in gas yield.

Effect of Carbonization Temperature on Yields of Products. The yields of the products of carbonization as functions of the carbonization temperature have been determined for more than 60 coals by the Bureau of Mines⁽³⁵⁾. A 13-inch retort was used in the test and the temperature reported was the wall temperature of the retort. The yield of gas increased steadily with temperature, from approximately one cubic foot per pound of coal at 483 °C (900 °F) to

six standard cubic feet per pound of coal at 982 °C (1800 °F). The tar yield decreased over the same range from 23 gallons per ton of coal to 12 gallons per ton of coal. The coke yield decreased from 79 per cent to 72 per cent over the same range.

Also, Taylor and Porter⁽⁹⁹⁾ have shown that 66 to 75 per cent of the volatile matter of the coal, as primary volatile products, is removed under 500 °C (932 °F). They also showed that at temperatures as low as 475 °C (887 °F) secondary decomposition of the tar into gases is appreciable.

Effect of Carbonization Temperature on Tar Composition. In tests performed on Pratt coal⁽³⁴⁾, the yields of tar over the range 500 to 700 °C (930 to 1292 °F) changed very little with temperature. The composition of the tar was affected by an increase in coke temperature; the paraffins and naphthenes decreased at a carbonization temperature of 600 °C (1112 °F), decreasing from 15 per cent to less than two per cent between 600 and 800 °C (1112 and 1474 °F). The yields of tar bases, olefins, and aromatics remained essentially constant over the range 500 to 1100 °C (930 to 2014 °F). Pryde⁽⁹¹⁾

states that there is a marked difference between the tar obtained from low-temperature carbonization and that from carbonization at higher temperatures. Tar distilled at 450 °C (842 °F) is oily, brown, and contains olefins, naphthenes, paraffins, phenols, and pyridines, while benzene and its homologues are generally absent. Tar obtained at 1100 °C (2014 °F) is black, and contains pitch, benzene, hydrocarbons, naphthalenes, and anthracenes, and only traces of aliphatic hydrocarbons.

Chemical Nature of Coal Tar

Coal tar is one of the primary products resulting from the destructive distillation of coal. Literature concerned with the compounds observed in coal tar is reviewed in this section.

The Effect of Types of Coal Carbonized on Tar Yield and Composition. In general⁽⁷⁵⁾, the yield of coal tar is affected by the rank of the coal carbonized, the higher rank coals yielding the least tar. Also, the nature of the coal tar is influenced by the type of coal when carbonized at low temperatures, but under high-temperature conditions, the effect of coal composition on the nature of the tar is negligible. The effect of coal composition at low temperatures is chiefly in the greater amounts of tar acids and paraffins found in the tars from low-rank coals.

Coal Tar Research. The only materials produced industrially from tar are benzene, toluene, pyridine, naphthalene, anthracene, phenol, o-cresol, and to a small extent in recent years, carbozole and acenaphthene⁽⁹⁾. Early investigations into the chemical nature of coal tar were retarded by the lack of techniques for the separation and identification of

the constituents. By the introduction of the alkali-melt technique, however, Weissgerber⁽¹⁰⁷⁾ paved the way to the preparation of previously inaccessible substances. Raschig⁽⁹⁴⁾ by his work on distillation, made possible the separation of homogeneous fractions having definite boiling ranges, which could be analyzed chemically with great success.

Substances Produced by Alkali-Melt Technique. In the alkali-melt technique⁽¹⁰⁾ a hydrocarbon is fused with an alkali metal, caustic alkali, or sodamide; a hydrogen atom of a reactive methylene group is substituted by an atom of the alkali metal. The hydrocarbon is then regenerated with water. Indene, and many of the homologs of indole, useful in the perfume industry, have been prepared from coal tar by this technique⁽¹⁰⁷⁾. Naphthene has been separated from naphthalene oil by variations of this technique, and diphenylene sulfide was proved to be in crude phenanthrene by this method⁽⁶²⁾.

Phenol Homologs. The homologs of coal-tar phenol, which occur mostly in the middle oil, have not been investigated to any extent. Several xylenols⁽¹⁵⁾ have been isolated, and in the cuminol

fraction, boiling at temperatures above 230 °C (445 °F), iso-pseudocumenol and sym-methyl-ethyl-phenol⁽⁶⁶⁾ have been isolated. From the heavy oils, 7-hydroxy-coumarone and 4-hydroxy-hydrindene and 5-hydroxy-hydrindene⁽⁶⁷⁾ have been prepared in the pure state. From anthracene oil, the phenols of the final coal tar fraction, 4-hydroxy-diphenyl, 2-hydroxy-diphenylene oxide, 2-hydroxy-flourene, and phenanthral⁽⁶³⁾ have been prepared in the pure state.

Compounds in Light Oil. Work published in 1931⁽⁶⁶⁾ on light oil in particular motor spirits, established the presence of chain and cyclic compounds accompanying benzene. The following olefins were identified: di- and tetra-hydrobenzene, and n-hexylene, and n-heptylene, and di-cyclo-pentadiene⁽¹⁾.

Compounds in Pitch. Pitch, in general, is composed of highly condensed, hydrogen-poor compounds. Substances involving methyl and hydroxy groups are not to be found in this pitch fraction; instead, there are heterocyclic oxygen compounds. By means of chromatographic analysis, Winterstein⁽¹¹²⁾ isolated the following compounds from pitch: naphthacene, 1:2 benzcarbazole, brazan, and triphenylene. Work

by other investigators⁽¹⁹⁾ led to the separation of the following: 3:4 benzpyrene, 1:2 benzanthracene, 1:2 benzpyrene, and perylene.

Thermal Cracking of Tar. Farkas⁽³³⁾ states that the thermal decomposition of saturated hydrocarbons involves principally the splitting of carbon-carbon and carbon-hydrogen bonds to form lower molecular weight hydrocarbons and unsaturated hydrocarbons. Deep cracking leads to secondary products of condensation and polymerization. At moderate temperatures, such as 400 to 600 °C (752 to 1110 °F), the splitting of carbon-carbon bonds in paraffins is selective toward the center bonds. Higher temperatures favor a more random splitting.

Naphthene cracking involves the ring as well as the side chains. The splitting of the side chain is very similar to that of the corresponding paraffin. The reaction of the ring involves dehydrogenation or ring rupture. Under severe cracking conditions, condensation of aromatic nuclei with the elimination of hydrogen occurs very extensively. Aromatic rings are extremely stable toward rupture even at very high temperatures, such as 700 °C (1292 °F).

Egloff⁽³¹⁾ investigated the thermal cracking of tar and tar oil on a pilot-plant scale, obtaining a gasoline having good anti-knock properties, and a high aromatic content. The yield was about 50 per cent of the original tar. In comparison with petroleum cracking, greater corrosion is encountered and smaller throughputs are obtained with coal-tar cracking. The gas produced is lower in heating value, but yields useful olefins.

Fuel Oil. The use of coal-tar creosote as a diesel oil has been studied, with the tar blended with petroleum oil⁽²⁶⁾. A new extraction solvent, a mixture of esters of high alcohols, is claimed⁽¹⁾ to give better results than the benzole or tricresyl phosphate methods.

Tar Bases. A pilot plant has been constructed in the United States to produce pyridine and picoline from coal tar. Also, two new bases, 1:2 benzacridine and 3:4 benzacridine, have been isolated by Kruber⁽⁶⁴⁾, and 3:4:5 trimethyl quinoline⁽⁶⁵⁾ has been found in the fraction boiling at 300 °C (572 °F).

Lubricating Oils. Synthetic lubricating oils are discussed by Pickstan⁽⁸⁹⁾. He gives a summary of the physical and chemical properties of the lubricating oils obtained from coal tar synthesis, or from water gas.

Other Processes. Weizmann⁽¹⁰⁷⁾ describes the vapor-phase aromatization at 600 to 700 °C (1112 to 1293 °F) of a low temperature tar oil to yield benzene, toluene, and xylene.

Penn-Lee Coal

The following section contains a discussion of the source of Penn-Lee coal, its classification, and its analysis.

Mine Location. Penn-Lee coal is obtained from the number 1 and number 4 mines of the Penn-Lee Coal Corporation located at Maness in Lee County, Virginia. The coal is mined from the Imboden bed which covers 32,845 acres and contains a reserve of approximately 192,143,250 tons⁽⁴⁴⁾.

Analysis of Penn-Lee Coal. Penn-Lee coal is approximately 37 per cent volatile matter, 54 per cent fixed carbon, 5.6 per cent ash, and 2.7 per cent moisture. The heating value of Penn-Lee coal is approximately 13,600 Btu per pound⁽⁴⁴⁾. The ASTM Classification of Coals by rank fixes Penn-Lee coal as a class two (bituminous), group four (high volatile B) coal⁽⁵⁶⁾.

Design Factors Affecting Heat Transfer

Two of the important factors to be considered in the design of a gas heater involving the transfer of heat from a solid to a gas, are the flow characteristics through the heater and the apparent heat transfer coefficient in the heater.

Fluid Flow Through Packed Beds. Leva⁽⁷⁰⁾ presents the following relationship for the determination of the type of flow in a packed bed.

$$N_{Re(M)} = D_p G / \mu$$

where:

$N_{Re(M)}$ = modified Reynold's number

D_p = particle diameter, ft

G = mass velocity based on pipe cross-section, lb/sec-ft²

μ = fluid viscosity, lb/ft-sec.

Leva states that laminar flow exists below a modified Reynold's number of ten, transitional flow between ten and 100, and turbulent flow above 100.

Heat Transfer to Gases in Packed Tubes. Apparent coefficients of heat transfer to gases flowing through externally heated tubes packed with granular materials have been determined⁽⁸¹⁾. The ratio of the observed apparent coefficients for the packed tube to that for an empty tube, depends on the ratio of the packing diameter to the inside tube diameter. For packing diameter to tube diameter ratios of 0.05 to 0.20, the ratios of packed-tube heat transfer coefficient to empty-tube coefficient varied from 5.5 to 7.5.

Application 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, second, 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 the experiment is called a factorial experiment⁽²⁹⁾.

The "F" Ratio. The "F" ratio is defined by the equation⁽²⁷⁾

$$F = \frac{S_1^2}{S_2^2}$$

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

In making use of the "F" ratio, the availability of tabulated "F" distributions⁽³⁰⁾ 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 textbooks⁽²⁶⁾.

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 means of subgroups are greatly different, the variance of the combined groups is much larger than the variances of the separate groups⁽²⁸⁾. For a more thorough introduction into the mechanics and basic theory of analysis of variance, the author would suggest any available statistics textbook⁽²⁶⁾.

Vapor-Phase Chromatography

Vapor-phase chromatography is a new analytical method for gases and liquids boiling up to 300 °C (572 °F). The principles of vapor-phase chromatography and the applications will be discussed in the following paragraphs.

Chromatography. Chromatography is a description for the process of separation, by differential sorption or solution, of the components of a flowing mixture, with respect to a stationary solid or liquid medium. Various forms of chromatography exist, including: (1) liquid chromatography in which the mobile phase is liquid and the stationary phase is either solid, or an immiscible liquid supported by an inert solid, and (2) vapor-phase chromatography, 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 chromatography.

Means of Separation. The two general mechanisms used to separate the components of a sample in a vapor-phase chromatographic column are (1) differential adsorption and (2) differential solution or

"partition." The apparatus and techniques are essentially identical, differing only in the choice of material used in the chromatographic column. Activated forms of charcoal, alumina, or silica gel are commonly used in adsorption columns, while an inert solid coated with a non-volatile liquid is used in partition columns.

Apparatus and Techniques for Vapor-Phase Chromatography. A simplified diagram of an elution analysis apparatus⁽⁸⁹⁾ is shown in Figure 3, page 51. The essential items in the apparatus are the carrier gas, the pressure controller, the chromatographic column, and the detector.

Carrier Gases. Three gases, nitrogen, helium, and hydrogen, have been most often used by the researchers in this field. Hydrogen and helium have high thermal conductivities and consequently show a high sensitivity to small concentrations of eluted components. Also, the fact that all the eluted components have lower thermal conductivities is an advantage as all scanning peaks will appear on the same side of the base line.

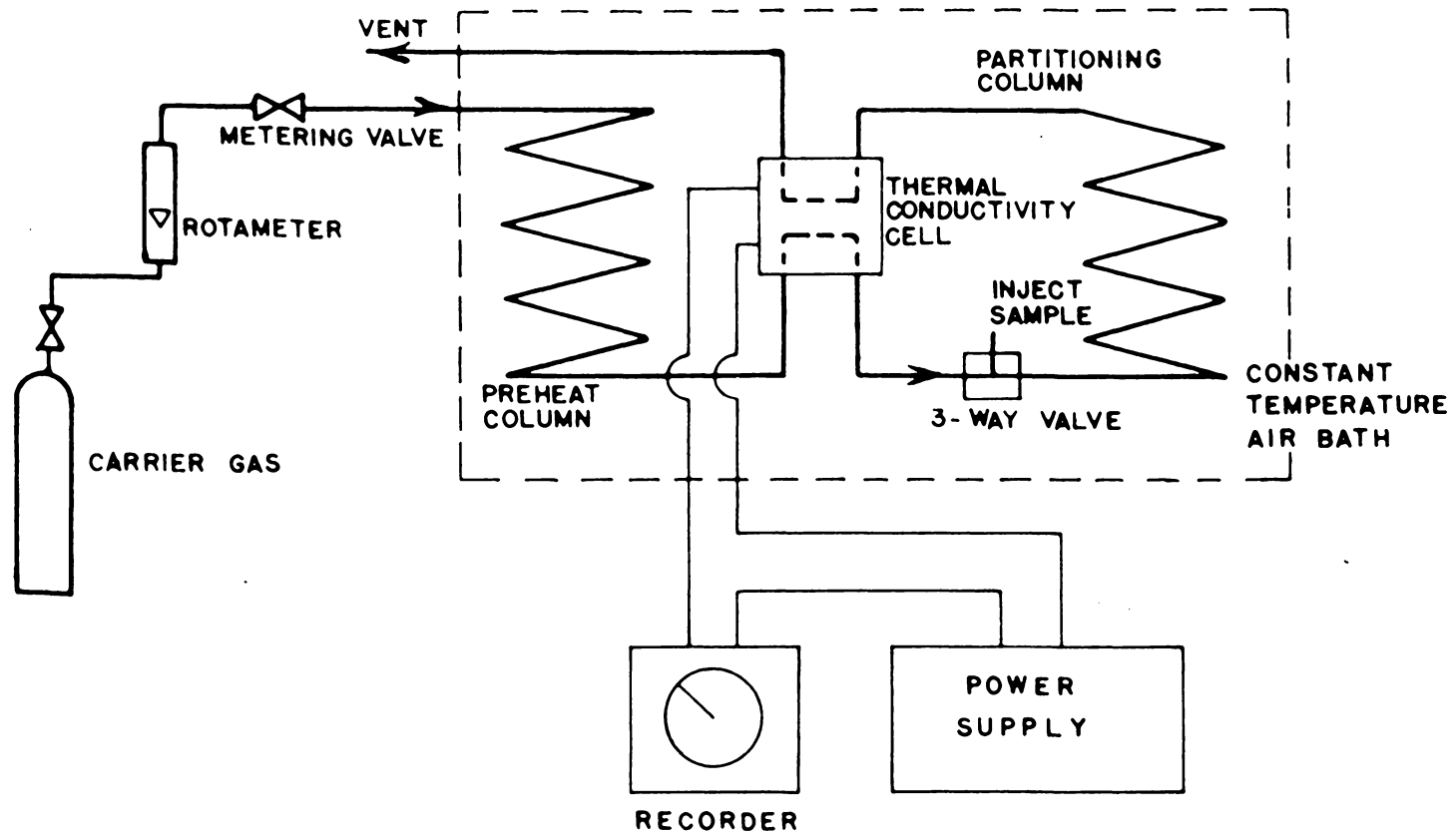


FIGURE NO. 3 SIMPLIFIED FLOW DIAGRAM FOR A LIQUID-VAPOUR CHROMATOGRAPH

Flow Rates. The flow rates of carrier gas used have varied from 5 to 150 milliliters per minute, depending on the type of sample to be analyzed.

Chromatographic Column. The columns in general use⁽⁸⁹⁾ vary from 3 to 14 feet in length, made from copper, stainless steel, or glass. The crushed material used in packing is usually 40-mesh or finer.

Partition Agents. Previous investigations have used a number of liquids⁽⁸⁹⁾ such as normal dodecane, dinonyl phthalate, benzyl diphenyl, hexatriacontane, tri-isobutylene, silicones, glycerol, liquid paraffin, and others. The liquid may be distributed over the packing by thorough mixing, or may be mixed with a volatile solvent and added to the packing, the solvent being subsequently removed by evaporation. Higher column temperatures are required to analyze high boiling components; however, the column temperature may be 50 to 100 °C (106 to 212 °F) 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)⁽⁸⁹⁾,

surface potential⁽⁴⁵⁾, infrared spectrometer, and titration where eluted substances exhibit acidic or basic reactions⁽⁴⁹⁾.

Application of Vapor-Phase Chromatography. Littlewood and Phillips⁽⁹⁰⁾ reported the separation of the common alcohols in columns packed with diatomaceous earth impregnated with silicone. Littlewood⁽⁹⁰⁾ has reported the separation of a variety of esters and Ray⁽¹⁰⁰⁾ has reported the analysis of mixtures of ketones using dinonyl phthalate. Van de Kramer⁽¹⁰⁰⁾ has reported the analysis of fatty acids by vapor-phase chromatography.

Analysis of Non-hydrocarbon and Light Hydrocarbon Gases. The separation and analysis of the non-hydrocarbon and light hydrocarbon gases⁽¹⁰⁰⁾ has been accomplished in columns packed with charcoal, alumina, silica gel, zeolites, and stationary phase liquids. Some of the separations that have been reported are shown in Table I, page 54.

Analysis of Hydrocarbons. The separation of olefins from paraffins is usually performed by using liquids such as dimethyl formamide or acetonyl acetone as the stationary phase⁽¹⁰⁰⁾. However, the presence

TABLE I
Chromatographic Analysis of Non-hydrocarbon
and Light Hydrocarbon Gases

	Approximate Retention Time on Charcoal	Approximate Retention Time on Activated Alumina	Approximate Retention Time on Charcoal
	min	min	min
Hydrogen	2	-	1.0
Oxygen	-	-	1.5
Carbon monoxide	4	-	-
Carbon dioxide	16	-	3.5
Methane	9	0.50	2.5
Acetylene	-	-	7.0
Ethylene	36	-	10.0
Ethane	51	1.00	15.0
Pentane	-	2.25	-
Iso-C ₄	-	5.50	-
Normal-C ₄	-	6.00	-
Column length	6 ft	110 cm	110 cm
Column temp., °C	20	60	180
Carrier gas	nitrogen	hydrogen	nitrogen
Flow rate	30 cc/min	-	-

Podbielniak, W. J. and S. T. Preston: Developments in
 Light Hydrocarbon Analysis, Oil and Gas Jour., p. 5,
 April 16, 1956.

of C₃ or C₅ paraffins will interfere with the analysis of a cracked C₄ fraction. Dinonyl phthalate or high molecular weight paraffins will generally resolve a hydrocarbon mixture in fractions according to the number of carbon atoms present.

Aromatic hydrocarbons are easily separated even when in the presence of paraffins or olefins. The reported results on aromatic hydrocarbons are summarized in Table II, page 56.

The paraffinic, olefinic, and cyclic hydrocarbons in the C₅ to C₁₀ range can be separated using a C₃₆ straight chain hydrocarbon as the partition agent⁽¹⁰⁰⁾.

TABLE II

Chromatographic Analysis of Aromatic Hydrocarbons

	Retention Time on Silicone Fluid	Relative Retention Time on n-Hexatri- acotane (n-pentane = 1)	Retention Time on Dinonyl Phthalate
	min		min
Benzene	3	4.19	8
Toluene	6	10.50	19
Ethyl benzene	12	21.97	38
m-Xylene	12	25.72	45
P-Xylene	12	26.02	45
O-Xylene	14	30.72	53
Isopropyl benzene	16	-	-
Sec-butyl benzene	28	-	-
P-Cymene	30	-	-
Indene	39	-	-
Tertiary pentyl benzene	45	-	-
Column length	1 m	4 ft	6 ft
Column diam., mm	5	4	4
Column temp., °C	132	78.5	80
Carrier gas	nitrogen	nitrogen	nitrogen
Flow rate, cc/min	12	-	20

Podbielniak, W. J. and S. T. Preston: Developments in
Light Hydrocarbon Analysis, Oil and Gas Jour., p. 7,
April 16, 1956.

III. EXPERIMENTAL

The experimental portion of this investigation consists of the purpose of the investigation, plan of experimentation, materials, apparatus, methods of procedure, data and results, and sample calculations.

Purpose of Investigation

The purpose of this investigation was to study the factors affecting the low-temperature carbonization of seam number one, Penn-Lee coal from southwestern Virginia, by determining the effect of pretreatment of the charge, temperature of the retorting gas, and time of retorting on the yields and properties of the products of carbonization.

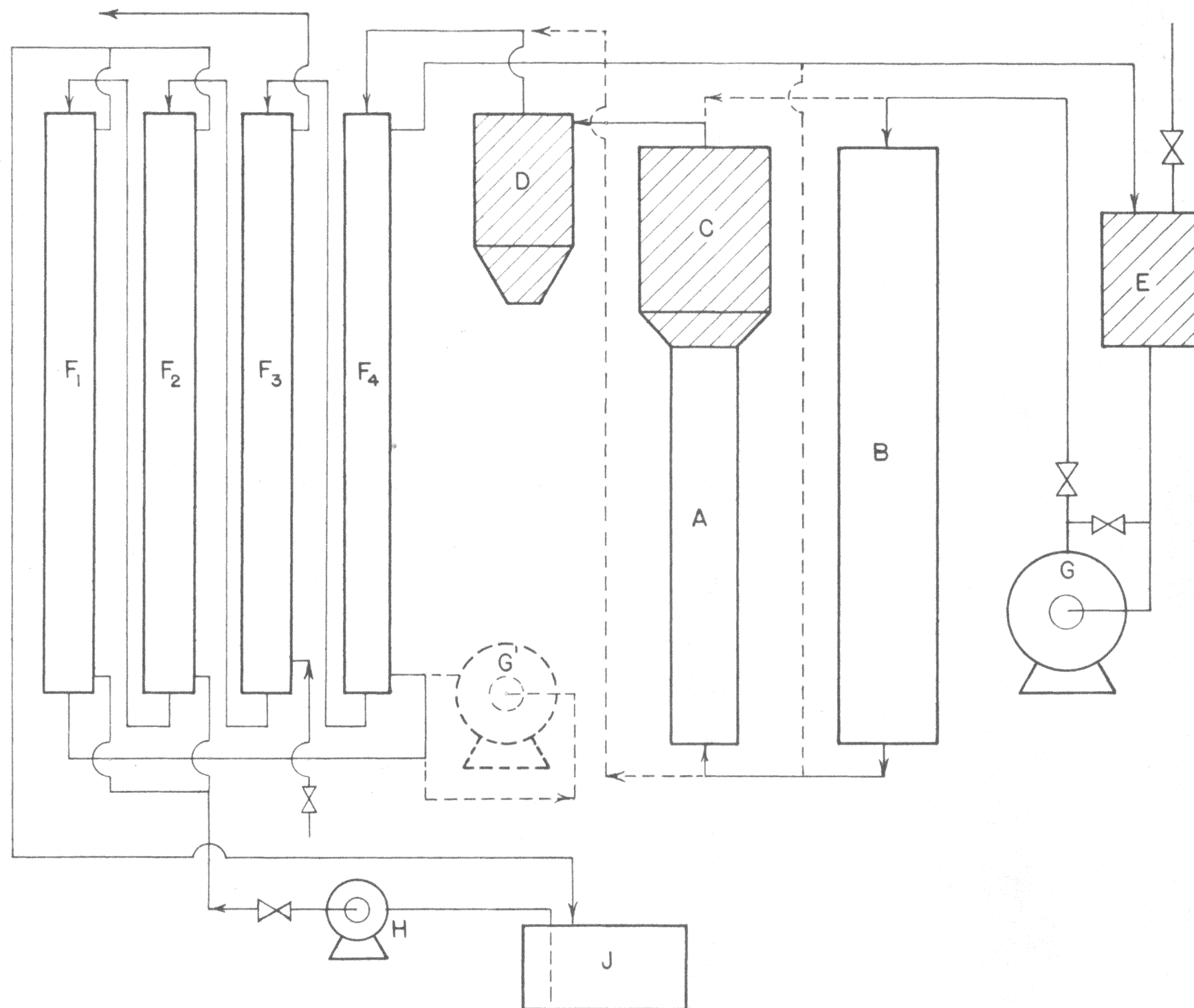
Plan of Experimentation

The plan of experimentation consisted of a survey of the literature, the re-design and modification of an existing fluidization unit for the retorting of lump coal, the experimental procedure, and the evaluation of the results.

Literature Survey. A literature search was made to obtain a general introduction to the field of coal retorting, to become familiar with the properties and compositions of the important types of coal available, to review the principles of heat transfer and fluid flow in packed beds, and to study various methods of analyzing and testing the products of carbonization.

Re-design and Modification of Existing Retorting Unit. The retorting unit constructed for this investigation consisted of a re-designed and modified fluidization unit. The modification was made (1) to create optimum conditions for packed bed retorting, rather than fluidized retorting, (2) to provide a higher temperature retorting gas, and (3) to provide a leak-proof retorting system. The retorting unit consisted of a retorting column, gas heating section, gas circulating pump, condensing system, gas flow measuring and pressure recording equipment, brine circulating system, and temperature measuring equipment as shown in Figure 4, page 59.

Existing Fluidization Unit. The available retorting fluidization unit consisted of a retorting column, gas heating section, condensers, gas flow measuring



LEGEND:

- A - RETORT
 - B - GAS HEATER
 - C - DISENGAGING SECTION
 - D - CYCLONE
 - E - SURGE TANK
 - F₁ & F₂ - BRINE COOLED CONDENSERS
 - F₃ - WATER COOLED CONDENSER
 - F₄ - GAS COOLED CONDENSER
 - G - GAS PUMP
 - H - BRINE PUMP
 - J - BRINE TANK
- CROSS SECTIONED AREAS ARE TO BE REMOVED.

DEPARTMENT OF CHEMICAL ENGINEERING
 VIRGINIA POLYTECHNIC INSTITUTE
 BLACKSBURG, VIRGINIA

PROPOSED CHANGES TO
 FLUIDIZED RETORT

SCALE: <i>None</i>	DATE: <i>15/4/56</i>	CASE NO:
DRAWN BY:		FILE NO:
CHECKED BY:		FIGURE NO: 4
APPROVED BY:	<i>4/16/56</i>	SHEET NO:

and pressure recording equipment, temperature control and measuring equipment, brine circulating system, surge tank, and knock-out and disengaging section. Certain modifications were performed on the equipment to convert it to a fixed-bed unit. These are described in later paragraphs.

Retorting Column. The retorting column assembly consisted of an insulated, vertical retort with thermocouple installations for measuring the bed and the gas temperatures, and manometer taps for obtaining the pressure differential across the packed bed. A distribution plate assembly was attached to the lower part of the retort.

Condensers. The liquid products from the carbonization were condensed in fractions. The first condenser was gas-cooled; the second and third condensers were water-cooled; and the fourth condenser was brine-cooled. The condensers were single-pass, double-type pipe exchangers, and the condensing system was essentially the same as in the existing fluidization unit.

Gas-Flow Measuring and Pressure Recording Equipment. Gas flow was measured by means of calibrated orifices. The pressure of the system was recorded on a round chart recorder. The pressure drop across the bed was measured by means of manometers.

Brine Circulating System. A brine-cooled condenser was employed to condense some of the gases leaving the water-cooled condenser. The brine was circulated from an ice-salt mixture maintained in a storage tank.

Temperature Control and Measuring Equipment. The temperature of the retorting gas was measured by a pushbutton potentiometer and controlled by means of a by-pass on the gas heating section which mixed varying amounts of cool, by-passed gas with heated gas. The temperature of the retorting gas stream could thus be set as desired by varying the ratio of hot to cool gas. Temperatures at various points in the system were measured by iron-constantan thermocouples.

Modifications. The modifications of the existing equipment included the replacing of flange connections

with welded connections, the substitution of a down flow system for the existing up-flow system, packing the gas heating section with one-inch crushed refractory brick, and locating the gas-circulating pump in a more advantageous position in the system.

Welded Connections. All of the flanged connections in the existing fluidization unit, except those on the retorting chamber itself, were removed and replaced with welded connections to prevent leaks.

Down Flow System. The system was designed so that the retorting gases flowed down through the packed bed rather than up through it, thereby causing the coolest section of the bed to be at the bottom and, as the coal was less plastic there, to better support the weight of the bed.

Gas Heating Section. The retorting gas was electrically heated in a heating section, packed with crushed refractory brick. The section was constructed originally for use in the fluidization unit, and it was believed that the refractory brick packing would lead to the higher temperatures that were desired, as the firebrick

packing possessed a smaller fraction of void space and would transfer heat to the retorting gas stream more rapidly. The section had electrical heaters inserted through the wall with the electrical leads passing through the wall of the section. Supplementary strip heaters were attached directly to the gas transfer line between the heating section and the retort.

Circulating Pump. During the previous investigation, using the fluidization unit, it had been found that the pump, placed between the gas cooled condenser and the heating section, was pumping gas at a temperature of 149 °C (300 °F). As the pump was oil-sealed, this led to leakage of gas through the pump itself. By placing the pump directly after the brine-cooled condenser, the gas that it handled would be at its lowest temperature. Thus, leaks through the pump would be prevented and the efficiency of the pump would be increased, as it would be pumping a more dense gas at the lower temperatures.

Experimental Procedure. The experimental procedure consisted of preoxidizing the coal, carbonizing the coal, determining the properties of the products, and of fundamental bench studies on oxidation of lump coal.

Bench Scale Studies. Bench scale tests were made on samples of Penn-Lee coal to study the effect of oxidation on the volatile matter, free-swelling index, and weight loss of the coal. The temperature levels were 205, 260, and 317 °C (400, 500, and 600 °F), and the levels of time were one, two, and three hours. Three replications of the data were made. Tests were then made to determine the temperature under which auto-ignition of the coal would occur. A study was made to determine the weight loss of a coal sample as a function of temperature. This was done to obtain information on the necessary temperatures for retorting the coal.

Pilot-Scale Study of Effect of Preoxidation. The effect of the preoxidation of coal at 338 °C (640 °F) for two and four hours, on the yields and properties of the products of carbonization, and plugging characteristics, was determined.

Pilot-Scale Study of Effect of Time and Temperature of Carbonization. The effect of time and temperature of retorting on the yields and properties of the products obtained were determined. The effect of temperature at levels of 444 and 510 °C (830 and 950 °F) was studied. The effect of time was studied, at levels of one, one and one-half, and two hours. The effect of the variables on the plugging characteristics of the bed was also determined.

Evaluation of Results. The results obtained were evaluated by comparing the yield of volatile material, the volume and composition of the gas generated, and the physical properties and yields of the tars produced as functions of the variables studied.

Statistical Analysis. A factorial design was used for the experimental work. Analysis of variance techniques were employed to determine the variables of major importance and the important interactions between these variables.

Materials

The materials used in this investigation are listed and described in this section.

Carbon Dioxide. Commercial grade. Obtained in cylinders from Southern Oxygen Co., Roanoke, Va. Used to provide an inert atmosphere for the carbonization studies.

Coal. Penn-Lee, washed, run-of-mine, 37 per cent volatile matter, 54 per cent fixed carbon, 5.6 per cent ash, and 2.7 per cent moisture. Obtained from seams No 1 and No 4 of Penn-Lee Coal Corp., Manass, Va. Used in the carbonization and pretreatment studies.

Dibutyl Phthalate. Normal, purified. Obtained from Fisher Scientific Co., Silver Spring, Md. Used as manometer fluid.

Helium. U. S. Bureau of Mines standard grade. Obtained in cylinders from Southern Oxygen Co., Roanoke, Va. Used as the carrier gas in the chromatographic analysis.

Molecular Sieves. No 5A, 1/16-inch pellets. Obtained from Linde Air Products Co., North Tonawanda Park, N. Y. Used as a column packing in the chromatograph.

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

Oxygen. Commercial grade. Obtained in cylinders from Air Reduction Sales Co., Charlotte, N. C. Used in Parr oxygen bomb.

Plastiseal. Expanding joint compound. Obtained from Tidewater Supply Corp., Roanoke, Va. Used in sealing joints in carbonizing unit.

Silica Gel. Lot No 753462, 6/16 mesh. Obtained from Fisher Scientific Co., Silver Spring, Md. Used as a column packing in the chromatograph.

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

Apparatus

The following list of apparatus was used in this investigation. A bill of materials used in the construction of the carbonizing unit is also included.

Apparatus. Free swelling. Built⁽⁹²⁾ 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, 1500 gram capacity, five milligram sensitivity. Manufactured by Seederer-Kohlbusch. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to weigh tar samples.

Balance. Analytical, chain-o-matic type, model 220-0, serial No N-13860, catalog No 1-967, 500 gram capacity. Obtained from Fisher Scientific Co., Silver Spring, Md. Used for weighing samples.

Balls. - Ceramic, 3/8-inch average diameter. Obtained from the Chemical Engineering Department, Virginia Polytechnic Institute. Used for packing in the tube heater for bench-scale pretreatment studies.

Bath. Fisher unitized constant temperature, catalog No 15-455-5. Obtained from Fisher Scientific

Co., Silver Spring, Md. Used to maintain tar samples at constant temperature for specific gravity measurement.

Crucibles. Free swelling, ASTM, vitreosil, catalog No 8-060. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to determine the effect of pretreatment on the free-swelling index of Penn-Lee coal.

Crucibles. Vitreosil, capacity 10 milliliters, catalog No 6-712. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to determine the volatile content of coal and char samples.

Desiccators. Pyrex, 6, 10, and 12 inch diameter, packed with drierite. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to store bench-scale samples.

Distillation Apparatus. Creosote and road oil, ASTM, catalog No 1-729. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to obtain distillation curves of Penn-Lee coal tar.

Distillation Apparatus. Gasoline and light oil, ASTM, catalog No 13-459. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to purify coal tar distillation fractions for analysis.

Furnace. Combustion, type 70 serial Nos 48882, 56260, and 50881. Manufactured by Hevi-Duti Electric Co., Milwaukee, Wisc. Used to heat gas in bench-scale studies.

Furnace. Hoskins, electric, type FD104, serial No 39158, catalog No 10-506. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to study the plugging characteristics of Penn-Lee coal.

Furnace. Fieldner type, ASTM, type FA 120, serial No 11577, catalog No 6-695. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to determine the volatile content of coal and char samples.

Glassware. Miscellaneous beakers, flasks, and cylinders. Obtained from Fisher Scientific Co., Silver Spring, Md. Used for storage and handling of the tar and char samples.

Materials of Construction. The materials used in the construction of the carbonizing unit are listed in Table III, page 71.

Meter. Precision wet test, 10,000 cu ft capacity in 0.025 cu ft increments. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to measure the gas evolved from the pilot-scale carbonization unit.

Partitioner, Vapor-Liquid Chromatographic.

Fisher-Gulf type, model FIS-IPH560-51-T24-T4-T82, serial No 622279. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to analyze gaseous products of carbonization.

Pipe. Stainless, type 18-8, 3/4-inch nominal diameter. Obtained from E. I. du Pont de Nemours Co., Inc., Belle, W. Va. Used for shell of gas heater in the pretreatment studies.

Potentiometer. Model 73PO21. Obtained from Lewis Manufacturing Co., Naugatuck, Conn. Used to measure the EMF in millivolts generated by thermocouples.

Sampling Bulbs. Pyrex, with stopcocks, capacity 250 milliliters. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to collect gas samples from pilot-scale carbonizing tests.

Scale. Platform, 115 pound capacity, one ounce graduations, model 31-0851, serial No 1788. Obtained from Toledo Scale Co., Toledo, O. Used to weigh coal charge for pilot-scale studies.

Sizing Screens. Three-eighths-, one-half-, three-quarters-, one-, and two-inch openings. Built in the Chemical Engineering Department, Virginia Polytechnic Institute. Used to size the coal samples for experimental studies.

Timer. Electric, range 0 to 10,000 minutes, graduated in hundredths of a minute. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to time the duration of a test.

Viscosimeter. Saybolt Furol, catalog No 13-566. Obtained from Fisher Scientific Co., Silver Spring, Md. 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 Co., Philadelphia, Pa. Used to make iron-constantan thermocouples.

Wire. Iron, No 20, B&S gauge, enamel insulation. Obtained from Leeds and Northrup Co., Philadelphia, Pa. Used to make iron-constantan thermocouples.

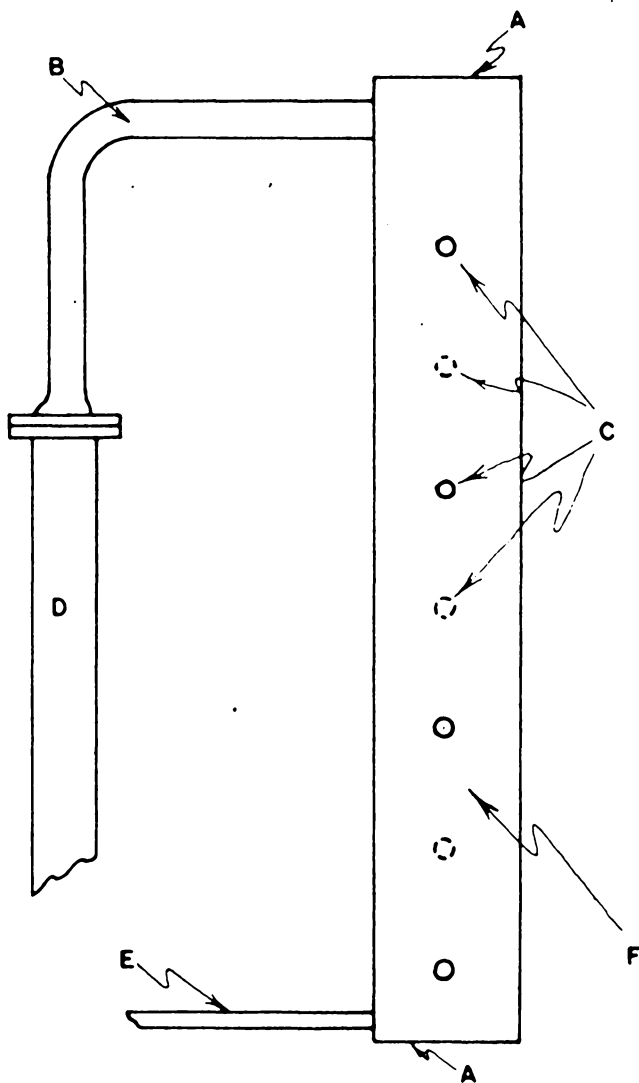
Method of Procedure

The following procedure was employed in investigating the effect of preoxidation on the yields and properties of the products of the low-temperature carbonization of Penn-Lee coal. This includes the procedures used in the bench- and pilot-scale tests, and in the analyses of the products obtained therefrom.

Modification of the Heating Section. The existing heating section used in the work of Carr⁽¹⁴⁾ was originally packed with knit monel metal mesh wire. The rate of heat transfer to the carbon dioxide gas stream was insufficient to obtain the desired gas temperature. It was believed, therefore, that a packing with a lower fraction of voids and higher bulk density would provide greater turbulence in the gas stream and, therefore, better heat transfer.

The monel packing was removed from the heating section and crushed firebrick, minus 1-1/4-inch, plus 3/4-inch, was randomly packed into the section.

The welding neck flanges at the ends of the section were cut off and flat, 1/4-inch steel plates were welded on the ends of the column, as shown in Figure 5, page 75.



LEGEND

- A- 1/4" STEEL PLATE WELDED IN PLACE.
- B- "L" SECTION, 2-1/2" STEEL PIPE
- C- 7 1250 WATT HEATERS
- D- RETORT
- E- RETURN GAS LINE, 3/4" IN. PIPE.
- F- CRUSHED REFRACTORY BRICK.

DEPARTMENT OF CHEMICAL ENGINEERING
 VIRGINIA POLYTECHNIC INSTITUTE
 BLACKSBURG, VIRGINIA

GAS HEATER FOR LOW-
 TEMP. CARBONIZATION UNIT

SCALE: 1" = 1'
 DRAWN BY:
 CHECKED BY:
 APPROVED BY:

DATE 4/15/56 CASE NO:
 FILE NO:
 FIGURE NO: 8
 SHEET NO:

4/26/56

A nine-inch length of 3/4-inch pipe was welded one inch from the bottom of the heating section to serve as an inlet for the carbon dioxide gas. An ell section, consisting of two 16-inch lengths of 2-1/2-inch pipe, one 2-1/2-inch, 90-degree ell, one 2-1/2 by four-inch eccentric reducer, and one four-inch welding-type slip-on flange, was welded approximately three inches from the top of the column to serve as an outlet for the hot carbon dioxide.

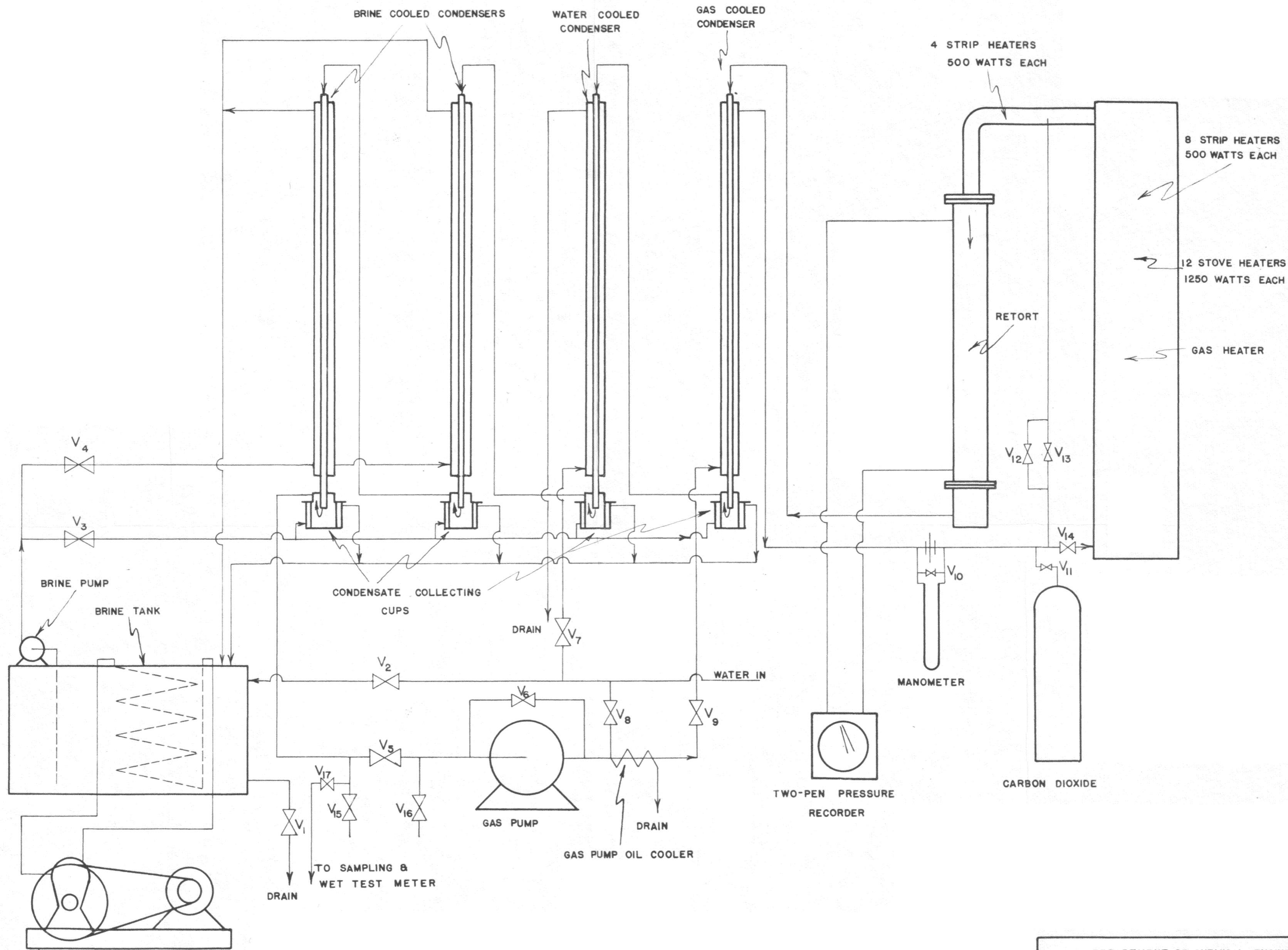
A platform was placed in the bottom of the heating section to support the packing. The platform consisted of a circular section of 1/8-inch steel plate, cut to fit the inside of the heating section and perforated with 1/8-inch holes to allow free passage of the gas stream. Four two-inch legs, made of 3/8-inch steel rod, were welded on the bottom of the circular sheet to complete the platform.

During the course of the investigation several of the internal heating elements burned out and the existing six-foot length of eight-inch pipe with eight heaters was replaced with a nine-foot length of eight-inch pipe with twelve heating elements. The section was then repacked with crushed refractory packing and re-welded.

Down-Flow Fixed-Bed System. It was decided for the purpose of this investigation to modify the existing upflow fluidization device into a fixed-bed, down-flow system. The flow diagram for this system is shown in Figure 6, page 78. In effecting this modification, the surge tank, the disengaging section, and the cyclone separator were all removed from the system. The other changes and modifications are included in this section.

Modification of Retort. A bed-support section was added at the bottom of the retort. This section consisted of a six-inch length of four-inch pipe with a flat 1/4-inch steel plate welded at the bottom and a four-inch, welding-type slip-on flange welded at the top. A platform was made consisting of a circular 1/4-inch steel plate, perforated with 1/8-inch holes and cut to fit the four-inch pipe, with three legs made from 3/8-inch by six-inch steel rod welded on. An outlet was provided by welding a nine-inch length of 3/4-inch pipe two inches from the base of the bed-support section as shown in Figure 6, page 78.

Modification of Condensate Collecting Cups. The facing plates at the bottom of the condensers were



2 1/2 TON REFRIGERATION UNIT

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FLOW DIAGRAM FOR LOW-TEMPERATURE CARBONIZATION UNIT		
SCALE: NONE	DATE 7/4/56	CASE NO:
DRAWN BY:		FILE NO:
CHECKED BY:		FIGURE NO: 6 and 10
APPROVED BY:	4/16/56	SHEET NO:

removed and replaced with plates made of $3/16$ -inch steel plate and otherwise identical to the original copper facing plates.

The collecting cups were also modified by the addition of an annular space to the outside of the cups to permit cooling with brine. This was accomplished by making the annular spaces of three-inch sections of three-inch copper pipe. The annular space was attached to the cup by silver-soldering a $1/8$ -inch copper plate to the bottom of the cup, and then to the three-inch section of copper pipe. The top of the annular space was closed by silver-soldering a donut-shaped piece of $1/8$ -inch copper plate to the cup and to the top of the three-inch copper pipe.

A $3/8$ -inch hole was then drilled at the top and bottom of the annular space and the flanges from $1/4$ -inch valves were silver-soldered in place to provide inlets and outlets for the brine.

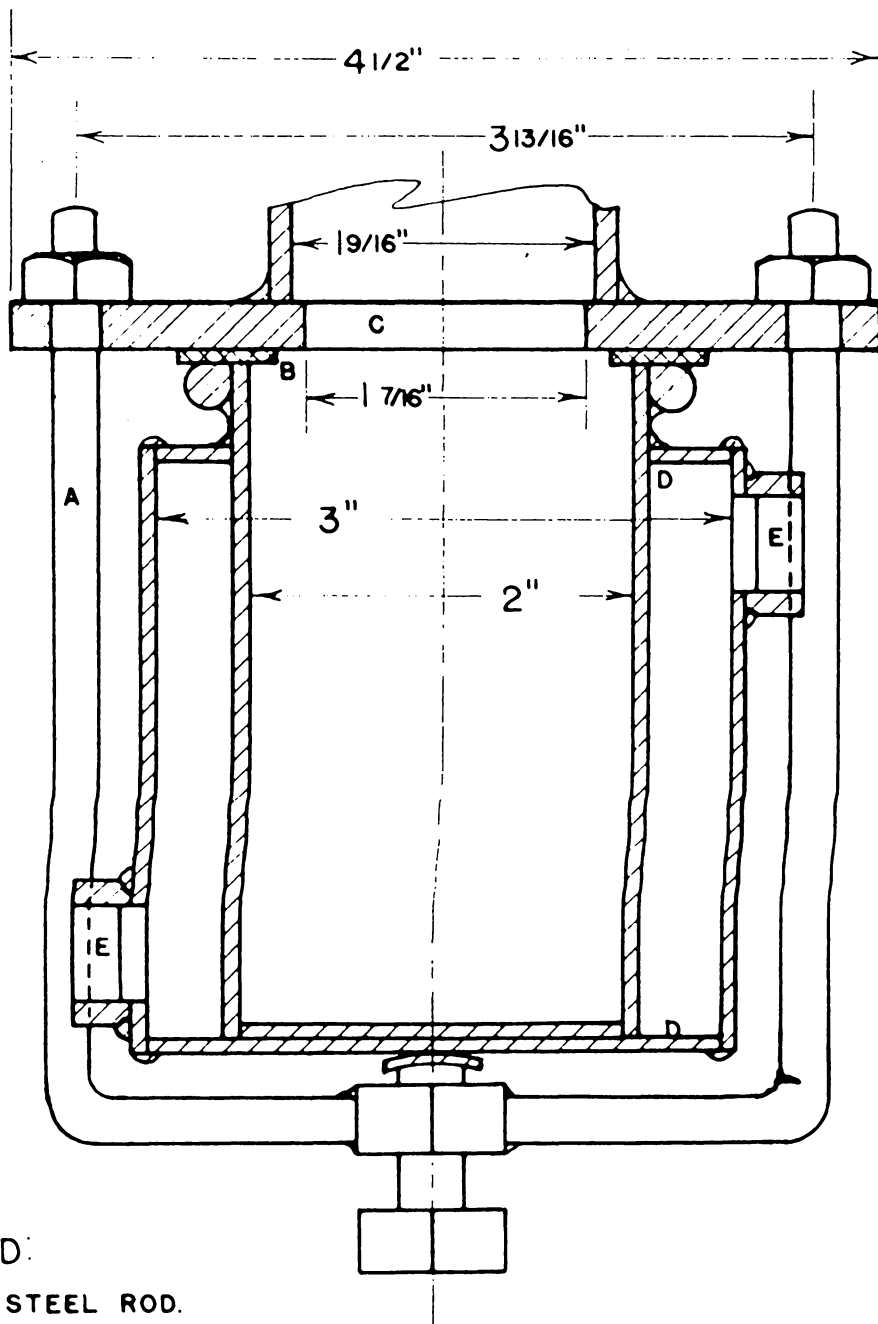
Inlet and exhaust manifolds were constructed of $1/4$ -inch and $3/8$ -inch copper tubing to supply and return the brine. The supply brine was taken from the brine supply line to the condensers and the flow was controlled with a $3/8$ -inch globe valve. The

headers were attached to the collecting cups with 1/4-inch copper tube fittings and 1/4-inch tubing to pipe adapters. The alterations are presented in Figure 7, page 81.

Relocation of Pumps. In order to increase pump efficiency, the gas pump was relocated so that it would pump the gas leaving the last brine-cooled condenser. The pump and motor, along with their mounts, were cut from their original positions with a cutting torch. The base was mounted on legs made from 1-1/4-inch black iron pipe, and placed in its new position, as shown in Figure 6, page 78. The four-inch pulley on the motor was replaced by a new pulley five inches in diameter resulting in a 20 per cent increase in gas flow. The pump was then enclosed with a guard rail constructed of 1-1/4-inch black iron pipe and one-inch angle-iron to prevent injuries resulting from catching limbs or clothing in the belts and pulleys.

The brine pump was placed on top of the brine tank to provide additional space needed for relocating the gas pump.

Modifications of Wiring and Thermocouples. The thermocouples in the retort were replaced with nine-



LEGEND:

- A- $\frac{1}{4}''$ STEEL ROD.
- B- GASKET.
- C- $\frac{1}{4}''$ STEEL PLATE
- D- $\frac{1}{8}''$ COPPER PLATE
- E- COPPER VALVE BUSHING FOR $\frac{1}{2}''$ PIPE.

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CONDENSATE COLLECTING CUPS FOR CARBONIZATION UNIT	
SCALE: FULL SIZE	DATE: <i>5/4/56</i>
DRAWN BY:	FILE NO:
CHECKED BY:	FIGURE NO: 7
APPROVED BY:	<i>4/16/56</i> SHEET NO:

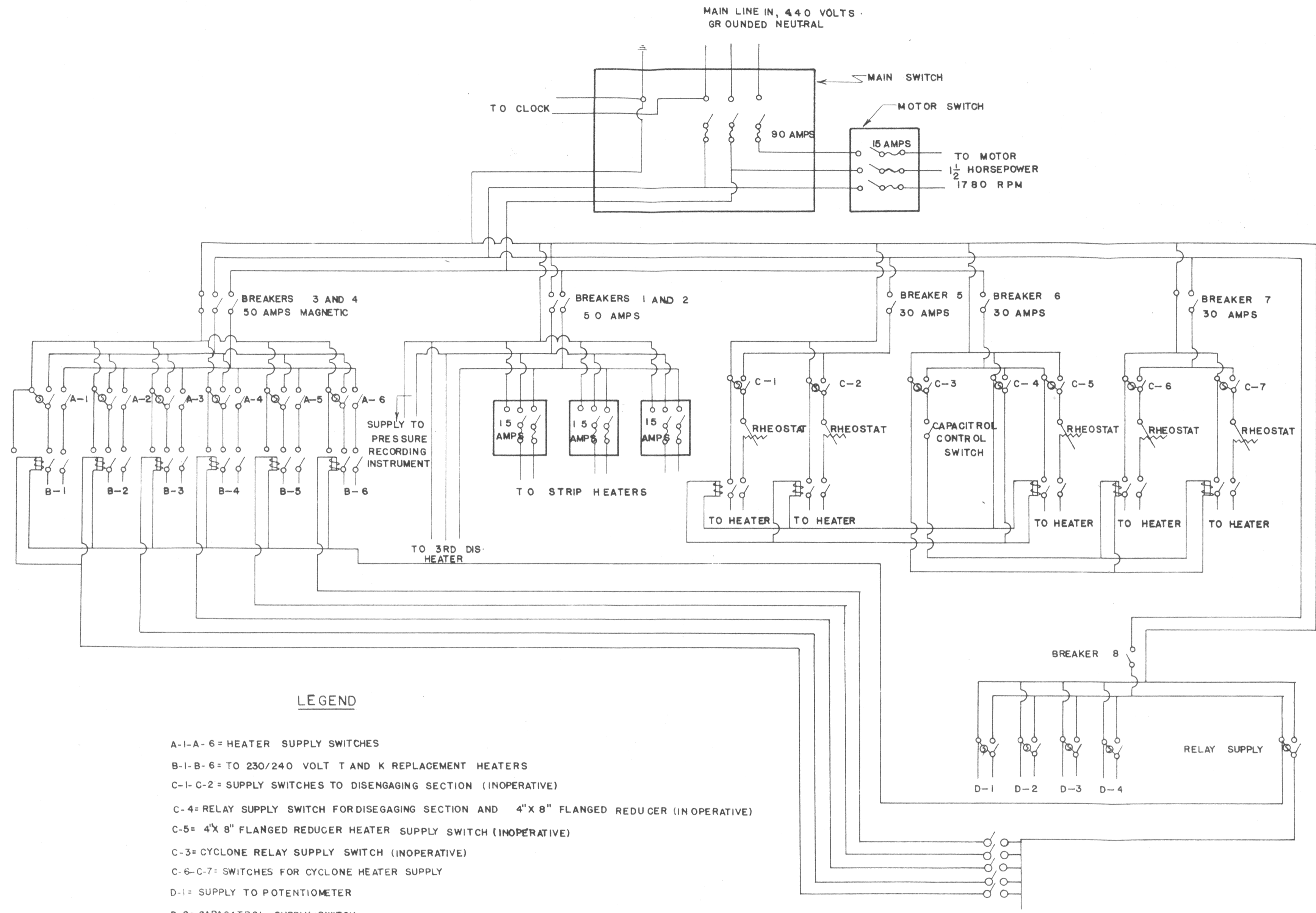
inch, iron-constantan thermocouples, in 3/4-inch steel wells, with 1/2-inch bushings welded two inches from the hot end. All excess wiring was removed, and the existing recording potentiometer was repaired. The thermocouples were calibrated at the freezing and boiling points of water. The wiring diagram for the system is shown in Figure 8, page 83.

Insulation. The heating section was insulated with one layer of 1-1/2-inch Kaylo insulation followed by 3-1/2 inches of type 900 fiberglass blanket. The retort and the ell section were insulated with four inches of type 900 fiberglass insulation.

During the course of the investigation, the Kaylo insulation proved unsatisfactory and was replaced with high-temperature pink Kaylo insulation.

Calibration of Orifice. The orifice measuring the gas flow rate through the system was located between condenser number one and the gas heater so that it measured the flow rate of the preheated gas entering the heating section.

The orifice was calibrated at retort temperatures varying from 149 to 538 °C (300 to 1000 °F), which corresponded to gas temperatures through the orifice of 49 to 104 °C (120 to 220 °F).



LEGEND

- A-1-A-6 = HEATER SUPPLY SWITCHES
- B-1-B-6 = TO 230/240 VOLT T AND K REPLACEMENT HEATERS
- C-1-C-2 = SUPPLY SWITCHES TO DISENGAGING SECTION (INOPERATIVE)
- C-4 = RELAY SUPPLY SWITCH FOR DISENGAGING SECTION AND 4" X 8" FLANGED REDUCER (IN OPERATIVE)
- C-5 = 4" X 8" FLANGED REDUCER HEATER SUPPLY SWITCH (INOPERATIVE)
- C-3 = CYCLONE RELAY SUPPLY SWITCH (INOPERATIVE)
- C-6-C-7 = SWITCHES FOR CYCLONE HEATER SUPPLY
- D-1 = SUPPLY TO POTENTIOMETER
- D-2 = CAPACITROL SUPPLY SWITCH
- D-3 = BROWN POTENTIOMETER
- D-4 = BRINE PUMP SWITCH

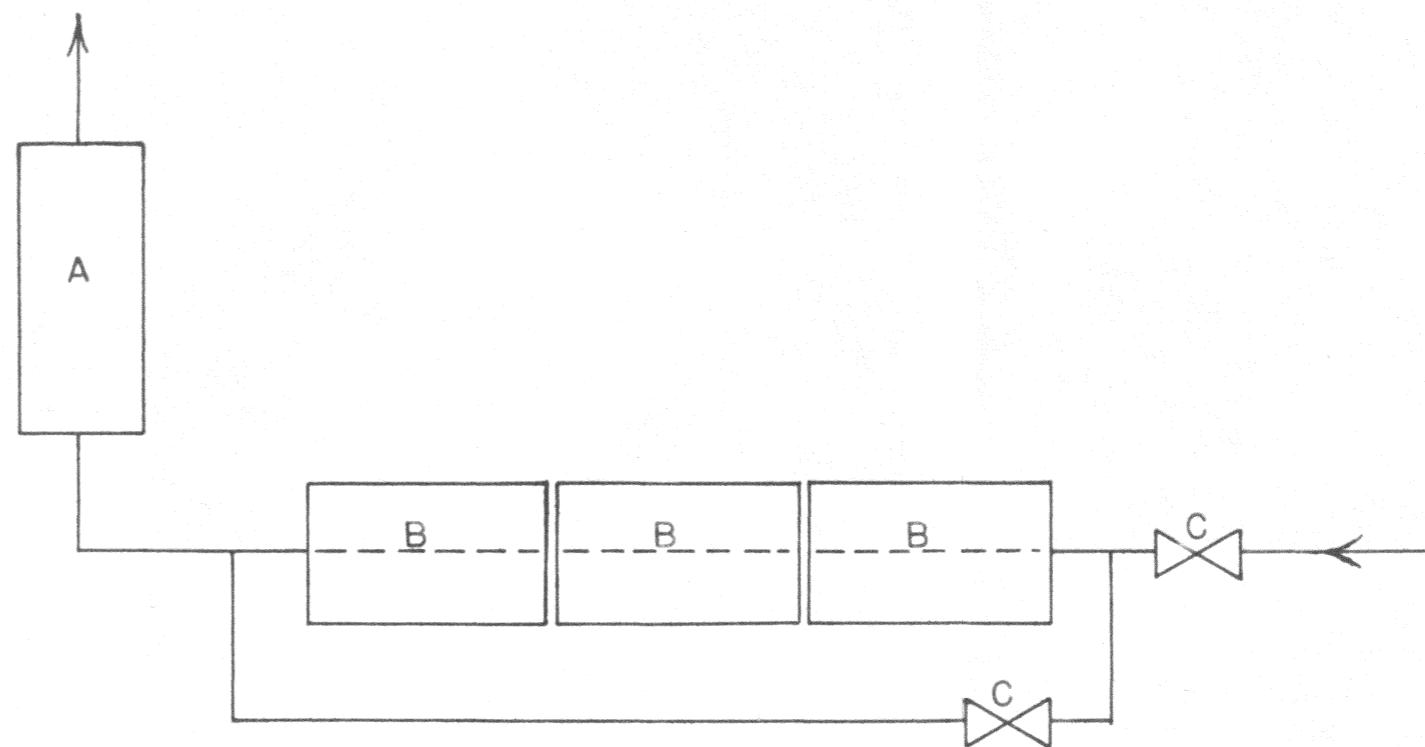
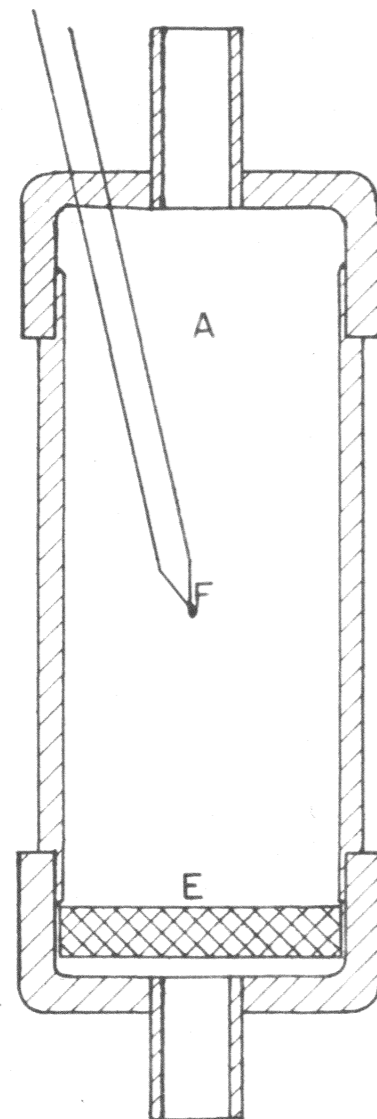
NOTES

- ① ALL BREAKERS ARE MAGNETIC TYPE IN ONE DISTRIBUTION PANEL
- ② SWITCHES WITH INDICATING BULB ARE MANUAL SWITCHES FOR OPERATION
- ③ RELAYS, POTTER AND BRUMFIELD TYPE, PR SERES 7A DOUBLE BREAK, NORMAL OPEN.
RATED AT 20 AMPS WITH SILVER, COIL VOLTAGE 110 VOLTS AC.

DEPARTMENT OF CHEMICAL ENGINEERING VIRGINIA POLYTECHNIC INSTITUTE BLACKSBURG, VIRGINIA	
WIRING DIAGRAM FOR CARBONIZATION UNIT	
SCALE: NONE	DATE: 10/2/56
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APPROVED BY:	SHEET NO:

Refrigeration for Brine Tank. A one-horsepower compressor was installed to cool the brine in the brine tank. The cooling coil was constructed from 50 feet of 1/2-inch copper tubing, and connected to the compressor with 1/2 by 5/8-inch flare nuts. This installation supplied three tons of refrigeration, and maintained the brine at -4 to -2 °C (25 to 29 °F).

Bench-Scale Preoxidation. Bench-scale preoxidation tests were performed at temperature levels of 204, 260, and 315 °C (400, 500, and 600 °F) for time intervals of one, two, and three hours. Three replications of these data were made. The tests were performed on 50-gram samples of coal sized to minus 3/4, plus 1/2 inch. The apparatus used is shown in Figure 9, page 85. The samples were weighed on an analytical balance to one ten-thousandths gram, and placed in the retort. The cap was screwed on, and the thermocouple connected. The gas pump was 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 was determined.



LEGEND:

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

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BLACKSBURG, VIRGINIA

BENCH-SCALE PRETREATMENT
APPARATUS

SCALE: <i>NONE</i>	DATE <i>4/4/57</i>	CASE NO:
DRAWN BY:		FILE NO:
CHECKED BY:		FIGURE NO: 9
APPROVED BY:	<i>4/4/57</i>	SHEET NO:

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 9, page 85. A 50-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 started and the inlet air heated to temperatures of 315, 329, and 343 °C (600, 625, and 650 °F). The flow rate of air was maintained at 12 ± 0.1 cubic foot per minute. The combustion temperature was taken as the inlet air temperature which resulted in bed ignition, which was visually observed.

Determination of the Decomposition Point. Two ground, sized to minus 250 mesh, weighed, coal samples, in covered crucibles, were placed in a Meeker type, electric furnace at successive 27.8 °C (50 °F) temperature intervals from 204 to 596 °C (400 to 1100 °F). At each temperature level, the samples were left in the furnace for seven minutes. They were removed, cooled, and weighed. The cumulative weight loss was plotted as a function of temperature. This plot is shown in Figure 15, page 105.

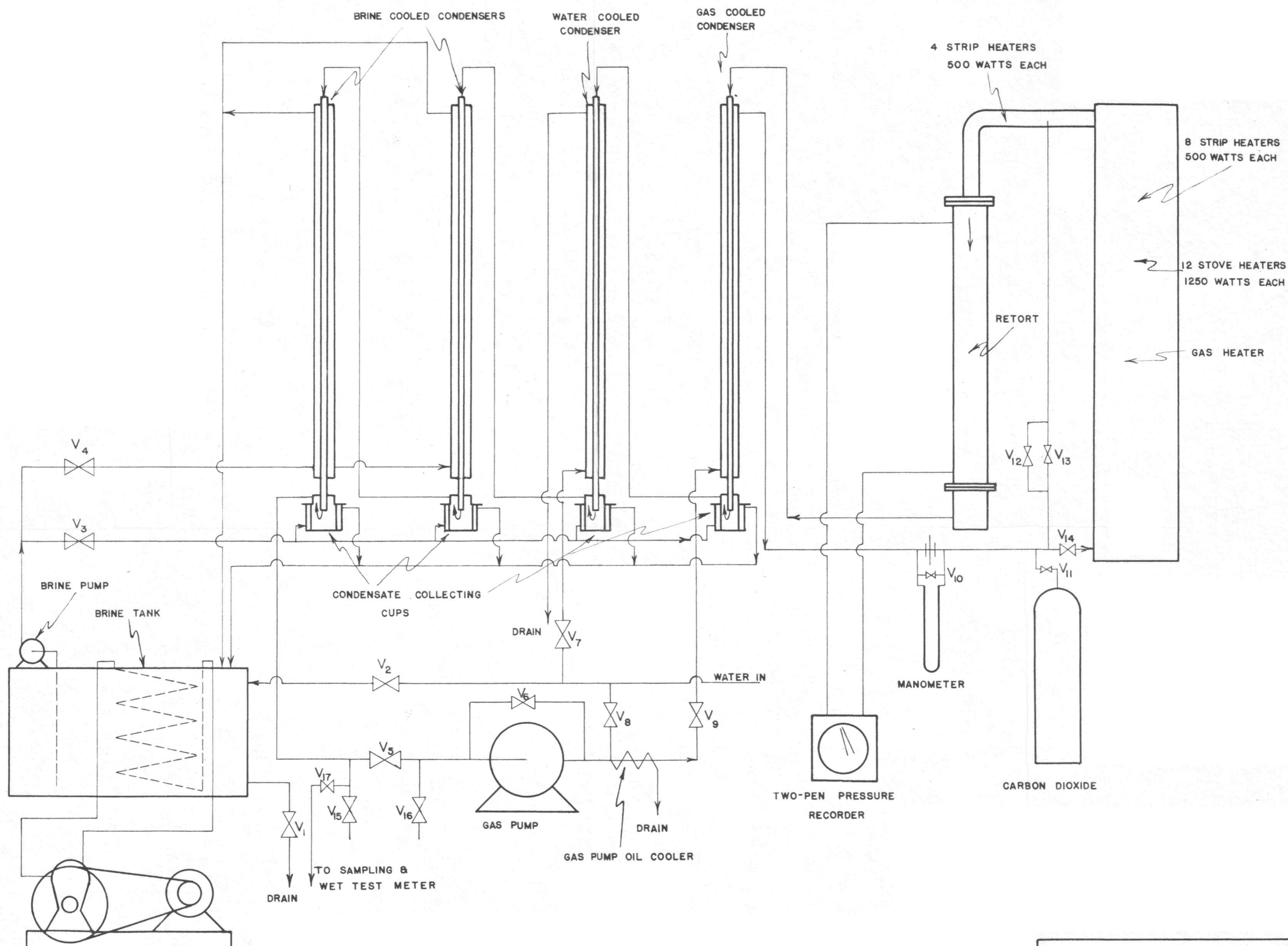
Pilot-Scale Preoxidation. Preoxidation tests were performed at a maximum bed temperature of 332 ± 8 °C (630 ± 15 °F). Coal, sized to minus two, plus one inch, was pretreated with air for times of two and four hours. The bed temperatures were measured with the retort thermocouples as shown in Figure 6, page 78. Samples of the exit gases were taken and analyzed in a Fisher-Gulf chromatograph. 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 the ignition may occur if the concentration of the oxygen in the retorting gas becomes too high at this temperature.

Pilot-Scale Carbonization. The pretreated samples were subjected to carbonization for time intervals of one, one and one-half, and two hours at temperatures of 443 and 510 °C (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 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, and the charge was removed, weighed, and stored.

Detailed Pilot Plant Procedure. The detailed procedure for the operation of the pilot plant, shown schematically in Figure 10, page 89, is as follows:

1. Load 5.5-pound charge into the retort, bolt retort in place with corrugated iron-asbestos gaskets coated with "plastiseal" between the flange faces, and insulate 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_g.



2 1/2 TON REFRIGERATION UNIT

DEPARTMENT OF CHEMICAL ENGINEERING
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 BLACKSBURG, VIRGINIA

FLOW DIAGRAM FOR LOW-TEMPERATURE
 CARBONIZATION UNIT

SCALE: NONE DATE 7/4/56 CASE NO:
 DRAWN BY: FILE NO:
 CHECKED BY: FIGURE NO: 6 and 10
 APPROVED BY: 4/16/56 SHEET NO:

6. Adjust gas flow rate to one inch of di-butyl phthalate measured on gas-flow manometer with valve V₆. Allow gas heater to heat for two hours.
7. Adjust flow to five and one-half inches of di-butyl phthalate measured on gas-flow manometer and allow bed to come up to retorting control temperature.
8. Control temperature at 332 °C (650 °F) by adjusting valves V₅, V₁₅, V₁₂, V₁₃, and V₁₄.
9. Sample bed exhaust gases by turning V₇.
10. After pretreatment is complete, turn off pump, purge system with carbon dioxide by opening valve V₁₁, with valves V₁₅, and V₁₆ 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 pump, and adjust flow rate to eight inches of di-butyl phthalate, measured on gas-flow manometer, with valve V₆.
12. Turn on pressure recorder, close brine pump switch.

13. Turn on water to water-cooled condenser using valve V₇.
14. Hold pressure in system at desired point by bleeding down through wet test meter, using valve V₁₇.
15. Control retort temperature by manipulating valves V₁₃ and V₁₄.
16. Collect resulting gas samples by turning valve V₁₇.
17. At the end of the carbonizing test, turn off relay switch, heater switch, gas pump switch, brine pump switch, potentiometer switch, and pressure recorder switch. Turn off water to water-cooled condenser with valve V₁, and pump cooling water with valve V_g.
18. Allow condenser to drain for at least five hours before removing cups and trap to collect condensate.
19. Measure gas evolved by reading wet test meter.
20. Remove insulation on retort. Allow retort to cool, and then remove and weigh remaining charge of product char.

PRECAUTION! Turn off 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⁽²⁵⁾.

Bulk Density Determination. The bulk density of the char product was determined by the American Society for Testing Materials method⁽¹⁶⁾.

Calorific Value Determination. The calorific value of the char samples was determined by the standard method suggested by the American Society for Testing Materials⁽¹⁷⁾.

Free Swelling Index Test. The free swelling index determinations were performed in accordance with the method⁽²²⁾ proposed by the American Society for Testing Materials 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 contained therein 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. The specific gravity of the tar was then 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 Fural viscosimeter⁽¹⁰¹⁾. The Saybolt Fural viscosimeter 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⁽²⁴⁾, with the following modification.

The tar sample was distilled until 60 per cent of its water-free volume had been collected. The water

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 distillate to an end point of 35 °C (662 °F) as prescribed by the American Society for Testing Materials.

Gas Analysis. The gas samples were analyzed in the Fisher-Gulf chromatographic partitioner. The carrier gas for the analysis was helium. The columns used for the analysis were filled with 5-A molecular sieves of silica gel. The 5-A molecular sieves were used for the separation of oxygen and nitrogen. Silica gel was used in all other cases.

The gas sampling bulb, with the sample to be analyzed, was fitted into a leveling bulb filled with water and a short length (about six inches) of tygon tubing. The water in the leveling bulb was allowed to flow into the sampling bulb thus slowly expelling the sample through the piece of tygon tubing, thus 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 thoroughly flushed with the sampled 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 of 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 and results obtained in this investigation are presented in the following tables and figures.

Calibration of Orifice. The data for the calibration of the orifice for measuring the flow rate of retorting gas are shown in Table IV, page 98. These data are plotted in Figure 11, page 99.

Bench-Scale Pretreatment. The data and results obtained in studying the effect of pretreatment with air upon the weight loss, volatile matter in the char, and the free-swelling index of the sample are shown in Table V, page 100. Plots of the data are given in Figures 12, 13, and 14, pages 101, 102, and 103.

Bench-Scale Study of Carbonization Temperature. The data and results obtained from the bench-scale study of the effect of temperature on the weight loss of coal are shown in Table VI, page 104. A plot of these data is given in Figure 15, page 105.

Pilot-Scale Carbonization. The data and results obtained from the low-temperature carbonization of Penn-Lee coal are presented in Table VII, page 106. Plots of the data are given in Figures 16, 17, and 18, pages 107, 108, and 109.

Distillation of Tar Samples. The data and results from the ASTM distillation of the tar samples obtained in the pilot-scale carbonization are presented in Table VIII, page 110.

Analysis of Variance Tables. The analysis of variance tables of all of the dependent variables statistically studied in this investigation, namely, weight loss, free swelling index, volatile matter, tar yield, gas yield, specific gravity of tar, bulk density of char, tar viscosity, and the 20 per cent distillation temperature, are shown in Table IX, page 111.

TABLE IV

Calibration of Orifice Measuring Gas Flow Rate
Through Low-Temperature Carbonization Unit

Reading No	Manometer Reading inches of di-butyl phthalate	Gas Flow Rate ^a cu ft/min
1	0.0	0.00
2	1.0	5.67
3	2.5	8.62
4	4.1	11.30
5	5.1	13.60
6	6.2	15.85
7	7.7	18.70

^a Gas flow rate corrected to 10 pounds per square inch, gage and 215 °F.

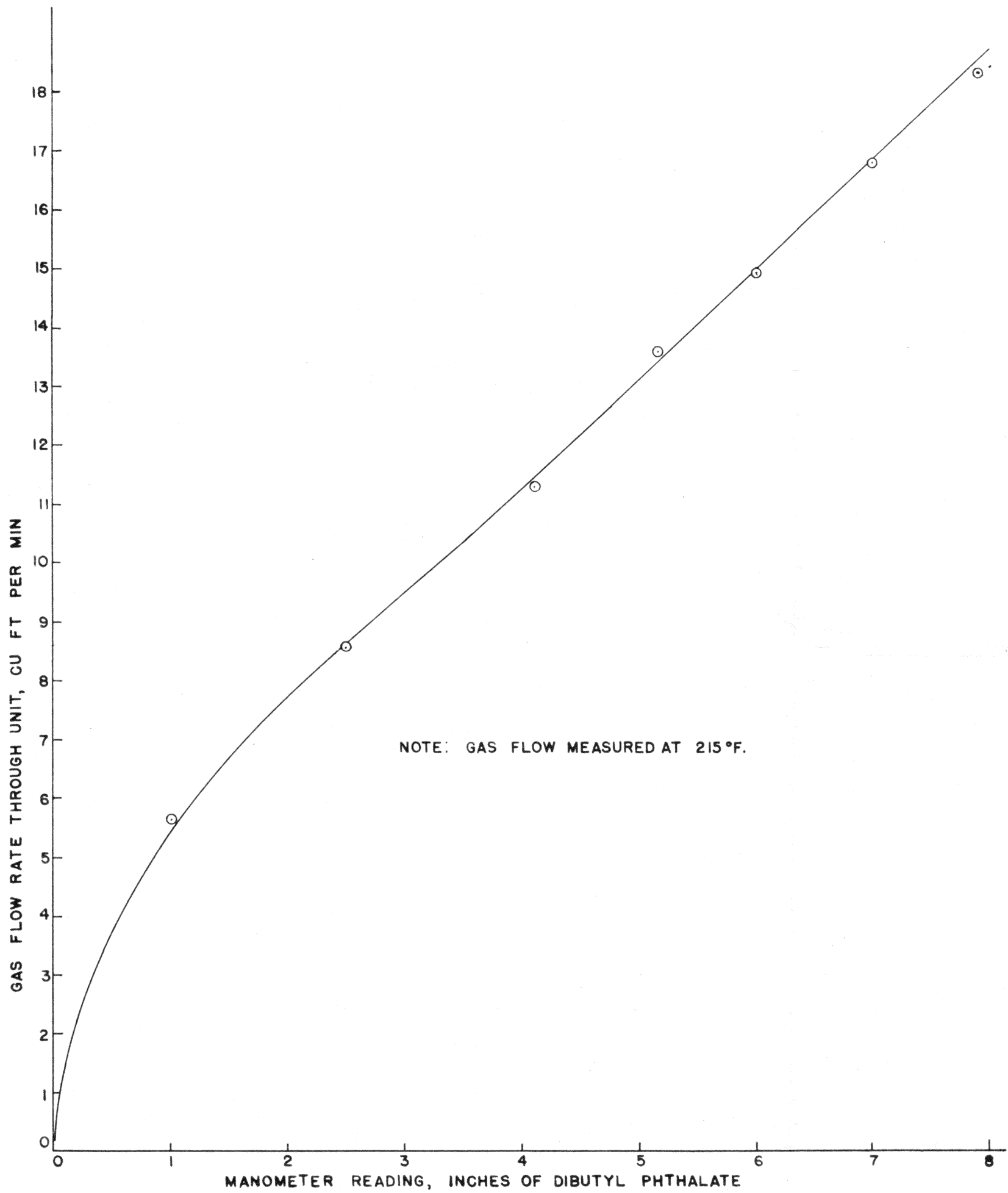


FIGURE 11 . CALIBRATION CURVE FOR ORIFICE MEASURING THE GAS FLOW RATE THROUGH CARBONIZATION UNIT

TABLE V

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

Test No	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

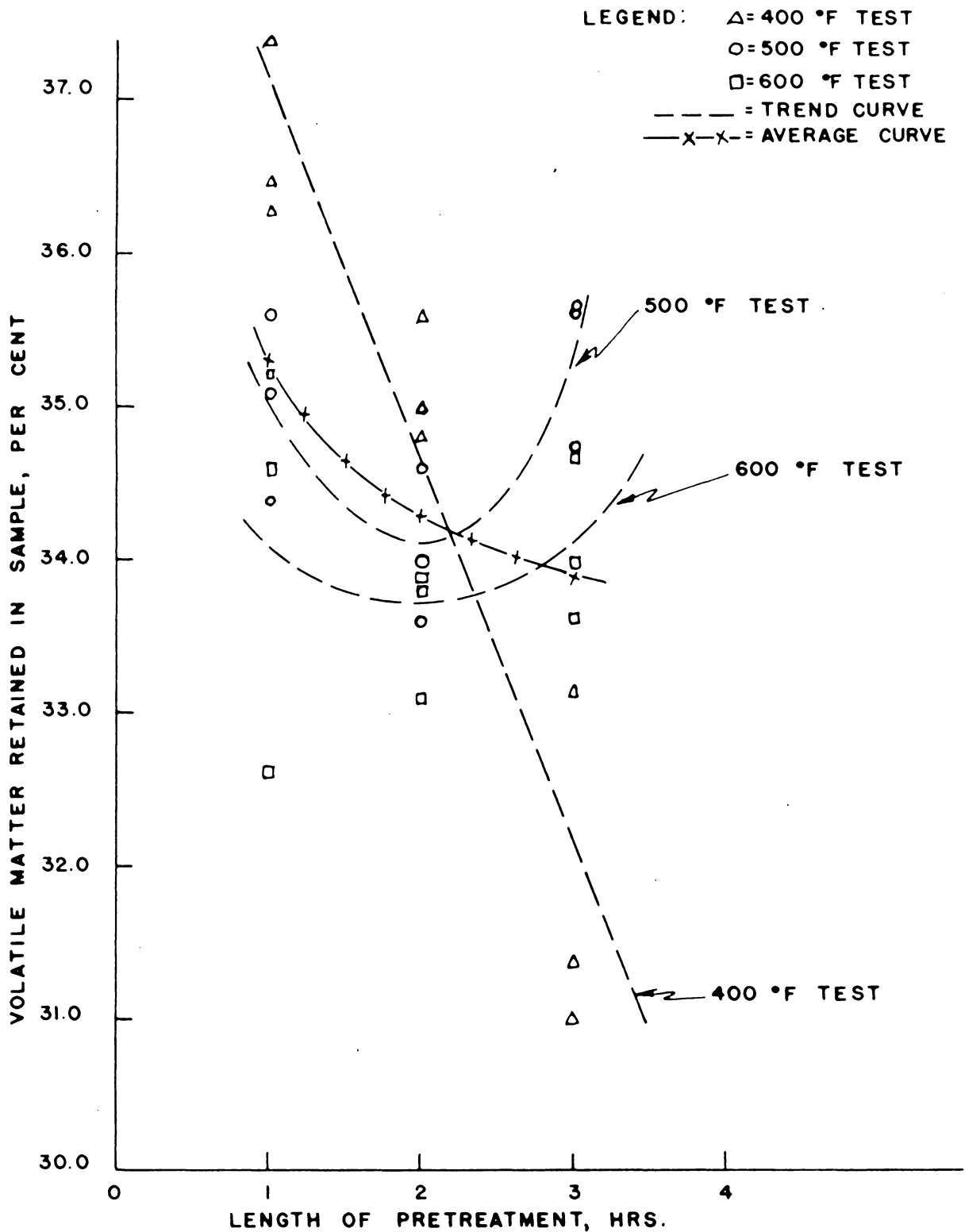


FIGURE 12 . THE EFFECT OF THE LENGTH OF PRETREATMENT ON THE VOLATILE MATTER RETAINED IN SAMPLES OF PENN-LEE COAL

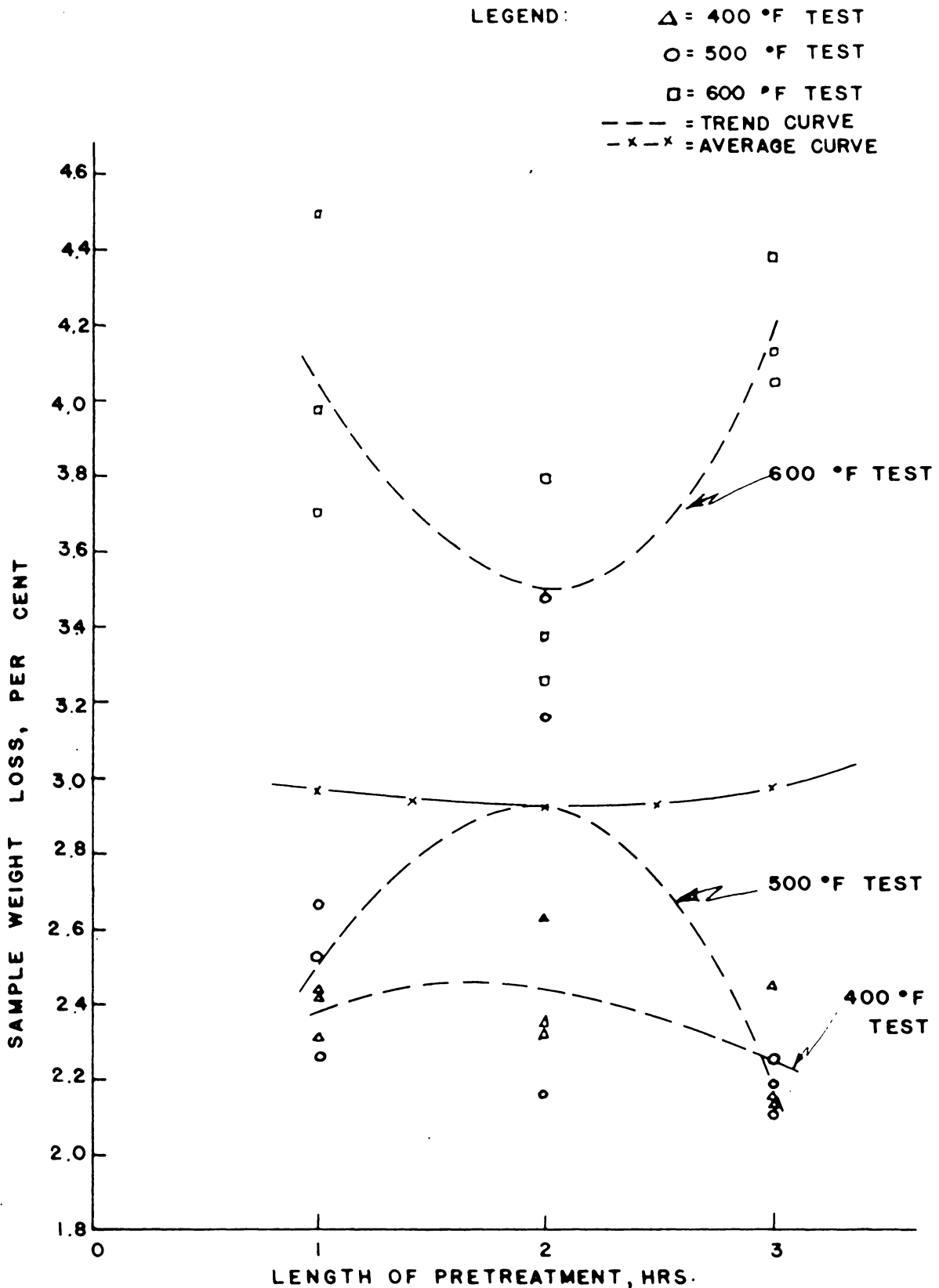


FIGURE 13 . THE EFFECT OF PRETREATMENT TIME ON THE SAMPLE WEIGHT LOSS OF PENN-LEE COAL .

LEGEND:

Δ = 400 °F TEST

O = 500 °F TEST

\square = 600 °F TEST

— — — = TREND CURVE

— x — x = AVERAGE CURVE

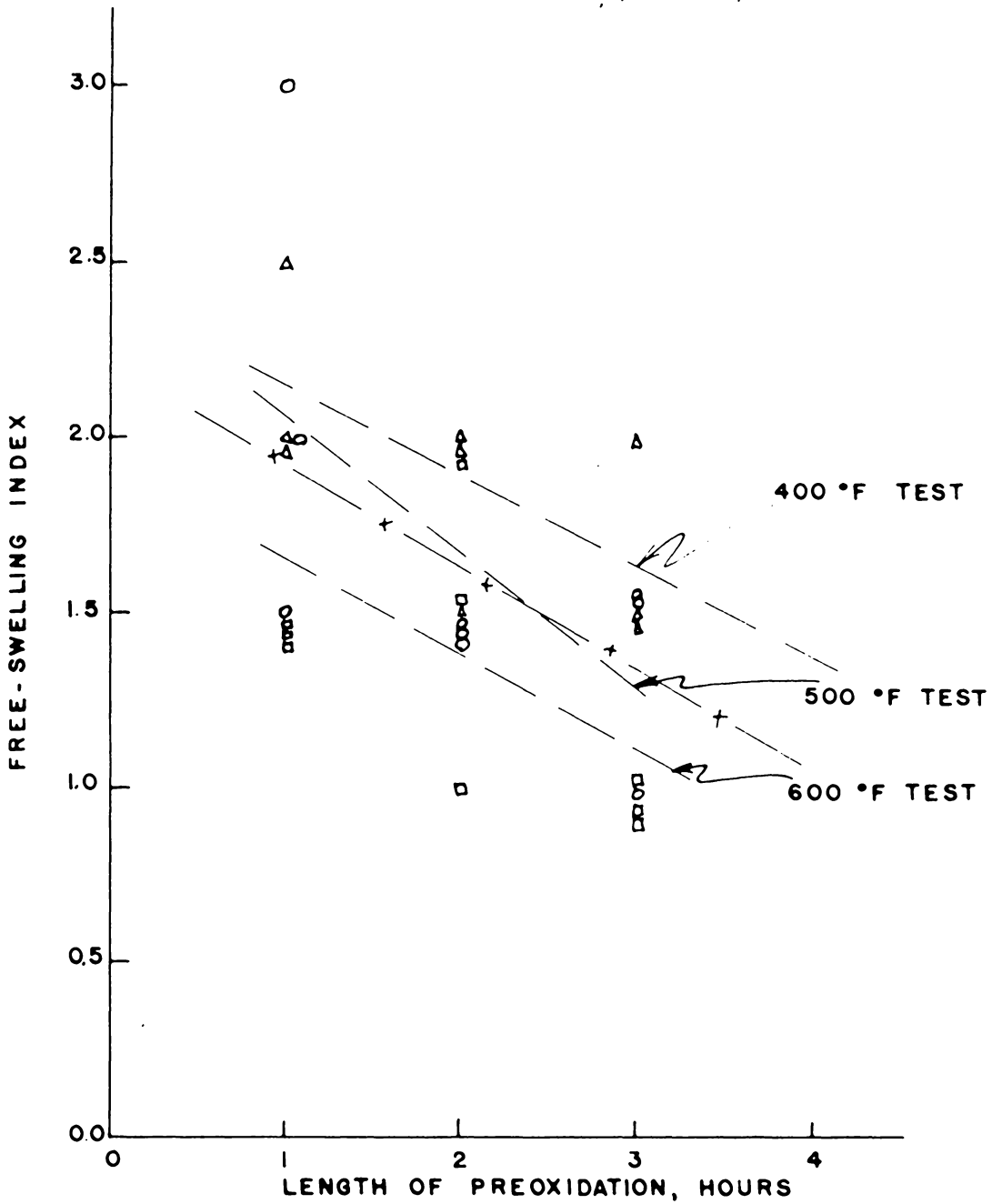


FIGURE 14 THE EFFECT OF THE LENGTH OF PRETREATMENT ON THE FREE-SWELLING INDEX OF PENN-LEE COAL

TABLE VI

Bench Scale Study of Effect of Carbonization
Temperature on Weight Loss of Coal

Cumulative Heating Time	Temperature of Carbonization	Sample Weight		Weight Loss	
		Sample No 1	Sample No 2	Sample No 1	Sample No 2
min	°F	gm	gm	%	%
0	--	1.0070	1.0130	--	--
7	400	0.9751	0.9852	3.1	2.8
14	450	0.9725	0.9831	3.4	3.1
21	500	0.9700	0.9801	3.7	3.5
28	550	0.9681	0.9739	3.9	3.9
35	600	0.9612	0.9699	4.4	4.2
42	650	0.9603	0.9631	4.7	4.9
49	700	0.9550	0.9584	5.1	5.4
56	750	0.9531	0.9579	5.4	5.5
63	800	0.9463	0.9528	6.1	6.0
70	850	0.7893	0.8038	21.6	20.7
77	900	0.7721	0.7954	23.2	21.6
84	950	0.7708	0.7881	23.7	22.3
91	1000	0.7625	0.7721	24.3	23.8

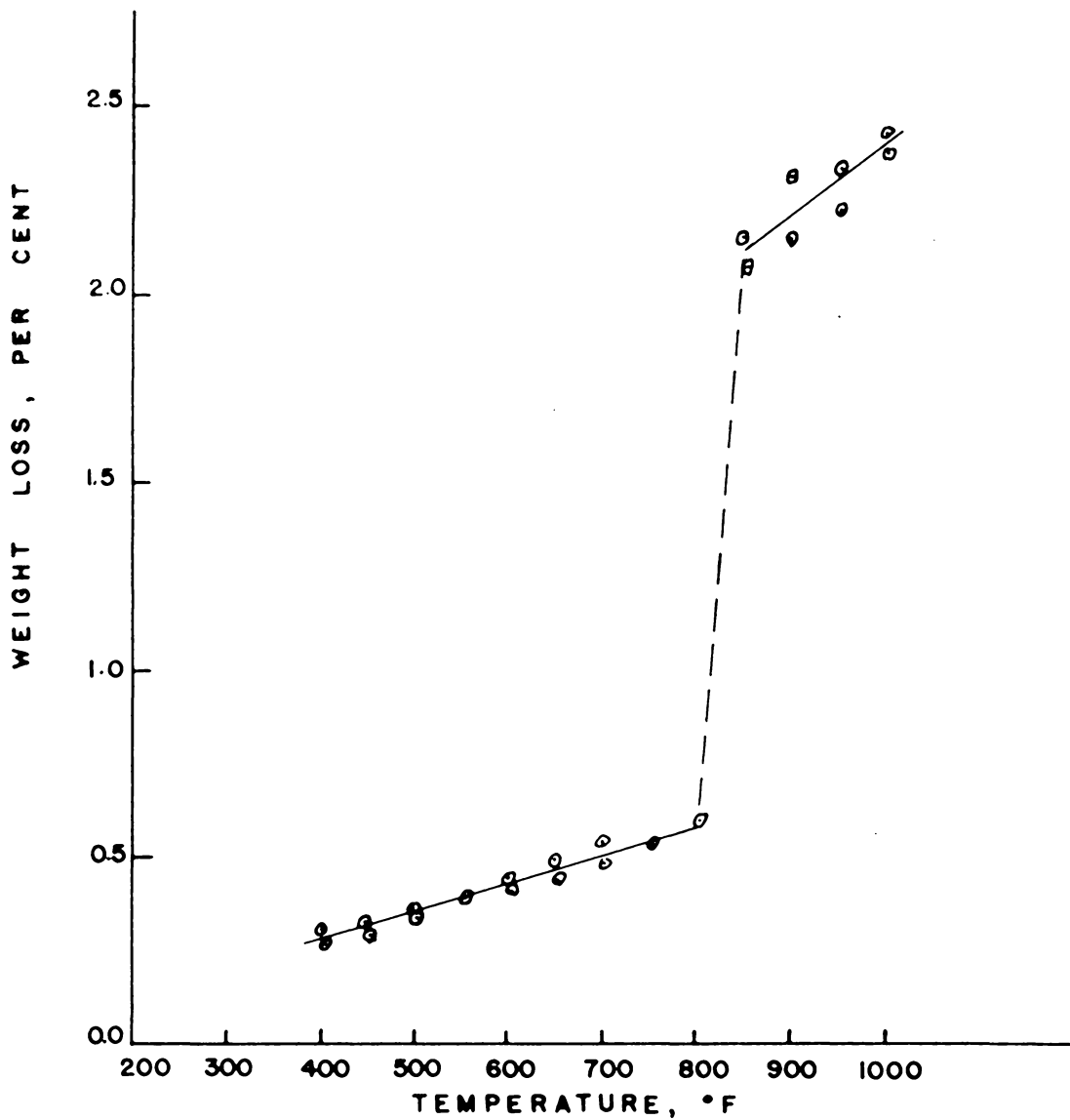
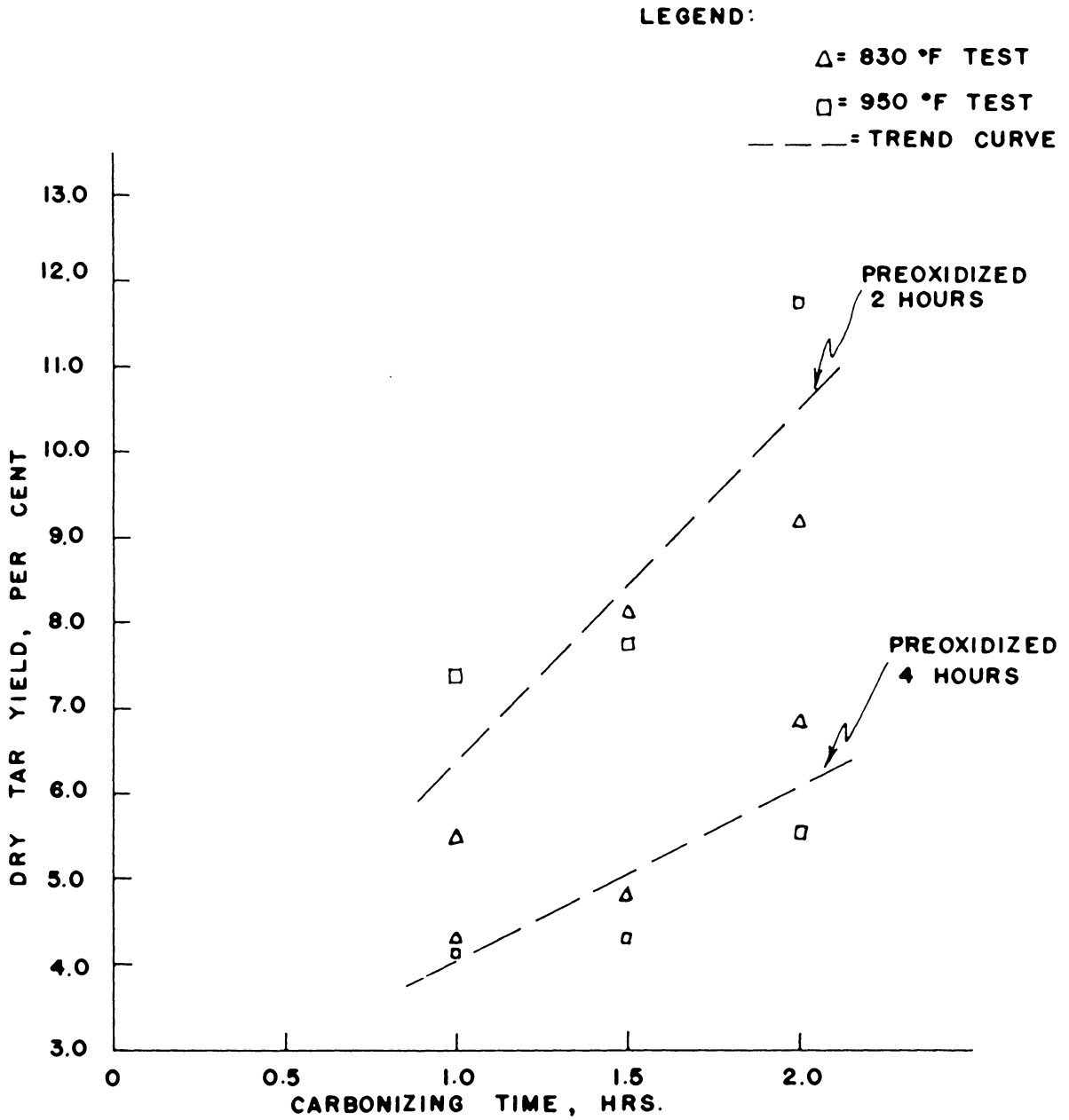


FIGURE 18 . THE EFFECT OF CARBONIZING TEMPERATURE ON THE SAMPLE WEIGHT LOSS OF PENN-LEE COAL

TABLE VIII

Pilot Plant Data
Results of Pilot-scale Carbonization Tests

Test 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	%
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	--



**FIGURE 16 . THE EFFECT OF CARBONIZING TIME ON THE
 DRY TAR YIELD OBTAINED FROM PENN-LEE COAL**

LEGEND:

△ = 830 °F TEST

□ = 950 °F TEST

— = TREND CURVE

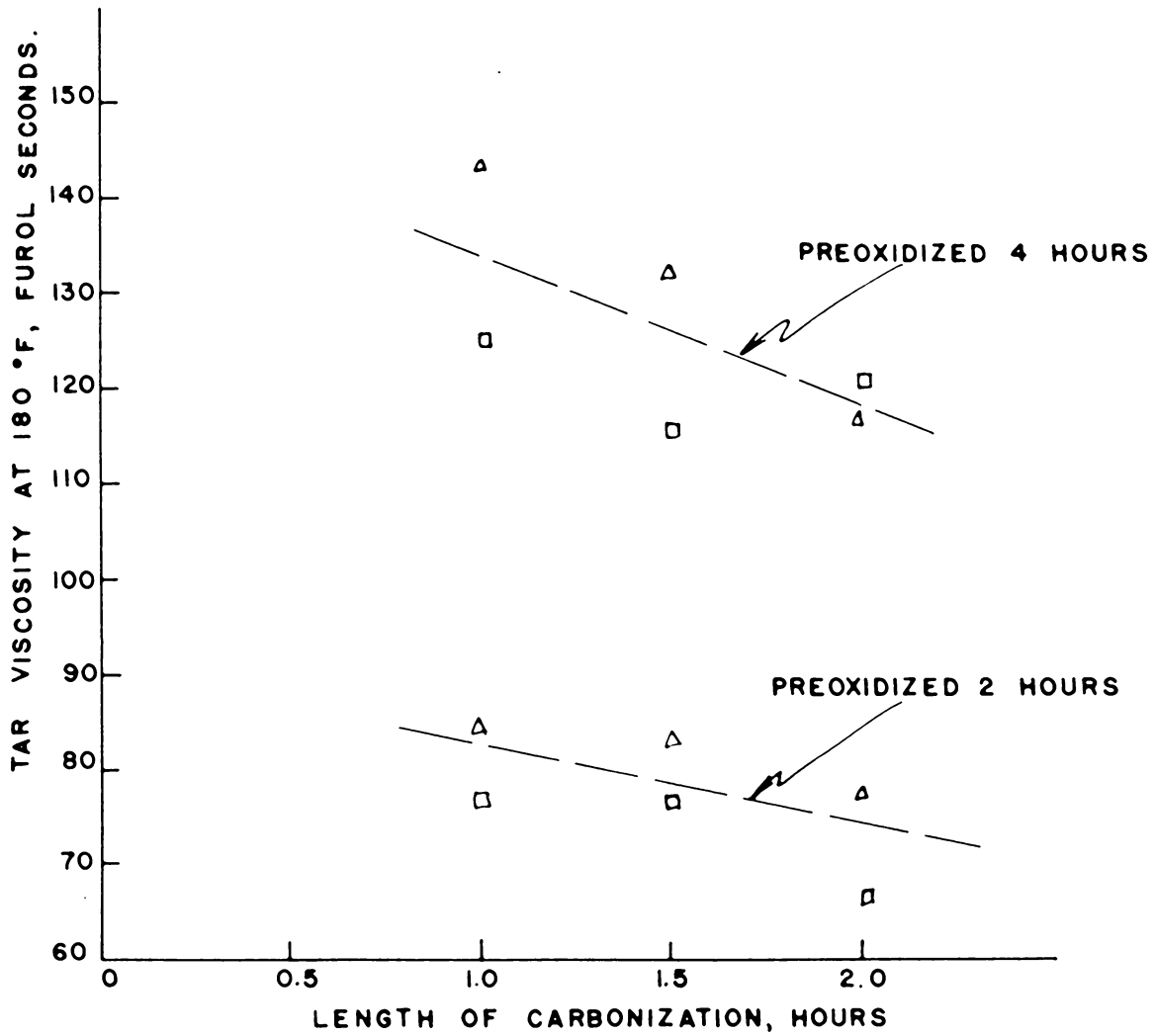


FIGURE 17. THE EFFECT OF THE LENGTH OF CARBONIZATION ON TAR VISCOSITY

LEGEND:

△ = ONE HOUR TEST
○ = ONE AND ONE-HALF HOUR TEST

□ = TWO HOUR TEST

— — — = TREND CURVE

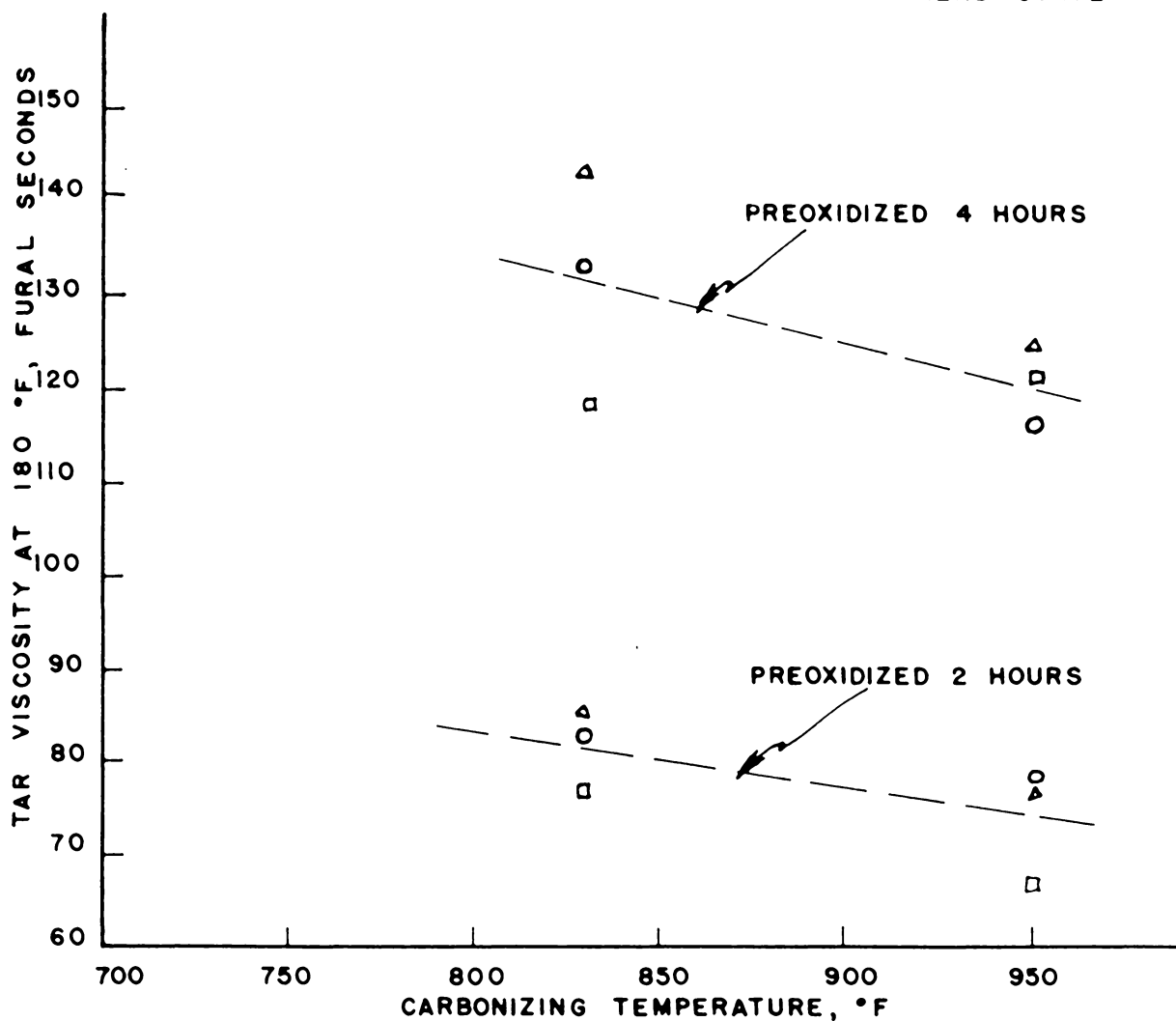


FIGURE 18 . THE EFFECT OF CARBONIZING TEMPERATURE ON THE VISCOSITY OF TAR OBTAINED FROM PENN-LEE COAL.

TABLE VII

Results of the Distillation of Coal Tar Samples

Test No	Preoxidation Time hr	Carbonization Time hr	Carbonization Temperature °F	20 Per Cent Distillation Temperature °C	Volume Per Cent Distilled at the Centigrade Temperatures Shown Below																				
					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	8.0	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 IX

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	0.001137	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

The sample calculations employed in the determination of the results of this investigation are presented 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, %
- W_d = weight of condensate, lb
- W_c = weight of charge, lb

$$y = 1.18/5.5$$

$$y = 21.5 \%$$

Determination of Volatile Matter. The calculation for the amount of volatile matter contained in a sample is shown below. The calculation is shown for T111, Table X, page 123.

$$x = W_1/W_s$$

where:

$$x = \text{volatile matter, \%}$$

$$W_1 = \text{weight loss of sample upon heating, gm}$$

$$W_s = \text{sample weight, gm}$$

$$x = 0.3765/1.007$$

$$x = 37.4 \%$$

Gas Analysis. The percentage of a given component in a gas sample was determined by the following calculation. The calculation is shown for carbon dioxide in the retorting gas in test number twelve, Table VII, page 106.

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

where:

x_c = amount of component in gas, %

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 VII, page 106.

$$S = \frac{W_t - W}{W_w - W}$$

where:

S = specific gravity of sample

W_t = weight of bottle plus tar, gm

W_w = weight of bottle plus water, gm

S = weight of bottle, gm

$$S = \frac{[53.7960 - 27.6438]}{[53.0734 - 27.6438]}$$

$$S = 1.028$$

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 seven, Table VII, page 106,

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

Determination of Calorific Value of Coke. The equation for determining the calorific value of the coke is

$$H = \frac{\Delta t(C_{we}) - [5(L) + 23(w_s \times S) + V]}{w_s}$$

where:

- H = calorific value of coke, Btu/lb
- Δt = corrected rempetature rise in calorimeter, °F
- C_{we} = water equivalent of calorimeter, Btu/°F
- L = length of fuse wire burned, cm
- w_s = weight of coke sample, gm
- S = per cent of sulfur in coke sample, %
- V = volume of sodium carbonate used in acid titration, ml

Substituting data from sample number six, Table VII, page 106,

$$H = \frac{(5.755)(2444) - [5(6.2) + 23(1.0 \times 0.8) + 23.2]}{1.0}$$

$$H = 13,992 \text{ Btu/lb}$$

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

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

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
- $H_{C_3H_8}$ = heat of combustion^a of propane, cal/gm mol
- 1.8 = conversion factor, gm mol-Btu/lb mol-cal.

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

Substituting data from sample number six, Table VII,
page 106,

$$H_g = [(0.193)(67,636.1) + (0.318)(212,798) \\ + (0.029)(372,870) + (0.0)(530,605)](1.8)$$

$$H_g = 164,764 \text{ Btu/mol.}$$

Coding Proportions. In the analysis-of-variance method, proportions have to be coded before they can be subjected to analysis. The proportions, 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 = proportion

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

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

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⁽²⁶⁾. This method of statistical analysis entailed the calculation of the sums of squares, degrees of freedom, and mean 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 the explanation, the author wishes to clarify the coding and terminology used hereafter. In this phase of the investigation, 27 tests were performed, at three levels of preoxidation time, three levels of preoxidation temperature, and with

three replications at each combination. 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 the 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 classes of sub-totals of the dependent variable values. Reference is made to the symbols presented in Table X, page 123. 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 27 individual test values. In this analysis, it is assumed that the replication effect, the interaction of replications with time, the interaction of replications with temperature, and the replication-time-temperature interaction comprise the sum of squares for the error term. These values were not determined separately, but were calculated collectively as an error term.

TABLE X

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	5.522
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

Calculation of the Sums of Squares. To conduct an analysis-of-variance test it was necessary to compute sums of squares for the length of pre-oxidation 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 X, page 123.

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

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

where:

SSA = sum of squares for temperature effect

T's = previously defined

n = number of observations in each total

N = total number of observations

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

$$SSA = 0.004$$

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

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

$$SSB = 0.0011$$

Sum of Squares for Interaction Between Time

and Temperature of Preoxidation. 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

$$\begin{aligned}
 SSAB = & \frac{(1.954)^2}{3} + \frac{(1.898)^2}{3} + \frac{(1.870)^2}{3} + \frac{(1.904)^2}{3} + \\
 & \frac{(1.869)^2}{3} + \frac{(1.855)^2}{3} + \frac{(1.799)^2}{3} + \frac{(1.912)^2}{3} + \\
 & \frac{(1.871)^2}{3} - \frac{(16.932)^2}{27} - 0.004 - 0.0011
 \end{aligned}$$

$$SSAB = 0.0034$$

Calculation of Error Sum of Squares. The error sum of squares was calculated as shown below:

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

where:

SSE = error sum of squares

SSA = temperature sum of squares

SSB = time sum of squares

SSAB = time-temperature interaction sum of squares

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

$T_{...}$ = 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 degrees of freedom that a variable is said to possess is one less than the number of levels at which the variable was studied. The degrees of freedom for an interaction between two variables is the product of the degrees of freedom of the two variables.

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

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

where:

MSSA = mean sum of squares for temperature

SSA = sum of squares for temperature

df = degrees of freedom for temperature

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

$$MSSA = 0.00055$$

Calculation of "F" Statistic. 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}" Statistic. The values of the "F" statistic can be found in tabular form in the work of 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

In the following paragraphs are contained a general discussion of the problems encountered in the investigation, a discussion of the results obtained in the investigation, recommendations for future work, and the limitations imposed during the investigation.

General Discussion

In the following paragraphs is contained a general explanation of the experimental work, and a general discussion of the problems and difficulties that arose in the operation of the equipment.

Experimental Work. In the following paragraphs, the reasons for treating the coal, the purpose of the bench-scale studies, and the experimental designs are discussed.

Pretreatment of Coal. The unique feature of the equipment used in this investigation lay in the fact that heat was supplied to the coal by means of a hot, inert gas stream. This type of heating provided a more uniform temperature throughout the bed than would have been possible

with direct heating of the retort shell. However, the plastic nature of the coal at temperatures above 427 °C (800 °F), caused the coal to melt and fuse together in the bed, preventing the passage of gas through the bed. Therefore, it was necessary to devise a method of treating the coal that would inhibit the tendency of the bed to fuse together. Among the various methods of treatment cited in the literature⁽⁸⁶⁾, pretreatment with air was chosen as the best possible method, since air was readily available, and could be contacted easily with the coal charge in the retort.

Difficulty in Coal Sampling. One of the problems indigenous to a lump-coal carbonization study lies in the difficulty of obtaining a representative, homogeneous sample. This difficulty does not arise in a fluid-bed study, because the finer particle size and the agitation occurring in the bed lead to both a more homogeneous sample and to a more uniform treatment of the entire bed. It was believed that the thorough mixing involved in both the original sampling

of the lump run-of-mine coal and in the sizing of the coal for testing would give as representative a sample as possible. Non-uniform pretreatment and heating in the fixed-bed retort were unavoidable, and it was hoped that a statistical approach would aid the author in the analysis of the data.

Bench-Scale Study. There was no information available in the literature concerning the ignition temperature, decomposition point, or caking properties of Penn-Lee coal. In order to obtain this information and to establish the effect of pretreatment with air on the swelling and fusing properties of the coal to be used, a series of bench-scale tests was planned. The levels of temperature of pretreatment were chosen as 204, 260, and 316 °C (400, 500, and 600 °F), as information from the literature indicated that air treatment had little or no effect on the caking properties of a coal below 200 °C (392 °F). The upper limit of 316 °C (600 °F) was chosen to be studied since temperatures much above 630 °C led to autoignition of the

coal studied. The time range of one to three hours was chosen as a sufficient range to show any trends that would occur with a varying time of treatment. The lower time limit was chosen on the basis of evidence from the literature. The upper limit of three hours was based on some preliminary qualitative tests that indicated that the swelling tendency of the minus three-quarter, plus one-half-inch coal samples was destroyed in this amount of time. However, the change in particle size from minus three-quarter, plus one-half-inch to minus two, plus one-inch in changing from bench-scale to pilot scale tests led to a somewhat different effect of pretreatment upon the plugging tendency of the coal. The pretreatment conditions which would definitely prevent plugging in the retort using the larger particle size coal still had to be established.

Pilot-Scale Study. The optimum pretreatment conditions obtained from the bench-scale investigation were found to be insufficient to condition the bed for the pilot-scale

carbonization tests. It was found that three hours heating in air at 316 °C (600 °F) would not keep the coal bed from fusing when subsequently heated to 400 °C (825 °F) in an inert gas stream. A series of trial-and-error pilot-scale tests using minus two, plus one-inch lump coal established the minimum pretreatment conditions to give a non-caking bed to be 342 °C (630 °F) for two hours. A four-hour treatment was inserted into the experimental design to measure the effect of increased preoxidation on the products of carbonization. Carbonizing temperatures were chosen to be 444 °C (830 °F) and 510 °C (950 °F). The 444 °C (830 °F) temperature was chosen as it was the minimum temperature at which the charge began to carbonize, i. e., the decomposition temperature. The 510 °C (950 °F) temperature was the highest temperature attainable in the pilot unit. The time range of one to two hours was selected since preliminary tests indicated that this range would bracket the time interval within which the carbonization would be complete.

The levels of variables discussed above proved later to have been satisfactorily chosen. No difficulties were encountered in attaining these levels in the subsequent operation of the equipment.

Equipment Operation. In the following paragraphs the problems involved in the operation of the equipment are discussed.

Inert Gas Heater. One major difficulty arose in the operation of the gas heater. The 1250-watt six-inch heating elements were welded into the shell of the gas heater as explained previously in the procedure. The proximity of the electrical leads to the hot shell frequently caused the leads themselves to burn off, thus rendering some of the elements useless. This situation became so pronounced, that a second heater, similar in construction, had to be built. In the second heater, four additional elements were welded into place, to serve as spare elements in case of "burnout" of any of the other eight.

Gas Circulating Pump. Although the gas pump was placed so that it would pump the cooled gases leaving the condensers, entrained tar frequently entered the pump through the gas line and caused stoppage. To eliminate the pump failure, a six-inch by one-foot knock-out tank was placed in the line between the condensers and the pump. The gas velocities, however, were apparently so high that tar was still carried into the pump. On the occasions that the pump froze, it was disassembled and cleaned with benzene. The most satisfactory preventive measure that was taken consisted of coating the inside of the casing with grease.

Thermocouples in Retort. The iron-constantan thermocouples in the three-foot retort, shown in Figure 6, page 78, were placed at approximately one-foot intervals. In the pre-oxidation stage of each test, the danger of a local, uncontrolled oxidation in a section of the bed was always present. If these "hot spots" occurred near a sensing element, they were detected and controlled. However, on

some occasions, "hot spots" occurred between thermocouples, resulting in local temperatures above the plastic point of the coal. The bed would then plug in that section and the test would have to be performed again. The heavy thermocouple well and large thermocouple bead led to a high degree of lag in the control of the process. In the operation of the unit, techniques were developed to compensate partly for the lag in the process.

Flanged Joint Leaks. Due to the necessity of removing the retort periodically to add or move the coal charge, it was constructed with flanged joints. Carr⁽¹⁸⁾ reported some difficulty in satisfactorily gasketing the flanged joints to prevent gas leaks from the system. A very satisfactory method of gasketing flanged joints for service in temperatures up to 538 °C (1000 °F), however, was employed in this investigation. Johns-Manville type 900 corrugated metal-asbestos gaskets coated with Johns-Manville "plastiseal" proved to be very satisfactory, and prevented high-temperature gas leaks from

the system. "Plastiseal" was also employed with success in coating all of the screwed fittings in the gas lines.

Discussion of Results

The results obtained from the bench- and pilot-scale studies on Penn-Lee coal obtained are discussed in the following sections.

Effect of Charge Weight on Plugging Characteristics of the Bed. In the early tests in the pilot-scale carbonization studies, six- to eight-pound charges of coal were carbonized. All charges weighing more than five and one-half pounds plugged the retort and stopped the flow of the retorting gas. One explanation of this plugging effect could be the additional weight of coal exerting added pressure at the bottom of the bed. However, as all of the early tests were subjected to a lesser degree of pretreatment, it cannot be definitely stated that the weight of the charge alone caused the coal in the bed to plug.

Preoxidation Needed to Condition Bed. The bench-scale investigation indicated that all of the swelling

properties of a minus three-quarter inch, plus one-quarter inch particle size of Penn-Lee coal would be removed by heating in an air stream for three hours at 315 °C (600 °F). However, in the pilot-scale study on a minus two-inch, plus one-inch particle size of coal, it was found that any pretreating temperature below 332 °C (630 °F) would not prevent the coal in the retort from plugging in a subsequent carbonization. If temperatures above 332 °C (630 °F) were used, autoignition would occur in the coal sample. Therefore, 332 °C (630 °F) was selected as the optimum temperature for preoxidation and the effect of the degree of oxidation on the various dependent variables was studied by testing at pretreatment time levels of two and four hours.

Effect of Retorting Conditions on Retorting Gas.

An increase in the degree of oxidation from two to four hours at 332 °C (630 °F) caused an increase in the average carbon monoxide content of the retorting gas from 12.6 per cent at the two-hour level to 15.7 per cent at the four-hour level. This is to be expected from a knowledge of the organic chemistry involved⁽⁴⁸⁾. Increasing the degree of oxidation

will lead to the formation of complex aromatic hydroxy-ketones, keto-acids, aldehydes, hydroxy-acids, and ketones. Many of these compounds decompose upon pyrolysis to form carbon monoxide or carbon dioxide. Hickenbottom⁽⁴⁷⁾ states that keto-acids decompose on heating to form carbon monoxide and water.

Hurd⁽⁴⁸⁾ states that benzaldehyde and dibenzylketone also form carbon monoxide upon heating.

It can also be seen in Table VII, page 106, that the maximum carbon monoxide exists in the gas at the end of the one hour tests. This indicated that all of the carbon monoxide liberating actions have occurred within the first hour of testing, and the ensuing decrease in carbon monoxide results from bleeding off and measuring the volume of the retorting gas. The methane concentration increased steadily with time of retorting, averaging 31.8 per cent at the end of one hour, and 76.5 per cent at the end of two hours. The increase in methane would indicate that the methane evolution is a direct function of the time of carbonization over the range of the variables studied. Methane evolution is probably

due to the thermal cracking of hydrocarbon side chains on the basic coal molecule⁽³⁾.

No evidence of hydrogen was found in the retorting gas. As the conditions of retorting were severe enough to cause condensation of the ring structures in the coal, with subsequent evolution of hydrogen⁽³³⁾, the appearance of hydrogen in the retorting gas was expected. However, any hydrogen formed could be dissipated in two ways: first, cracking of any uncondensed hydrocarbon fractions could easily occur in being recycled through the heating section of the test unit; cracking would lead to two lighter molecules, one saturated and one unsaturated; hydrogen could then be used in saturating the light olefin molecules; second, Georgiadis and Gaillard⁽⁴³⁾ show that all of the oxygen in coal is driven off below 1100 °C (2012 °F), with the maximum rate of oxygen evolution occurring at 840 °C (1005 °F). In the case of a strongly oxygenated coal, the evolved oxygen could easily react with any hydrogen present to form water.

Gas Evolved in Carbonization. The effects of preoxidation and temperature of retorting were

found statistically to have an insignificant effect on the amount of gas evolved during carbonization. Increasing the level of preoxidation caused an increase in the average volume of gas evolved from 1.05 cubic feet with two hours treatment, to 1.37 cubic feet with four hours treatment. Increasing the temperature of retorting showed a similar increase in the volume of gas evolved. At a retorting temperature of 443 °C (830 °F), the average volume of gas was 0.04 cubic feet, and at 510 °C (950 °F) the average volume of gas formed was 1.38 cubic feet. These increases in volumes of gases produced, however, could have occurred by chance, as is shown in the statistical analysis. Time of carbonization, naturally, had a significant effect. The gas evolved at the end of one hour averaged 0.615 cubic foot; at the end of two hours, however, the gas yield had increased to 1.87 cubic feet.

Effect of Pretreatment on Dry Tar Yield. An increase in the time of pretreatment caused a marked decrease in the yield of tar obtained from a subsequent carbonization. In this investigation it was found that an increase in pretreatment time from two

to four hours decreased the dry tar yield upon subsequent carbonization from an average value of 8.3 per cent for coal treated for two hours to an average value of 5.0 per cent for coal treated for four hours. This decrease could have been caused by several factors. First, an increase in the total oxygen addition to the molecules in the coal would have increased the molecular weight of those molecules⁽⁵⁷⁾ and caused them to be relatively less volatile at the carbonization temperature. Second, the prolonged heat treatment during the preoxidation stage could have caused some polymerization⁽¹⁰³⁾ in the distillable coal tar. This action could also tend to render these tars less volatile at the carbonization temperature. Third, the extensive heating and oxidizing surface treatment could have induced a case-hardening effect which would offer a physical resistance to the diffusion of vapors and liquid to the surface of the coal. It would be very difficult to say which of these possibilities played the major role, but it is likely that they all affect the tar yield to some degree.

A statistical analysis of the variance of the data gave an "F" value of 47.9 when tested against the three-way interaction term. A value of 18.5 was needed to show significance at the 95 per cent level. The assumption was made in this case, that the three-way interaction term was equivalent to the error term for the experiment. This "F" value serves to substantiate the strong effect of preoxidation on tar yield.

Effect of Carbonizing Temperature on the Dry Tar Yields. The effect of carbonizing temperature on the dry tar yields was very closely related to the degree to which the coal had been pretreated. For example, coal pretreated in air at 316 °C (630 °F) for four hours showed a decrease from an average dry tar yield of 5.3 per cent to one of 4.7 per cent, with an increase in carbonizing temperature from 443 to 510 °C (830 to 950 °F). However, coal treated for two hours showed an increase from a yield of 7.6 to 9.0 per cent over the same range of temperatures. This apparent anomaly is not easily explained. There appears to be an interaction between an increase in carbonizing time and the degree of pretreatment, but

the physical significance corresponding to this interaction is unknown.

An increase in the temperature caused an increase from an average dry tar yield of only 6.5 to 6.8 per cent with an increase in carbonizing temperature from 443 to 510 °C (830 to 950 °F), and an analysis of the data variance gave an "F" ratio of only 0.386 for the main temperature effect. The pretreatment temperature interaction gave an "F" value of 4.23, however, and although it was not significant at the significance level chosen for testing, there is a strong suggestion that a more highly-replicated experiment may substantiate the interaction effect that was observed in inspecting the data.

Effect of Pretreatment on Dry Tar Yields at Different Time Levels. An increase in the time of pretreatment had the same effect on the tar yield at one, one and one-half, and two hours, the three levels of carbonizing time studied. Doubling the time reduced the average dry tar yields 41, 42, and 36 per cent, respectively. The theoretical basis for this treatment effect lies in the polymerization of the coal tar molecules as explained before. The

fact that the effect is similar at different levels of carbonizing time serves to substantiate results obtained on the dry tar yields.

Effect of Time of Carbonization on Dry Tar Yields. An increase in the time of carbonization from one to one and one-half and two hours caused a marked increase in the dry tar yields. In general, the appearance of the tar yield versus time of carbonization curve was linear. Increasing the time of carbonization from one hour to two hours caused a 56 per cent average increase in the dry tar yield. An increase of this type would be expected, until the volatile matter in the coal had been driven off. However, close study of the dependence of tar yields on carbonization time showed that changing the degree of pretreatment caused a change in the rate at which the tar was produced in a subsequent carbonization. For example, at pretreatment levels of two and four hours, doubling the time of carbonization caused a 62 per cent change in the former case, and only a 50 per cent increase in the latter. This suggests a case-hardening effect in the pretreatment stage,

which retards the passage of vapor through the surface of the coal.

An analysis of the variance of the data showed an "F" value of 13.5 for the effect of time of carbonization upon the dry tar yields. At the 95 per cent level a value of 19.0 was needed to show significance, and at the ten per cent level a value of only nine was needed. By the very nature of the carbonization process, it is obvious that an increase in carbonization time must increase the net tar yield. However, it is interesting to note that doubling the time from two to four hours has roughly three times the effect on the data variance as increasing the time of carbonization from one to two hours.

Effect of Treatment on Tar Viscosity. Doubling the time of treatment caused a 62.5 per cent increase in the average drained tar viscosity. "Drained tar," as used in this investigation, refers to the crude tar distillate after the water which occurred with it had been decanted. This drained tar, still contained 40 per cent water, which could be removed by distillation to 300 °C (572 °F) and by careful separation of the two distilled phases. This increase in viscosity

can be explained in a similar manner to that for the explanation for the decrease in the dry tar yield with increasing pretreatment. That is, the addition of oxygen to various volatile tar molecules would tend to increase the molecular weight of these molecules, or to induce a degree of polymerization in them. In fact, it has been stated⁽⁶⁵⁾ that heating alone, without the presence of oxygen can induce polymerization in coal tar molecules. A heating and oxidizing action, then, could easily lead to an increase in the viscosity of the distilled coal tar product. An analysis of variance test on the data gave an "F" value of 151.36, with a value of only 18.5 needed for significance at the 95 per cent level. This serves to substantiate the strong effect of preoxidation on tar viscosity.

Effect of Carbonizing Temperature on Tar

Viscosity. An increase in the temperature of carbonization from 443 to 510 °C (830 to 950 °F) caused a ten per cent decrease in the average drained tar viscosity. This decrease was essentially the same at pretreatment levels of two and four hours, and at carbonization times of one, one and one-half, and two

hours. One possible explanation for this action could lie in some degree of thermal cracking of the coal tar molecules at the higher temperature. Thermal cracking should lead to the formation of more gas at the higher temperature, more hydrogen in the gas, a less viscous, lower molecular weight product, and higher product yields. The results from an analysis of the variance of the data, however, did not strongly support the apparent action of carbonization temperature on tar viscosity. An "F" value of 5.69 was obtained upon testing the temperature effect against the three-way interaction. A value of 18.5 was necessary to show significance at the 95 per cent level. However, if the insignificant two-way interactions are pooled with the three-way interaction and used as an estimate of error, an "F" value of 9.48 is obtained. In this case, a value of only 5.59 would be needed to show significance at the 95 per cent level. As one would expect⁽¹¹⁶⁾ the cracking rate to double with every 12 °C (22 °F) rise in temperature in this range of temperatures, it would seem that pooling may be justified as one would expect a significant cracking effect from the theoretical standpoint.

Effect of Carbonizing Time on Tar Viscosity. An increase in the carbonization time from one to two hours decreases the average tar viscosity approximately 11 per cent. This effect is of the same order of magnitude as the effect of temperature upon tar viscosity and suggests that the two are roughly interchangeable in the cracking reaction. For example, heating at 444 °C (830 °F) for two hours could give a product of approximately the same viscosity as heating at 510 °C (950 °F) for one hour. As in the case of the temperature effect, the effect of time was barely substantiated by statistics. When the time effect was tested against the three-way interaction an "F" value of 5.25 was obtained. A value of 19.0 was needed to show significance at the 95 per cent level. However, if the variances of the two- and three-way interactions were pooled, and it was assumed that this was a measure of the error variance, an "F" ratio of 8.73 was obtained. A value of only 4.74 was needed to show significance at the 95 per cent level. The same argument for pooling could be applied in this case as was applied before; that is, since from the theoretical standpoints

cracking would be expected, the assumptions made to allow pooling in these cases may be justified.

Effect of Pretreatment on the Tar Distillation Curves. Doubling the time of pretreatment from two to four hours caused an increase in the average 20 per cent distillation point temperature from 255 °C (491 °F) to 326 °C (628 °F). This would suggest that the previously mentioned effects of pretreatment, such as a decrease in the dry tar yield and an increase in the viscosity, are brought about at the expense of the lower boiling tar constituents. That is to say, that the tar yields decrease because of a sharp decrease in the relative amounts of low-boilers rather than an overall decrease in the tar constituents over the entire boiling range. This statement is substantiated by the action of pretreatment on the tar viscosity. For example, if the tar yields were decreased because of a general oxidation over the entire boiling range, the viscosity of the products obtained should be the same at any level of oxidation. However, since in this case the viscosity increased strongly with increasing oxidation, the idea that the lighter components

are sacrificed at higher pretreatment levels is well substantiated. The results of an analysis of variance showed an "F" value of 64.16 for the ratio of the preoxidation effect to the three-way interaction. The "F" value necessary to show significance at the 95 per cent level in this case was 18.5.

The Effect of Carbonizing Temperature Upon the Tar Distillation Curves. An increase in the temperature of carbonization from 443 °C (830 °F) to 510 °C (950 °F) caused a decrease in the average 20 per cent point temperature from 295 °C (563 °F) to 286 °C (547 °F). This decrease is in the direction that would substantiate the cracking effect which was found in the case of the tar viscosity. An analysis of the variance of the data, however, shows an "F" value of only 0.92, with a value of 18.5 needed to show significance at the 95 per cent level. Therefore, the trend shown with temperature increase could very well be caused by random error in the experiment. However, since there is good reason to believe that cracking would occur with an increase in temperature⁽³¹⁾, the possibility exists that a significant increase in the lighter component might be found at

some higher distillation temperature. That is to say, the heavier coal tar molecules may crack thermally to give distillable products. These products, however, may still be in a boiling range above 350 °C (672 °F). The possibility also exists that the cracked products may polymerize and condense to form higher boiling compounds⁽¹⁰³⁾. This particular effect was not evident in the 20 per cent fractions but could have occurred in the higher boiling fractions. As the American Society for Testing Materials methods for distillation of tars only proceeds to 350 °C (662 °F), the largest distillation fraction that could be compared between samples was the 20 per cent boiling fraction. The distillations were discontinued at 350 °C (662 °F) as severe thermal cracking in the tar itself begins above this temperature.

Effect of Carbonization Time on Tar Distillation Curves. An increase in the time of carbonization from one to two hours caused a decrease in the average 20 per cent distillation temperature from 301 °C (574 °F) to 280 °C (536 °F). Carbonization time shows the same general effect as temperature within the range that was studied, and suggests again that increasing of

temperature is roughly interchangeable with increasing of time. However, this further supports the supposition that the cracking action takes place in the higher boiling fractions, as the effect on the 20 per cent point was in the direction that would occur with cracking, but statistically insignificant. The "F" value obtained for the time effect was 1.85, with a value of 9.0 required for significance at the 95 per cent level.

Effect of Pretreatment on the Specific Gravity of the Tar. An increase in the time of pretreatment from two to four hours caused an increase in the average specific gravity of the tar product from 1.026 grams per cubic centimeter to 1.040 grams per cubic centimeter. An analysis of the variance of the data showed an "F" value of 114.17 for the effect of pretreatment when tested against the third order interaction. The effects of temperature and time were insignificant over the range of variables that was studied.

The pretreatment effect could be due partly to the addition of oxygen to the volatile molecules in the coal which could increase the molecular weight,

and also to an oxygen bridge condensation of any cyclic compounds present⁽⁵⁷⁾.

Water Formed During Carbonization. The total amount of water formed during carbonization averaged 7.8 per cent of the total coal charged to the retort. As the moisture content of the coal was only 3.7 per cent, water undoubtedly was formed in the carbonization process. Orchin⁽⁸⁵⁾ suggests that condensation reactions may occur at hydroxy groups in coal molecules that form water as a by-product. Also, water could have been produced in the reaction of hydrogen in the retorting gas stream with any oxygen that was driven off from the coal. The absence of hydrogen in the retorting gas at the end of the tests could be accounted for in this manner. Oxygen would also react with any hydrocarbon gases present to form carbon dioxide or carbon monoxide and water.

Effect of Pretreatment on the Volatile Matter Retained in the Coal. An increase in the length of time of pretreatment from one hour to three hours caused an average decrease in the volatile matter remaining in the coal of from 35.3 per cent volatile matter after one hour of treatment to 33.8 per cent

after three hours of treatment. This could have been brought about in two ways. First, moisture could have been driven off from the coal by the pretreatment temperatures, and second; the polymerization and oxygen addition could have caused the average molecular weights of the distillable elements in the coal to increase and thus cause them to be less volatile. An analysis of the variance of the data gave an "F" value of 8.25. A value of 3.55 was necessary to show significance at the 95 per cent level. Therefore, there is definite statistical confirmation of the effect of time of pretreatment on residual volatile matter.

The total effect of temperature of pretreatment on residual volatile matter was found to be statistically insignificant. An "F" value of 3.00 was obtained upon analysis of the variance of the data. A value of 3.55 was necessary to show significance at the 95 per cent level. A time-temperature interaction term "F" value of 12.75 was obtained in the statistical analysis. At the 95 per cent level, a value of only 2.93 was needed to show significance. This gives statistical credence to the interaction effect shown in Figure 12, page 101.

It can be seen that at a pretreatment temperature of 204 °C (400 °F) an increase in pretreatment time causes a sharp decrease in the residual volatile matter. At 315 °C (600 °F), however, an increase in pretreatment time has little effect on the residual 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, 204 °C (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. These other reactions, the simple addition of oxygen⁽⁵⁷⁾, could be of an opposing type, in the sense that 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 12, page 101, would indicate this type of a mechanism.

The Effect of Pretreatment on the Sample Weight Loss. As can be seen from Figure 13, page 102, the

204 °C (400 °F) and 260 °C (500 °F) parameters both show a gradual increase in the amount of weight lost by a sample in the first two hours of treatment. This is probably due to the loss in moisture from the coal. Opposing this loss, however, is the additive action of oxygen on the coal surface. This opposing action can explain the maximum in the two isotherms at approximately two hours. Exactly the opposite effect is found in the 315 °C (600 °F) isotherm. The only explanation that can be suggested for this is that the evolution of moisture was complete before one hour of treatment was ended; therefore, the moisture loss was out of the range of the variables studied. The minimum in the curve can only be explained by a change in mechanism of the oxygen reaction after two hours. Possibly the addition of oxygen to the unsaturates at a double-bond type which would cause a gain in weight⁽⁵⁷⁾, is opposed by a more complete oxidation, which would result in a loss in weight. As no additional data were taken to support this proposed mechanism, it is only offered as one possible explanation of the effect of preoxidation on the sample weight loss. A statistical analysis

of the variance of the data gave an "F" value of 1.37 for the overall time effect. At the 95 per cent level a value of 3.55 was necessary for significance. This means that the total time effect over the range of variables studied is not significant. The effect of time at various levels of pretreatment temperature is significant, however, as is shown by the temperature-time interaction "F" ratio of 3.85. At the 95 per cent level a value of 2.93 was needed to show significance. The above "F" ratio gives a degree of substantiation to the different shapes of the time versus weight loss curves at different pretreatment temperatures. The effect of pretreatment temperature showed a rapid increase in weight loss above 260 °C (500 °F). From 204 °C (400 °F) to 260 °C (500 °F) the weight loss of the sample increased from an average of 2.35 per cent at the lower temperature and to 2.63 per cent at the higher temperature. From 260 °C (500 °F) to 315 °C (600 °F), however, the average weight loss increased from 2.63 to 3.90 per cent. The total temperature effect was strongly significant, having an "F" value of 53.72,

when a value of only 3.55 was necessary to show significance at the 95 per cent level.

Effect of Bench-Scale Pretreatment Conditions on Free Swelling Index. An increase in the time of pretreatment from one hour to three hours was found to decrease the average free swelling index⁽²²⁾ of the treated coal from 1.94 to 1.33. An increase in the temperature of pretreatment from 204 °C (400 °F) to 315 °C (600 °F) was found to decrease the average free swelling index of the treated coal from 1.89 to 1.33. The free swelling index of the raw coal was 3.0, and a one-hour treatment at 315 °C (600 °F) would halve this to 1.5. An analysis of the variance of the data gave an "F" ratio of 6.91 for the temperature effect and 8.27 for the time effect. A value of only 3.55 was required to show significance at the 95 per cent level. This gives strong statistical substantiation to the trends shown in the data above. Also, there is a strong indication that time and temperature are roughly interchangeable in this reaction, within the range of the variables that was chosen. That is, that the same results may be obtained by increasing the length of reaction time

at constant temperature, and by increasing the temperature at a given length of reaction time. This observation is well supported by both theoretical principles⁽¹¹⁵⁾, and statistical analysis, i. e., the close "F" values for both time and temperature effects.

The reason for this action of pretreatment on the swelling property of a given coal is probably due to the polymerization, caused both by heat and oxygen addition, of the volatile matter in the coal. If this material were to become less volatile and more viscous, there would be a definite decrease in the bubbling and flowing action in the bulk coal. This conclusion is further substantiated by the pilot scale tests. The more strongly pretreated coals gave smaller yields of a more viscous tar at a given time and temperature of carbonization.

Effect of Carbonizing Conditions on the Bulk Density, Yield, Calorific Value, and Volatile Matter of the Char. The average bulk density of the char product was 16.85 pounds per cubic foot with an increase in preoxidation time from two hours to four hours. Temperature, and time of carbonization also

were found to have little or no effect on the bulk density of the char. The bulk density of raw coal, however, was found to be 38.7 pounds per cubic foot, while the average bulk density of the pretreated and carbonized char was 16.8 pounds per cubic foot. Therefore, the time of carbonization of at most one hour roughly halves the bulk density of the raw material. Carbonizing beyond one hour has little or no effect on the bulk density of the product.

Preoxidation conditions and carbonizing temperature conditions appeared to have little or no effect on the yields of char product. The time of carbonization seemed to have a marked effect on the amount of char remaining after carbonization. The average char yield based on the original charge after one hour of carbonization was 84.7 per cent, after one and one-half hours the yield was 79.9 per cent, and after two hours the yield decreased to 78.4 per cent. This loss was undoubtedly caused by the loss of the distilled tars and gases.

The average calorific value of the char product formed in the carbonization of Penn-Lee coal was found to be 13,860 Btu per pound. The variables

involved in the carbonization, such as degree of pre-treatment, carbonizing temperature, and time of carbonization appear to have no effect on the calorific value of the char. The product is seen to have been up-graded somewhat from the raw coal, which was found to have a calorific value of 13,550 Btu per pound.

The average amount of volatile matter remaining in the char product after carbonization was 7.9 per cent. In the volatile matter tests upon the char, it was observed that no soot or smoke was evolved upon heating the char sample to 950 °C (1742 °F).

Recommendations

In the recommendations for future studies, considerations of improvements to the carbonization unit and further investigations in certain phases of carbonization and pretreatment are necessary to advance the study of low-temperature carbonization.

Suggested Changes in Carbonization Unit. The suggested changes in the carbonization unit for improving its operation are listed under the appropriate headings in the following paragraphs.

Redesign of Heater. Two basic possibilities exist for the redesign of the existing gas heating section. If a non-recycle system is desired, the better method would be to heat the coal charge with hot flue gas from the combustion of pulverized coal, oil, or natural gas. The advantage of this method of heating lies primarily in the fact that the retorting gas neither changes composition during a test, nor is there danger of cracking the non-condensed gases in a re-cycle pass through the gas heater. This method would also closely approximate any realistic process for carbonizing with a hot

inert gas stream. The carbonizing gas would consist of carbon monoxide, carbon dioxide, and nitrogen.

The second design would be an electrical heater with improved heat transfer characteristics. It would consist merely of a series of "s" bends. Heat would be supplied to the section with 500-watt strip heaters attached to the walls of the heater. The heater should be packed with crushed firebrick as is the existing heater. It is recommended that the heater be constructed from 2-1/2-inch stainless pipe to increase the superficial gas velocity from 0.0818 pound per second per square foot to 0.845 pound per second per square foot, and thus increase the heat transfer coefficient. With a heater of this type, retorting gas temperatures in excess of 649 °C (1200 °F) could probably be attained. The advantages of electrical heating are primarily the ease of operation and the ease of control.

Modification of Retort. To increase the speed with which the retort can be removed from

and inserted into the system, clamps similar to those on the Pfaudler type "P" reactor should be used to hold the retort in place rather than bolted flanges. Also, a hoist should be installed above the retort to increase the ease with which it can be raised into position.

Gas Pump. The sliding vane pump in the existing system proved to be entirely unsatisfactory. The capacity of 20 cubic feet per minute was not enough to give flow rates through the heater that would result in good heat transfer. Although an entrainment trap was placed in the gas line between the condensers and the gas pump, tarry material continued to enter the pump, and led to a freezing action of the vanes against the inner casing wall. A Roots-Connersville rotary positive blower with a 50 cubic foot per minute capacity is recommended for future studies.

Insulation. White "Kaylo" was found to be unsatisfactory for insulating the gas heater and it is recommended that pink (high temperature) "Kaylo", with a layer of glass wool, be used in

all further studies. White "Kaylo" is not recommended for use at temperatures above 538 °C (1000 °F). As the skin temperature of the gas heater reached an estimated 983 °C (1800 °F), the white "Kaylo" failed within several tests. Skin temperature of this magnitude was not expected in the original design.

Draining Condensers. Some difficulty was encountered in draining the product condensers. Five to six hours were necessary for all of the condensed tar to drain out into the cups. Therefore, it is recommended that steam be piped into the annular space of the condensers to increase the fluidity of the condensate and speed up the draining operation.

Condensate Cups. The condensate cups were found to be too small for the amount of condensate collected. The volume of the cups was 100 milliliters, and in some instances 80 to 90 milliliters of product would be condensed into a single cup, nearly filling the cup to overflowing. It is therefore recommended that a small

drain with a valve be welded into the bottom of each cup to drain off the condensate during a test whenever desired.

Vapor Line from Retort. It was found during the investigation that some "high-boiling" tars would condense in the vapor line from the bottom of the retort to the first condenser, shown in Figure 10, page 89. This would cause a build-up of tarry material in the line which would eventually stop the flow of retorting gas through the system. It is therefore recommended that this line be heated with 500-watt strip heaters to prevent any condensation of this type.

Piping. In general, the three-quarter-inch piping on the carbonization unit would be too small to allow much increase in the flow rates. To decrease the pressure drop that would arise from increasing the gas flow rate, all of the existing three-quarter-inch pipe should be replaced with one and one-half inch lines.

Metering Air into System. The air entering and leaving the system during pretreatment should be metered and analyzed. This would provide the

investigator with a quantitative estimate of the amount of oxygen reacted with the coal. A calibrated thin plate orifice should be installed in both the air inlet and exhaust lines.

Controlling Preoxidation. A control system should be installed in the preoxidation stage, so that the bed would be maintained at 332 °C (630 °F) plus or minus 8.3 °C (15.0 °F). High-response thermocouples placed at three-inch intervals in the retort could serve as sensing elements. The control element would be a control valve in the re-cycle line. If the temperature should rise above the control point, the re-cycle valve would open, and if the temperature should fall, the re-cycle line would close, thus letting more oxygen into the intake line. The suggested valving arrangement is shown in Figure 10, page 89.

Pilot Scale Studies. Recommendations for further pilot-scale work on the carbonization of Penn-Lee coal are listed in the following paragraphs.

Effect of Temperature. The effect of temperature on the yields and properties of the

products of carbonization should be studied over a temperature range of 443 to 649 °C (830 to 1200 °F). Over a range of this magnitude, the effects of cracking could be shown more graphically than over the range studied in this investigation.

Gas and Condensate Evolution. The evolution of gas and condensate should be determined as a function of time at short intervals over a four-hour range, to determine the optimum time of carbonization and to provide fundamental information concerning carbonization processes. It is recommended that this be accomplished by draining the condensate from the collecting cups and measuring the gas evolved at ten-minute intervals for four hours. Also, the composition of the product gas should be determined at ten-minute intervals over the same range. The vapor-liquid chromatograph can aid the investigator in the rapid analysis of the product gases.

Fluidized Bed Studies. In this investigation, fixed beds of large particle size led to

a troublesome sampling error. In further studies, it is recommended that fluidized beds of particle size less than 30-mesh be employed, rather than fixed beds. The fluidized bed technique would insure a more uniform charge and more equal treatment for all portions of the charge.

Effect of Pressure. There is a possibility that pressures may have an effect on the products of carbonization. The effect of pressure on the carbonization of Penn-Lee coal should be studied at a pressure of ten atmospheres.

Other Treatments. It is recommended that other types of pretreatment, such as oxidation with nitric acid, or solvent extraction with benzene be studied and compared with the air treatment used in this investigation. This comparison should be made on both an operational and an economic basis.

Bench Scale Tests. Recommendations for further bench-scale studies are presented in the following paragraphs.

Rate of Oxidation. The rate of oxidation with air at various temperatures should be

studied on the basis of acid formation in the coal⁽⁶⁰⁾. The acids formed in the coal can be determined by dissolving the sample in diluted sodium hydroxide, and then by oxidizing the solution with permanganate. The amount of acid formed is proportional to the amount of permanganate required for oxidation.

Humins and Bitumens. It is recommended that the effect of pretreatment with air on the relative amounts of humins and bitumens be determined. This can be done by dissolving the treated sample in dilute sodium hydroxide and the residue in benzene. The weight loss⁽⁶¹⁾ in sodium hydroxide is proportional to the amount of humins in the sample, and the weight loss of the residue in benzene is proportional to the amount of bitumens in the sample.

Dry Coal. It is recommended that all bench-scale tests be made on coal that has been thoroughly dried. If this is not done, loss of moisture on a subsequent hot air treatment may mask any effect the air itself

may have on the change in weight or volatile matter of the coal.

Varying Coal Rank. It is recommended that the variables mentioned in this section be extended to studies of other coals of varying rank. In this way, the results may be correlated to include coals of other ranks and types.

Pretreatment with Inert Gases. In order to divorce the effect of heating alone from the oxidizing effect, and determine the relative importance of the two on the properties of the coal, the effect of heating should be studied as a separate pretreatment method. It is recommended that the previously mentioned variables be studied with pretreatment in an oxygen-free, i. e., pure nitrogen or carbon dioxide stream.

Products of Pretreatment. Provisions should be made to measure both the liquid and gaseous products of the bench-scale pretreatment. The water vapor can be condensed, and the gaseous products should be metered and analyzed for carbon dioxide, carbon monoxide, hydrocarbons, and oxygen.

Vapor-Liquid Chromatograph. It is strongly recommended that the chromatograph be modified to analyze high-boiling coal tar fractions. At the existing column temperature (140 °C), analysis of coal tar fractions is prohibited by exceedingly long elution times and poor resolution. A column temperature of 200 °C to 250 °C (392 °F to 488 °F) should be satisfactory for the larger part of the coal tar distillate. This would enable the investigator to study the effect of pretreatment and carbonizing conditions on the individual components of the tar, and could lead to a more fundamental understanding of the carbonization phenomenon.

Limitations

The investigation of the factors affecting the low-temperature carbonization of Penn-Lee coal was conducted under the following limitations.

Coal. The coal used throughout the investigation was seam number one, Penn-Lee coal from Maness, Virginia. The analysis of the coal was 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 throughout the investigation was 5.5 pounds.

Gas Flow Rate. The gas flow rate used in both the pilot-scale and bench-scale studies was 12 (plus or minus 0.1) cubic feet per minute.

Carbonization Independent Variables. The effect of length of time of carbonization was studied over the range of one to two hours. Tests were made for carbonization times of one, one and one-half, and two hours. The carbonizing temperatures studied were 443 °C (830 °F) and 510 °C (950 °F) plus or minus 8.3 °C (15.0 °F).

Pilot-Scale Pretreatment Variables. The pretreatment studies were made at a temperature of

332 °C (630 °F) plus or minus 8.3 °C (15.0 °F). Tests were made at time levels of two and four hours. The pretreating medium was air.

Particle Size. The particle size of the coal used in all of the pilot-scale studies was minus two inches, plus one inch.

Retorting Atmosphere. The retorting gas medium in which the carbonizing tests were begun consisted of 98 per cent carbon dioxide, with the remaining two per cent air. During the course of a test, the composition of the atmosphere changed as a function of the time of treatment, and could not be independently controlled.

Recycle Design. A recycle-type carbonizing unit was employed in all of the pilot-scale tests. As a result of this design, all of the product gases were recycled back through the gas heater and thus caused the composition of the retorting stream to change from its original composition.

Pressure. The pressure under which the pilot scale tests were performed was 10 (plus or minus one) pounds per square inch, gage.

Condenser Temperatures. The brine in the brine-cooled condensers was maintained at -2 to 0 °C (28 to 32 °F). The water in the water-cooled condensers was at 20 °C (68 °F).

Bench-Scale Charge Size. In all of the bench-scale tests, approximately 50 (plus or minus one) gram samples were used. This included both pretreatment and ignition tests.

Bench-Scale Particle Size. In all of the bench-scale studies, coal of particle size minus three-quarters inch, plus one-half inch was employed.

Bench-Scale Variables. In the bench-scale pretreatment studies, tests were made at temperature levels of 204 °C, 260 °C, and 316 °C (400 °F, 500 °F, and 600 °F). The effects of time levels of one, two, and three hours were investigated. Three replications of the data were made at each level of time and temperature. Air was the only pretreating atmosphere studied.

Chromatograph. The gas samples from the investigation were analyzed in a Fisher-Gulf chromatograph. Silica gel and 5A molecular sieves were used for the column packing. The flow rate of the carrier gas was

30 milliliters per minute. The column temperature was maintained at 50 °C (122 °F). The sample sizes varied from 0.1 to 0.4 milliliters. Helium was used as the carrier gas.

V. CONCLUSIONS

Carbonization studies were made on Penn-Lee coal, using a standardized technique of operation developed in the study and employing carbonization temperatures of 443 and 510 °C (830 and 950 \pm 15 °F); carbonization times of one, one and one-half, and two hours, and pretreatment times of two and four hours at 332 °C (630 \pm 15 °F). These tests were performed on charges of five and one-half pounds. The retorting gas flow rate was 12 cubic feet per minute. The tests were performed on a minus four, plus two-inch size of coal at ten pounds per square inch, gage. The unit used for carbonization was of a gas recycle-type design. In the bench-scale study, tests were performed on 50-gram samples of Penn-Lee coal at temperatures of 204, 260, and 316 °C (400, 500, and 600 °F). The time levels studied were one, two, and three hours. Three replications of the data were made. In all cases, a Fisher-Gulf chromatograph was used for the analysis of gas samples. The following conclusions were made from this study.

1. In the bench-scale tests, both temperature and time of pretreatment had significant decreasing effect upon the free-swelling index of the coal. "F" values of 8.29 and 6.91 were determined for the effects of time and temperature, respectively, with a value of 3.55 required to indicate significance at the 95 per cent level. Three hours of treatment were found to be sufficient to completely destroy the swelling properties of minus three-quarter, plus one-half inch samples of Penn-Lee coal.

2. In the bench-scale tests, the temperature of pretreatment had significant effect upon the loss in weight of Penn-Lee coal. An increase in the temperature of pretreatment from 204 °C (400 °F) to 316 °C (600 °F) caused an average increase in the weight loss of from 2.32 to 3.89 per cent. An "F" value of 53.72 was found for the effect of pretreatment temperature on weight loss. A value of 3.55 was required to show significance at the 95 per cent level.

3. The time of pretreatment was found to have a significant effect on the volatile matter remaining in Penn-Lee coal after pretreatment. An increase

in the time of pretreatment from one to three hours caused a decrease in the amount of volatile matter remaining after pretreatment of from 35.5 to 33.8 per cent. An "F" value of 8.25 was found for the effect of time of pretreatment upon volatile matter. A value of 3.55 was required to show significance at the 95 per cent level. Also, a significant interaction between time and temperature of pretreatment was observed. An "F" value of 12.75 was found for the time by temperature interaction effect on volatile matter, with a value of only 2.99 required to show significance at the 95 per cent level.

4. In the bench-scale study, the decomposition point of Penn-Lee coal was found to lie within the temperature range of 427 to 454 °C (800 to 850 °F).

5. Penn-Lee coal undergoes autoignition when heated above 332 °C (630 °F) in air.

6. In the pilot-scale study, the dry tar yield was only affected by the time of pretreatment. An increase in the pretreatment of from two to four hours caused a decrease in the dry tar yield of from 8.4 to 5.2 per cent. The "F" value found for the effect of time of pretreatment was 47.90, with

a value of 15.5 required to show significance at the 95 per cent level. The effects of time and temperature of carbonization were found to be significant.

7. The viscosity of the tar product was significantly affected by the time of pretreatment. An increase in the time of pretreatment of from two to four hours caused an increase in the tar viscosity from 78.1 to 126.3 Furol seconds. An "F" value of 151.36 was found for the effect of preoxidation time on tar viscosity, with a value of only 18.5 required to show significance at the 95 per cent level.

8. The specific gravity of the tar product in the carbonization of Penn-Lee coal was significantly affected by the time of pretreatment only. An increase in the time of pretreatment of from two to four hours caused an increase in the tar specific gravity from 0.026 to 1.041. An "F" value of 114.17 was found for the effect of preoxidation time on the specific gravity of the tar, with a value of 18.5 required to show significance at the 95 per cent level.

9. The 20 per cent distillation temperature of the tar produced from the carbonization of Penn-Lee

coal was affected significantly by the preoxidation time alone. An increase in the pretreatment time of from two to four hours caused an increase in the 20 per cent distillation temperature from 255 °C (473 °F) to 321 °C (610 °F). An "F" value of 64.16 was obtained for this effect, with a value of 18.5 required to show significance at the 95 per cent level.

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

VI. SUMMARY

The purpose of this investigation was to study the factors affecting the low-temperature carbonization of seam number one, Penn-Lee coal from southwestern Virginia, by determining the effect of pretreatment of the charge, temperature of the retorting gas, and time of retorting on the yields and properties of the products of carbonization.

An examination of the literature was made of available information on coal carbonization and the reactions of coal with oxygen. This information was of great value in analyzing the results of this investigation.

A pilot-scale unit for the carbonization of Penn-Lee coal was constructed. The construction of the unit consisted partly of the modification of an existing fluidization unit. The inert gas heater and the retort were reconstructed, and the location of the gas circulating pump was changed. Heat was supplied to the coal charge by a hot inert gas stream, which was heated electrically in an eight-inch by ten-foot gas heater, packed with crushed

refractory brick. For the satisfactory operation of the equipment various auxiliary apparatus were required. Among these were the pressure recorder, the twenty-four-point temperature indicator, the refrigeration unit, the brine circulating system, and the piping and valves.

A series of bench-scale tests was performed to study the effects of pretreatment with air upon the free-swelling index, the weight loss, and the volatile matter in Penn-Lee coal. Twenty-seven tests were performed in which time of pretreatment at levels of one, two, and three hours, and temperatures of pretreatment at levels of 204, 260, and 315 °C (400, 500, and 600 °F) were studied. 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 by temperature effect were found to show a significant effect upon the volatile matter remaining in the coal after pretreatment. Also, the decomposition point of the Penn-Lee coal was found to lie between 427 and 454 °C (800 and 850 °F).

Twelve pilot-scale tests were performed to study the effect of preoxidizing time, carbonizing time, and carbonizing temperature on the products of carbonization. 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 within the range studied, upon the volatile matter in the char products, the bulk density of the char, or the calorific value of the char.

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VIII. ACKNOWLEDGMENTS

The author is deeply indebted to Dr. F. W. Bull for the advice and encouragement offered in the course of the investigation. The author wishes further to express his sincere appreciation to Mr. Herbert Rhinehart for his aid and assistance throughout the investigation.

The author also wishes to express his gratitude to Dr. F. C. Vilbrandt for his guidance which was so enthusiastically and generously granted.

The author wishes to thank the entire staff and graduate body of the Department of Chemical Engineering for their helpful comments and criticisms.

Finally, the author wishes to extend thanks to Mr. M. B. Smith for his help in the construction of the gas heating section of the carbonizing unit.

Thanks are also given to the author's wife, Gaye, for her aid in typing and proofreading the rough copy of the thesis.

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