

A STUDY OF SOME OF THE THERMAL CHANGES INVOLVED IN
COAL CARBONIZATION AND THE EFFECT OF
CHEMICAL PRETREATMENT ON THESE THERMAL CHANGES AND
UPON COKE STRUCTURE

By

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PART I - HISTORICAL

SECTION I

THE ORIGIN OF COAL, THE CLASSIFICATION OF COAL, AND THE GEOGRAPHICAL LOCATION OF COAL DEPOSITS

Hendricks (22) has pointed out that as early as the latter part of the eighteenth century von Beroldingen (50) and Deluc (10) held the belief that coal was formed from plant debris which had accumulated in swamps and had subsequently undergone changes that resulted in the sequence of coals ranging from peat to anthracite. Since that time numerous researches have extended and have confirmed these preliminary ideas.

Probably the most significant contributions to the theories on the origin of coal were made by Thiessen (53) from microscopic study of coal structures. Two consecutive and fundamentally different processes were proposed to account for the transformation of fresh vegetable matter into coal: 1) the biochemical process; and 2) the dynamochemical process.

According to these, during the first process the accumulating vegetable matter becomes partially disintegrated or decomposed and reduced and many of the organic chemical compounds of the original material are partially decomposed, depending upon the conditions at the particular locality. This process has been termed "biochemical" inasmuch as the more important transformations take place under the influence of, or in conjunction with, the vital activities of certain microorganisms. The operation of this process varies considerably even

within the same bed, depending on the varying conditions of deposition of organic matter as well as on its composition. This "biochemical" process ends with the cessation of the anaerobic microbial action as a result of oxygen depletion of the matter or as a result of the development of exterminative toxins. The observation of coal and peat show that the biochemical process may be cut short with only partial decomposition of the vegetable matter. This is shown by the lignites of North Dakota and by woody or fibrous peat. The process may proceed further, as in the case of densely laminated coal, resulting even in the complete obliteration of most of the plant structure, as in the case of "amorphous" coal or peat. The conditioning limits of depth or age at which bacterial action ceases undoubtedly vary with the rate of growth of the peat, the concentration of toxic constituents, the porosity of the ground, the water composition, the temperature, and probably other factors. It is quite likely that anaerobic action may continue at considerable depths in the peat bog and for a time after the peat deposit has been covered with sedimentation, especially if the latter is coarse and porous. The primary residual product of the biochemical process is a peat or its equivalent in rank.

At the end of the biochemical process, the product is only an unconsolidated, nondehydrated peat occluding methane together with fluid decomposition products that have not made their escape. At more advanced stages it is a black or "mature" peat in which most of the plant matter has decayed, or an "amorphous" peat; if the matter is less advanced, the peat contains much wood or another matter largely undecomposed and is brown and less "mature".

The dynamochemical process covers the chemical and physical alterations of the coal-forming matter induced and controlled by geodynamic influences. This process follows the "biochemical", but it may at times be conceived to slightly overlap the latter. The accumulation of heavy strata of rock and soil gives a much more compact peat, with consequent expulsion of a part of the water and consolidation of the residual substances. In the early stages of this pressure application the mass is compacted, gases are further expelled, and the liquid putrefaction products that form the cementing material or binder for the coal are partly hardened, probably through polymerization and condensation type reactions. The fuel mass, much reduced in volume, assumes its more typical geological relation as a stratified mineral sediment. The reduction of an average peat to a low grade lignite represents a loss of three-fourths of the weight of the original peat mass, original peat containing about 90 per cent water and the lignite containing about 40 per cent water. The transformations of the mass to the higher ranks of coal are accompanied by further reduction of the water content.

With the expulsion of water comes also the escape of gases, mainly methane from the peat. Some carbon dioxide and hydrogen sulphide are also liberated. As the process proceeds, additional changes in chemical constitution occur, some of the residual products of the biochemical process are further altered, and plant elements not previously affected are decomposed or altered, with consequent losses of water and light hydrocarbons. The exact nature of these chemical changes are not known, inasmuch as the exact chemical constitution of coal cannot be definitely postulated.

During this dynamochemical process the volatile matter content of

the carbonaceous mass progressively decreases as determined by standard conventional methods. This progressive devolatilization of the coal is due to the geodynamic process. The ultimate stage of the process would be the complete elimination of oxygen, nitrogen, and hydrogen, so that little of the organic matter remains except carbon in the form of graphite.

During the past century, many attempts have been made to classify coals according to the geologic metamorphism in terms of certain numerical values from the proximate and ultimate analyses (20). Proposed classifications have used volatile matter, fixed carbon, total carbon, hydrogen, and oxygen in various combinations. However, some systems failed to classify properly high-rank coals and others failed when applied to low-rank samples. The final solution appeared to be the use of two separate factors for the proper classification of all ranks. The system developed by Parr (40) and later used as the basis for the A.S.T.M. classification has proved quite satisfactory in this respect. After extended study Parr recognized that mineral matter content had little if any relation to the rank of a particular coal, hence a classification is best made on a mineral-matter-free basis. The moisture content is also an extraneous variable. The remainder after subtracting mineral matter and moisture is the dry, mineral-matter-free basis. This has been designated "pure" or "unit" coal, and on this basis the volatile matter and fixed carbon add up to 100 per cent. High rank coals were found to be well distinguished by their heating value which is actually closely related to the oxygen content. The latter two items are really inverse functions of one another.

The Parr classification has not been much used in the form in which it was presented, but the simplicity and advantages of the general method

were at once apparent, and the A.S.T.M. classification which is summarized in Table 1, page 6, resulted from these fundamental principles. This scheme has been utilized to a large extent in recent years and has been generally accepted as the standard for the North American coals.

For the United States as a whole, approximately forty per cent of the total generated and harnessed energy consumed in 1948 was obtained from coal, the other primary sources being petroleum, natural gas, and hydroelectric power (9, page 275). This country is indeed fortunate in the fact that it has huge coal resources, totalling approximately 47 per cent of the world's known supply. Table 2, page 7, shows the relative coal resources of the world by continents as estimated in 1948.

The distribution of coal resources of the United States are shown in Figure 1, page 8. The general areas covered by this illustration are as follows: (21, page 89)

1. Eastern Province includes: (a) the anthracite regions of Pennsylvania and Rhode Island; (b) the Atlantic coast region, which takes in the fields of Virginia and North Carolina; and (c) the Appalachian region, which extends from northern Pennsylvania into Alabama, and includes parts of Ohio, Maryland, Virginia, West Virginia, Kentucky, Tennessee, and Georgia.
2. The Interior Province includes: (a) the northern region, containing the Michigan coal fields; (b) the eastern region containing the Illinois, Indiana and western Kentucky fields; (c) the western region, containing the coal fields of Iowa, Missouri, Nebraska, Kansas, Arkansas, and Oklahoma; and (d) the southwestern region of Texas.
3. The Gulf Province includes: (a) the Mississippian region, which embraces the coal fields of Louisiana, Mississippi, and Alabama; and (b) the southwestern region, which takes in certain regions of Arkansas and Texas.
4. The northern Great Plains Province includes the coal fields in the Great Plains east of the Front Range

TABLE 1. A.S.T.M. Classification of Coals by Rank* (1)
F.C. = fixed carbon; V.M. = volatile matter

CLASS	GROUP	LIMITS OF FIXED CARBON OR B.t.u. MINERAL-MATTER-FREE BASIS	RELATIVE PHYSICAL PROPERTIES
I. Anthracitic	1. Meta-anthracite	Dry F.C., 98% or more (dry V.M., 2% or less)	Non-agglomerating †
	2. Anthracite	Dry F.C., 92% or more and less than 98% (dry V.M., 8% or less and more than 2%)	
	3. Semianthracite	Dry F.C., 86% or more and less than 92% (dry V.M., 14% or less and more than 8%)	
II. Bituminous §	1. Low-volatile bituminous coal	Dry F.C., 78% or more and less than 86% (dry V.M., 22% or less and more than 14%)	Either agglomerating or non-weathering ¶
	2. Medium-volatile bituminous coal	Dry F.C., 69% or more and less than 78% (dry V.M., 31% or less and more than 22%)	
	3. High-volatile A bituminous coal	Dry F.C., less than 69% (dry V.M., more than 31%); and moist ‡ B.t.u., 14,000 or more	
	4. High volatile B bituminous coal	Moist ‡ B.t.u., 13,000 or more and less than 14,000	
	5. High volatile C bituminous coal	Moist B.t.u., 11,000 or more and less than 13,000	
III. Subbituminous	1. Subbituminous A coal	Moist B.t.u., 11,000 or more and less than 13,000	Both weathering and non-agglomerating
	2. Subbituminous B coal	Moist B.t.u., 9500 or more and less than 11,000	
	3. Subbituminous C coal	Moist B.t.u., 8300 or more and less than 9500	
IV. Lignitic	1. Lignite	Moist B.t.u., less than 8300	Consolidated
	2. Brown coal	Moist B.t.u., less than 8300	Unconsolidated

* This classification does not include a few coals that have unusual physical and chemical properties and come within the limits of fixed carbon or B.t.u. of the high-volatile Bituminous and subbituminous ranks. All these coals either contain less than 48 per cent dry mineral-matter-free fixed carbon or have more than 15,500 moist mineral-matter-free B.t.u.

† If agglomerating, classify in low-volatile group of the bituminous class.

‡ Moist B.t.u. refers to coal containing its natural bed moisture but not including visible water on the surface of the coal.

§ It is recognized that there may be non-caking varieties in each group of the bituminous class.

|| Coals having 69 per cent or more fixed carbon on the dry mineral-matter-free basis shall be classified according to fixed carbon, regardless of B.t.u.

¶ There are three varieties of coal in the high-volatile C bituminous coal group, namely, variety 1, Agglomerating and non weathering; variety 2, agglomerating and weathering; variety 3, non-agglomerating and non-weathering.

TABLE 2. Estimated Coal Resources in 1948, by Countries in Per Cent
of World Tonnages (According to Minerals Yearbook 1949).
(9, page 28)

North America

Canada	1
United States	47
Other North American Countries	1

Europe

Germany	7
U.S.S.R.	24
United Kingdom	4
Other European Countries	2

Africa

British Commonwealth	5
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Asia

China	7
India	2
	<hr/>

World Total	100
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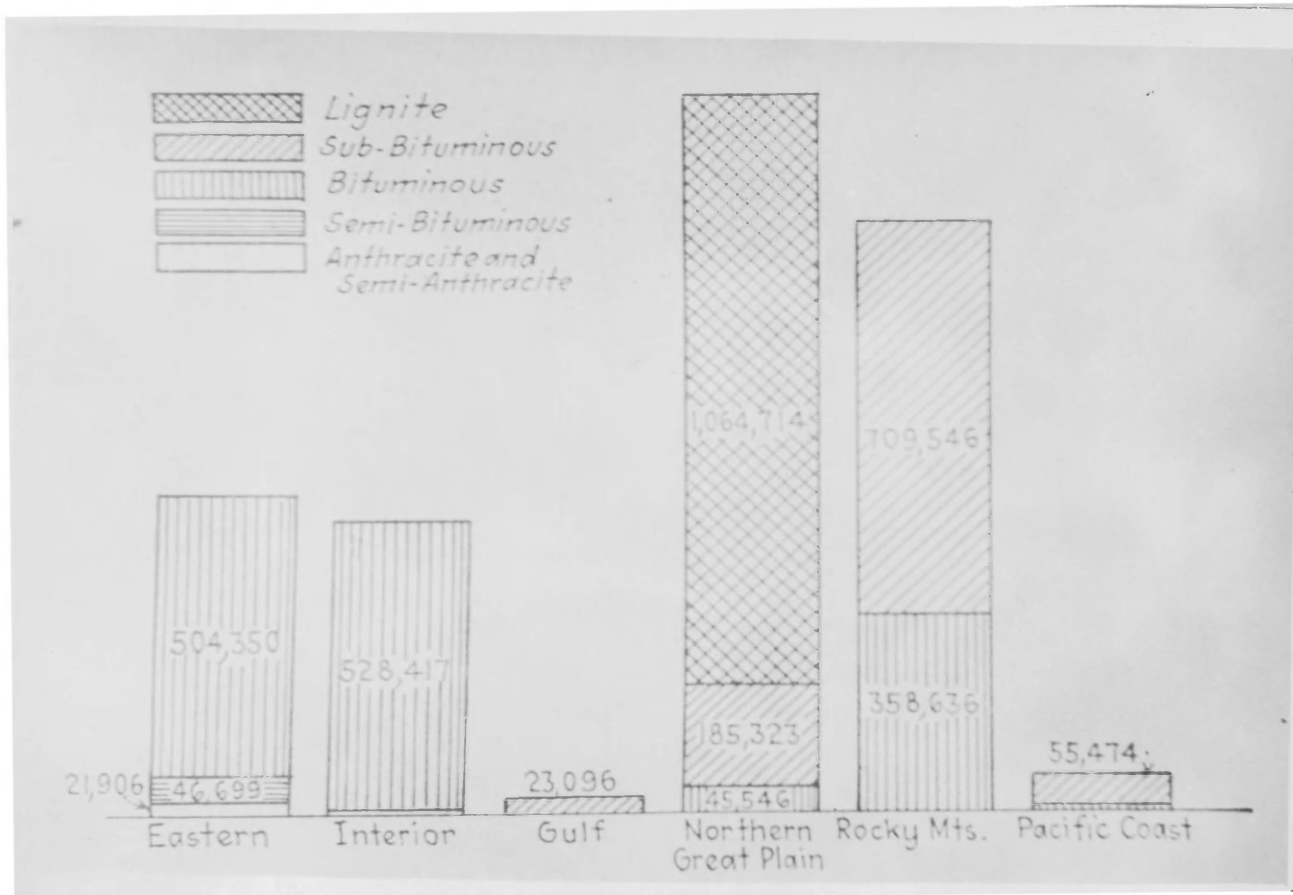


FIGURE I

ESTIMATED COAL RESOURCES OF THE UNITED STATES

FIGURES ARE IN MILLIONS OF NET TONS

(ACCORDING TO HASLAM AND RUSSELL 1926) (21, page 94)

of the Rocky Mountains. These are: (a) the Fort Union region, with the northern Wyoming field and the lignite fields in the Dakotas and eastern Wyoming; (b) the Black Hills region in Wyoming; (c) the Judith Basin and the Assiniboine regions of Montana; (d) the Denver region in Colorado; and (e) the Raton Mesa region of Colorado and New Mexico.

5. The Rocky Mountain Province includes (a) the Yellowstone region of Montana; (b) the Big Horn, Hama Fork, and Green River regions in Wyoming; (c) the Uinta region of Utah and Colorado; (d) the San Juan River region of Colorado and New Mexico; and (e) the southwestern Utah region.
6. The Pacific Coast Province includes the coal fields in California, Oregon and Washington.

In general it can be seen that the lower grades of coal are located in the western section of the nation. The better grades of coking coals are located in the eastern area and the development of this supply has made possible the concentration of the heavy industrial enterprises in this section.

The production of coal in the United States is approximately 35 to 45 per cent of the entire world's output and is of the order of magnitude of 600,000,000 tons annually.

SECTION II

THE CHEMICAL COMPOSITION OF COAL

The chemical constitution of coal has received much attention by many workers and its extremely complex structure has prevented any complete elucidation of the problem. Studies have been directed in specific directions in order that the reactions of coal might be compared with families of compounds yielding similar reactions, hence of an analogous structure. This work has been covered in considerable detail by Weiler (51,52) and Howard (24) and only a brief review of their conclusions will be presented. The conclusions covering the chemical constitution of coal were obtained by the following reaction types:

(1) Reduction reactions; (2) Halogenation reactions; (3) Oxidation reactions. Each of these resumes is covered briefly as follows:

(1) The studies of the destructive hydrogenation of known organic compounds and the kinetics of the destructive hydrogenation of coal make it possible to associate certain types of chemical structure or groups of atoms with certain phases of coal hydrogenation and the products obtained.

The primary liquefaction that occurs below 370° C. is probably a combination of solution and depolymerization of high-molecular-weight substances formed during the coalification process. In the coalification process condensation reactions or polymerization of unsaturated structures resulted from loss of water.

Above 370° C. the temperature coefficient of liquefaction is such a very high energy requirement for the reaction indicating the breaking of strong primary bonds, either carbon-to-carbon or carbon-to-oxygen or

both.

It is not evident what is the nature of the structures involved in the thermal decomposition of the coal substance occurring just above 370° C. giving the loss of 60 per cent of the oxygen of the coal primarily as carbon dioxide and water but partly as low molecular weight phenolic compounds. The reaction occurs simultaneously with the liquefaction reaction occurring in the same temperature range. The carbon dioxide and some of the water obtained are probably derived from the decomposition of carboxylic acids; the formation of low-molecular-weight phenols suggests the breaking of linear ether linkages. The simultaneous liquefaction and oxygen-removal reactions may be a coincidence and the elimination of water may be partly a continuation of the coalification process, that is, condensation to larger molecules or the formation of unsaturated linkages. The fact that liquefaction occurs in spite of the possible continuation of the coalification process is an indication that the rate of cleavage of molecules overshadows the rate of condensation on the one hand and the presence of hydrogen saturates the double bonds preventing polymerization on the other hand.

The further deoxygenation is slower and is partly the decomposition of nonvolatile phenols previously formed in the early stages of the oxygen removal process.

The evolution of gaseous hydrocarbons, particularly ethane, has been associated with the hydrogenation cracking of cyclic hydrocarbons.

With the above discussion in mind it is possible to arrive at a probable picture as to the hydrogen, carbon, and oxygen linkages. The condensation process involves the elimination of water and carbon dioxide, resulting in essentially condensed polynuclear (five and six-membered

rings) carbon skeletons of high molecular weight. The degree of completion of this reaction is indicated by the quantity of retained oxygen.

Owing to the high hydrogen-to-carbon ratio of the original plant material, the hydrogen content of the coal even after prolonged coalification is far in excess of the quantity required for a completely aromatic structure. It is believed that much of the polynuclear ring structure must be saturated in the form of hydroaromatics or partially saturated to give rise to olefinic double bonds.

(2) Exhaustive chlorination has been utilized as an approximate measure of the carbon distribution in coal between complex condensed ring structures on the one hand and aliphatic and simple cyclic structures on the other. Chlorination of the coal using a hundred fold weight of antimony pentachloride at temperatures up to 400° C. yielded the aliphatic and simple ring structures in the form of chlorinated hydrocarbons, C_8Cl_6 , C_2Cl_6 , and CCl_4 , leaving the condensed ring system as a highly chlorinated nonvolatile residue. By this reaction it was estimated that 80 per cent of the carbon of a bituminous coal is present in complex condensed ring structures.

Much more work has been carried out on halogenation reactions of a nature similar to that noted above and the following conclusions concerning the structure of coal have resulted: A large portion of the carbon is present in condensed ring systems. These ring systems are largely of the naphthenic type and are probably to a large extent hydroaromatic, that is, composed of six membered rings. Much of the hydrogen and lower hydrocarbons resulting from coal carbonization is due to the dehydrogenation of these naphthenic linkages to aromatic systems. It

is impossible to determine an answer to the probable nature of the oxygen linkage from halogenation reactions.

(3) The mild oxidation of bituminous coals results in the formation of a mixture of relatively simple alkali soluble "humic acids". These primary oxidation products have not yet been definitely characterized but are believed to be chiefly of condensed cyclic structure, some of the cycles containing only carbon atoms, and others containing some oxygen, nitrogen and sulphur. The carboxyl and hydroxyl groups are responsible for the alkali solubility. The carboxyl content is of sufficient amount to lead to average equivalent weights of 200 to 300. Severe oxidative degradation yields simple water-soluble acids such as carbonic, acetic, oxalic, succinic and members of the benzenecarboxylic acid series. The oxidation products of the lower-rank coals yield larger proportions of carbonic acid, the simpler aliphatic acids, and the low members of the benzene-carboxylic series. These results tend to indicate a series of structures ranging from vegetable debris of mixed aliphatic, heterocyclic, and carbocyclic structure, to graphite, the completely condensed structure.

It can be seen that each of the above treatments is much different but yields approximately the same general type of configuration for the complex coal substances. Realizing that coal is undoubtedly a heterogeneous system comprised of a multitude of chemical species, it is advantageous for many purposes to deal with an average or representative molecule which can be assumed from the research data available. Fuchs and Sandhoff (18) have postulated such a representative molecule as shown in Figure 2, page 14. This is compatible with the proximate and ultimate analyses of bituminous coals and with the experiences of oxidation,

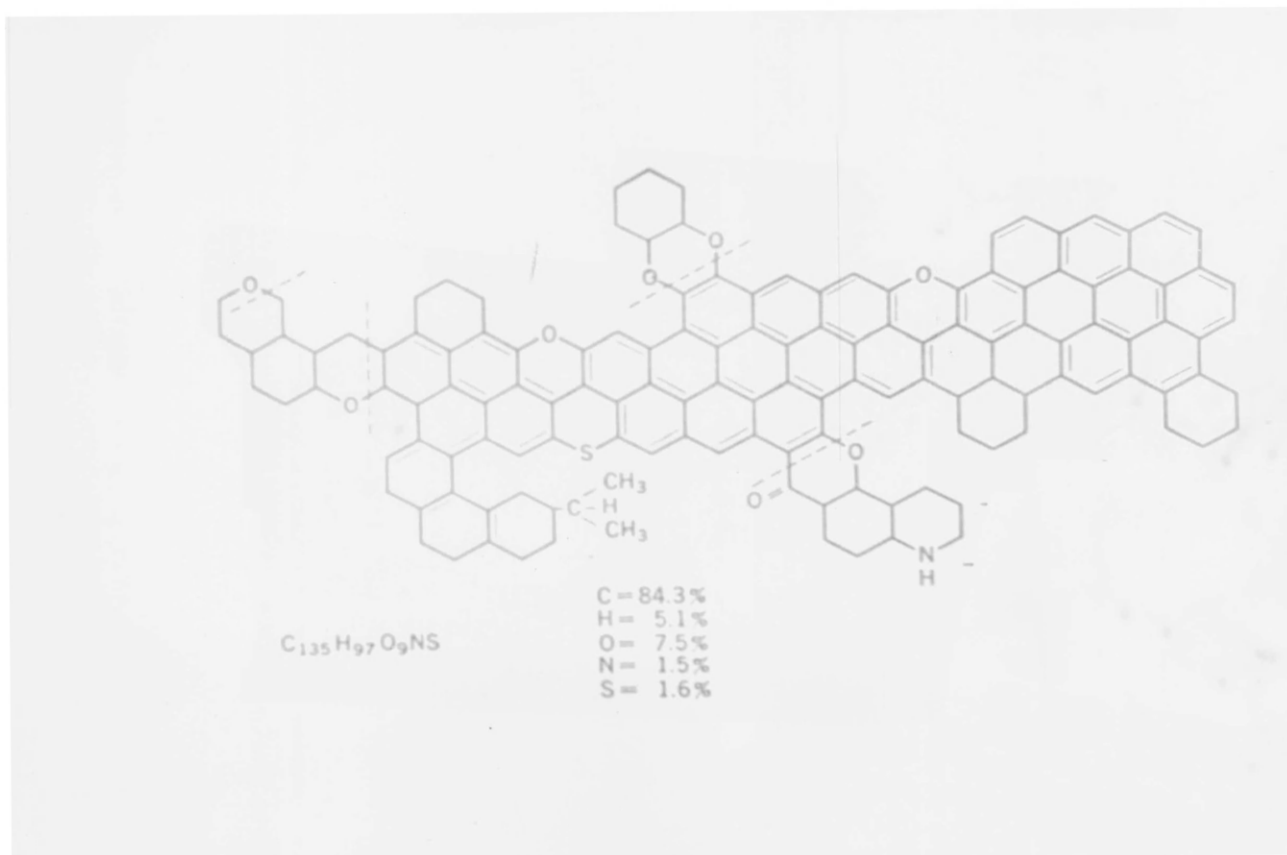


FIGURE 2

A TYPICAL COAL MOLECULE

(ACCORDING TO FUCHS AND SANDHOFF) (18)

reduction, halogenation, and thermal decomposition.

Finally, observation of such a complex hypothetical molecule gives an indication of the difficulty involved in obtaining definitive interpretable data in any research on reactions occurring with coal.

SECTION III

THE CARBONIZATION OF COAL

GENERAL DISCUSSION AND PRINCIPLES

The carbonization of coal is extremely important inasmuch as 15 to 20 per cent of the coal produced in the United States is processed in this manner. The primary use of the coke produced in this process is for metallurgical purposes with secondary application as a smokeless fuel.

Scientifically, coal carbonization can be defined as destructive distillation; decomposition by heat, in the absence of air, causing an increase in the carbon content, at the expense of other constituents volatilized as gases or vapors. (42, page 23) It is a process of modifying a crude, raw fuel into better fuels, of extracting valuable by-products -- ammonia, light oils, tar -- before they are destroyed in the burning, of converting the raw smoke-producing inefficiently handled coal, into smokeless fuels, efficient in their use and distribution.

The heating of coal with the exclusion of air initiates chemical reactions that are highly complex and that yield a variety of new substances in place of the original coal. These products are in three phases -- the solid altered residue or coke; liquid products, water and tars; and gas.

In bulk carbonization it is doubtful whether any of the initial products liberated from the coal are obtained as final products. Among the primary products occur many secondary reactions, which follow well known physical-chemical laws. It must be kept in mind that the components of such a system are so many and so complex that application of laws of

chemical statistics and dynamics as a whole is extremely difficult if not impossible.

The process of coal carbonization may be divided into various steps, as follows: first, the liberation of the primary volatile matter at relative low temperatures (350° - 500° C.) which leaves the coal substance as a partly carbonized solid; second, the liberation of volatile products from the altered residue by heating to higher temperatures; and finally, thermal reactions among the primary volatile products, which greatly influence the composition of the final products from the coal. The work of Taylor and Porter (49) in their experiments on the mechanism of coal carbonization can be summarized as follows:

1. Approximately two-thirds of the organic substance of coal is decomposed below 500° C. Coals vary in their ease of decomposition, the older eastern coals being less easily and rapidly broken down than the younger western coals.
2. The first decomposition to occur as the temperature is raised is the breaking of certain oxygen containing substances related to cellulose, the products being primarily water and carbon dioxide.
3. It is believed that coal breaks down more or less at all temperatures but the point of large decomposition is considerably above room temperature.
4. The formation of liquid and gaseous paraffin hydrocarbons begins at low temperatures, but proceeds slowly and at 450° C. the volatile matter is chiefly paraffins for bituminous coal. Younger coal types such as the subbituminous produce chiefly water and carbon dioxide up to at least 450° C.

5. Paraffin hydrocarbons of the C_nH_{2n+2} series higher than methane are predominant below $400^{\circ}C$.

6. The thermal decomposition of the primary volatile matter takes place readily at temperatures above $750^{\circ}C$. yielding an increase in the quantity of permanent gases, hydrogen and hydrocarbons.

7. Above $750^{\circ}C$. the distillation yields gases in which hydrogen predominates, whether secondary reactions are prevented or not.

8. The tar yields may be markedly increased by distillation at lower temperatures. For example, a Pittsburgh type coal may yield approximately 13 per cent of its weight as tar at temperatures below $500^{\circ}C$. This is more than twice the amount obtained in commercial high-temperature equipment.

9. Water of decomposition is produced at temperatures above $250^{\circ}C$. with the greater portion below $500^{\circ}C$. In high-temperature carbonization it is probable that this water vapor may react with tar vapors and gases passing out of the heated retort.

10. Sulphurous gases (H_2S , etc.) are produced at temperatures as low as $250^{\circ}C$. and with increase in temperature reach their maximum before the maxima for hydrocarbons and hydrogen are reached.

11. Bituminous coals of different oxygen content but similar volatile matter content yield volatile products of very different character. The coal of greater oxygen content yields less tars and more gas, the excess gas consisting primarily of carbon dioxide and carbon monoxide.

12. At a temperature of approximately $900^{\circ}C$. the volatile matter of a Pennsylvania bituminous coal is practically all driven off in the time required to reach this temperature. This time could be as low as five

seconds under favorable conditions, but in practice is a function of the temperature gradient and the thickness of the charge.

13. Small-scale experiments normally cannot be truly reliable for the determination of coke quality.

Morgan and Soule (36) have presented a theory of coal carbonization with emphasis upon the mechanism of tar formation. Their theory has been expanded and modified by Fuchs and Sandhoff (18) to give the following points:

1. The decomposition of coal substance when subjected to the action of heat is a process of progressive step-by-step decomposition, in which pyrogenetic syntheses play only a secondary part.

2. Homocyclic and heterocyclic ring systems characterize coal as well as the entire series of its decomposition products. The decompositions during carbonization are essentially reactions effecting the elimination of heterocyclic complexes and progressive aromatization.

3. The average molecular weights of the volatile intermediate products constantly decrease as the temperature of carbonization rises. This decrease is marked by the evolution of water, carbon monoxide, hydrogen, methane, and other hydrocarbons.

4. The initial decomposition of coal, giving semi-coke and low-temperature tar, is brought about by (a) splitting off of radicals containing heterocyclic and homocyclic rings, (b) opening of some heterocycles to intermediate aldehydes which give rise to phenols, amines, and naphthenic compounds, (c) progressive dehydrogenation and splitting off of side chains by the action of the developing hydrogen.

5. Final decompositions are at a maximum between 600° and 800° C. and are marked by (a) loss of hydrogen and other simple gases from semi-coke and hydroaromatic volatile compounds, (b) hydrogenation of phenols to aromatic hydrocarbons with the formation of methane, ethane and water, and (c) formation of higher aromatics from semicoke proper and by secondary pyrogenetic synthesis.

From this discussion one can readily see that the carbonization of coal yields reactions of an extremely complex nature and reactions which can readily be altered by the conditions of carbonization utilized.

INDUSTRIAL COAL CARBONIZATION

Coal carbonization processes might readily be divided into three fundamental categories dependent upon the temperatures involved in the operations: (1) low-temperature carbonization, 700 to 1100° F., (2) high-temperature carbonization, 1800 to 2000° F., and (3) mid-temperature carbonization, 1200 to 1500° F. The first and second temperature ranges will be discussed at this point while the mid-temperature method will be covered in a later section.

(1) The aims of low-temperature carbonization are four-fold, as follows: (13)

- (a) The production of a greater yield of liquid fuels than can be obtained in high temperature operation.
- (b) The production of a dry, easily pulverizable, highly combustible, low volatile material for use in pulverized fuel furnaces, and at the same time obtain the valuable by-products.
- (c) The production of an easily ignitable smokeless fuel for domestic purposes.
- (d) The production of a substitute for low volatile bituminous coal for mixing with high volatile swelling bituminous coal for the manufacture of suitable dense metallurgical coke.

The primary difficulty in this type of coal carbonization is transfer of heat to the coal in a reasonably short period of time with the relatively low temperature gradient at hand. Coal is actually a poor conductor of heat and the lower temperature gradient markedly decreases the rate of

heat transfer from the retort walls through the coal charge. The cost of the operation is dependent upon the installation charges per ton of coal carbonized, hence it is necessary to effect a large through-put for a given time. This may be done by using a thin layer of coal, agitating the coal, or by passing hot gases through the coal mass. All of these methods increase the rate of heat transfer to the material.

Low temperature carbonization processes may be classified according to the method of heating and oven construction as is shown in Table 3, page 22.

Many methods of low-temperature carbonization have been studied but none have gained wide industrial acceptance. The only process now in operation in this country is the Disco Process which is described in Section V, Part 1. One low-temperature carbonization method is reported in operation in England for the up-grading of domestic fuels. At a later date it may prove feasible to carry out such processes if the need for smokeless fuels and for more liquid products increases.

(2) The primary methods of carbonization utilized today are of the high-temperature type and can be further classified as beehive or by-product. The first of these methods is very inefficient and the only product obtained is the coke. The second method, which utilizes externally heated ovens, is more desirable since in addition to the coke, gaseous and liquid products are also recovered.

The characteristic feature of beehive coking is the production of the heat required for carbonization by combustion within the oven. This type of oven is the oldest form which has been used for coal carbonization. In the year 1916 as much as 120,000 tons of coal per day were carbonized in the beehive oven; during the depression years this figure

TABLE 3. Classification of Low-Temperature Carbonization Systems (13)

- A. Externally heated retorts - coal in thin layers, not stirred
 - 1. Vertical layers of coal in narrow retorts
 - 2. Horizontal thin layers of coal
- B. Externally heated retorts - coal stirred in contact with heated surfaces
 - 1. Vertical retorts
 - 2. Horizontal retorts
 - a. Stationary retorts with internal stirrers
 - b. Rotating cylinders
 - 3. Retorts with coal stirred on a flat heated surface
- C. Internally heated retorts - coal in direct contact with hot gases or liquids
 - 1. Hot gases generated by air or air and steam blown into the retort
 - a. Coal charged in lumps or briquets
 - b. Coal charged in pulverized form
 - c. Complete gasification
 - 2. Hot gases or vapors generated outside the retort
 - a. Combustion products
 - b. Producer gas
 - c. water gas
 - d. Coal gas
 - e. Superheated steam
 - f. Combinations of the foregoing
 - 3. Melted lead in contact with coal
- D. Two-stage carbonization to control the sticking properties of coal

fell to less than 1,000 tons per day; and in January 1941, it increased to 19,000 tons per day (11). In 1948 the production of beehive coke had dropped to 9,350 tons per day (9, page 404). The trends in production of coke by means of the beehive and by-product methods are shown in Table 4, page 24.

Actually, although the beehive oven is a very inefficient means of coal carbonization, it will probably be used considerably in times of great coke demands, because of its relatively low capital cost.

The older types of beehive ovens were built of fire brick and stone. Coal is charged at the top through a charging door, and the charge is leveled off through a side door. Gases are driven off by means of the sensible heat remaining in the floor, oven walls, and roof from the previous run. Air is admitted into the oven through openings in the side door. The products of combustion are vented through the charge door at the top. The progress of the carbonization is downward through the coal charge and it is very important that the air supply be carefully controlled to prevent combustion of a considerable amount of the coke itself. The oven is usually charged with 5 to 6 tons of coal and the coking operation requires from 48 to 72 hours.

The beehive oven has tended to become obsolete, primarily because of the complete loss of the volatile products evolved from the coal and also as a result of the objectionable character of the waste gases discharged (55). Table 5, page 25, gives a heat balance based on a pound of coal charged to a beehive oven and is indicative of the large heat loss experienced in this process.

This large loss of heat led to a modification of the original oven type so that use could be made of some of the sensible heat leaving in

TABLE 4. Production of Beehive and By-Product Coke in the United States,
1880-1949. (Minerals Year Book 1949) (9, page 404)

Year	Coke Produced (Thousands of Tons)	
	By-Product	Beehive
1880	0	3,300
1895	19	13,315
1900	1,076	19,458
1905	3,462	26,769
1910	7,139	34,570
1915	14,073	27,508
1920	30,834	20,511
1925	39,912	11,355
1930	45,196	2,776
1935	34,224	917
1937	49,211	3,165
1941	58,048	6,704
1943	63,743	7,933
1945	62,094	5,214
1946	53,929	4,568
1948	68,284	6,577
1949	60,222	3,414

TABLE 5. Heat Balance in Beehive Coking. (42, page 109)

	B.t.u.	B.t.u.
Original heating value		13,500
Remaining in 0.63 lb. coke		8,060
Burned in oven to carbonize the coal:		
0.07 lb. coke	900	
0.06 lb. tar and oil	1,000	
5.5 cu. ft. gas	<u>3,200</u>	
Total used for coking		5,100
Miscellaneous losses		<u>340</u>
Total		13,500

the gases at the top of the oven. A waste heat flue leading to a waste heat boiler was located at the oven charging hole. Applications such as this would show a recovery of approximately 1800 B.t.u. per pound of coal charged in the above heat balance.

By-product coke ovens are long, narrow, silica brick chambers in which coal is coked by the combustion of a fuel gas in flues built in the refractories which separate the ovens (55). The products of combustion of the fuel gas and the volatile products of carbonization are kept separated from one another at all times. In order that heat and space may be conserved, by-product ovens are built in batteries, with ovens and division walls containing the flues alternating from one end of the battery to the other. The primary limitation upon this method of carbonization is the high initial cost involved in the construction of the ovens. At present day inflated prices the cost of an industrial oven and its accessories would be in the neighborhood of \$225,000. (25) A battery containing 60 of such ovens would cost \$13,500,000.

A coke oven battery is a stable mass of brickwork, carefully insulated to prevent loss of heat. The battery is supported on a concrete foundation, or mat, by concrete or brick arches and piers or by structural steel work. The oven is a narrow chamber usually 38 to 40 feet long, 10 feet high, and is tapered in width from 17 or 18 inches at one end to 15 or 16 inches at the other end. (47, page 85)

The individual oven is intermittent in its operation but each oven in the battery is started and finished at different times so that the operation of the entire block produces continuously a gas of good average composition. The finely crushed coal is dropped from a lorry car through

charging doors in the top into the oven where the walls are at a temperature of approximately 2000° F. The initial rush of gas, steam, and air is vented to the atmosphere through an outlet valve in the uptake pipe which rises from the top of the oven. The coal is then leveled through the charging holes after which the holes are covered and the gas evolved is turned into the collecting main. Heating is carried on and the charge is left in the oven until the coal is completely carbonized and the evolution of the volatile matter has ceased. The average temperature at the center of the charge at the end of the heating period is normally about 1800° F. and the average temperature in the flue is about 2350° F. The temperatures in the oven vary with the conditions of operation, the coking time, the width of the oven, the type of coal used, its moisture content, and the fineness of the coal.

At the end of the coking period the doors at the ends of the oven are opened and the entire red-hot mass is pushed rapidly out by means of an electrically operated ram. The coke falls into a quenching car of sufficient size to hold the charge from one oven. The car then travels to a quenching station where an overhead nozzle sprays cooling water on the charge. Many plants are now equipped with inert gas quenching devices. Here an inert gas such as carbon dioxide or nitrogen is used to cool the coke, hence the term dry quenching. In a method of this nature it is said that seventy to seventy-five per cent of the sensible heat of the coke may be recovered and it is claimed that the coke gives better fuel efficiency than that which is wet quenched. (47, page 86)

The gas from the coal being carbonized together with entrained particles, passes upward through a cast iron gooseneck into a horizontal

steel trough which is connected to all the ovens in series. This trough is known as the hydraulic main or collecting main. A slight suction is maintained on the main by means of a mechanical exhaustor located beyond the primary condenser. The tar, overlaid by an aqueous liquid containing ammonia and its compounds, collects in the bottom of the main. The liquids are pumped away as they collect, though part of them may be recirculated for cooling-flushing.

The types of ovens differ mainly in the arrangement of their heating flues, whether vertical or horizontal, the method of applying the regenerative principle to preheating the air for combustion, and also in the arrangement for introducing the heating gas and air to the flues. In yields, qualities of products, and methods of operation there is essentially no material variation among the several by-product ovens.

Many papers have been written concerning the construction of the various types of by-product ovens but no discussion will be undertaken here on any of such details as they do not directly apply to the problem at hand.

At this point it seems desirable to discuss briefly the progress of carbonization in the ovens, after which the inherent difficulties with the method of carbonization will be seen. When the coal is placed in the hot oven, that portion of the charge in immediate contact with the hot walls is heated rapidly to a high temperature. A thin layer of this coal softens, becomes plastic, and melts. This plastic zone travels toward the center of the oven as the temperature of the oven is raised. In this zone and on either side of it, destructive distillation of the coal takes place, some of the gaseous products forcing their way out of the plastic material, hence imparting the cellular structure which appears in the final coke.

On the wall side of the fusion zone, the plastic layer hardens into a cellular residue which is further devolatilized as the temperature rises during the remainder of the coking process. At the inner face of the fusion zone, as it travels away from the hot wall, the relatively cool, raw coal from the center of the charge is melted and carbonized. Finally, the fusion zones initially formed at the two walls will meet at the center of the charge.

The gases evolved from the fusion zone force their way either to the walls of the coking chamber or pass into the cool, uncarbonized, raw coal. The volatile matter driven into the center of the charge will have the tar, oils and water condensed out, to be distilled again when the plastic layer reaches the particular point at which they were deposited. The gases forcing their way through the hotter face of the plastic zone, however, pass through cracks in the coked coal up along the incandescent oven or retort walls, and finally through the hot free space at the top of the charge. The heat to which these materials are subjected during their travel causes considerable thermal decomposition. During the latter part of the coking period this process is intensified, for the path of the gases becomes longer and the coke hotter as the fusion zone progresses toward the center of the oven. As a result of this progression, the thermal decomposition of the products becomes more severe. The gases become much richer in hydrogen and the coke becomes silvery-gray in color, due to the deposited particles of retort carbon formed by the breaking down of the hydrocarbons and tars. Evans (12) has pointed out that a knowledge of chemistry does not help very much in the interpretation of this operation - in fact, it rather tends to complicate matters because the better appreciation of the complex reactions is offset by the confusion

which results from a consideration of the almost limitless range of reactions that could take place.

Having briefly covered the by-product coking process, an examination will now be made of some of the factors which have influenced the design of the oven. Inasmuch as it is extremely difficult to obtain a rapid flow of heat into the coal charge during carbonization, the belief has arisen that the plastic zone is a very poor conductor of heat. The facts which are available apparently tend to support this belief. Figure 3, page 31, shows the temperature throughout a coke oven of 18 inch width at various periods of time after the coking operation has been started. It is seen that even after 10 hours of operation, the temperature at the center of the charge is only 425° F. which indicates a lag of approximately 1500° F. to that of the oven wall. The actual drop in temperature across the fusion zone is of the nature of 900° F.

At the time a fresh charge of coal is dropped into a hot oven, the rate of heating at the wall is very high, and as long as the fusion zone is near the wall, its rate of travel into the green coal will be fast because the heat has a very small resistance through which to travel in order to reach it. As the fusion zone proceeds toward the center of the charge, heat flows into it much more slowly because heat is absorbed by the coke which has been formed and by gases which are passing to the foul gas main. In addition to the fact that the zone is receiving less heat from the oven walls, it is also being cooled by the cold coal which lies before it. As the center of the charge becomes heated, a point is reached where this sensible heat absorption begins to diminish due to the decreasing temperature difference and the rate of travel of the fusion zone actually increases.

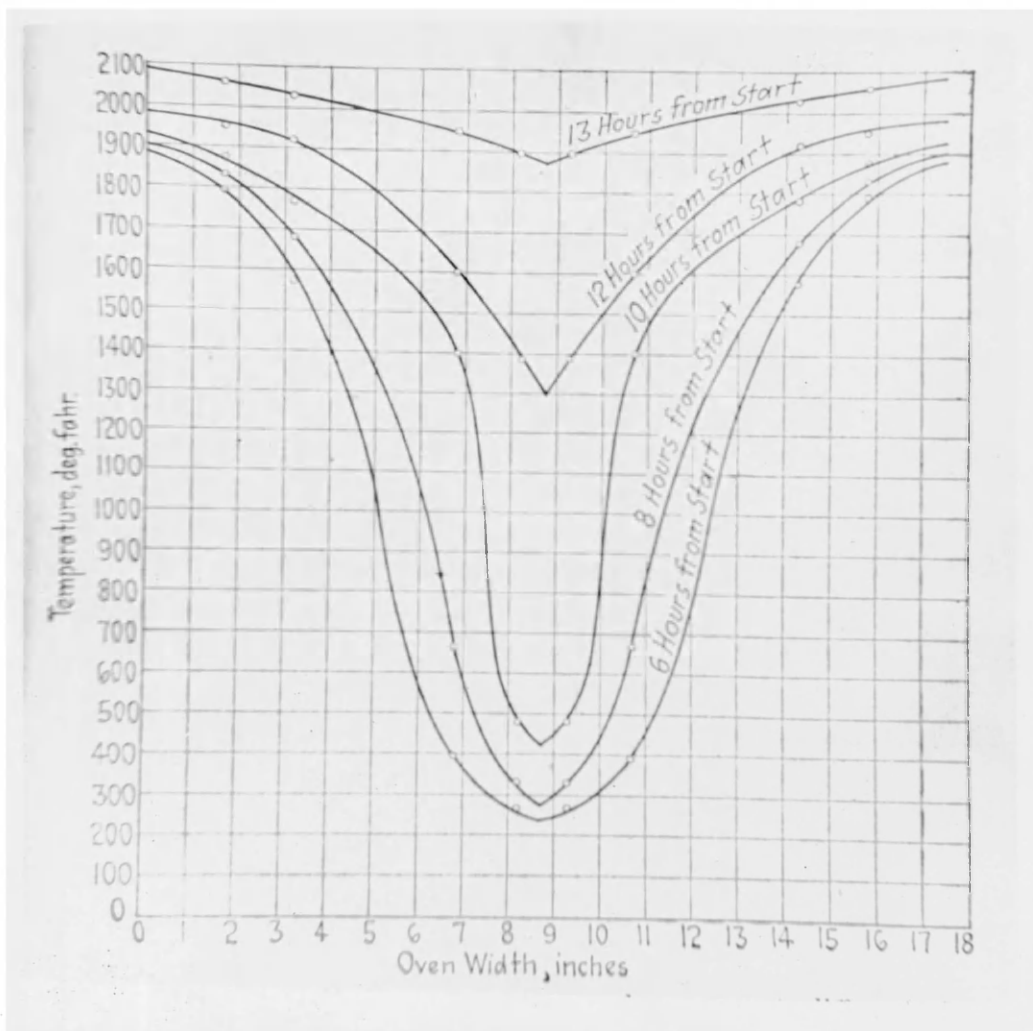


FIGURE 3

TEMPERATURE GRADIENTS ACROSS A COKE OVEN
 AT DIFFERENT INTERVALS DURING THE COKING PERIOD
 (ACCORDING TO HASLAM AND RUSSEL) (21, page 657)

Figure 4, page 33, illustrates the difference in the rate of heating curve for a 16 inch and a 20 inch oven. This curve indicates that the additional 4 inches of oven width are traveled at a rate lower than the minimum reached in the 16 inch oven. The result is to increase the time required for coking to a much greater extent than in direct proportion to the increase in oven width.

An economic balance must be made between cost of construction, the properties of the coke produced, and the capacity of the oven in order to arrive at the optimum size unit to utilize. The trend in American practice is toward the narrower ovens which allow a greater capacity by virtue of the increased coking speed.

From this discussion it is apparent that one of the major difficulties in any coal carbonization process is the transfer of heat across the fusion zone. The ideal coking process would be one which would exclude this difficulty and which would as a result of decomposition yield heat from within the coal sample itself.

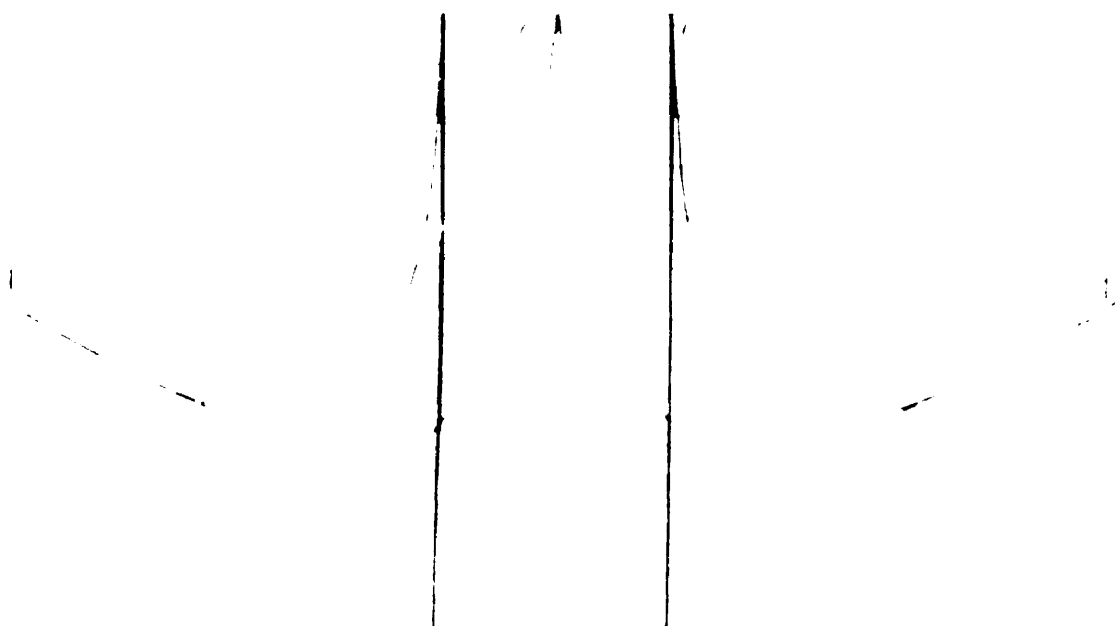


FIGURE 4

DIAGRAM ILLUSTRATING THE EFFECT OF INCREASING COKE-OVEN
WIDTH ON THE RATE OF TRAVEL OF THE FUSION ZONE
(ACCORDING TO HASLAM AND RUSSELL) (21, page 660)

SECTION IV

THERMAL EFFECTS OBSERVED DURING COAL CARBONIZATION

The thermal reactions of coal during carbonization have received considerable interest. The problem is quite complex, since the original coal is a heterogeneous material which upon decomposition yields solids, liquids and gases which are likewise complex.

Over the entire range of the carbonization period the net resulting heat effect is normally only slightly endothermic or exothermic. However, this is only because appreciable exothermic and endothermic reactions are found to be taking place simultaneously. Work on the subject has been carried out by Mahler in 1891, Euchene in 1900, Constan and Kolbe, and Schlapfer in 1908 and 1909, by Hollings and Cobb in 1914 and 1915 and others (30, page 103).

Mahler used a heat balance method of measurement. By means of a bomb calorimeter he determined the heat of combustion of the coal, and also that of all the products of carbonization. He found that the heat of combustion of the products was less than the heat of combustion of the original coal by some 459 B.t.u. per pound, which is about 2-1/2 per cent of the heat in the original coal.

Euchene compared the heat of formation of the products of distillation with a heat balance of a retort setting for a coal with an analysis similar to that used by Mahler and found a net exothermic effect of 114 B.t.u. per pound. This is of the order of 0.6 per cent of the heat of combustion of the coal. Euchene carried out determinations on three types of coal which differed in their oxygen content and also in their

volatile matter. All of these showed a liberation of heat during carbonization. The quantity of heat liberated in these experiments was very small (always less than 1 per cent of the heat of combustion of the coal) and was actually of an order comparable with the percentage error to be expected in this type of experimentation.

Hollings and Cobb (23) carried out experiments in order to determine the character of these thermal effects, using a method wherein the temperature changes which occur in a coal sample when it is heated and distilled by a definite inflow of heat were compared with those which occurred during the heating of a similar sample of inert material by a similar inflow of heat. By this means they were able to trace the course of the exothermicity or endothermicity of the reactions which take place over the entire range of temperature from 25° to 600° C. This method is superior to the one used by former investigators in that it gave an indication of precisely the location of these thermal effects. Bituminous coals, anthracites, cannel, and cellulose were examined and it was readily seen where well-defined zones of reaction predominated, displaying the location of the endothermic or exothermic regions.

Although the overall reactions associated with high temperature carbonization seem to be exothermic, it does not necessarily follow that the net heat effects at low temperature need also be the same. In the case of the coal used by Hollings and Cobb, it was seen that endothermic reactions began at 250° C. and continued up to 610° C., with a break between 410° C. and 470° C., during which there existed a short exothermic stage. For this particular coal, it was probable that the overall reactions during low temperature carbonization were either neutral or

perhaps slightly endothermic.

Burke and Parry (4) gave the following statement regarding the heat of distillation of coal:

This "heat of carbonization" - that is, the integrated thermal quantities resulting from exothermic or endothermic chemical reactions, or both, which occur during coal distillation, while of considerable importance to the chemist in his endeavor to elucidate the chemical phenomena occurring during coal carbonization, it is of relatively slight importance to the engineer, who is concerned with the design or operation of apparatus for effecting carbonization. The reason is the trifling magnitude of the thermal quantities involved even in the most extreme cases, although in certain critical cases they may be of real importance to the mechanism of the carbonization process.

The method of Burke and Parry for their determination of the heat effects during coal carbonization involved the passage of a hot inert gas through a charge of coal with means of measuring the heat content of the gas before and after passage through the coal. This was actually an adiabatic furnace in which no heat was lost by radiation. They found the following values of heats of carbonization: Utah coal 85 B.t.u. per pound, Lignite 37 B.t.u. per pound, and Pittsburgh coal 7 B.t.u. per pound. The results of these determinations are questionable since the process was not continuous, only average exit temperature values were used for calculation of heat of carbonization, and values of specific heats over the range of temperature involved were assumed. The results of this work agreed well with the long held hypothesis that the order of exothermicity was related to the geological age of the coal.

The classic work on the thermal effects during coal carbonization was carried out in 1922, 1923, and 1924 by Davis (7) by means of calorimetric studies in twin adiabatic calorimeters. Also at the same time Place and Davis carried out a qualitative study of the thermal effects

by means of a heating rate method. They list the following methods for carrying out such determinations: (8)

1. The indirect calorimetric method, in which the reaction heat is taken as the difference between the combustion heat of the coal and that of its distillation product.
2. The direct calorimetric method, which involves the use of calorimetric apparatus adopted to the measurement of the reaction heat while the reactions are in progress.
3. The heat balance method as applied to commercial-scale coke ovens, and also to experimental carbonizing operations.
4. The heating rate method, wherein the heating rate of coal indicates its reaction heat when compared with that of an inert substance such as coke. The same heating conditions are maintained for coal and coke over the carbonizing range, and variations in the temperature of the coal relative to that of the coke are ascribed to reaction heats developed at the temperature in question; where the coal heats faster than the coke, positive reactions predominate and vice versa.

The primary disadvantage of the heating rate method is the fact that it is only qualitative. It does have one important advantage over other methods, namely, it shows the actual trends in the reactions over the entire range of temperature involved. The other methods show only the net effect over the entire carbonization process.

The apparatus used by Davis and Place for their qualitative study consisted of a resistance furnace wound with platinum resistance wire of sufficient size to admit a 19 mm. quartz tube. The quartz tube which was sealed at one end was 38 cm. long. Thermocouples were placed in the bottom of the furnace and in the center of the coal sample for measurement of temperatures. Two 250 cc Erlenmeyer flasks, one of which served as a tar receiver and the other which acted as a pressure regulator, were placed in series with the tube leaving the quartz tube. In this work a 20 gram sample of coal was heated as rapidly as possible over the temperature range 25° to 750° C. This operation required about eight minutes.

Actually it was realized that this rapid rate of heating might mask the effect of small thermal reactions, but the time was chosen in order that the results might be compared with calorimetric determinations which were carried out for a similar length of time. The coals tested in this apparatus were Minnesota peat, Texas lignite, Utah bituminous, Pocohantas bituminous and Pennsylvania anthracite. They also carried out determinations using pine sawdust as a comparison.

The results of these tests can be summarized best as follows: (8)

In general, all the coals tested, the anthracite excepted, show strong absorption of heat at or near 100° C. This was undoubtedly due to the latent heat required to vaporize the uncombined water in the coal. The sharp positive turns under 100° C. are probably due to the action of absorbed oxygen, particularly in the case of the lower rank coals. Such coals are known to be particularly liable to spontaneous combustion, and a high capacity for the absorption of oxygen may doubtless be expected. No attempt was made to remove adsorbed gases or water from any of the coals before making the tests; they were taken in the air-dried condition. As observed by Hollings and Cobb in their tests most of the coals gave curves with inflection points around 150° C. An "endothermic turn" around 300° C. is noticed only in the case of the Utah and Pocohantas coals; for the lignite it begins around 400° C., and for the Illinois coal at about 325° C. The slopes of all coal curves, except that for anthracite, between 400° and 750° C., are in the positive direction, indicating exothermic reactions, and perhaps to some extent increase in thermal conductivity, this being in practical agreement with the findings of Hollings and Cobb. The strong exothermic reaction obtained for pine sawdust would be expected from the work of Klason and others who found exothermic reactions in the distillation of wood cellulose so strong at 270° C. that the temperature of the charge rose 80° above that of the furnace in which it was being heated.

The twin adiabatic calorimeter, as devised by Davis for the determination of the reaction heat of coal during carbonization consisted of two calorimeter bombs which were exact duplicates of one another. The heating elements and calorimeter could be interchanged without appreciable change

in results. Differential thermopiles were part of the unit. A coal sample was placed in the heating capsule of one bomb and the other heating unit was left empty. The temperature was then raised through the distillation range, and the difference in heat developed in the two calorimeter units was the heat of reaction of the coal.

The theory of this adiabatic calorimeter is of particular interest and note will be made of it at this time. Consider twin calorimeters enclosed within a water jacket; one designated as a and the other as b, a being the active calorimeter and b the reference. The rate of change of the temperature difference between the two is

$$\frac{d(T_a - T_b)}{dt} = K_a (C - T_a) - K_b (C - T_b) \mp (k_a \mp k_b) (T_b - T_a) \mp W_a - W_b$$

T_a and T_b being the temperatures of calorimeter a and b and C the temperature of their common jacket; K_a , K_b and k_a , k_b are cooling factors of the calorimeters relative to the jacket and to each other respectively; W_a and W_b are temperature changes per unit time due to evaporation and stirring. If the jacket completely encloses both units and they are similar in temperature, K_a becomes almost equal to K_b and k_a to k_b ; furthermore, if evaporation is eliminated and the stirring energy is the same in both cases, W_a and W_b can be neglected. The equation then becomes:

$$\frac{d(T_a - T_b)}{dt} = (K \mp 2k) (T_b - T_a)$$

which is a usable form once the value of the factor $(K \mp 2k)$ is determined. This can be done by maintaining temperatures T_a and C equal and constantly observing the cooling rate in calories per minute for various temperature differences.

Figure 5, page 40, is a schematic diagram of this adiabatic calori-

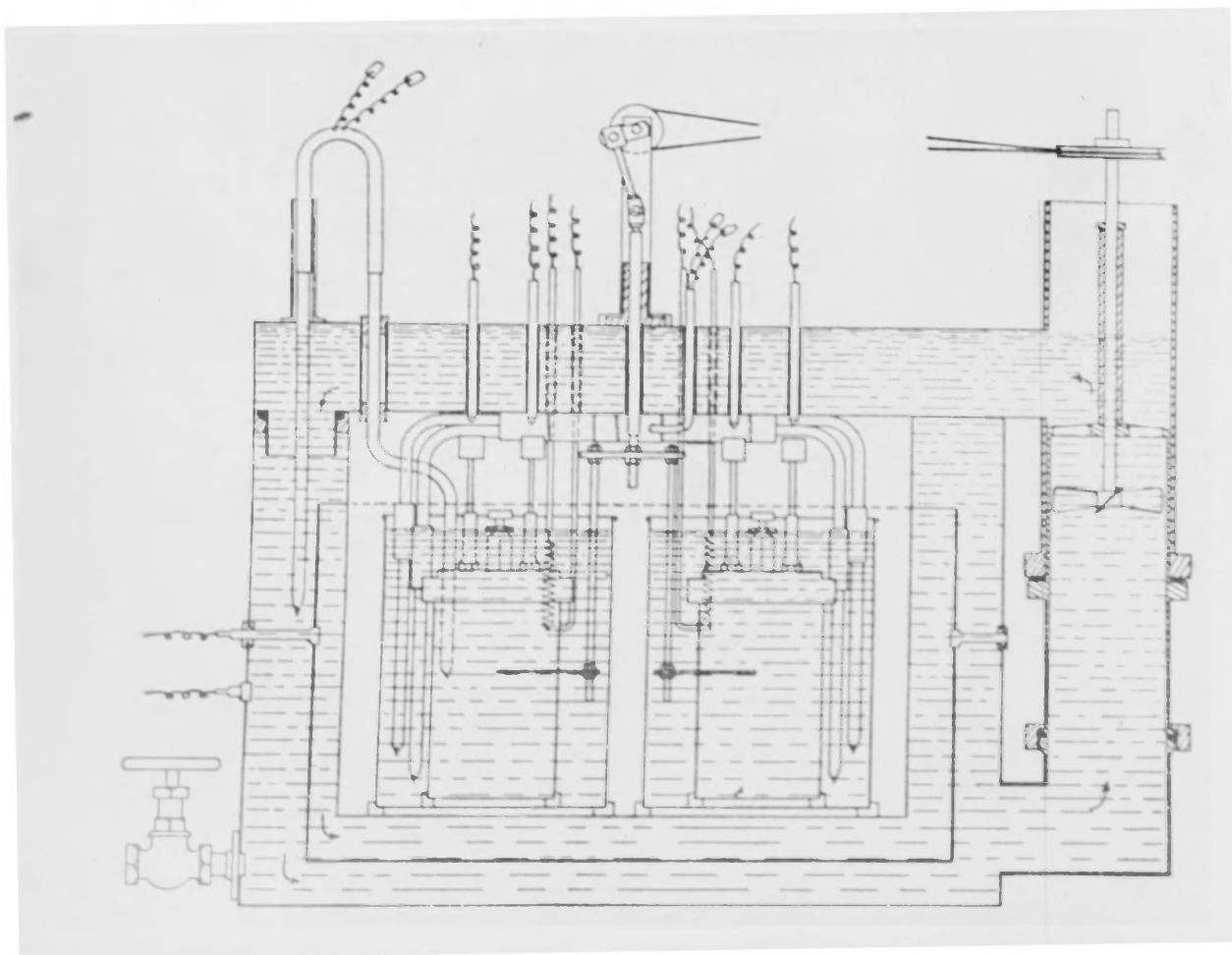


FIGURE 5

CALORIMETRIC APPARATUS FOR HEAT OF DISTILLATION OF COAL

(ACCORDING TO DAVIS) (7)

meter assembly. The results of this investigation are summarized as follows:

Material	Heat of Carbonization (cal./g.)
Sawdust	180
Peat	85
Ohio Coal	46
Utah Coal	45
Lignite	42
Illinois Coal	30
Pocahontas Coal	7
Anthracite	2

This work indicated that the reaction heats of coal were very small compared with the total heat effects involved in the carbonization process. The reaction heats given above were determined in a nitrogen atmosphere. A further investigation by Davis in hydrogen atmospheres yielded reaction heats which were of smaller quantity and in some cases actually became endothermic. This writer endeavored to construct an apparatus of this type but encountered so many and such varied difficulties that it was abandoned.

McBride (34) has carried out a study of the heat required to carbonize a coal sample by heat balances over three types of coking units. The three units which were used in this study were: by-product coke ovens, horizontal retorts, and vertical retorts. The results obtained were as follows: (Heat required to carbonize the coal)

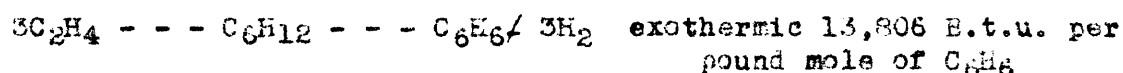
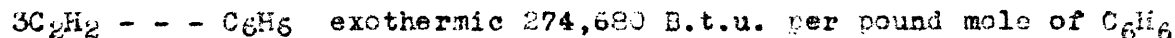
Coke ovens	1320 B.t.u./lb.
Horizontal retorts	1420 B.t.u./lb.
Vertical retorts	1485 B.t.u./lb.

The age of the retorts and their inherent inefficiency was probably responsible for their higher heat requirements.

Herty, Wilson and Forest (54) made a study of the thermal operations of a modern sixty-oven battery of regenerative coke ovens fired by a part

of the gas produced from the coal. The results of this study show an exothermic effect of 450 B.t.u. per pound of dry coal from a heat balance over the oven.

Denig (11) discusses the thermal effects occurring in a by-product coke oven and states that an exothermic effect of 200 B.t.u. per pound has been obtained. The error in these tests was believed to be within the order of 4 or 5 per cent. The difference between Davis' calorimetric value of 40 to 50 B.t.u. for a similar coal is too large to be attributed to faulty methods. An explanation for this variation may be exothermic heat of cracking. The path of the gases in the commercial apparatus is much longer and more opportunity for secondary reactions is present. If the decomposition of the coal should yield C_2H_2 , C_2H_4 , H_2 , etc., the following exothermic reactions may occur:



Such dehydrogenation reactions in general are exothermic. The large amount of hydrogen present in coke oven gas indicates the probability of exothermic reactions due to dehydrogenation.

From this discussion it is evident that a large part of the experimental data is actually controversial so far as the net thermal effects are concerned. Well defined ranges of reaction have been observed and any work of a practical nature with these heats will be within a particular exothermic range.

This survey of the literature indicates that the exothermic effect is most predominant at the plastic temperature of the coal. This fact is the basis of at least one low temperature carbonization process. This

process was developed by Prof. S. M. Parr at the University of Illinois (37, 38, 39, 41).

The desire of this process was to eliminate the heat barrier caused by the plastic zone. If the plastic zone could be restricted to just one transformation over the entire coal sample, this difficulty could be eliminated.

In this process the charge of coal is preheated to 35-50° C. below the plastic zone (the point of strongly exothermic reaction). The preheated coal is then transferred to a much hotter retort where the heat rapidly penetrates the charge of warm, dry coal in sufficient quantity to cause the entire mass to become plastic practically at the same time owing to the large temperature gradient. This sudden change in temperature of the coal "trips off" the exothermic reactions and the entire charge shows about 70° C. increase in temperature. When the exothermic reaction takes place it releases about 65 B.t.u. per pound of coal. The coal used was an Illinois type which was high in oxygen content and prior to that time had not yielded a high strength coke.

To arrive at the reason for the pretreatment which the Parr Process employs it is best to study the actual zones which occur during this mid-temperature process. Parr has listed the following distinct zones: (38)

1. First 100° of temperature are required to drive off free moisture, and until this work is completed the temperature does not rise above 100° C.
2. Below 300° the coal is still in the granular or non-pasty stage. Below the pasty stage there has been no decomposition. There is, however, a rearrangement or condensation of organic constituents carrying hydroxyl and carboxyl groups of such a nature as to split off CO₂ and water.

The resultant heat of reaction over this range was endothermic. The

latent heat of this decomposition was decidedly affected by the manner in which the heat was applied to the coal during this thermal pretreatment. The studies of Farr definitely indicated also that the rate of these low temperature reactions had a decided effect on the reactions which occurred at elevated temperatures. A very slow accession of heat over the endothermic range greatly reduced, and in some cases completely annulled, the exothermic effect at the plastic zone. The effect of this prolonged heating can be illustrated by a few examples of Farr's data which showed when the exothermic effect took place. Three samples were treated over the same temperature range for periods of 7-1/2, 10-1/2, and 12-1/2 hours respectively and the following values are the temperatures at which the exothermic reactions occur: 350° C., 400° C., and 450° C. This pretreatment data definitely indicated that a straight line relationship existed between temperature and time.

The fundamental objective of this method of carbonization was to produce a gas yield which would be attractive to the gas maker and to produce a coke, especially from Illinois coals, which would be readily salable on the domestic market or directly available for complete gasification or for power purposes. The coke produced was apparently not of sufficient quality to be utilized for metallurgical purposes.

SECTION V

SOME CHEMICAL TREATMENTS OF COAL

There seems to be no indication in the literature that the effect of chemical pretreatment of coal has been studied from the standpoint of the thermal reactions occurring. The Disco process (35) is probably the most notable advance in the pretreatment of coal. This process has been applied on an industrial scale primarily for the following purposes:

1. To upgrade cleaned coal fines of relatively low market value.
2. To prepare a smokeless lump fuel which could be utilized for domestic and industrial furnaces.
3. To provide a smokeless fuel which can be easily burned.
4. For the formation from the coal of liquid products which have a good market value.

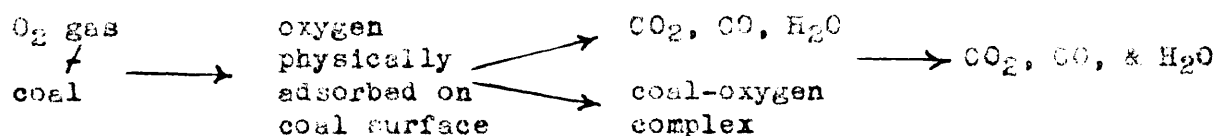
The following steps describe the process: a. Predrying, b. "Roasting", c. Carbonizing in retorts, d. Cooling and screening. Probably the most important step in this process is the "roasting". This step preheats the coal and partially oxidizes it by exposure to controlled quantities of air. The coal in this pretreatment reaches a temperature of 600° F. The coal is removed from the conveyor and drops into another vessel where it is quickly heated to the plastic temperature and the formation of lumps begins. These lumps then roll around the inside of the shell and work their way down to the discharge end of the unit.

The coke produced in this process is of inferior quality for metallurgical purposes but does serve as an outlet for material which

normally would be lost as waste. The primary purpose of the air pretreatment is to control the excessive coking characteristics of this high grade bituminous coal. These excess coking characteristics are satisfactory for high temperature carbonization processes but produce a very fluffy, friable material upon low temperature carbonization.

Dr. Illingsworth (30, page 144) in England, succeeded on a small scale in producing a rather hard low temperature coke. However, he used coals unsuitable for low temperature carbonization in their raw state unless given a preliminary treatment. The method of pretreatment was similar to that used in the Disco process to remove the excess bituminic material so that a more dense coke might be obtained.

Several investigations have been carried out concerning the action of oxygen on coals (6, 28, 44, 45, 46). The mechanism of the reaction between gaseous oxygen and coal at low temperature is relatively complex. It can probably be expressed somewhat by the following reaction:



It is generally accepted that the first of these reactions is quite rapid and that the second and third steps actually control the quantity of oxygen which is consumed. Aerial oxidation at a temperature of 150° C. gives a relatively low oxygen content product though prolonged exposure at this temperature will give products of considerably higher content. The properties of the "coal-oxygen complex" are not well known, but work by Yohe shows that coal which has been treated with oxygen contains organic peroxide substances (36). This was demonstrated by placing the coal substance in contact with sensitized plates. The plates were

affected so that dark spots or images appeared. Russel noted that this was due to the presence of organic peroxides. A review of the literature seems to indicate that these peroxides are very unstable; however, storage of these treated coals at low temperature does not seem to appreciably affect their composition.

Schmidt, Elder, and Davis (46) have concluded that the volatile matter content of coal changes only slightly and in an irregular manner as oxidation progresses at a temperature of 99.3°C . It was noted that the detailed analysis of tar, coke, and light oil did not change greatly with the amount of oxidation to which the coals were subjected. The analysis of the coke, including percentage of sulfur, showed no appreciable change with oxidation. The yield of ammonia was increased. A decrease in the yield of tar was noted but the sum of the yields of tar and coke varied but slightly with extent of oxidation. This indicated that oxidation of coal changes the original tar-forming constituents in such a way that upon carbonization they decompose to form coke and a small quantity of gas instead of distilling as tar. In this same work, a slight decrease in light oil yield was observed.

Künle (29) reported that the heating of a bituminous coal for 10 hours at 225°C . raised the oxygen content from 9.9 to 23.9 per cent and increased the volatile matter content by 1 per cent.

Products of higher oxygen content are obtained by submitting the coal or air-oxidized coal to treatment under suitable conditions with a variety of oxidizing agents, including nitric acid, potassium permanganate, and hydrogen peroxide. These processes are not only capable of producing products of higher oxygen content but are much more rapid than air oxidation.

The action of nitric acid on coal is very violent and the rate of reaction is many times that of air. It is a highly exothermic reaction evolving copious quantities of nitrous fumes due to the nitric acid reduction. Friswell (16) in using cold dilute (49%) nitric acid, observed this heating up which occurred with bituminous coal during the primary reaction. Anderson (2) measured the increase in weight obtained on evaporating several samples with dilute nitric acid as follows:

Coal	V. V. (%)	Gain in Wt. (%)
Ell.	33.3	11.47
Main	35.8	10.47
Splint	36.2	17.91
Gas	38.2	16.33
Virgin	33.5	13.19
Kilsyth Coking Coal	28.4	23.51

Fuchs (17) has patented a method for producing these highly oxidized coals utilizing a three-step procedure:

1. Oxidation in air at about 350° C.
2. Oxidation in air at a lower temperature and in the presence of a catalyst such as ammonium nitrate.
3. Treatment with nitric acid.

It is said that this type of treatment reduces the quantity of nitric acid required to approximately one-tenth of that needed when oxidizing with nitric acid alone.

All workers are agreed that the primary action of nitric acid is to convert the greater portion of the coal into a substance soluble in alkalies and resembling the ulmins. The product is of considerably higher nitrogen content than the original coal. It is probable that this nitrogen is present primarily as nitro groups but partly in the nitroso and isonitroso state.

A number of investigations have been made on the effect of added inorganic material on the products of coal carbonization. Lessing (31) stated that the course of the decomposition of coal is affected by the catalytic influence of some of its constituents and also by the nature of the retort material with which the hot gases come in contact. He stated that the composition of the mineral matter is of utmost importance in this connection.

Lessing's views were based upon his own researches and upon the existence of several patents which made claims of the improvement of carbonization yields. Rollason (43) claimed that addition of 3 to 5 per cent of finely divided limestone to coal carbonized at 500° C. gave increased yields of oils and Jowet (26) claimed the production of a better coke and a better illuminating gas by treatment of coal with potassium chlorate and potassium permanganate.

Lessing and Banks (32) published the results of their investigations of the influence of inorganic additives on the carbonization of cellulose, sugar, and coal in 1924. The effect was usually to increase the coke yield to a greater or lesser extent. The greatest changes were generally obtained with the use of the salts of strong acids and weak bases.

Inorganic compounds added to the coal included sodium chloride, sodium sulphate, ferric chloride, ferrous sulphate, sodium carbonate, potassium carbonate, sodium oxalate, sodium silicate, the oxides of silicon, aluminum, iron, calcium and magnesium, and sulphuric acid. The gas yield seemed to be practically unaffected by all these treatments, but the tar yield was reduced on carbonization at 900° C. The yield of retort carbon was reduced and the coke yield increased. Ferric chloride, ferrous sulphate and sulphuric acid produced the greatest change, with

sodium silicate and sodium carbonate producing a similar but smaller change.

Gauger and Sauley (19) investigated the effect of inorganic additions on the carbonization of a North Dakota lignite. The additions decreased the tar yield in all cases and increased the coke yield with the exception of sodium carbonate which showed a marked increase in gas yield.

King and Edgcombe (27) made a study of the influence of retort materials on carbonization of coal. Coke, carbon, silica, alumina, chromium and stainless steel showed no effect on carbonization yields, however, copper, nickel, cast iron and steel became sulphided and hence reduced the hydrogen sulphide content of the gas. Sulphides such as pyrites and marcasite, reduced the yield of tar and of gas and the coke produced was barely coherent.

From this brief review it can be seen that certain modifications can be made to the reactions which occur during coal carbonization.

SUMMARY OF FOREGOING INFORMATION AND

STATEMENT OF THE PROBLEM

This review of previous researches on coal chemistry and coal carbonization is indicative of the vastness and complexity of the general problem. The equipment utilized commercially for carbonization today is extremely expensive and the through-put per unit time is relatively low.

The process of Farr seems to be the only one which has been developed to utilize specifically the thermal effects involved in coal carbonization to speed the coking process. This process has received no significant industrial application and this may be partially due to industry's inherent reluctance to adopt new methods until they have been proven.

This literature review brought forth the proposal that these reactions might be affected by certain inorganic additions in such a way as to make more extensive utilization of the thermal effects, either as a method of autogeneous coking or as a means of markedly increasing the capacity of present industrial units.

PART II - EXPERIMENTAL

SECTION I

EQUIPMENT AND ANALYTICAL PROCEDURES UTILIZED IN RESEARCH

A. EQUIPMENT

Before a study of the thermal effects involved during coal carbonization could be made it was necessary to consider the variables which could affect the reactions which occur, and determine what means could be used to control these variables through the design of equipment.

In the previous discussion four methods as presented by Davis and Place were set forth. Each of the methods has its limitations, as follows:

1. The indirect calorimetric method, in which the reaction heat is determined by difference between the heats of combustion of the products of distillation and the original coal sample, is not suitable because of the difficulty in recovering all products in such an apparatus. As the process is intermittent, after distillation all of the tars must be recovered and weighed and a representative sample must be taken for thermal value determination. This procedure must also be utilized for the gases and coke recovered. As relatively small differences in reaction heats were expected, this type apparatus was not adopted.

2. The direct calorimetric method is the best for such calorimetry because the products do not have to be handled after the distillation is completed. The primary difficulty is the small net heat of carbonization as compared to the heat required to raise the coal to the carbonization temperature. The values of Davis show a heat evolved of from 2 to 180 cal./gram with a total heat input to the apparatus of approxi-

mately 8500 calories to effect the carbonization. In addition, it is doubtful whether these results actually have a quantitative significance since they could not be duplicated on a large scale.

3. The heat balance method as applied to commercial scale equipment is automatically eliminated because of the expense involved. It has one decided advantage in that the thermal quantities observed would be those actually obtained in practical applications. It is understood, however, that such observations are extremely difficult for accurate determinations.

4. The heating rate method, wherein the heating rate of the coal indicates its reaction heat when compared to an inert substance such as coke is the preferred method for laboratory research in that it gives the trends in reaction heats over the entire range of carbonization. Any commercial application of such thermal effects will undoubtedly be in the range of strong exothermicity.

With these preliminary considerations as guides, a qualitative approach to the problem was adopted. The primary variables of concern in this were fluctuations in the rate of heating and in the distillation pressure. The first was eliminated by a constant voltage heating current; the second by a pressure regulator.

First Qualitative Apparatus

The first apparatus consisted of a 1-1/2 inch diameter steel pipe, 12 inches in length, which was first wrapped with asbestos paper and then with sufficient #24 gauge (E. & S.) nichrome wire to give a total resistance of 25 ohms. The pipe was then lagged with wet ground asbestos. Transite rings were placed in the top of this furnace and at a point about half the length of the furnace. Holes of 25 mm. diameter were

drilled in the center of these transite rings in order that a 26 mm. quartz tube might fit into them. The purpose of these rings was to insure that the tube was in exactly the same location during each run.

A quartz tube of 26 mm. diameter and 12 inches in length was used as the reaction vessel. The tube extended three inches out of the top of the furnace when the apparatus was assembled for a determination. A rubber stopper was placed in the top of the tube in order to prevent escape of tars and gas. Thermocouples were placed in the furnace below the tube and in the coal sample. The thermocouple in the coal sample was protected from the reducing atmosphere by means of a six millimeter vycor tube extending through the rubber stopper in the top of the quartz vessel. An additional nine mm. tube led from the rubber stopper to two 250 ml. Erlenmeyer flasks, one of which served as a tar receiver and the other which acted as a pressure regulator. One tube from the pressure regulator led to a water aspirator by which a vacuum was applied to the system. One end of the other tube of the regulator was open to the atmosphere, the other end being submerged in three inches of water. This insured a vacuum pressure of three inches of water at all times.

The results of the determinations made in this apparatus were limited in their degree of reproducibility. Extreme conditions of pre-treatment of coal samples could be readily distinguished but mild treatment showed an overlapping of characteristic observations. Two factors were believed to be the cause of the variation experienced in similar runs:

1. The thermocouple within the coal sample may not be located in exactly the same place from experiment to experiment.

2. Condensation of tar in the upper extremity of the reaction tube with subsequent "drain back" onto the sample may contribute a marked thermal effect.

Second Qualitative Apparatus

Utilizing the first hypothesis, another reaction vessel was constructed of vycor (high silica) glass with a fixed thermocouple well. In this apparatus, the tip of the thermocouple rested approximately in the center of the sample and was always in the same location. The coal sample was supported on a nickel screen upon which an asbestos mat had been laid. The drain back was eliminated by a removable pyrex header on the reaction tube by means of a graded vycor to pyrex joint. This section was wound with a sufficient length of #24 (B. & S.) gauge nichrome resistance wire to provide 100 watts of power at 35 volts. Heat from this maintained the exit portion of the tube at a temperature of 300° C.

To secure a more even distribution of radiant heat upon the sample the tube was wound with nichrome wire over the portion which contained the coal sample. Figure 6, page 56, shows this apparatus, with furnace open, after assembly for a determination. Figure 7, page 57, illustrates the tube with the nichrome resistance wire removed to show the thermocouple well.

The nitrogen and oxygen used in this system were supplied from standard high pressure cylinders. The gases passed through a reducer valve, a drying tube of activated alumina, and then through a manometer to the reaction vessel.

In addition, the nitrogen was passed through a chain of oxygen

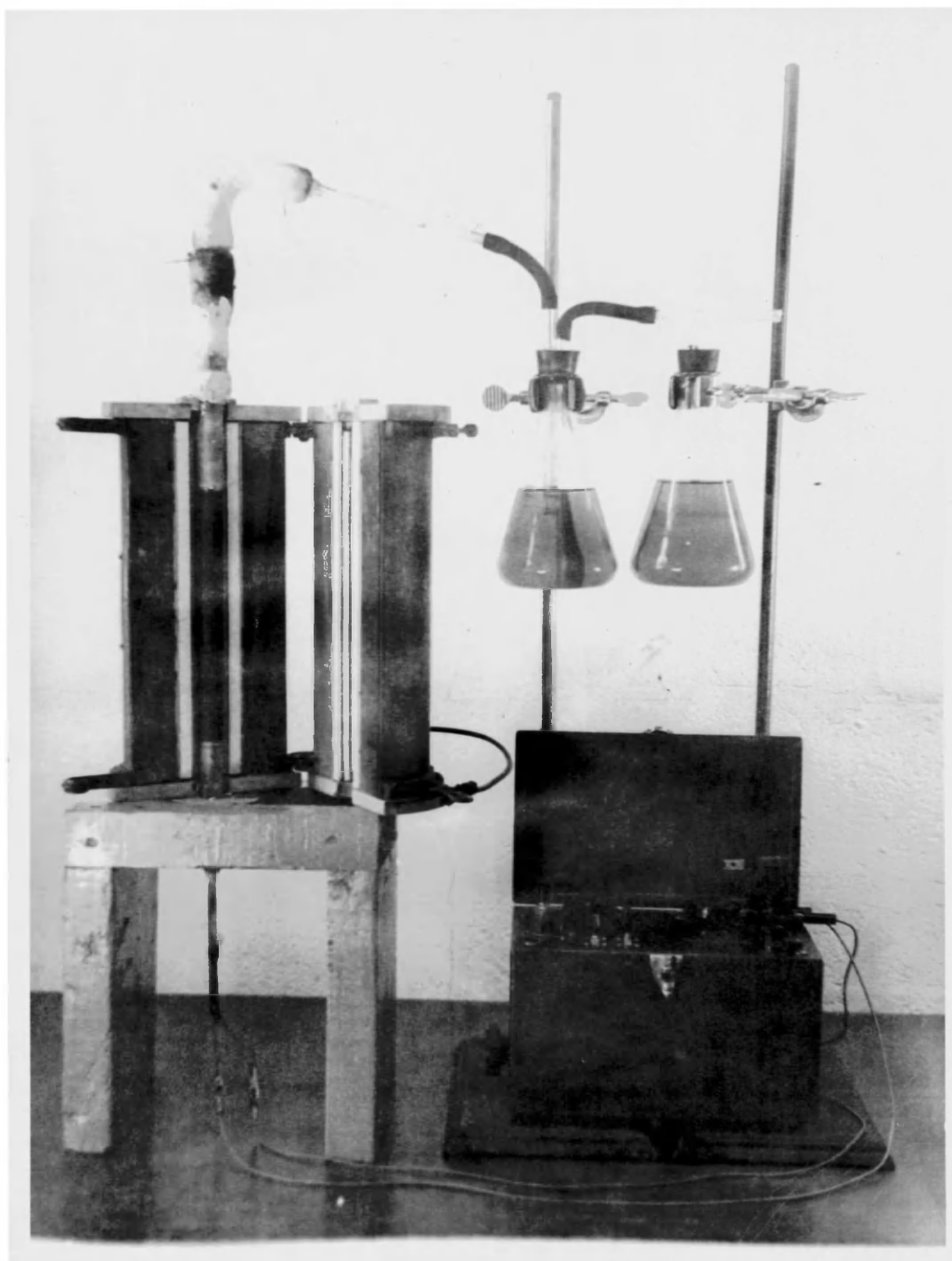


FIGURE 6

APPARATUS WITH PROVISION FOR CONDENSING TARS

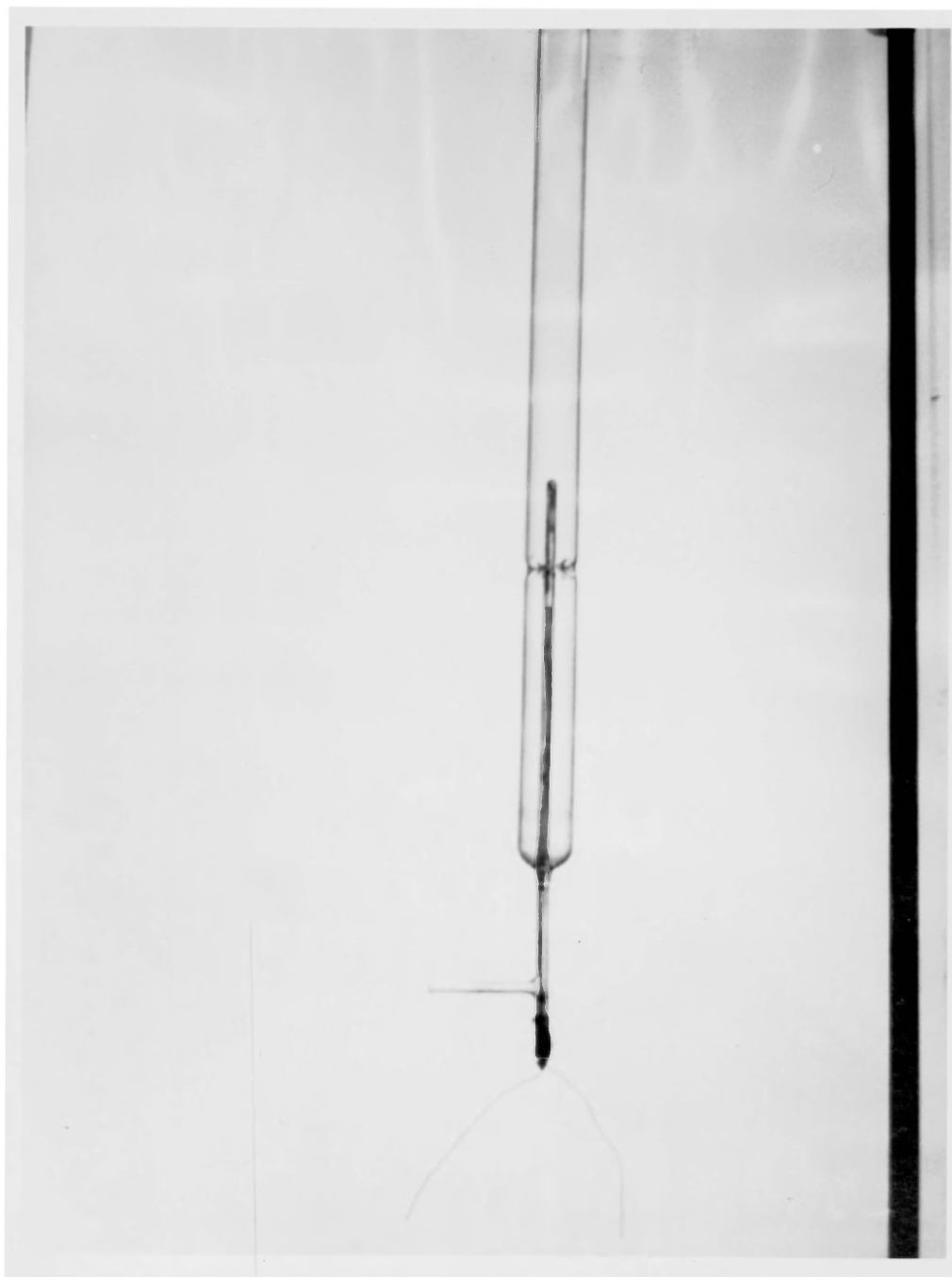


FIGURE 7

APPARATUS WITH NICHROME WIRE REMOVED TO SHOW
THERMOCOUPLE WELL

scrubbers containing potassium pyrogallate for removal of traces of oxygen.

Apparatus for Softening Point Determination

The apparatus for the determination of the softening temperature of the coal was based on the theory that any substance which passes from a granular state to a coherent mass by application of heat must pass through a molten or at least a pasty stage. The apparatus consisted of a pyrex glass tube 19 mm. in diameter with its reaction zone jacketed by a vertical tube furnace. A copper screen was provided in the center of the 12 inch long tube to support the coal sample. The furnace used for this determination is the same as that provided for the first qualitative thermal effect determinations. A thermocouple was located at the center of the sample for the measurement of temperature. A rubber stopper containing a six mm. pyrex tube was placed into the bottom of the 19 mm. tube. This tube led to a vessel of nitrogen which was under a constant water head of four feet. A water filled manometer was placed in this line between the gas flow and the atmosphere in order to measure any change in pressure during the determination. The increasing back pressure built up by the resistance to flow through the sample is an indication of a change in consistency of the coal sample.

Pretreatment Furnace

The furnace utilized for gaseous pretreatment of coal samples was fabricated from a three inch diameter aluminum bar, 12 inches in length. A 3/4 inch hole was provided through the center of this bar and tapped at each end for standard 3/4 inch pipe. A galvanized nipple was placed

at each end. The resulting tube was wound with sufficient #24 (B. & S.) gauge nichrome wire to give a total resistance of 100 ohms. Sheet asbestos was used as insulation between the aluminum and the nichrome.

To make accurate temperature control available at all times, a Fenwall thermostat (No. 471631) was connected in series with the furnace resistance and placed in a well which was drilled in the aluminum, parallel to the center hole. A well was provided in the mid-section of the cylinder so that a thermometer could be placed in the center of the coal sample. The sample was supported on a No. 200 copper screen which was placed in the center of the aluminum tube.

A 9 mm. pyrex tube, which led to a 250 ml. Erlenmeyer bubbling flask, was provided at the exit of the furnace through a rubber stopper. A similar tube was provided at the bottom of the furnace, leading to the source of oxygen, nitrogen, nitrous oxide, etc. An activated alumina drying tube was placed in the gas line before the furnace to insure removal of any water vapor present in the gas. Figure 8, page 60, is a photograph of this pretreatment furnace.

Operating Procedure for Equipment

First qualitative apparatus. This apparatus was used solely for determination of the heat effects for Pittsburgh bed, Westmoreland County coal. These coal samples were pretreated for various periods with oxygen, nitrogen and nitrous oxide.

A sample of ten grams of coal was placed in the quartz tube, which was positioned in the furnace, and the system was preconditioned to insure removal of oxygen. This was done by evacuating the tube to a vacuum of 28 inches Hg by means of a water aspirator. Dry nitrogen was then bled slowly into the tube in order to again achieve atmospheric

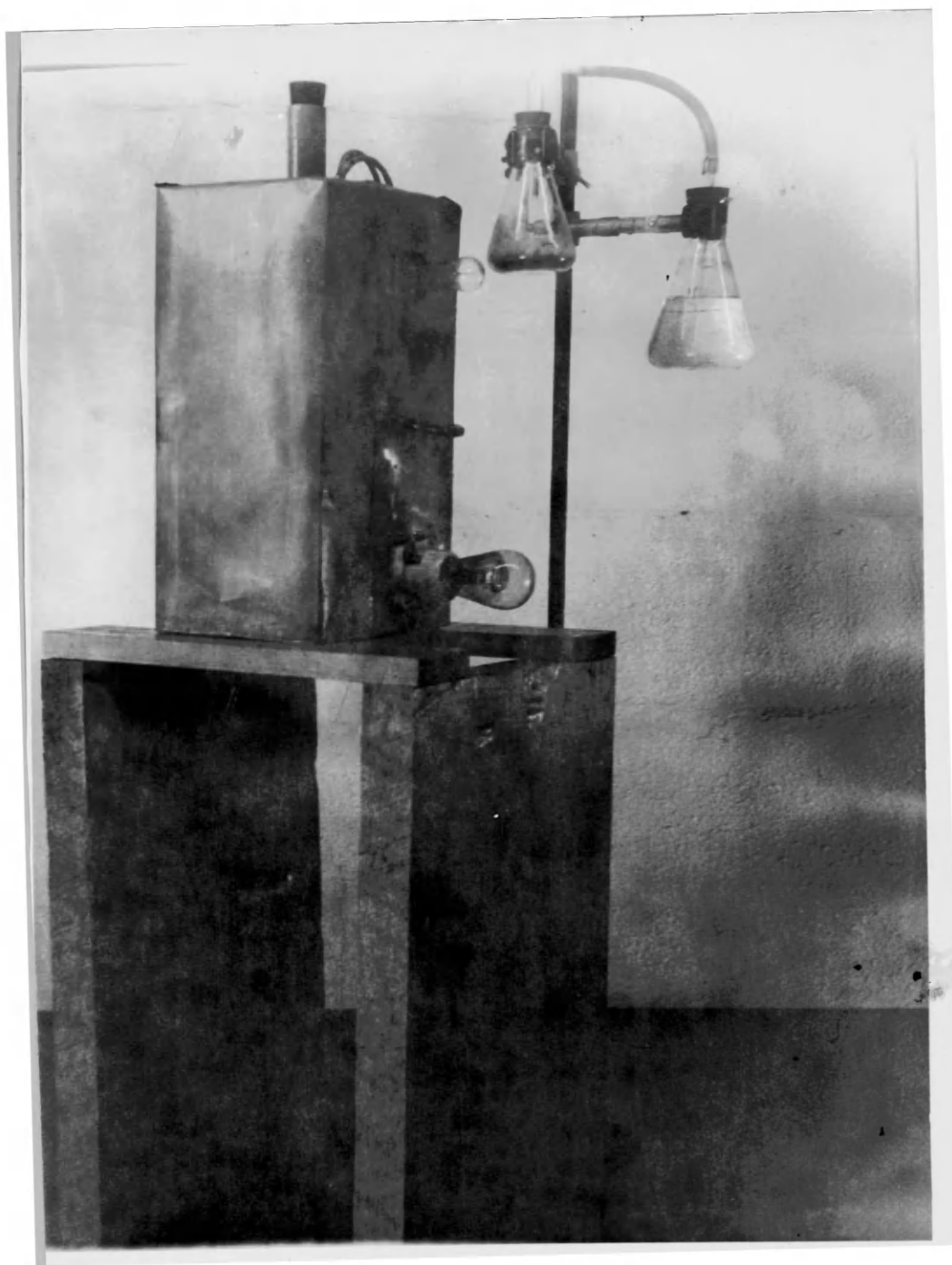


FIGURE 8

PRETREATMENT FURNACE

pressure and to provide a neutral atmosphere. A vacuum of three inches water was placed on the system by drawing from a water aspirator through the pressure regulator flask. This pressure was maintained throughout the determination. The sample tube was heated at a constant furnace voltage of 115 volts (A. C.) over the temperature range of 25° to 700° C. The heating operation required approximately twenty-five minutes.

Upon completion of the heating period, the quartz tube was removed from the furnace and allowed to cool to ambient temperature. Readings of the temperatures were made at thirty second intervals throughout the run. Leeds and Northrup portable potentiometers were used for these temperature measurements.

Second Qualitative Apparatus. The operation of this apparatus is quite similar to that of the previous one. The primary differences are the preconditioning used and the effect of the modification incorporated to compensate for condensing tars.

A sample of ten grams of coal was placed on the asbestos mat provided in the vycor tube. The tube was then set in the furnace and the system was evacuated to a vacuum of 28 inches Hg by use of a water aspirator. Nitrogen was then bled in slowly until atmospheric pressure was attained. A purge period was then provided wherein dry nitrogen at the rate of 0.93 cubic feet per hour was passed up through the coal sample. This purge was of twenty minutes duration. Upon completion of the purge, the current to the heating coil at the upper extremity of the tube (35 volts A. C.) was turned on. This heating was continued for twenty minutes before the determination began in order to attain a temperature of 300° C. in this section of the apparatus. During this period of heating a vacuum of three inches water was placed on the

system through the pressure regulator tube, and this pressure was maintained throughout the determination.

After the forty minute preliminary conditioning and preheating period, the sample tube was heated by a constant voltage of 115 volts A. C. As in the case of the first qualitative apparatus the heating operation required approximately twenty-five minutes. Readings of the potentiometer were made at thirty second intervals.

Apparatus for Softening Point Determination. A ten gram sample of coal was placed on the copper screen provided in the pyrex tube. A purge was provided during which 0.1 cubic foot of nitrogen was passed up through the coal sample to insure removal of air. At the end of this purge period the sample was heated by a constant furnace voltage of 115 volts A. C. from room temperature to a temperature of approximately 100° C. above the temperature at which the plastic zone appeared. Thermocouple readings and gas pressure readings were taken at thirty second intervals. The point at which the gas pressure reached its peak was taken as the point of maximum fluidity. The greatest resistance to the flow of nitrogen occurred as the material passed from the porous to the viscous condition. At higher temperatures, the material again became porous and the resistance to flow diminished.

Pretreatment Furnace. The pretreatment furnace required a "warm-up" period of approximately two hours prior to its use. The primary reasons for this were the large heat capacity of the aluminum tube and the high resistance of the furnace windings. This type of furnace was chosen because it was conducive to close temperature control. After attaining the desired temperature, fifteen grams of coal were weighed

and placed in the furnace. The sample was allowed to stand for twelve minutes in order to reach the furnace temperature.

At the completion of this period, the gas which was being used for pretreatment was turned into the bottom on the unit. The exit gas passed into a bubbling bottle, then it was released to the atmosphere. In cases where corrosive gases were utilized the material was neutralized or absorbed after leaving the furnace. At the end of this pretreatment period the sample was removed and placed in bottles, sealed, and cooled to room temperature.

B. ANALYTICAL PROCEDURES

Carbon and Hydrogen Determinations

Only brief mention will be made of this method of determination inasmuch as it is given in detail in A.S.T.M. D 271-48. The determination was made by combustion of a weighed quantity (0.2 g.) of sample in a standard combustion furnace. The products of combustion were thoroughly oxidized by passing them over red-hot CuO and Pb CrO_4 . They were then cooled and absorbed in standard U-tubes. Moisture was absorbed with granular calcium chloride and the carbon dioxide was absorbed by a combination of soda-lime and calcium chloride. Calcium chloride was placed in the exit leg of the U-tube to prevent loss of water formed by the reaction of soda-lime and carbon dioxide.

The purifying train used consisted of the following purifying reagents arranged in order of passage of air and oxygen through them: H_2SO_4 , KOH solution, soda-lime, and granular CaCl_2 .

The calibration of this apparatus was carried out on reagent grade

benzoic acid. The data obtained were closely reproducible and in agreement with the standard values.

Nitrogen Determination

The method used for nitrogen was a modification of the standard Kjeldahl-Gunning method (A.S.T.M. D 271-48). It is believed that much of the nitrogen was in the nitro or nitroso form, hence the standard procedure, which is primarily for amino nitrogen, was modified.

A one gram sample of coal was placed in a standard Kjeldahl digestion flask, five ml. of hydriodic acid, sp. gr. 1.7, were added and the mixture was gently boiled for 45 minutes. The mixture was then vigorously boiled until the volume was reduced appreciably. After cooling, five ml. of concentrated sulphuric acid, 5 ml. of water and 7-10 g. of K_2SO_4 were added and the mixture was heated to distill out the water and to liberate iodine. The mixture was cooled, another 5 ml. of water were added and the water and iodine were again distilled off. This process was continued until no more iodine was apparent. This procedure insured that the nitrogen was in the reduced form. At the end of the preliminary treatment 0.6 g. of mercury and 30 ml. of concentrated sulphuric acid were added. From this point the analysis was similar to the standard method and will not be described further.

Volatile Matter Determinations

The volatile matter determinations were made with standard prescribed equipment as set forth in A.S.T.M. D 271-48. Platinum crucibles of 10 ml. capacity, 25 mm. diameter and 30 mm. height were used. The furnace used was an electrically heated, muffle type (Hoskins Type FA120).

The heating cycle used was somewhat different than that prescribed

by the A.S.T.M. method. This change was made to obtain a coke sample that would be more representative of that produced by the heating cycle utilized in the carbonization studies herein described.

A one gram sample of coal was weighed into the platinum crucible, closed with a cover and placed in nichrome wire supports in the furnace chamber. The temperature of the furnace was at 1200° F. when the sample was inserted and 1400° F. at the end of the 8 minute heating period.

The sample was removed from the furnace at the end of this time, cooled and weighed.

SECTION II

OXIDATION EXPERIMENTS USING OXYGEN AND NITROUS OXIDE

The treatment of coal with oxygen has been discussed to some extent in Part I, Section V. The fact that coal is changed markedly by heating in the presence of oxygen has been studied extensively in the hope of obtaining valuable products such as organic acids (14, 15). Oxygen is a relatively inexpensive reagent and is known to have considerable effect on coal. These considerations led to its selection as the first reagent studied in this research.

The coal used for these experiments was supplied by the Pittsburgh Station of the U. S. Bureau of Mines. The analysis is given in Table 6, Page 67. All coal samples were sized to pass a No. 60 U. S. Standard Sieve and be retained on a No. 100 U. S. Standard Sieve.

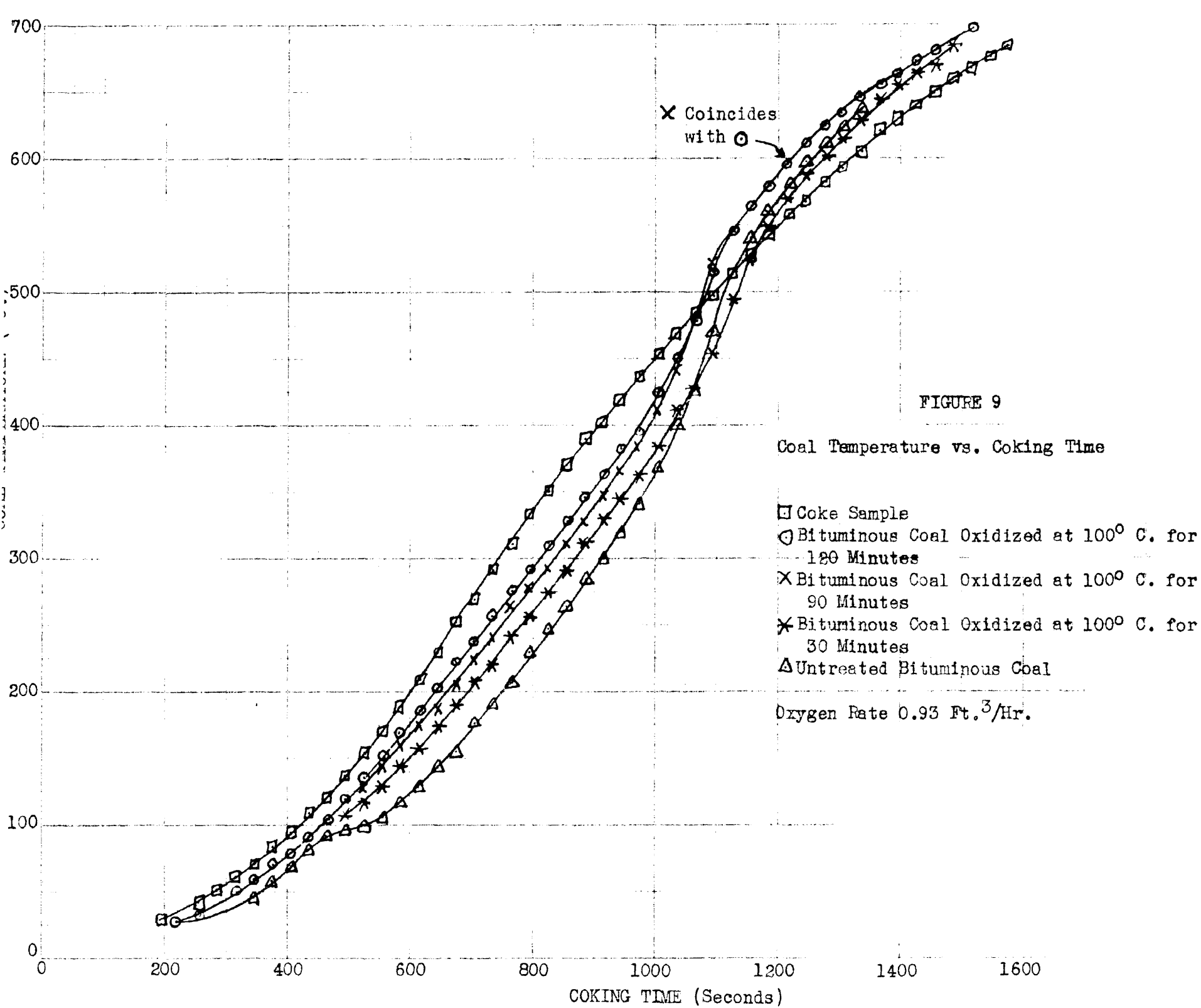
Samples containing 15 grams of coal were oxidized at 100° C. with an oxygen rate of 0.93 cubic feet per hour for periods of 30, 90 and 120 minutes respectively. The results of the carbonization tests on these samples are shown in Figure 9, page 58, which is a plot of coal temperature vs. the time which has elapsed during the carbonization. The carbonization was carried out in the first qualitative apparatus described in Part II, Section I, which is similar to that used by Davis and Place (9) in their experiments. An untreated coal sample and a sample of coke were also heated through this same temperature range for comparison purposes.

In the instance of the untreated coal sample, a sharp decrease in heating rate is observed at 100° C. The trends in the curves indicate that below the plastic zone the oxygen pretreatment decreases the effect

TABLE 6. Coal Analysis Report (U. S. Bureau of Mines)

State: Penna.; County: Westmoreland; Bed: Pittsburgh; Town:Suterville.

	Air Dried	As Received
Moisture	1.3	2.2
Volatile matter	34.8	34.5
Fixed carbon	57.6	57.1
Ash	6.3	6.2
Hydrogen	5.3	5.4
Carbon	78.8	78.0
Nitrogen	1.6	1.6
Oxygen	7.1	7.9
Sulphur	.9	.9
Heating Value (BTU)	14,020	13,890
Specific Gravity	1.32	



of the endothermic reactions, inasmuch as the curves approach that of coke upon longer exposure of the coal to oxygen. The plastic zone for this coal begins at 412° C. and continues through 470° C., with the point of maximum fluidity at 435° C. This is shown graphically in Figure 10, page 70. The method of determination has been described in Part II, Section I, page 58.

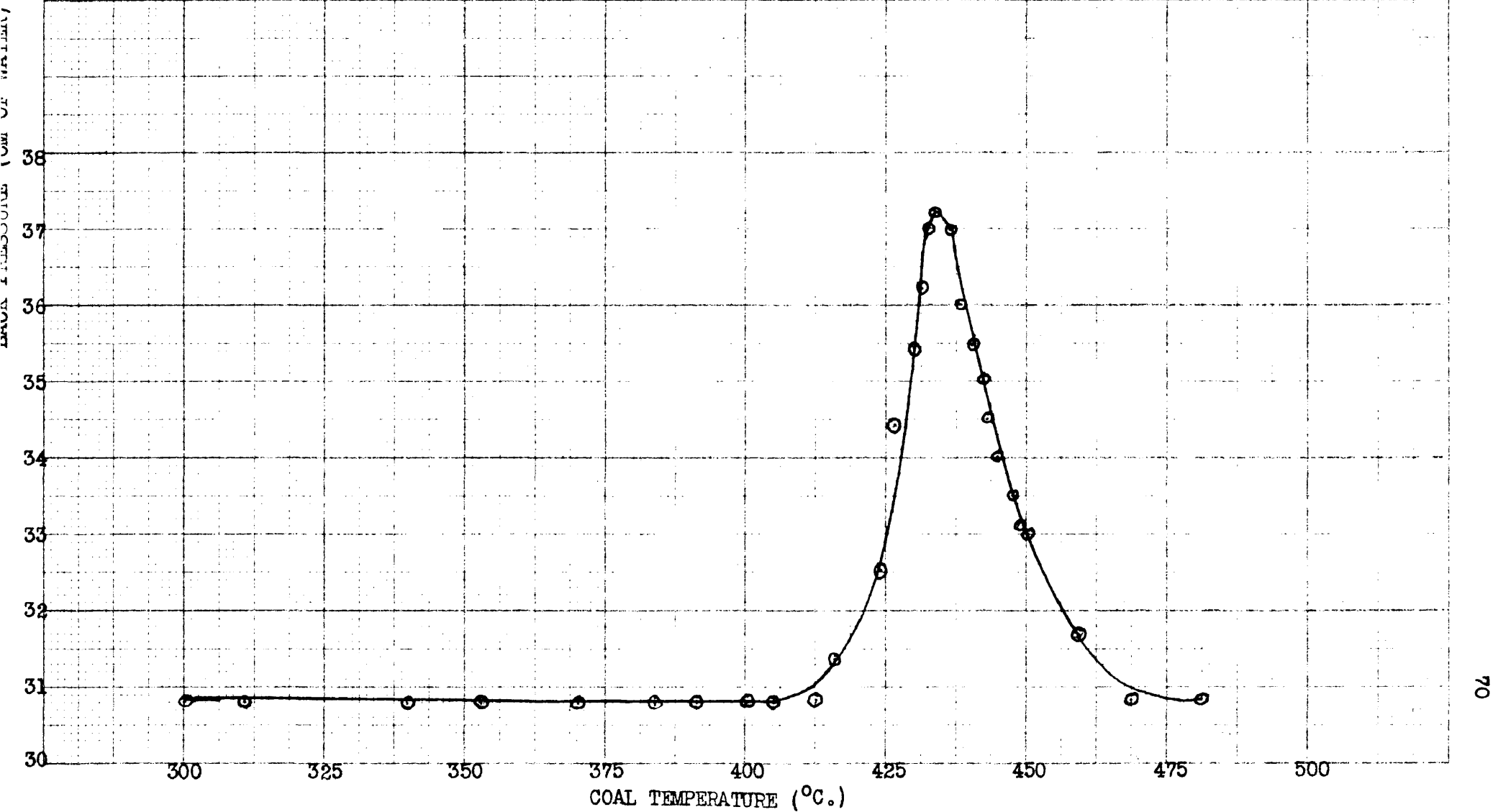
After the more prolonged oxidation treatment, the rate of heating above the plastic zone is greater than for the untreated sample. These results indicate that decompositions liberating heat begin at temperatures as low as 375° C. and continue to a limited extent throughout the carbonization process. These exothermic effects undoubtedly nullify the endothermic effects of other reactions occurring within the coal mass.

Mid-temperature coke buttons were made from these oxygenated samples. Much more compact and stronger cokes were obtained by the oxidations. The coke of the sample treated for 120 minutes was of exceptionally good quality.

These experiments suggested that a more profound oxidation of the samples might be desirable. The method previously used was modified in an effort to improve the reproducibility of results. The modified procedure involved the reheating of the coke sample obtained from each run with the same furnace voltage as utilized in carbonization. The temperature difference between the coal sample and the coke at corresponding furnace temperatures was determined. The temperature of the coke was made a baseline and plots were made of temperature difference vs. time. For all points on the curves below the coke baseline, a change in slope toward this line indicates exothermic reactions predominating, while a divergence from this line indicates that endothermic reactions

FIGURE 10

Plastic Zone Determination
Back Pressure vs. Coal Temperature



are predominant.

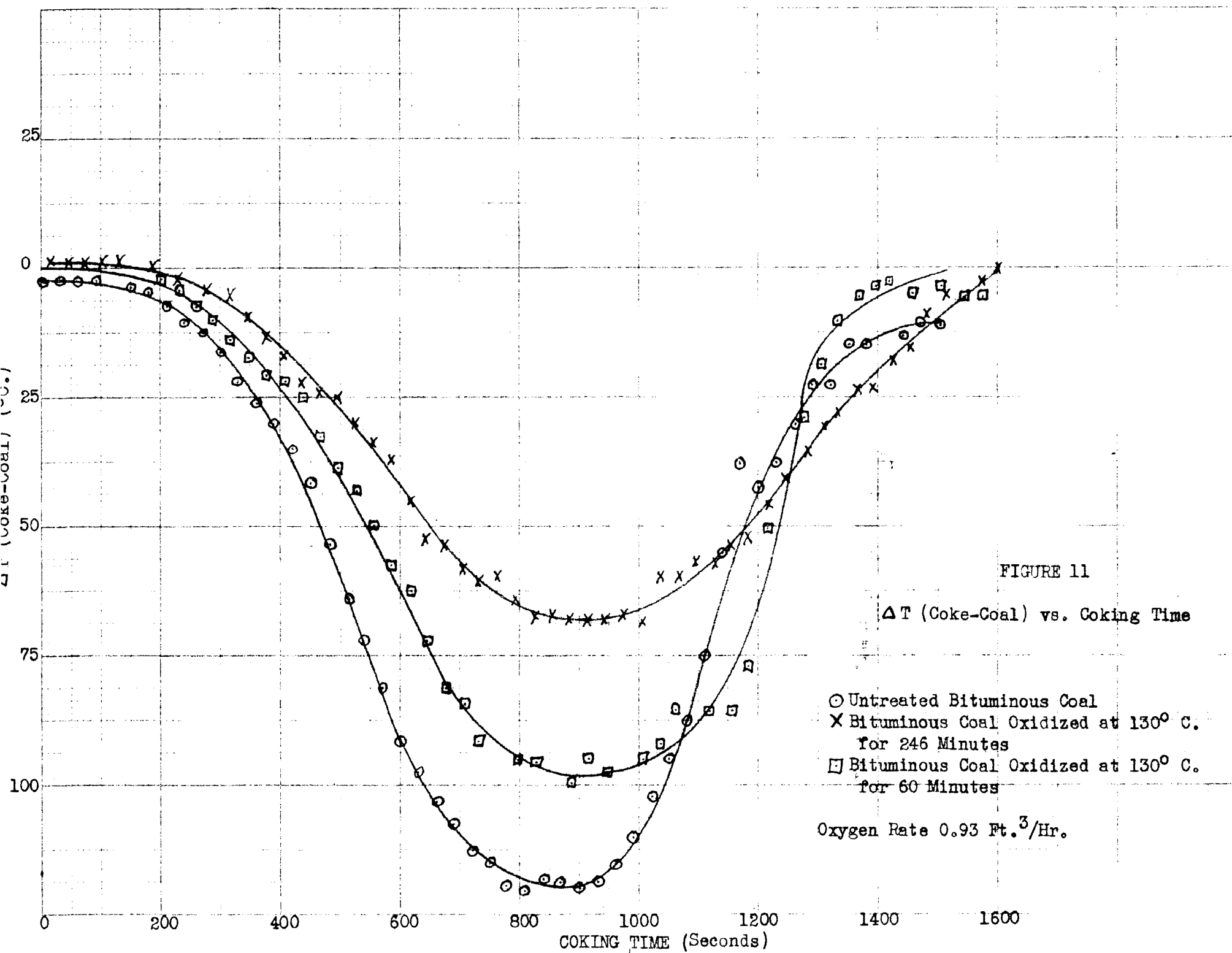
Samples of coal were treated in oxygen atmospheres for periods of one, two and four hours at 130° C. The results of the carbonization tests on these samples are given in Figure 11, page 72. Treatment was also effected in nitrous oxide for one and five hours respectively. The results of the carbonization tests on these samples are shown in Figure 12, page 73. The purposes of these pretreatments were:

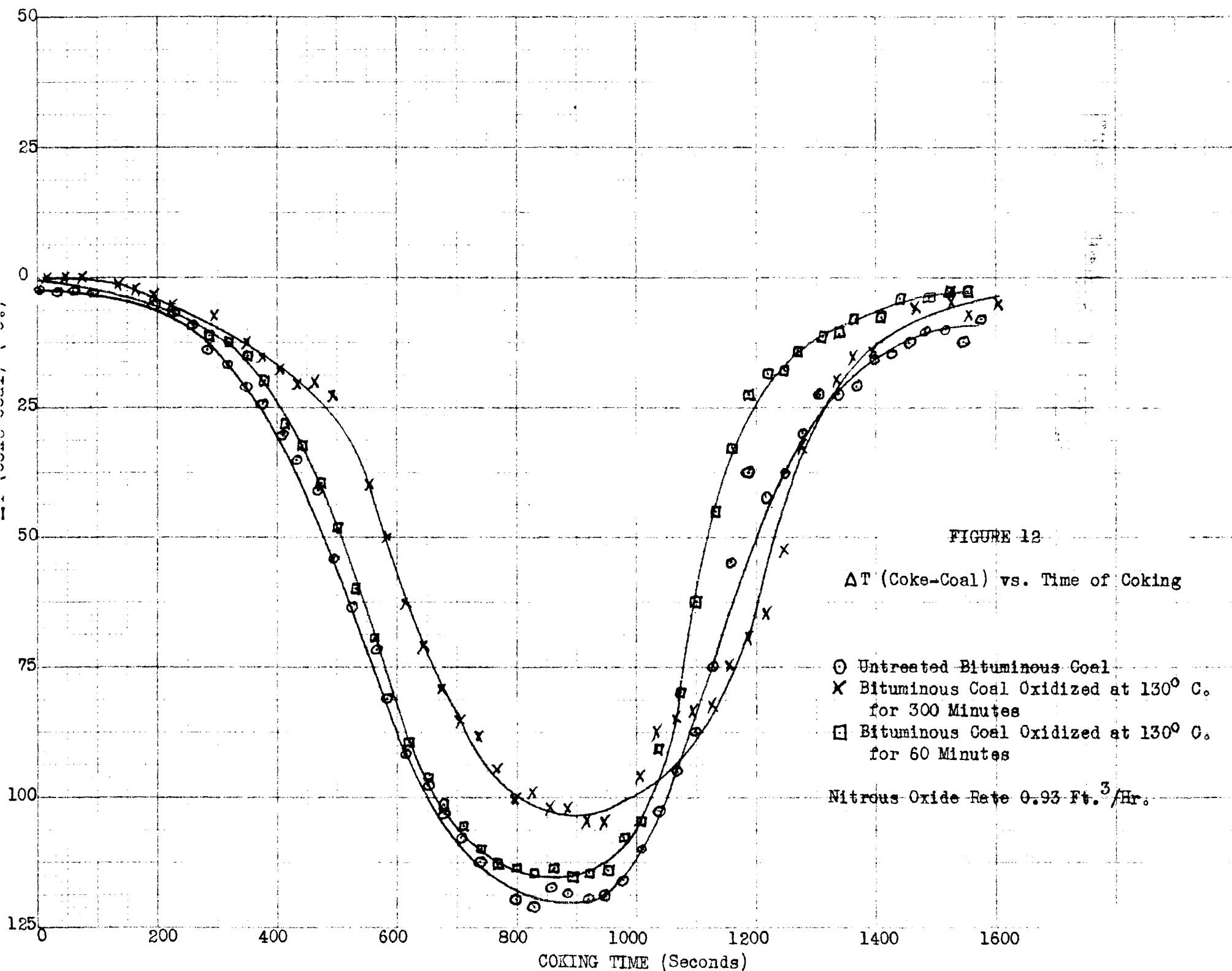
1. To adsorb oxygen physically and chemically in such a way that upon coking sufficient heat would be liberated at the coal particle by reaction of the oxygen with certain hydrocarbons to cause local overheating which would tend to break down the complicated long chain aromatic linkages and so initiate the coking reactions at a lower external temperature.

2. To weaken during the pretreatment process the chain linkages of the coal molecules.

In addition to the oxygen and nitrous oxide pretreatments, samples were also treated with aqueous solutions of ammonium nitrate, ammonium persulphate, and potassium fluoride. The solutions consisted of 0.8 g. of the appropriate salt dissolved in 10 ml. of water. This solution was mixed with 15 g. of coal. An aqueous solution was used to secure as intimate a contact of the reagent with the coal as possible. The resulting suspension was evaporated to dryness at 112° C. It was hoped that the ammonium nitrate, upon thermal decomposition at a relatively high temperature, would result in the liberation of nitrous oxide and oxygen which would readily react with the more highly activated coal substance.

As can be seen in Figure 12, the results obtained with oxygen





pretreatment for one hour show moderate deviations from the untreated coal. The results for the sample pretreated for two hours do not differ appreciably from those of the one hour pretreatment and have not been plotted. The four hour oxygen pretreatment resulted in a much faster heating rate up to furnace temperatures of approximately 450° C. The major exothermic trends in all cases occurred between 350° and 600° C. The coke samples obtained show an increase in quality within the range of pretreatment utilized. The coke obtained from the sample treated with oxygen for four hours actually resembles that produced at much higher temperatures.

The thermal effects during carbonization for the coal samples treated in nitrous oxide atmospheres show only small deviations from the untreated coal and the resulting coke was very weak structurally due to its high porosity. The thermal effects in the samples treated with ammonium nitrate, potassium fluoride and ammonium persulphate are nearly identical with the untreated coal, and hence are not shown on separate plots. The coke sample produced in the case where ammonium nitrate was used is about the same grade as untreated coal; however, those resulting from samples pretreated with potassium fluoride and ammonium persulphate were of an inferior quality.

It appeared that the temperature of the pretreatments given these coal samples might not have been sufficiently high to activate the coal molecules. Inasmuch as occluded gases and water of constitution begin to be evolved at temperatures in the vicinity of 150° C., this was believed to be a desirable temperature for pretreatment because the removal of other adsorbed gases would give the oxygen a greater chance of reaction

with the coal. The removal of water of constitution may also result in a weakening of the chain linkages and so permit the oxygen to enter the molecule with greater ease.

There is much discussion in the literature concerning the heating of the coal during carbonization. It seems to be a general consensus that the faster heating rates produce the best quality of coke. Some writers have stated that the plastic property is practically nullified if the rate of heating is unduly long. Utilizing this general principle, coal samples were pretreated at 150° C. for various periods of time in an oxygen atmosphere, then placed in the quartz reaction vessel. The quartz vessel was plunged into a furnace which was already at 638° C. A standard time of eight minutes was given the carbonization; hence not all the samples reached the same ultimate temperature due to the difference in thermal conductivity and thermal effects occurring within the coal sample itself. The heating rates which resulted from this experimental procedure were so great that thermal effects were so masked that no conclusive data could be obtained. In addition to these pretreatments, a two-hour heat pretreatment was given to a sample of coal at 150° C. The results of these pretreatments on coke structure are given in Table 7, page 76.

It is doubtful whether the increase of coke quality upon heating in oxygen for periods of one, two and three hours is a result of any weakening of the bond structures of the coal. It would rather seem that it is actually a partial destruction of the excess bitumens in the coal substance. Upon further oxygen treatment it is seen that the bonding constituents are completely destroyed.

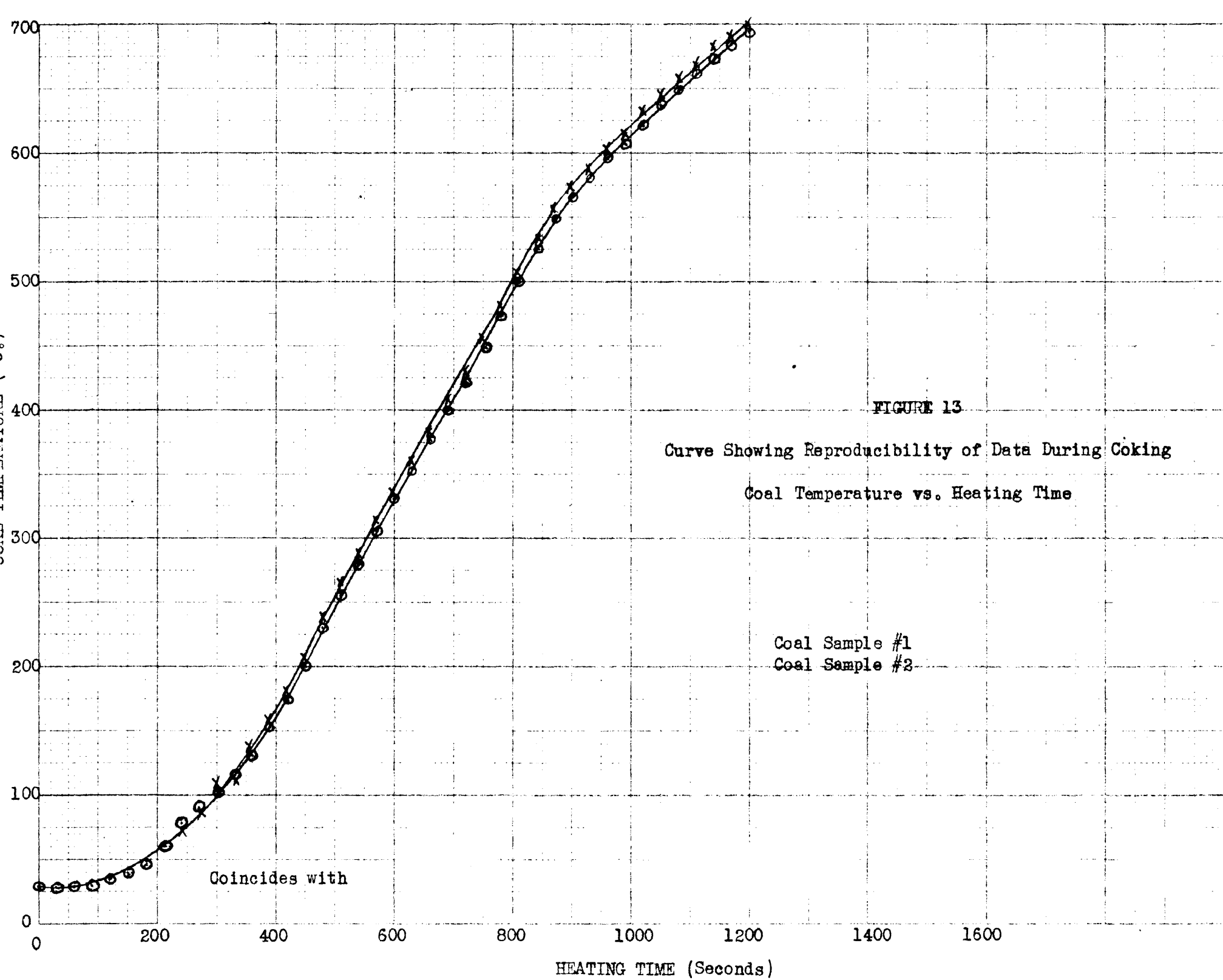
TABLE 7. Result of Pretreatment with Oxygen on Coke Structure
Utilizing a Rapid Method of Heating.

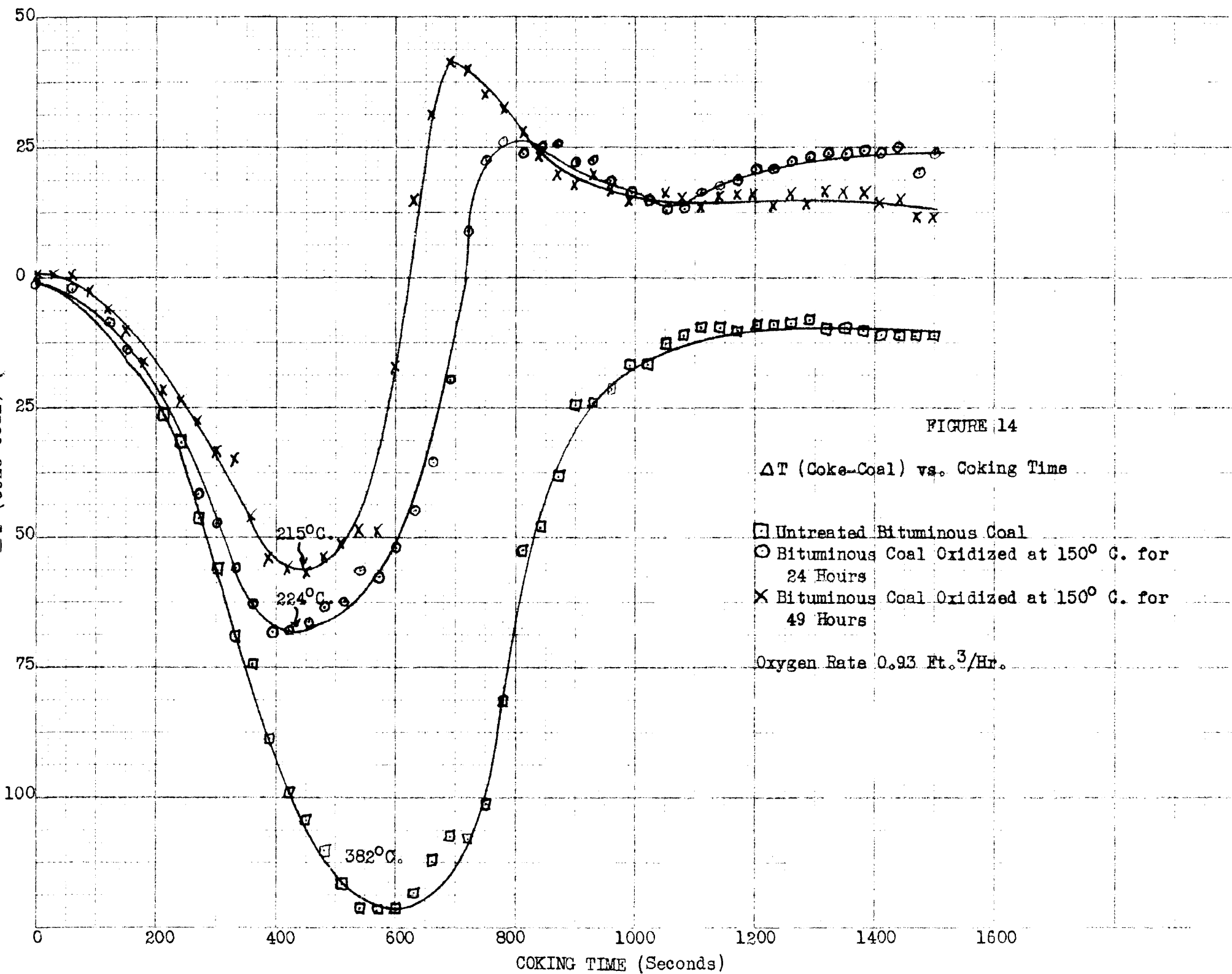
Pretreatment	Quality of coke
1. None	Fluffy coherent mass of very porous structure
2. 2 hr. heat treatment (150° C.)	More dense and less porous than above
3. 1-1/2 hr. O ₂ treatment (150° C.)	More dense than with only heat treatment
4. 2 hr. O ₂ treatment (150° C.)	Good quality coke. quite dense and strong
5. 3 hr. O ₂ treatment (150° C.)	Same as above
6. 4 hr. O ₂ treatment (150° C.)	No coke (bonding property destroyed)

Utilizing this rapid heating method, samples were coked after treatment with ammonium nitrate, aluminum chloride and cobaltous chloride, respectively. The treatment was made with 15 g. of coal and 0.2 g. of salt in aqueous solution with subsequent drying at 112° C. The results indicated no apparent change in coke structure and, as before, the heating rates were so rapid that the thermal effects were unduly masked.

These preliminary experiments suggested that the degree of reproducibility could be increased by certain changes in the qualitative apparatus. As has previously been noted, the overlapping of data after the plastic zone was believed due to condensing tar and difficulty in locating the thermocouple in exactly the same position during each run. The results of the changes made to compensate for these difficulties can best be shown by two identical heating cycles carried out on identical untreated coal samples. These are shown in Figure 13, page 78. A small deviation might be expected since it is extremely difficult to obtain exactly similar samples from such a heterogeneous system.

Samples of Pennsylvania bituminous coal were treated in oxygen atmospheres for periods of twenty-four and forty-nine hours at 150° C. with an oxygen rate of 0.93 cu. ft. per hour. The samples were carbonized in the modified apparatus and the results of these studies are given in Figure 14, page 79. It is seen that strong exothermic reactions begin respectively at 215° C. and 224° C. The strong exotherm for the untreated coal sample shown for comparison does not begin until a temperature of 382° C. is reached. The sharp change in slope of the heating rate curve for these oxidized samples after the initial strong exotherm would indicate an endothermic predominance which decreases the rate of heating of





the coal with respect to the rate of heating of the coke sample. This is believed not to be the case in this instance. The initial strong exotherm has carried the temperature of the sample to such a high value, that upon the decrease of the exotherm, the temperature difference between the furnace walls and the coal is small compared to that of the inert coke sample. As a result of this fact, the coke sample heats more rapidly than the coal being coked.

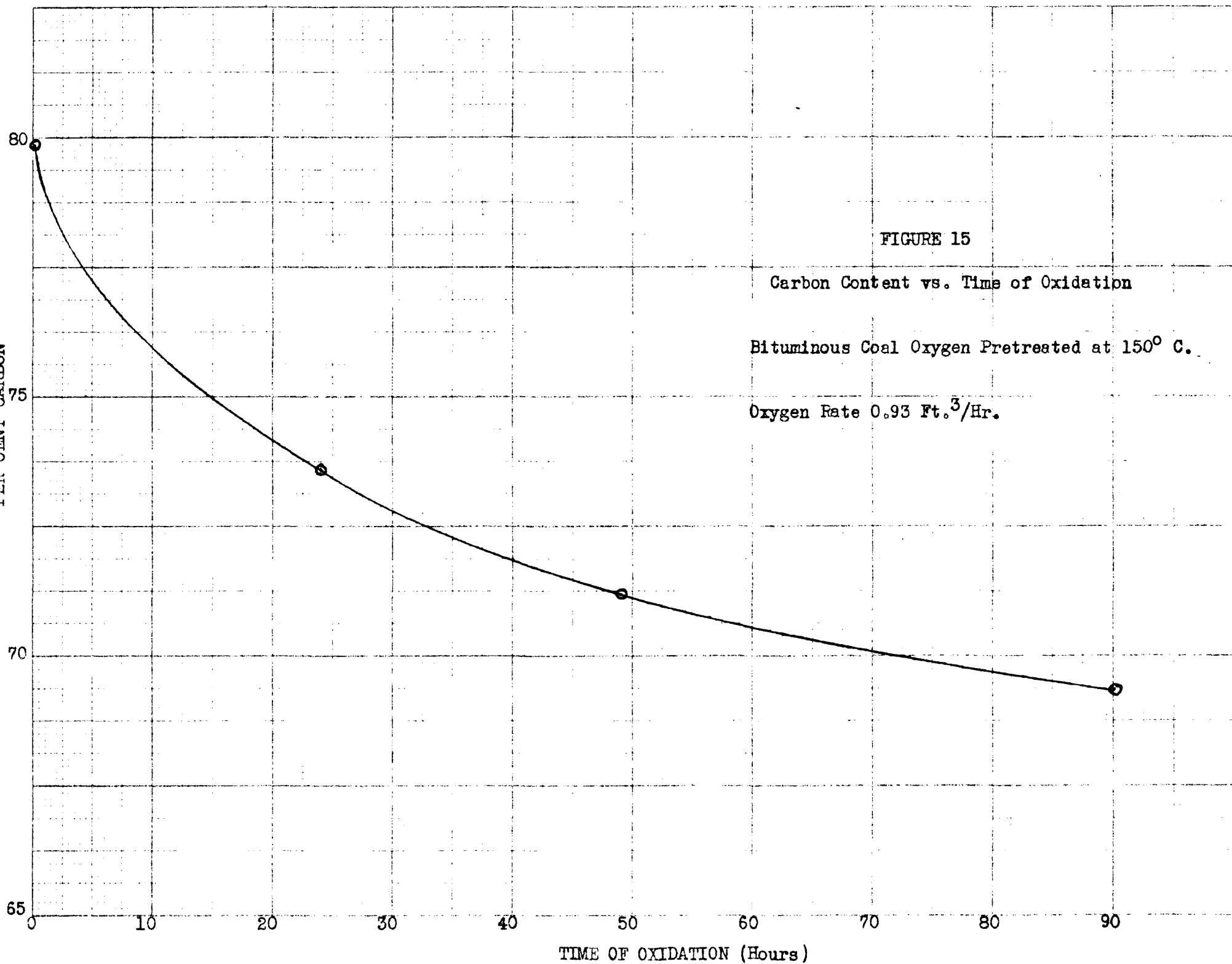
This condition continues until a point where the temperature of the two samples are approximately the same value, at which time the exothermic effects of decomposition again begin to predominate. This is indicated by another change in sign of the slope of the heating rate curve.

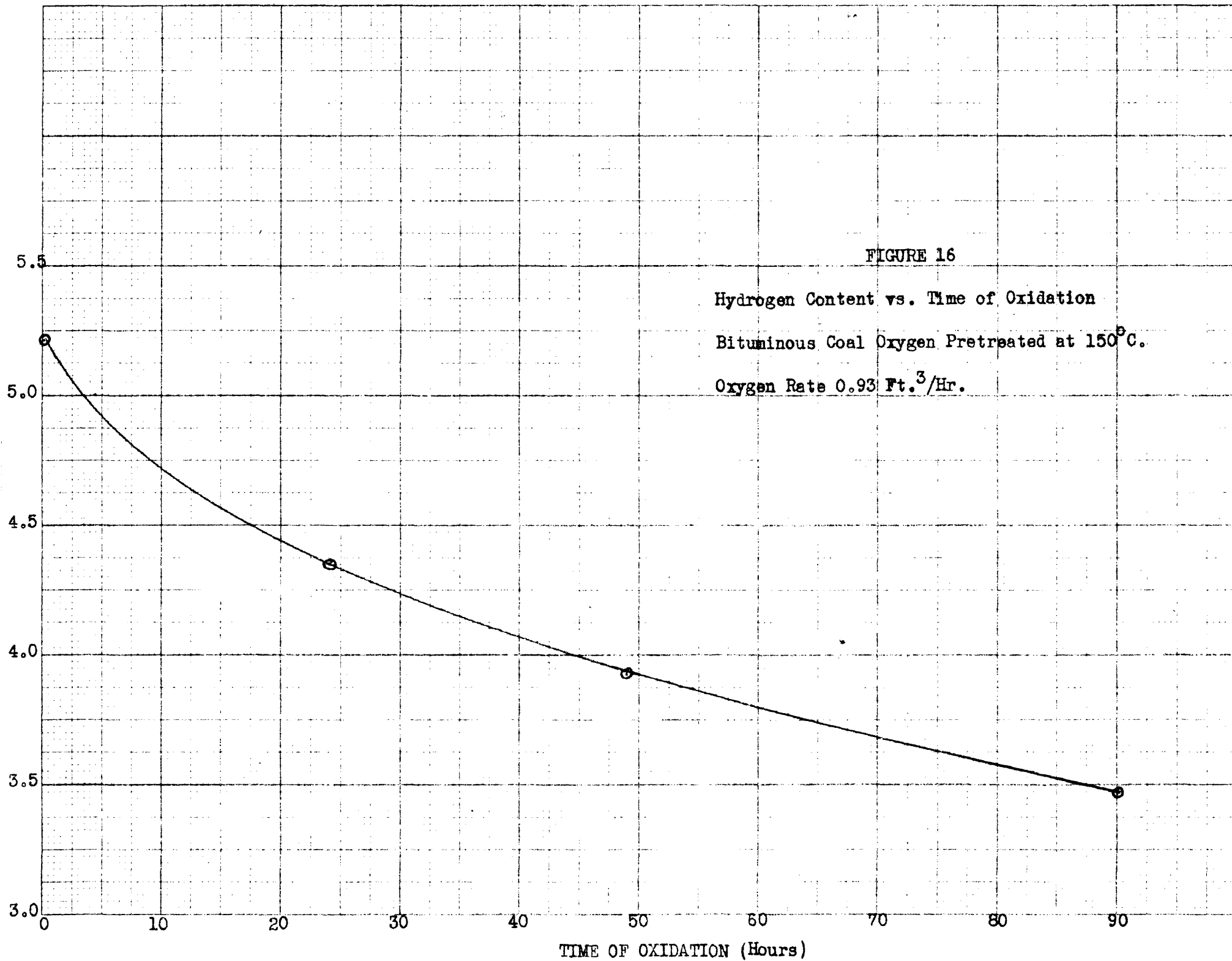
From this carbonization data it can be also seen that the stability of the oxygen treated coal is an inverse function of the degree of oxidation.

Figures 15, page 81, and 16, page 82, indicate the change in carbon and hydrogen analyses respectively for the oxidations at 150° C. At temperatures in excess of 150° C. it becomes very difficult to carry on controlled oxidations of bituminous coal in an oxygen atmosphere. Controlled oxidation was attempted at higher temperatures but ashing of the samples resulted.

The experiments thus far described indicate that the thermal reactions occurring during carbonization can be altered by a preliminary oxygen treatment of the coal. In addition, it is concluded that oxidation up to a certain critical point increases the quality of the coke that can be produced from a bituminous coking coal. After this point is reached, further oxidation is detrimental to coke structure.

PER CENT CARBON

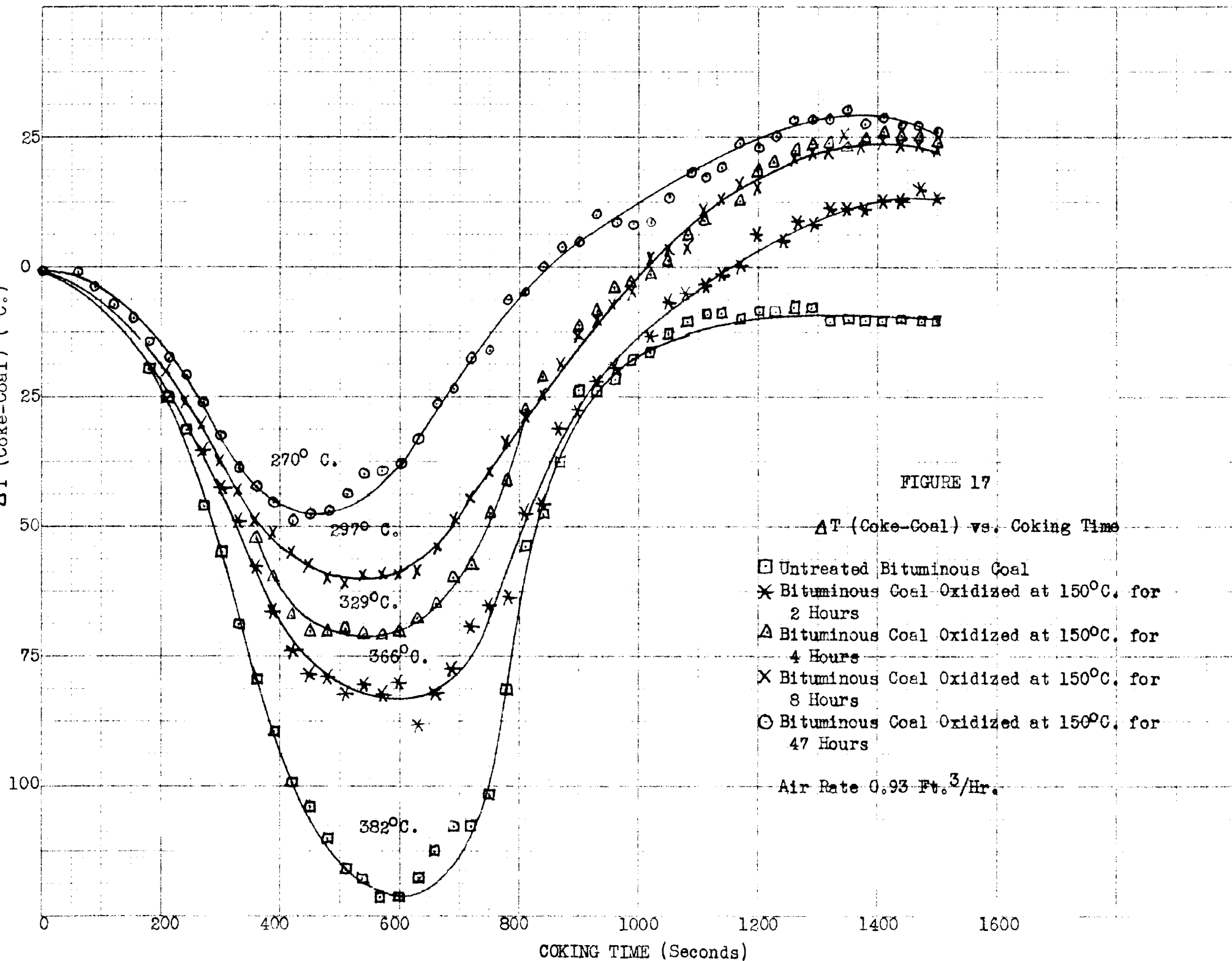




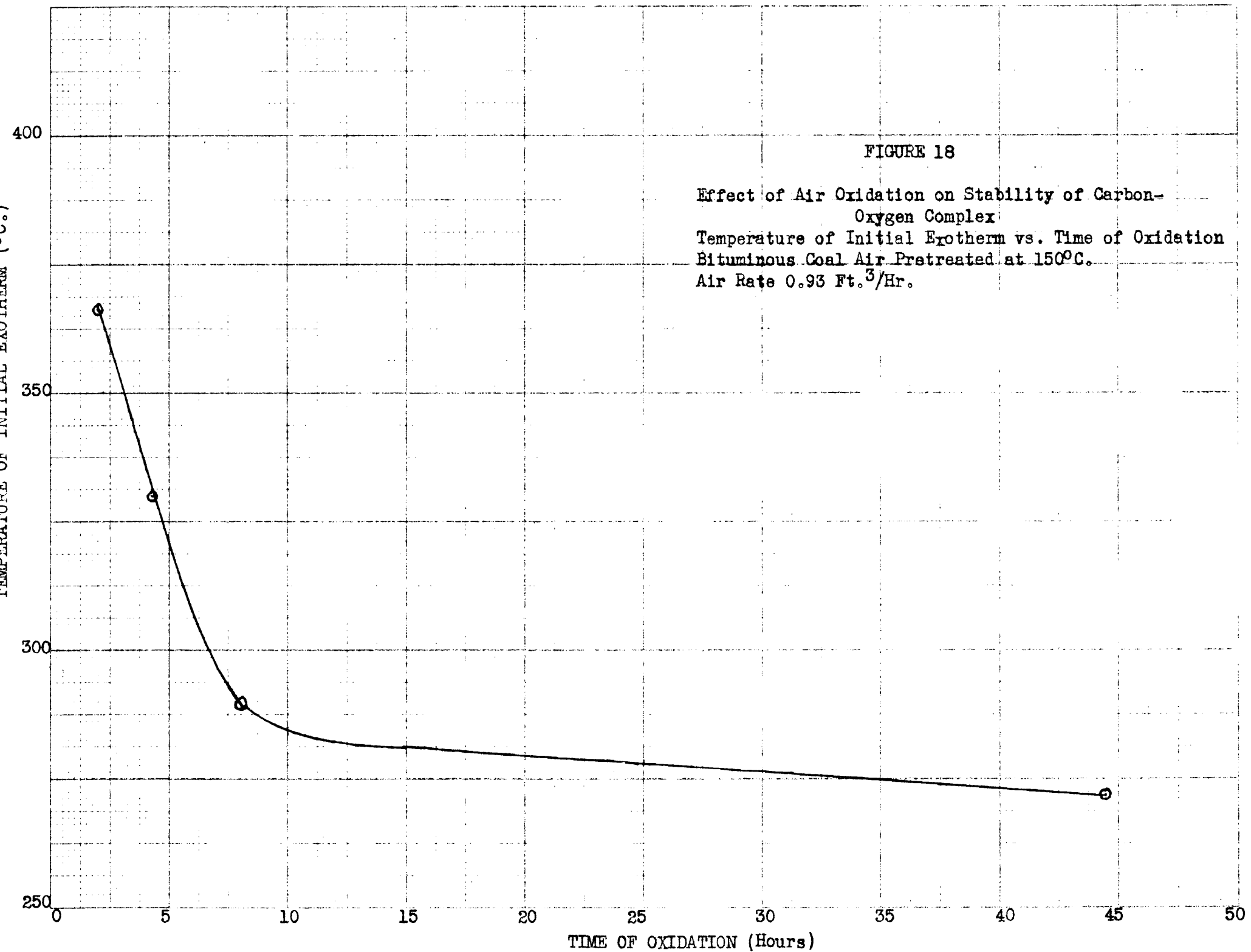
SECTION III

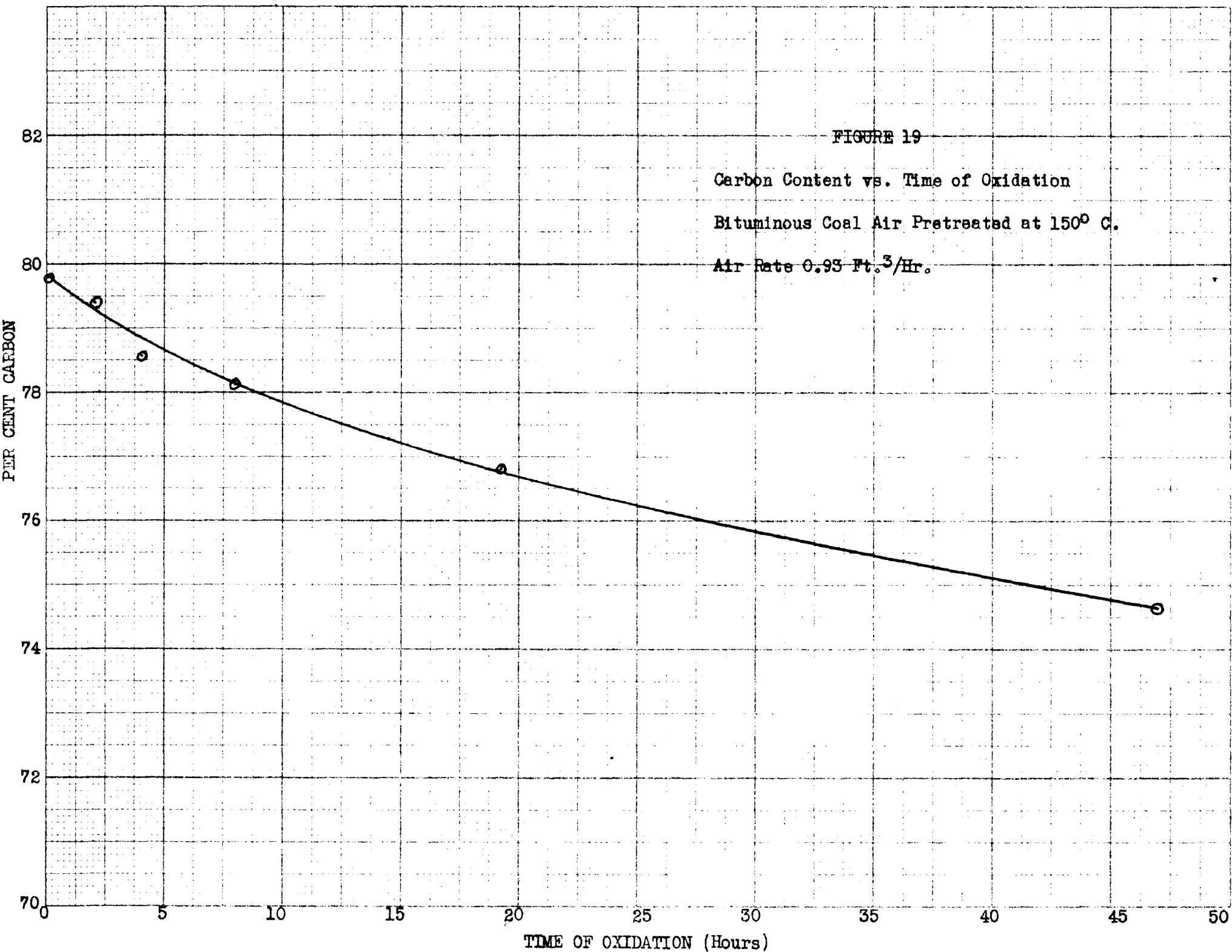
EXPERIMENTS WITH AIR OXIDATION

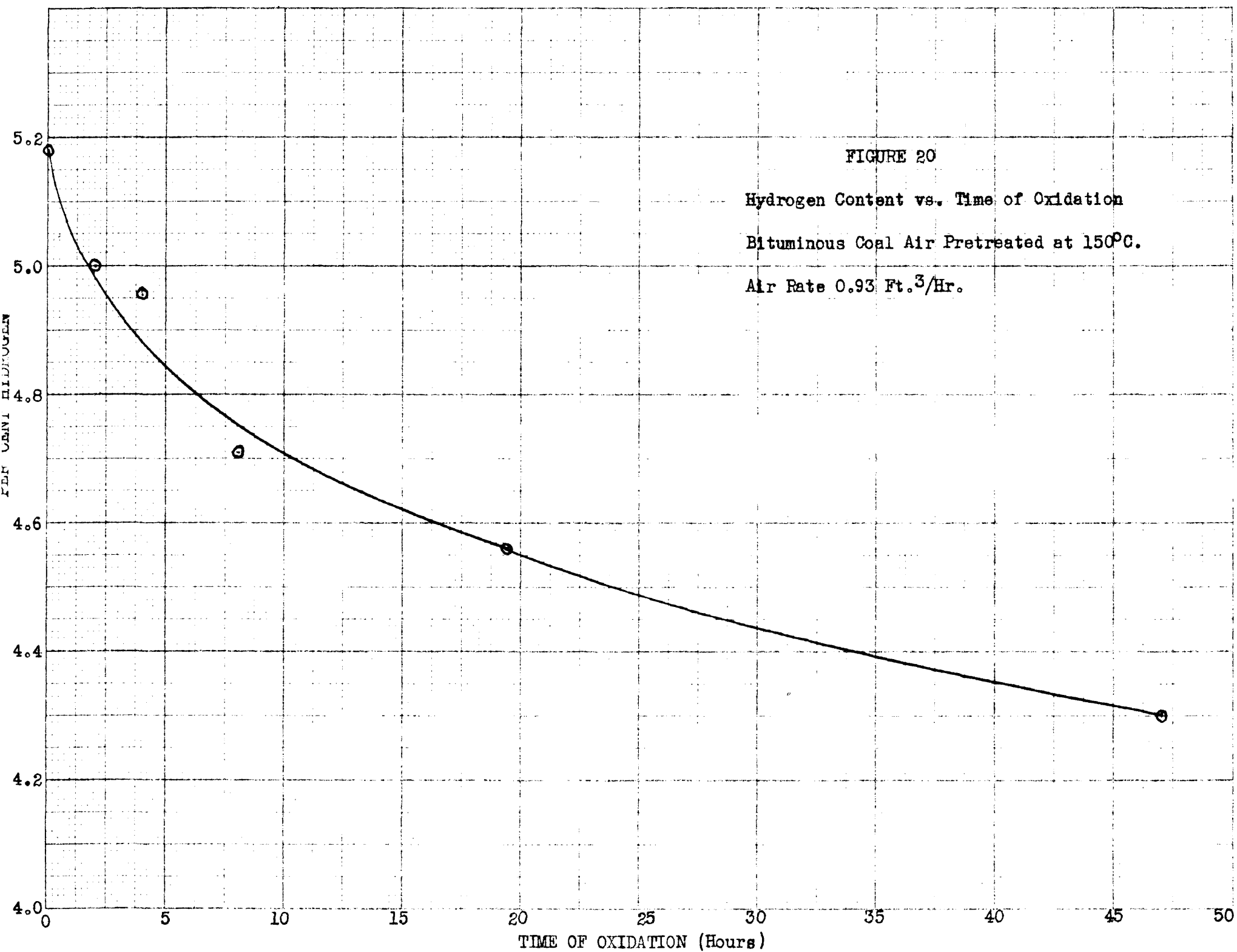
Air is the most economical source of oxygen for pretreating any large quantity of coal on an industrial basis. This fact led to the study of the effect of mild air oxidation on the thermal effects involved during carbonization. The previous experiments with oxygen indicated that 150° C. would be a desirable temperature for the pretreatment. Pretreatments were made for periods of two, four, eight and forty-seven hours respectively, at an air rate of 0.93 cubic feet per hour, using 15 g. coal samples. The results of carbonization studies on these samples are shown in Figure 17, page 84. These experiments show definite trends due to the effect of the pretreatment on the thermal quantities. The pretreatment tends to decrease the endothermic reactions occurring in the preliminary portion of the carbonization and in general the exothermic effects become more pronounced as oxidation is increased. It is interesting to note that the minimum points on these curves occur at a progressively lower temperature with increased oxidation. This is shown graphically in Figure 18, page 85. It appears that the stability of the reaction products formed during the pretreatment is in inverse relation to the degree of the oxidation. This can be further substantiated by the results of the carbon and hydrogen analysis of the samples after oxidation as is shown in Figures 19, page 86, and 20, page 87. These curves are actually inverse functions of oxygen "pickup" because oxygen is determined by a method of difference and previous research has indicated that the percentages of nitrogen and sulphur present are not



TEMPERATURE OF INITIAL EXOTHERM (°C.)







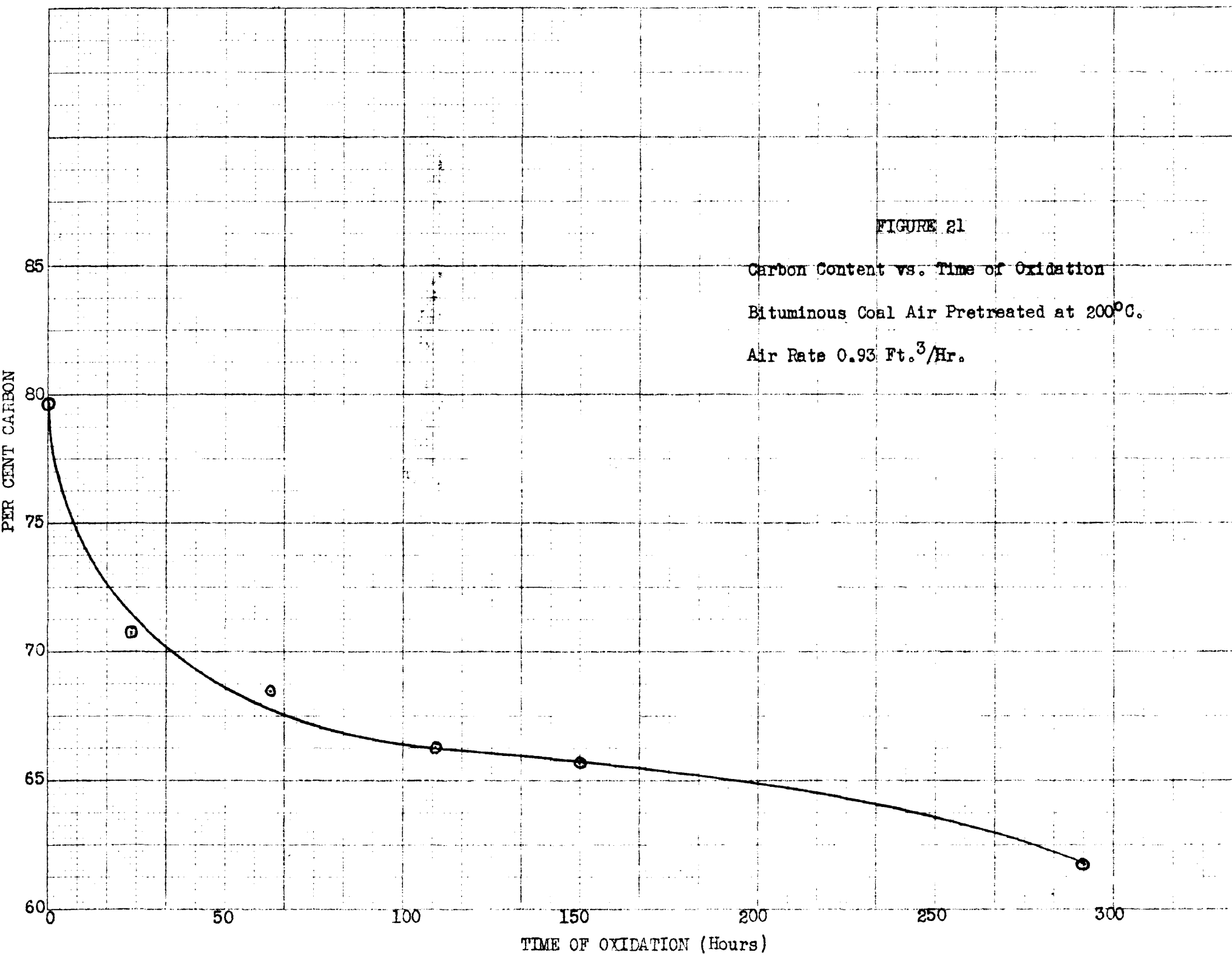
appreciably affected by an oxidation at these temperatures. The curve of decomposition is roughly of the same type as the curves showing the carbon and hydrogen analysis, indicating a relatively rapid oxygen "pickup" in initial periods of oxidation. Upon prolonged oxidation a straight line relationship is approached.

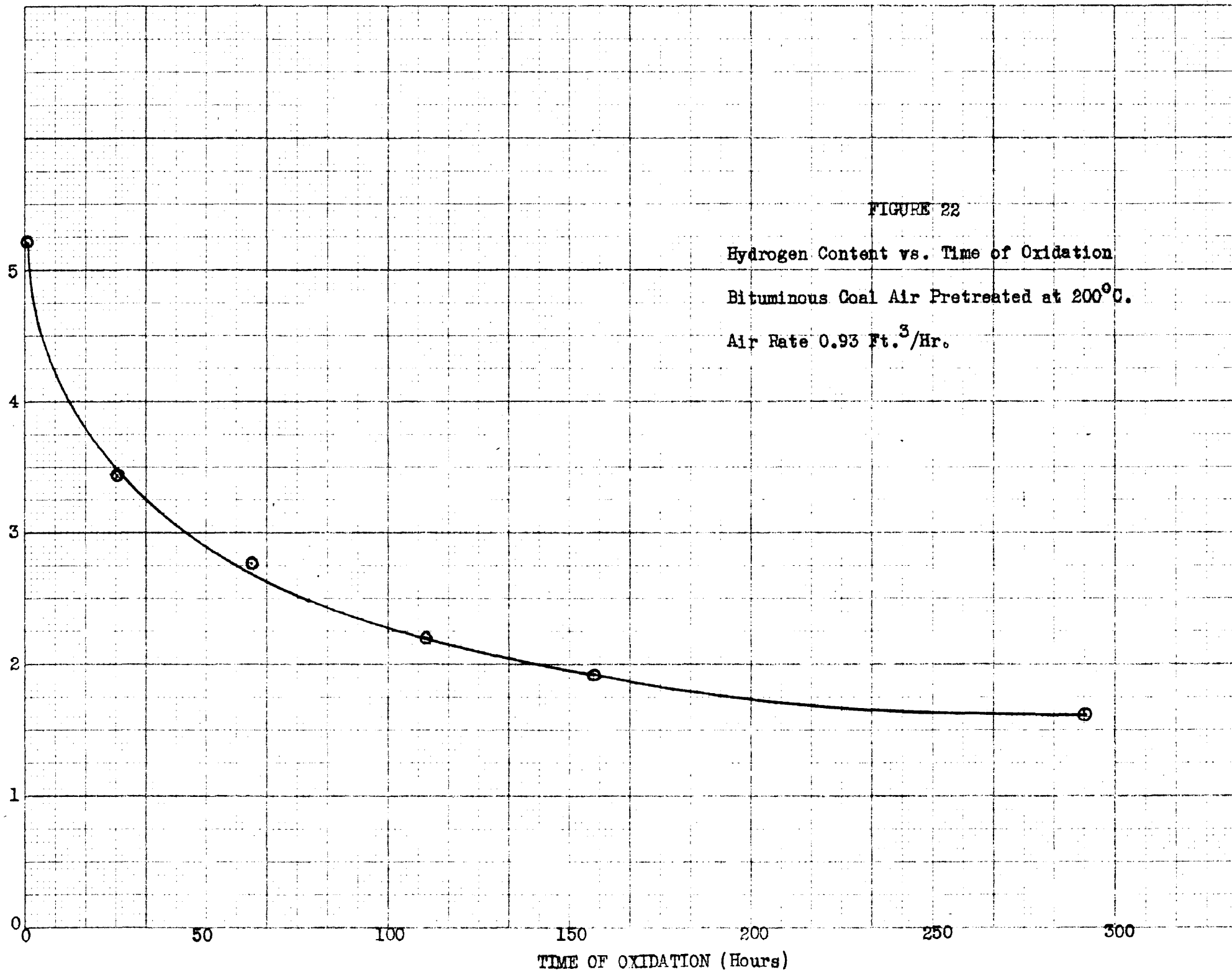
In general it can be concluded that the major changes in the thermal effects occur immediately before and during the plastic period. At temperatures in excess of 500°C . the major portion of the carbonization is a dehydrogenation process and it is quite probable that practically no oxygen is present in the coal after this point. Any reactions occurring after this temperature would probably not be affected appreciably by the oxygen pretreatment.

Controlled oxidation of this Pennsylvania coking coal can be carried out readily at temperatures up to 200°C . At temperatures above 200°C . the heat of reaction is extremely difficult to control. Figures 21, page 89, and 22, page 90, indicate the changes in carbon and hydrogen analyses respectively after air oxidation at 200°C . The oxidation was carried out on 15 gram coal samples for periods of 24, 61, 110, 150 and 291 hours at an air rate of $0.93\text{ ft.}^3/\text{hr}$.

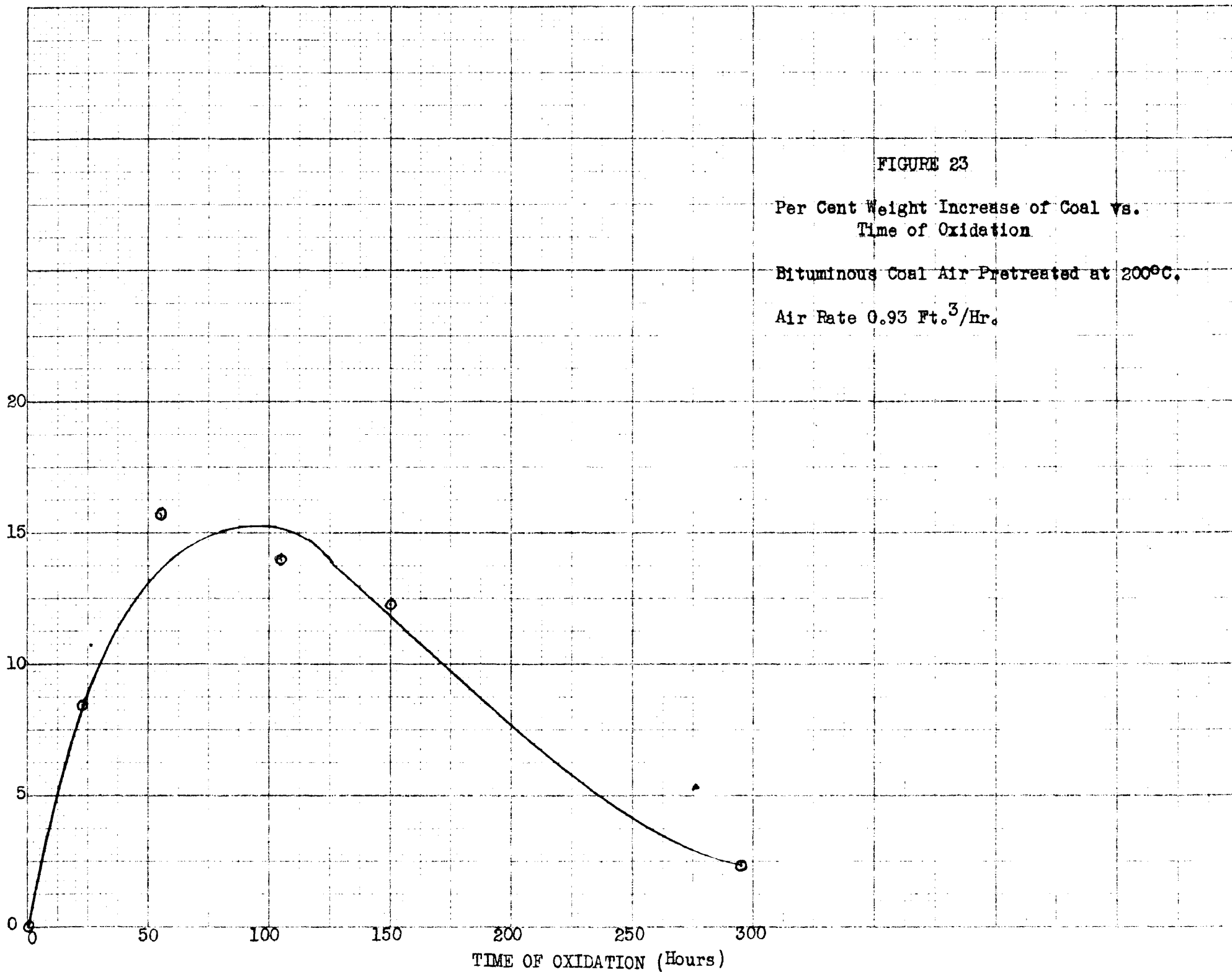
The effect of this oxidation at 200°C . on the weight of the original coal is shown in Figure 23, page 91. It is seen that the weight increase reaches a maximum after approximately 75 hours of oxidation. No apparent change in volatile matter content was observed after these pretreatments.

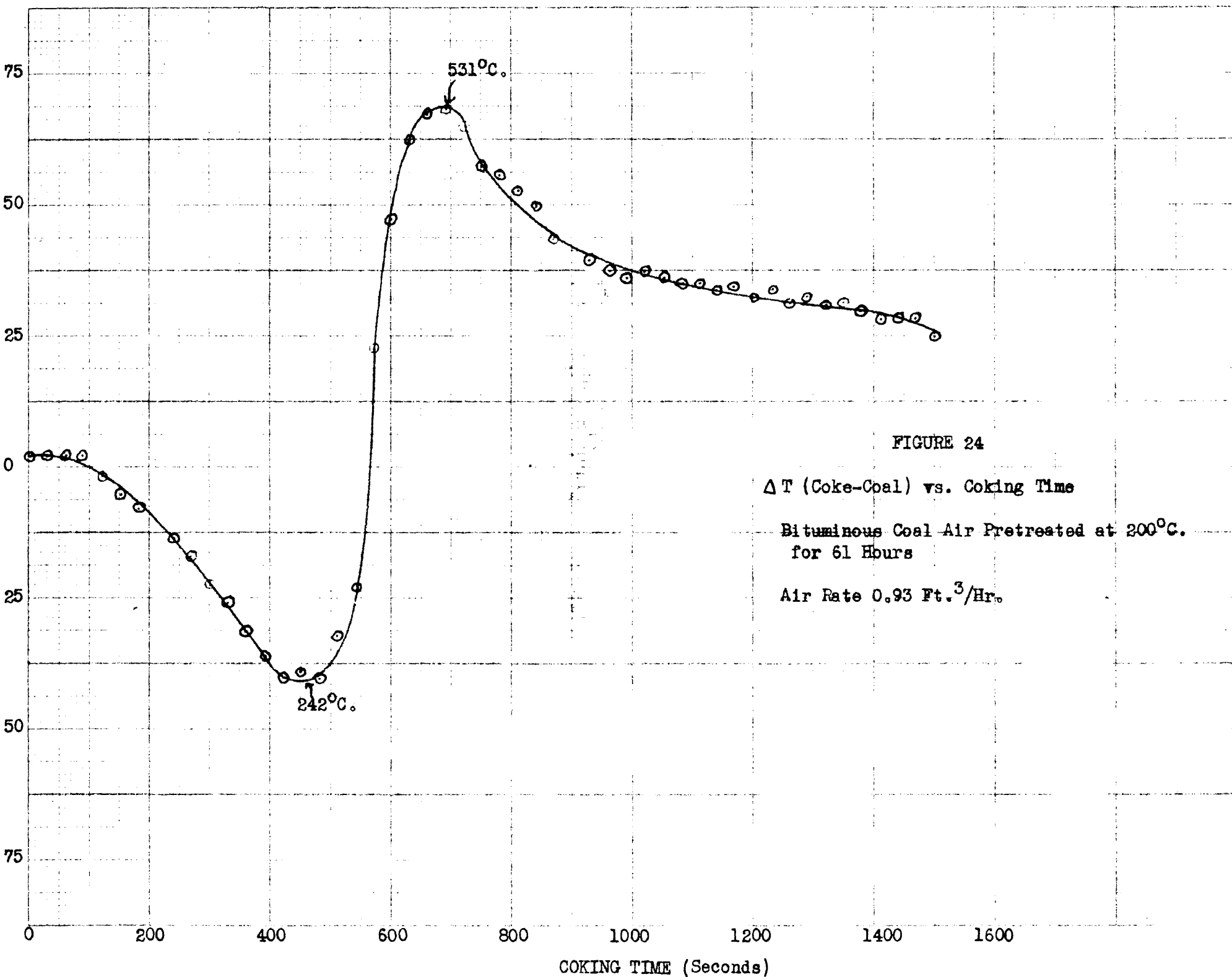
The sample which had been treated for 61 hours at 200°C . was selected for carbonization studies. The heating curve for this sample is shown in Figure 24, page 92. It is seen that extremely strong exothermic predominance begins at 242°C . The upper portion of the





PER CENT WEIGHT INCREASE OF COAL





curve is similar to those previously experienced with oxygen pretreated samples. No coke was produced during the carbonization. The bonding property had been completely destroyed.

In order that a coherent coke sample might be obtained, a blend of 5 grams of this oxidized sample and 5 grams of untreated coal was coked. The heating rate curve for this sample is shown in Figure 25, page 94. The strong exotherm begins as in the previous case at 242° C. and continues throughout the carbonization. A good coherent coke button was obtained. The gas liberated in this operation was collected in six aliquot portions and was analyzed. The analyses of the gas collected plotted versus coal temperature are shown in Figure 26, page 95. The composite analysis is as follows:

Carbon dioxide and other acidic gases	16.7%
Unsaturation	1.2%
Oxygen	3.5%
Hydrogen	30.0%
Carbon monoxide	13.5%
Methane	11.7%
Nitrogen (by difference)	23.4%

A similar analysis was made on the gas collected from an untreated coal sample. The analyses of the gas collected plotted versus coal temperature are shown in Figure 27, page 96. The composite analysis is as follows:

Carbon dioxide and other acidic gases	3.2%
Unsaturation	2.4%
Oxygen	.5%
Hydrogen	35.1%

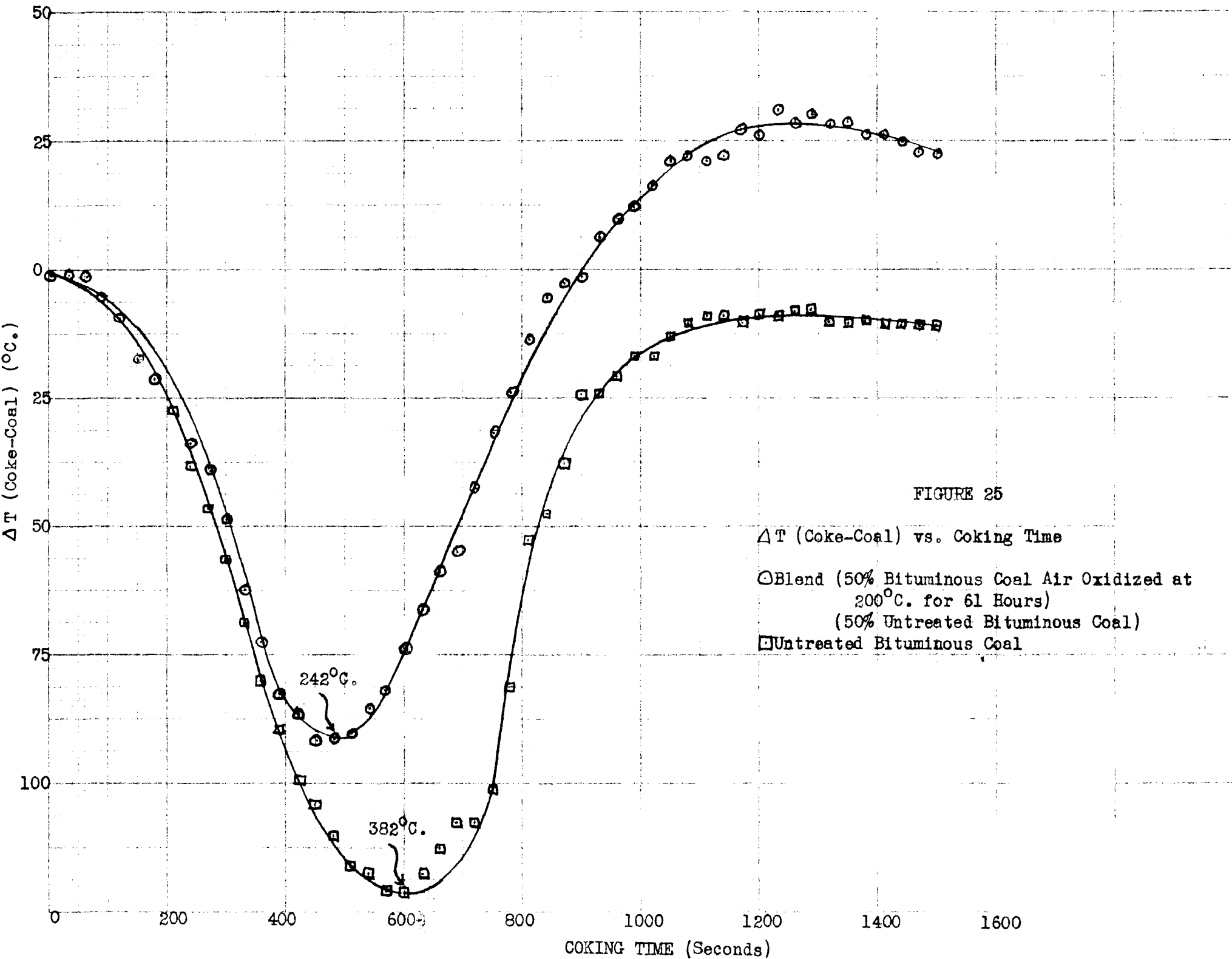


FIGURE 26

Gas Evolution vs. Carbonization Temperature

50% Untreated Bituminous Coal

50% Oxidized Bituminous Coal (61 Hr. Air
Oxidation at 200°C.)

Air Rate 0.93 Ft.³/Hr.

- Carbon Dioxide
- * Hydrogen
- Carbon Monoxide
- △ Methane

GAS EVOLUTION (% of Total)

