INITIAL STEPS IN THE COALIFICATION PROCESS
PLANT CONSTITUENTS AND THEIR DEGRADATION TO THE PEAT STAGE

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Organic matter is produced in nature at a rate on the order of 10^{17} grams per year. The vast majority of this is annually passed back into the cycle in both marine and terrestrial environments, yet during the course of geologic time a fraction has escaped to form the fossil fuels. In terrestrial organic sedimentation, ultimately leading to coal, one of the most significant contributions is that made by woody tissues of plants. It becomes of interest, therefore, to examine in some detail the structural and chemical alteration of woody plant material in the early stages of alteration to peat and ultimately to coal. This paper deals with the histological and histochemical processes in the degradation of wood in the early stages of organic accumulation.*

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THE TRANSITION FROM PEAT TO LIGNITE

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A completely satisfactory distinction between peat and lignite is seldom made in coal classification schemes and often peat is excluded entirely from the category of coal. It is not difficult to understand why this situation exists, but the failure to formally recognize peat as a form of coal has an effect which is lamentable, in that it creates a "no-man's land" between the provinces of the biochemist on one hand and the coal chemist on the other. Few biochemists find it rewarding to work in this fringe area and coal chemists are in general abhorred by the thought of concentrating their efforts in the study of peats.

In contrast with the above, the common absence of an adequate differentiation of lignites (or brown coals) and peats in coal classifications is obviously not to be viewed with alarm. It seems apparent that any such distinction will be an arbitrary one and no great need exists at the moment for establishing a firmly fixed line of demarcation. The analytical data present in the literature contrasting the composition of peats and lignites are useful and often informative, at least in a general way. Among other things, these data show that peats commonly contain significantly higher percentages of moisture and nitrogen. However, few would feel prone to assert that air dried peat is lignite, or that lignite can be produced from peat merely by leaching the nitrogeneous substances from the mass. From this it is evident that such data represent the average effect of the actual changes which occur in the transition from peat to lignite. A true understanding of the transition can hardly be achieved without inspecting the nature of the various individual changes, each of which may affect the average moisture, nitrogen or carbon content in a different manner. The materials undergoing the changes are the minerals which are composed of inorganic substances and the macerals which are fabricated of organic material.

The mineral substances present in coal seams occur in discrete masses which usually possess well-defined boundaries by virtue of their mode of origin. Equally discrete are the masses of material formed of maceral substances and, as in the case of the mineral masses, the discreteness obtains because of the manner in which the substance or aggregate of substances has been formed. In some instances these boundaries are inherited from the source materials as in the case of detrital rock fragments and fragments of cell or tissue systems. In other cases, the boundaries are determined by the size and shape of the space in which a newly formed mineral or maceral may be emplaced. Figure 1 of Plate I illustrates this point by showing the clearly defined boundaries of the maceral material which has been formed, in situ, through the alteration of material composing the secondary wall of the vessels. Within the vessel cavity another maceral substance occurs and the size and shape of the mass have been determined by the shape of the cavity and the volume of the intruding material. Comparison of Figure 1 with Figure 2 (Plate I) leaves little doubt as to the in situ development of the buff colored, anisotropic maceral material which now makes up the remnant of the original vessel wall. The latter was initially colorless and has taken on the buff hue during coalification in the peat stage.

The evolution of maceral substances in the peat - lignite transition can be observed readily but little is known concerning the chemistry of these changes. Certain

of the materials composing peat are typically stable during the transition, as suggested by the photomicrographs presented as Figures 3 and 4 of Plate I. The illustrations indicate that fusinite as well as certain anthraxylous macerals belong in this category. The observations made thus far suggest that essentially all of the maceral suites possess macerals which are usually stable through this transition.

Although many materials appear to be common to lignites and peats, comparative studies make equally obvious the numerous changes which contribute to the general properties taken on by the newly formed coal type. Plate II depicts some of the organic substances encountered in peat. These include a great variety of materials ranging from colorless and chemically unaltered substances on the one hand to drastically modified opaque and highly colored macerals on the other. As is to be expected, the colorless organic substances are uncommon in lignitic coals but are commonly encountered in thin sections of peat. Lignified and suberized tissues yield a number of materials, some of which appear to provide lignites with their slacking properties. Several of these develop out of the colorless materials encountered in peats and the resultant macerals may be buff, yellow-brown, red-brown or brown in color. Maceral materials of the buff and brown types do not appear to contribute to the slacking of lignitic masses. The bulk of the yellow-brown and red-brown materials are physically disrupted when placed in a dessicating environment, whereas masses of material composed of buff or brown maceral substances remain unaffected.

Tannic and phenolic substances are conspicuous in many peat types and the latter group of materials or their derivatives appear as reddish and brownish macerals in lignites (compare Plate I, Figure 1 with Plate II, Figure 2). The fate of the brilliant red tannins is not clear but in this investigation they have not been observed to occur as such, in other than peat masses. Crystalline inclusions which are found in the cells of a variety of plants appear to be destroyed in the peat environment for, so far as could be determined, they have not been observed in lignitic coals.

With respect to the mineral content of peats and lignites, the most interesting contrast appears to be that associated with the occurrence of pyrite. This mineral is a common component in lignite seams and in other coal beds of higher rank. It is often present in microscopically visible masses and as such is readily detected. In the peats examined, pyritic material is conspicuous by its absence. Although detailed studies have not been made, it seems evident that if pyritic material is present in the peats being studied, it is disseminated in minute particles within the organic substances. The more conspicuous masses previously referred to must be developed during or subsequent to the peat - lignite transition.

Burial of a peat mass beneath a thick cover of other sedimentary materials normally results in the thinning of the peat seam, largely through the loss of water. This presumably includes the loss of both "inter-particle" water and "intra-particle" water. The removal of the inter-particle water obviously places adjacent particles in more intimate contact and causes them to adhere to one another to a certain extent. Wherever plastic substances are present the coherency of the mass is increased and it is further augmented by the "matting effect" encountered in peats containing sizeable concentrations of fibrous material. A truly coherent or "consolidated" mass cannot be produced until the bulk of the material is altered to maceral substances which will behave plastically under the impact of the forces produced by the weight of the overburden. It seems reasonable to assume that the plastic deformation of an individual mass results in an increased adhesion with adjacent particles and an "inter-lacing" of particles through the actual flowage of material into inter-particle spaces. The actual impregnation of a foreign particle by a mobile material appears to be restricted to migration into any voids which may be present in the gross structure of the invaded particle. No evidence was found suggesting an "inter-molecular" mingling of the invading and invaded substances, hence, this type of

impregnation is not thought to play a major role in the forming of consolidated coals.

The size, shape and texture of the discrete masses of material comprising lignite seams provide evidence as to which of the macerals have had a plastic phase in their history. Of the macerals derived from lignified or suberized source materials certain of the buff, yellow-brown and red-brown macerals appear to show the greatest effects of having been plastic or mobile at some stage in their development. Volumetrically these materials comprise the larger part of most lignite seams. It seems possible, therefore, that the development of these macerals or their plastic progenitors is essential to the consolidation of a coal seam. If they fail to develop, a poorly consolidated mass of "brown coal" results. Their development appears to be characteristically associated with the peat - lignite transition. Macerals which exhibit plastic properties under the normal pressure conditions encountered in coal measure strata are undoubtedly present in higher rank coals but the above mentioned materials are apparently of primary importance in bringing about the initial consolidation of a coal seam.

All of the preceeding implies that it is profitable to view coal seams as a mixture of macerals and minerals. The rank, the degree of consolidation, the slacking properties and all other characteristics are then a function of the relative concentrations of the constituent macerals and minerals. The importance of understanding the physical and chemical nature of these components and the properties of the natural maceral assemblages is self-evident and research in this field should be accelerated in the interests of achieving the greatest benefits from the exploitation of our coal reserves.

Figure 1: Transverse section of lignitized wood (Persea sp.) from the Brandon lignite. Vessel walls are composed of a buff-colored anisotropic material. (410x)

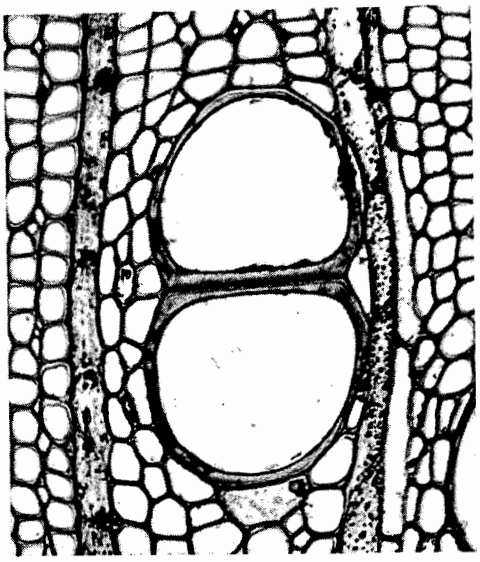

Figure 2: Transverse section of wood of Persea borbonia. Vessel walls are colorless. (310x)

Figure 3: Section of peat from Okefenokee Swamp, Georgia. Opaque fusinite is shown in lower right, yellow-brown to reddish anthraxylous material occupies remainder of photograph. (112x)

Figure 4: Section of lignite from Harding County, S.D. Opaque fusinite is shown in lower right, yellow-brown to reddish anthraxylous material occupies remainder of photograph. (95x)

PLATE I

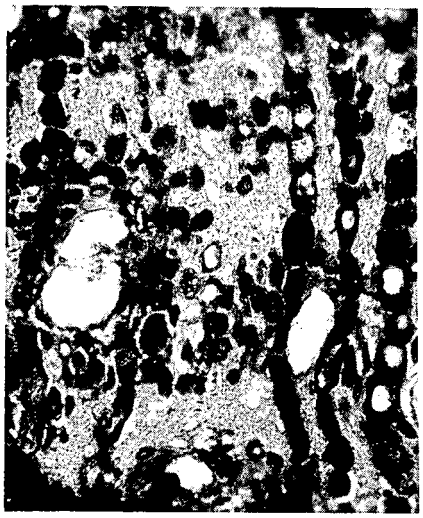

Figure 1: Thin section of materials encountered in peat from Okefenokee Swamp, Ga. (20x)

Figure 2: Wood from peat of Shark River area, southern Florida. Brown phenolic substances in rays are inherited from source material. (84x)

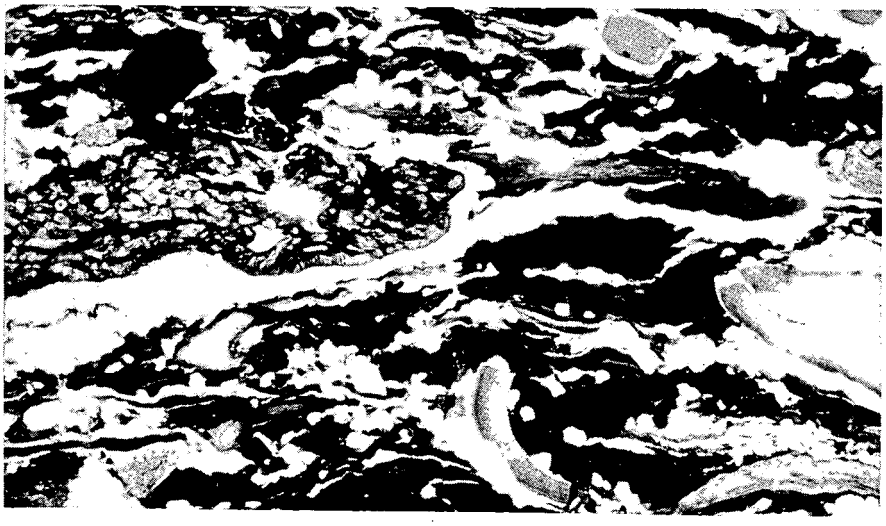

Figure 3: Typical assortment of substances composing Nyssa swamp peat. Materials vary from colorless to a variety of yellow-brown, red, and opaque materials. (27x)

PLATE II

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THE CHEMICAL CONSTITUTION OF A LIGNITIC RESIN

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Natural resins are formed in trees as a protective measure when the bark is injured. An exuded viscous liquid covering the injury looses its more volatile components and apparently undergoes polymerization and condensation. These rather stable substances appear to occur in low rank coals in a state similar to their original structure. The lack of chemical investigation of coal resins is undoubtedly associated with the tacit assumption of their similarity to the natural resins and with the observation that their physical appearance suggests less alteration than any other maceral.

Although microscopic resin-forms exist in resin ducts observed in most coals, certain coals contain some macroscopic particles which are probably the coalified product of the original exuded resins. The latter can usually be freed from the associated coal by proper comminuition and separated by gravity methods, although preparation of a "pure" fraction is difficult.

Most studies on coal resins have been limited to their physical description and considerations of recovery techniques. These resins range in color from light yellow to deep brown and in specific gravity from 1.00 to about 1.25. They possess varied solubility characteristics although consistently water insoluble. A wide melting range between 120 and 400 $^{\circ}$C, contrasts with a nearly constant elemental analysis: 80% carbon, 10% hydrogen and 10% oxygen. A generalized constituent classification representing functional group composition includes: resin acids, resin alcohols, resin esters and resenes. The latter represents hydrocarbons.

The experimental data evaluated in this investigation includes: solubility in alkali and in organic solvents, equivalent weights, melting points, elemental analyses, saponification, correlation with abietic acid and amber properties, 2,4-dinitrophenylhydrazine reaction and absorption spectra.

The coal employed in this study was a North Dakota lignite, of the Paleocene Fort Union formation whose analysis appears in Table 1. The resins studied were recovered from the crushed lignite by a sink-float procedure employing a mixture of n-heptane and carbon tetrachloride (specific gravity, 1.15) as the separation medium. A yield of 0.6 g. of pure resins was

obtained from one kilogram of lignite. The resins varied in color from light yellow to deep red and were arbitrarily separated into the three classes: yellow-light orange, orange, and dark orange-red.

Table 1

Proximate Analysis of Sentinel Butte Lignite

Moisture	20.0%
Ash	8.8%
Volatile Matter	47.5%
Fixed Carbon	23.7%
Moist B.T.U.	7500

Figure 1 shows the reprecipitated acid fraction of the resin color classes to possess essentially identical vibrational characteristics. This is also true for the original resin color classes. The only major dissimilarity appears in the 3 micron region. The darker colored resins apparently have an increased degree of associated hydroxyl vibration. The assignments given to the various absorptions are shown in Table 2. The ultraviolet absorption spectra, Figure 2, show equal similarities between color classes. However, the darker-colored resins undoubtedly have a higher chromophoric concentration. The 215 millimicron absorption maximum and the visible absorption data (Figure 8) suggest a conjugated carbonyl structure. This possibility is confirmed by a positive test for a ketone by formation of a dark orange-red 2,4-dinitrophenylhydrazone.

Table 2

Infrared Absorption Assignments of the Resins and Resin Acids

Wavelength (microns)	Vibrational Assignment
2.93	O-H stretch (unassociated)
3.05	O-H stretch (associated)
3.42	C-H stretch (aliphatic)
5.80 (shoulder)	C=O stretch
5.89	C=O stretch
6.81	C-H bend (aliphatic)
6.88	C-H Bend (aliphatic)
7.25	CH_3 symmetrical bend
8.0-9.0	C-O stretch
9.19	ring vibration
9.72	ring vibration
10.26	C-H bend, or ring vibration
11.30	C-H bend

The noted variation in the dark colored resins is consistent with other observations. The equivalent weights have lower values (Table 3) as do the melting point ranges (Table 4). In addition, the dark-colored resins are more soluble in a number of common organic solvents (Table 5).

The melting range and solubility data indicate the dark-colored resins to be a lower molecular weight material. However, since the spectral data indicate all the resin color classes to have essentially the same structure, it appears that differences in molecular weight must result from varying degrees of condensation of some basic structural unit. Saponification studies are in agreement with this conclusion. The saponified products of both the orange and yellow-light orange resin acids have common equivalent weights. It is suggested that the major portion of these resins, the resin acids, are at least in part composed of a basic unit structure condensed in the form of an ester.

In considering the nature of this basic unit, it seems logical to pursue an investigation of abietic acid which has been studied extensively in dealing with natural plant resins. The oxidation tendencies of abietic acid are especially significant.

As abietic acid undergoes slow air-oxidation (Figure 3) its infrared absorption spectra becomes increasingly similar to that of the resin acids. The major changes are associated with the higher oxygen content (lower carbon and hydrogen values - Table 6) and the decreased crystallinity (amorphorous appearance and lower melting range - Table 4) of the oxidation products. A second carbonyl band appears at 5.80 microns, and the absorption in the 8.0 to 9.0 micron region, corresponding to C-O stretching vibrations, is increased. The decrease in the crystalline nature of oxidized abietic acid is also markedly reflected in the infrared spectra. The destruction of at least part of the unsaturated structure by oxidation is indicated by the decreased band at 7.82 microns, corresponding to the $> C = CH$ group.

Related effects are noted in the ultraviolet absorption spectra (Figure 4). These are in general associated with the conjugated double bonds. The 241 millimicron band maximum decreases and a new absorption appears at 215 millimicrons indicating that the total unsaturated character is not destroyed, but that one of the double bands remains in conjugation with the carbonyl group formed by the oxidation.

Although similar, the infrared absorption spectra of the resin and that of air-oxidized abietic acid are not identical. The resin apparently has a higher aliphatic C-H content and possesses three unique bands at 9.72, 10.26 and 11.30 microns. These latter absorptions are found in amber, a natural resin which is considered to be a mixture of succino-abietic acid and esters of succinic acid. It is characterisitcally insoluble in acetic acid.

The resins yield a glacial acetic acid-soluble fraction which is darker in color, has a lower melting range and lower carbon-hydrogen content than the original. The infrared spectra of the acetic acid-soluble resin fraction and the air-oxidized abietic acid (Figure 5) are very similar,

Table 3

Equivalent Weight Determinations

Sample		Equivalent Weight
A. Precipitated resin acids		
1. Yellow-light orange		726
		748
	Average	737
2. Orange		648
		660
	Average	654
3. Dark orange-red		556
		535
	Average	546
B. Saponified resin acids		
1. Yellow-light orange		325
		341
	Average	333
2. Orange		327
		332
		340
	Average	333
C. Glacial acetic acid insoluble fraction		
1. Yellow-light orange		495
2. Orange		433
		444
	Average	439
D. Abietic acid		
1. Pure		299
		301
		303
	Average	301
2. "Air-oxidized", 15 years		336
		337
		334
	Average	336

Table 4

Melting Point Data

Sample	Melting Range(°C)
A. Resins	
1. Yellow-light orange	185-210
2. Orange	180-205
3. Dark orange-red	170-190
B. Precipitated resin acid (orange)	180-210
C. Acetic acid soluble fraction (orange resins)	141-167
D. Acetic acid insoluble fraction (orange resins)	220-295
E. Abietic acid	
1. Pure	162-164
2. "air-oxidized" for fifteen years	91-95
F. Amber	245-325

Table 5

Resin Solubility Tests in Organic Solvents

Solvent	Yellow-Light Orange	Orange	Dark Orange-Red
Acetone	Slightly soluble	Very soluble	Completely soluble
Chloroform	Insoluble	Slightly soluble	Slightly soluble
Ethanol	Slightly soluble	Very soluble	Completely soluble
Glacial Acetic Acid	Very soluble	Very soluble	Very soluble
Benzene	Insoluble	Slightly soluble	Slightly soluble

Table 6

Results of Elemental Analyses and Mol. Wt. Determinations

Sample	%C	%H	%N	%S	%Ash	Mol. Wt.
Resin (orange)	78.8	10.0	0.8	none	none	---
Precipitated resin acids (orange)	78.5	10.1	0.3	---	---	635
Glacial acetic acid soluble fractions						
1. Yellow-light orange	75.8	9.4	---	---	---	---
2. Orange	75.0	9.4	---	---	---	---
	75.1	9.6	---	---	---	---
Abietic Acid						
1. Pure	79.6	10.2	---	---	---	---
	79.5	10.1	---	---	---	---
a. Theoretical	79.4	10.0	---	---	---	---
2. "Air-oxidized" for two years	77.1	9.6	---	---	---	---
	77.1	9.5	---	---	---	---
3. "Air-oxidized" for for fifteen years	70.3	8.4	---	---	---	---

especially in respect to the decreased absorptions at 9.72, 10.26 and 11.30 microns which are related to amber. The infrared spectra of the glacial acetic acid-solubles and insolubles are strikingly different. The latter closely approximates the spectrum of natural amber. The strong hydroxyl band at 2.93 microns, in the amber spectrum, is a dissimilarity, but is in agreement with the less intense carbonyl bands observed. Supporting evidence is indicated in the ultraviolet absorption spectra of the soluble compound, Figure 6, and of the insoluble fraction, Figure 7. The data suggest complete isolation of these compounds was not attained.

By assigning the 11.30 micron absorption to amber, the spectra of the original resin color-classes may be interpreted to indicate a constant level of amber concentration. Therefore, the variation in equivalent weights of the differently colored resin acids, cannot be related to varying amber concentrations. The difference in the equivalent weights of the amber-like fraction (acetic acid-insoluble) obtained from the yellow-light orange, and orange resins is not diverse enough to account for the difference in the equivalent weights of the corresponding resin's acids. Since it has been indicated that slight mutual contamination exists in the two acetic acid-solubility fractions, one may conclude that the equivalent weight of the amber is constant, but that of the oxidized-abietic acid fraction varies. This property of the oxidized-abietic acid-like fractions (acetic acid-soluble) decreases with increasing resin color intensity.

Since it has been shown earlier that saponification reduces the equivalent weights of the differently colored resin acids to a common value, it seems that the "oxidized abietic acid-like" material exists as an ester. This is possible, since the oxidation products of abietic acid have been shown to have hydroxyl groupings, and could enter into self-condensation reactions. A possibility of an abietate other than a self-condensation product is discounted because of the simplicity of the spectra, and because of a high molecular weight alcohol would have been insoluble in the alkaline solution after saponification. Such a self-condensation reaction could also account for the differences in color of the resins and their corresponding acids, if the condensation involved a secondary hydroxyl group that might otherwise be oxidized to a chromophoric carbonyl group.

It is concluded that the resins separated from this North Dakota lignite have undergone only a moderate degree of alteration during the coalification process, that they are composed of a mixture of amber (succino-abietic acid and esters of succinic acid) and a form of oxidized-abietic acid. It is suggested that the oxidized-abietic acid component has undergone self-condensation to form an ester.

ACKNOWLEDGEMENT

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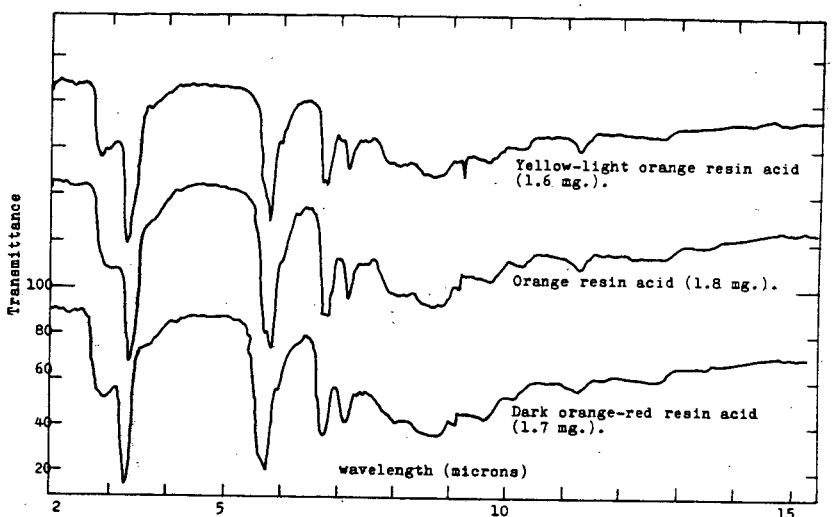

Figure 1 Comparison of resin acids.

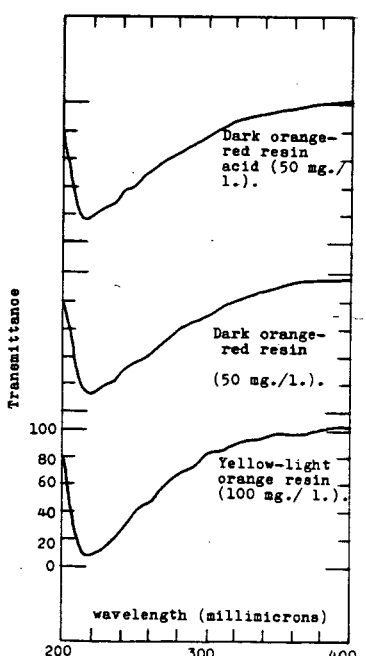

Figure 2 Comparison of dark-orange red resin and resin acid with yellow-light orange resin.

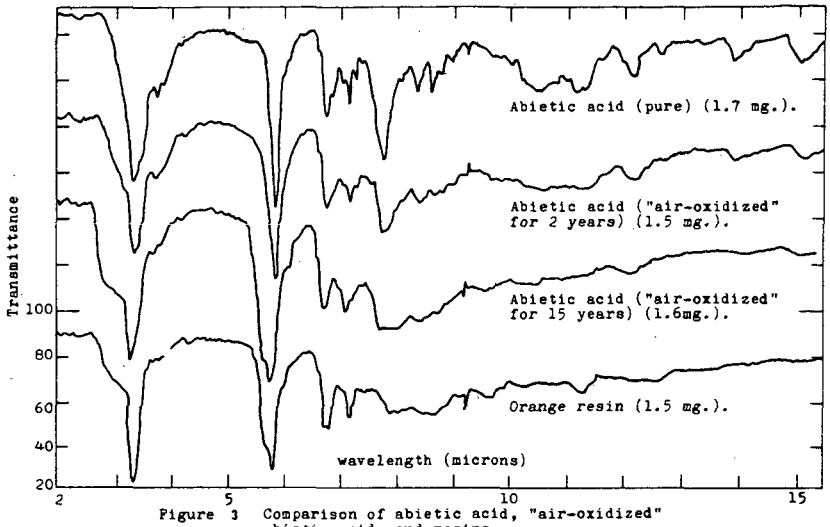

Figure 3 Comparison of abietic acid, "air-oxidized" abietic acid, and resins.

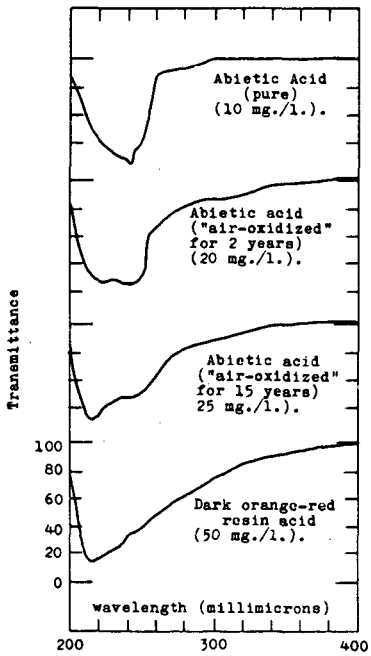

Figure 4 Comparison of abietic acid, "air-oxidized" abietic acid, and resin.

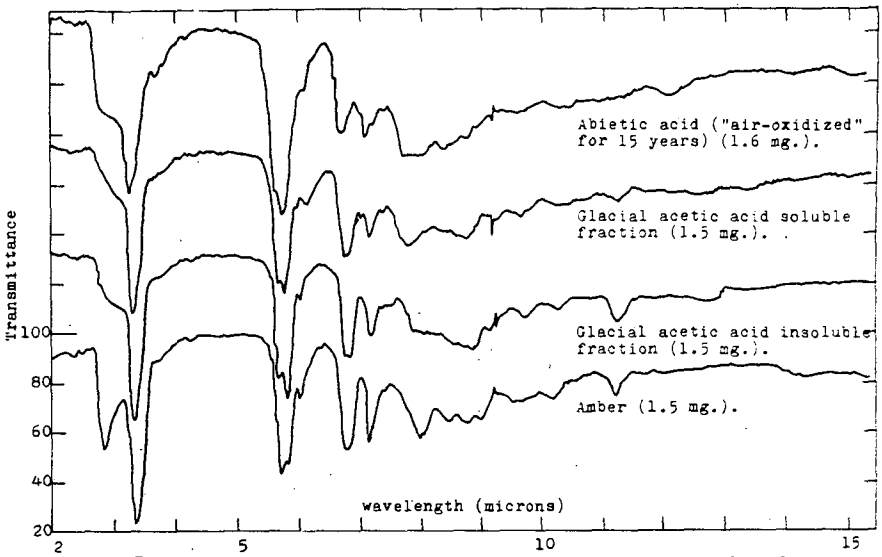

Figure 5 Comparison of "air-oxidized" abietic acid and glacial acetic acid soluble fraction, and glacial acetic acid insoluble fraction and amber.

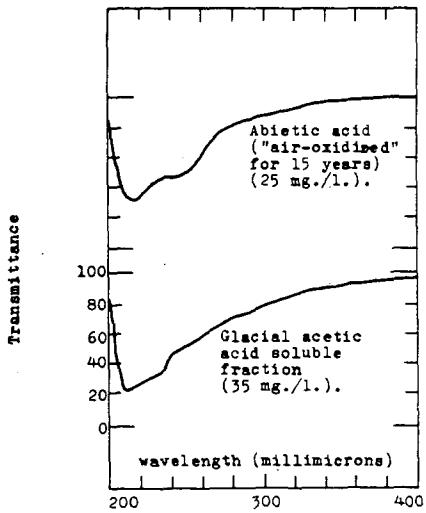

Figure 6 Comparison of glacial acetic acid soluble fraction and "air-oxidized" abietic acid.

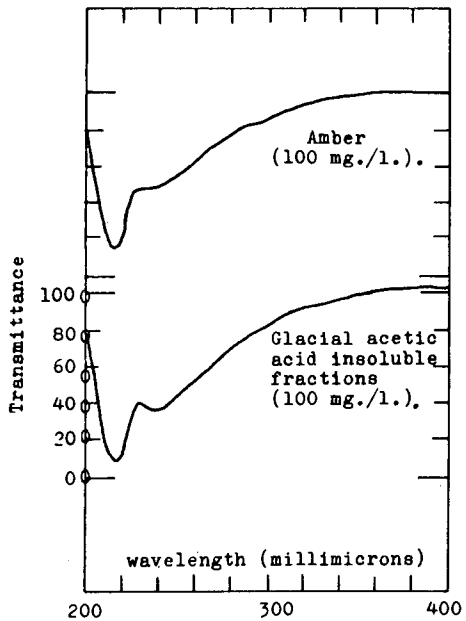

Figure 7 Comparison of amber and glacial acetic acid insoluble fraction.

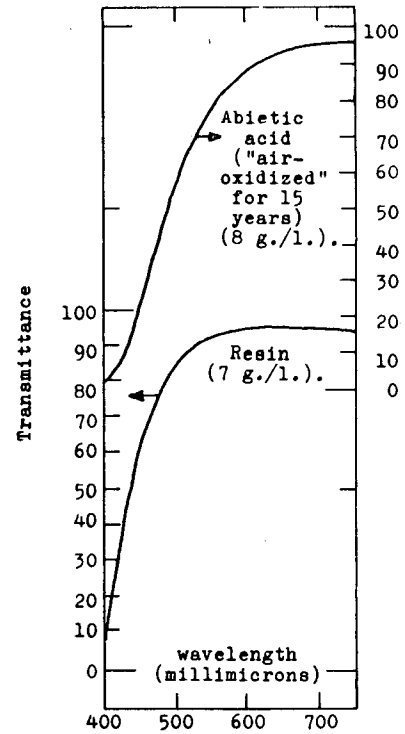

Figure 8 Comparison of resin and "air-oxidized" abietic acid.

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The Principal Geological, Chemical and Physical Factors Controlling the Mineral Content of Coal

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Coal is essentially a near end-member of a homologous series with 100 percent carbonaceous matter at one end of the series and with 100 percent mineral matter at the other end. This is tacitly recognized by chemists in their common usage of the mineral-matter-free basis for treatment of coal analyses in experimental work and in process industries.

Whenever classification of coal has been subject for discussion or study (1,2,3)*, the mineral matter content of coal is mathematically removed from consideration--and rightly so for such a purpose. But mathematical elimination of mineral matter does not eliminate the fundamental problem of mineral matter in coal.

Minerals are an integral part of a coal bed. Once this fact gains general acceptance the genetic relations of the minerals found in coal can be properly appreciated. Many papers on the kinds of minerals (4,5,6,7), the distribution of minerals(8,9), and the mode of occurrence of minerals (10) in coal have been published. The biochemical and geochemical origins of ash forming ingredients in coal, the fate of mineral elements leached from degraded plants, and the origin of minor elements in coal are the subject of a previous paper (11). The present paper discusses the interrelationships of the geological, chemical, and physical factors which control the mineral content of coal.

Coal is a rock which is of great economic value and its grade is largely determined by the percentage of minerals present. Most persons concerned with coal are familiar with the mineral matter content of coal only through the residue remaining after combustion. But geologists are concerned with coal as a rock as well as its value as a commodity, and in mapping coal formations throughout the world they are faced with the problem of whether what appears to be coal should be called coal or something else. In such a situation Schopf's (12) definition of coal becomes very important. Here is his definition:

> "Coal is a readily combustible rock containing more than 50 percent by weight and more than 70 percent by volume of carbonaceous material formed from compaction or induration of variously altered plant remains similar to those in peaty deposits. Differences in the kinds of plant materials (type), in degree of metamorphism (rank) and range of impurity (grade) are characteristic of varieties of coal."

On a weight basis, Schopf extends the definition of coal to include one half of the homologous series discussed at the beginning of this paper. The lateral gradation of a coal seam with only a relatively small percentage of mineral matter into a carbonaceous shale is not uncommon in Cretaceous and later coal beds of the western United States. Many thinly bedded deposits are not considered to be coal beds nor would they be included as such according to Schopf's definition, yet these kinds of deposits probably contain a far greater

*Figures in parentheses refer to references listed at end of paper.

geologic reserve of carbonaceous material than do the coal beds now included in reserve data compiled by the U. S. Geological Survey (13).

Geological factors of sedimentation are the primary controls of the mineral content of coal beds. Purely chemical control of mineral deposition problably occurs only during the peat stage and during the early diagenetic stages of the coalification process. During the subsequent history of a coal bed certain physical factors become important in controlling mineral deposition--but these operate directly in conjunction with chemical processes.

GEOLOGICAL FACTORS

The accumulation of peat in sufficient quantities to permit the ultimate formation of a coal bed of commercial importance requires a degree of stability short of equilibrium. Organic material must accumulate at a rate somewhat greater than that at which complete degradation occurs. But minerals are continuously being supplied to the swamp, and with only a relatively small percentage of organic matter accumulating a carbonaceous shale forms, rather than a coal bed. A coal swamp, throughout its life, is a basin of deposition into which minerals are being brought by water and wind. These are mainly hydromica and kaolin minerals with minor amounts of quartz and traces of resistant accessory detrital minerals such as zircon, garnet, tourmaline, and other minerals as reported by Gauger, Barrett, and Williams (7).

The clay minerals that occur as persistent partings in so many coal beds are typical of the geological control of sedimentation operating on a very large scale. The so-called "coal balls," which are large masses of limestone or dolomite found in great abundance within certain coal beds owe their presence in coal to geological controls.

Once again it must be emphasized that geological conditions and geological processes are the primary controls in establishing the grade of an incipient coal bed. But even beyond this first stage of development of coal, beyond the purely sedimentary stage, geological factors have an influence on the chemical and physical controls which are to be discussed.

CHEMICAL FACTORS

The chemical environment of the coal swamp can be effective in modifying the composition of minerals.

The acidity of swamp waters is certainly an important factor in influencing the ultimate disposition of the suspended and detrital mineral matter brought into the peat bog. The acidity of 64 samples of peat taken 0.5 foot below the surface in 15 Minnesota peat bogs had an average pH of 4.2. The pH data are given in Table I and are taken from Passer's report (14).

These data are probably typical for most peat bogs not located in limestone or dolomite terranes. The high acidity of these peat bogs is probably surprising to most chemists and this is why these data have been presented. Coastal swamps, which may be brackish or which may alternate between fresh water and marine water environments must have an entirely different range of acidity but pH data are lacking for such swamps.

Generally, the pH of samples from any given peat profile will decrease from a minimum value near the top to a maximum at or near the soil base. One example is a peat profile from Rice Lake Bog in St. Louis County, Minnesota, where the pH varies from 3.6 to 5.5 as indicated in Table II.

TABLE I. pH OF 64 SAMPLES TAKEN FROM 15 MINNESOTA PEAT BOGS LOCATED IN FIVE COUNTIES (14)

PEAT BOG	COUNTY	NO. SAMPLES	pH (0.5 ft below surface)
Rice Lake	St. Louis	17	3.8, 3.6, 3.3, 3.9, 3.4, 3.3, 3.4, 3.2, 3.2, 3.1, 3.3, 4.0, 3.9, 3.4, 3.5, 5.3
Floodwood State	St. Louis	8	4.1, 4.4, 4.6, 5.1, 4.3, 5.1, 4.0, 4.2
Corona	Carlton	5	3.0, 4.1, 4.1, 3.4, 3.4
Cook	St. Louis	3	3.9, 3.8, 3.9
Cusson	St. Louis	1	4.0
Big Falls	Koochiching	3	5.3, 5.3, 5.5
Red Lake 1	Beltrami	6	5.2, 5.2, 5.8, 4.7, 4.8, 5.5
Red Lake 2	Beltrami	2	5.5, 3.5
Rapid River	Lake of the Woods	3	4.5, 4.9, 5.2
Canyon	St. Louis	3	5.6, 5.6, 5.4
Elmer	St. Louis	3	4.6, 3.8, 3.9
Zim	St. Louis	3	4.4, 5.4, 4.8
Cotton-Shaw	St. Louis	3	3.3, 3.1, 3.0
Payne	St. Louis	3	4.7, 5.8, 5.1
Prosit	St. Louis	1	4.8

TABLE II. PROFILE OF pH AT POSITION CV, RICE LAKE BOG ST. LOUIS COUNTY, MINN. (Ref. 14, p.4)

DEPTH	pH
0.5	3.6
1.5	3.5
2.5	3.5
3.5	4.1
4.5	4.0
5.5	3.9
6.5	4.1
7.5	4.4
8.5	4.5
9.5	4.4
10.5	5.1
11.5	5.0
12.5	5.5

A relatively low pH may be an important factor in altering the character of the clay minerals deposited in a coal swamp. Grim (15) believes that the leaching of alkalies and alklaine earths under such circumstances may account for the dominance of kaolinite in fresh water lake sediments. The intense acid leaching of clays associated with coal beds may well account for the origin of the high grade fire clays so commonly found with coal beds. Carroll (16) experimented with precisely this type of system in the laboratory and found that under anaerobic conditions in fresh water as much as 62 percent of the ferric oxide present on the clay minerals tested were removed in only 23 days. By the action of anaerobic bacteria the pH generally was reduced 2 units or more. This demonstrated that by chemical activity the character of the sedimentary minerals may be changed and iron made available for further chemical reaction.

Bacteria are factors in the chemical control of mineral matter in coal. Sulfide minerals, and especially pyrite and marcasite, are among the most important minerals to be found in coal. The roles of these minerals in affecting the utilization of coal are too numerous to be mentioned in this paper. Bacteria are active in two ways here--one group of organisms will attack the protein in the plants and as a consequence of that activity will ultimately release hydrogen sulfide; while yet another group of bacteria, the Desulfovibrios of Zobell and Rittenberg (17), reduce sulfate ions to sulfide ions. Quantitatively the contribution of sulfide ion from reduced sulfate is far more important and has previously been discussed by Deul (18). Even insofar as the composition of surface waters entering a peat swamp is concerned there are geological overtones. In basins of limited extent geological controls are effective determinants of the chemical nature of the surface waters in a drainage area. An outstanding example is given by Davis (19) in a discussion of the geologic control of the mineral composition of surface waters of the Southern Coast Ranges of California. Davis shows that the ratio of bicarbonate to sulfate concentrations are related to the lithology of the rocks exposed in the tributary drainage area and that the ratio may vary from 0.8 to 6. (dominantly bicarbonate) to a ratio of 0.02 to 0.7 (dominantly sulfate).

The nature of the minerals deposited in the peat swamp and the chemical modification of these sedimentary minerals have been briefly discussed. It is now necessary to consider the interaction of physical and chemical forces in further transformations which may take place subsequent to the peat stage. When equilibrium is interrupted and a peat is buried under an increasing load of sediment, water is squeezed out of the peat and from the underlying sediments. The expelled water migrates either laterally or vertically upward under the compressive forces. During this stage of burial and compaction, called the early diagenetic stage, chemical conditions are constantly changing. The expelled waters probably are concentrated in iron, silica, and in sulfide ions as compared with water in a peat swamp. Replacement of organic structures by pyrite and quartz may well take place at this stage. Replacement phenomena are far too complex to discuss in the light of present knowledge but the fact of replacement as a process cannot be denied.

PHYSCIAL FACTORS

Once a coal has been formed and the bed moisture is reduced to below 20 percent, as in a subbituminous rank coal, cleating of coal becomes a prominent physical feature. Cleats are closely spaced parallel vertical joints; their origin is attributed to pressure phenomena, to tectonic forces, and to forces of contraction following devolatilization (20). These cleat surfaces are often coated with thin layers of mineral matter. Regardless of the mode of origin suggested for the cleats in coal all observers agree that cleating occurs late in the history of a coal bed. Cleating is a physical phenomenon and only after cleats have formed can minerals be deposited in the voids formed by fracturing. In these voids are deposited minerals of a high degree of purity and whichcan be easily

identified. Pyrite, kaolinite, calcite, gypsum and halite are minerals which have been found on cleat surfaces of coal. Their origins obviously are similar despite the great difference in composition of the minerals. Pyrite and kaolinite were formed by recrystallization from solution of minerals already present in the coal beds; calcite, gypsum, and halite were in part formed from ions migrating through the coal from outside the coal bed.

Erosion, a geological factor, may expose a coal bed to the atmosphere, and under such conditions cleat fractures in coal may be enlarged by physical forces. Weathering processes now impose an entirely new set of chemical conditions upon the coal bed. Atmospheric oxidation and the action of ground waters effect changes in the mineral matter of coal which are even more startling than the changes in the organic matter. Whole new suites of minerals are formed while pyrite may be completely destroyed. Minerals like gypsum, jarosite, melanterite, copiapite and many other sulfate minerals are formed from the oxidation products of pyrite. Allophane, an amorphous clay mineral which is chiefly a hydrous mixture of alumina and silica, may be an extreme alteration product of clay minerals within the coal and in the overlying sediments (21).

SUMMARY AND CONCLUSION

Geological controls are the primary factors in determining the grade of coal insofar as the mineral content is concerned. These primary controls, operative in the geologic past, have influenced current practices in coal utilization. The chemical environment of the coal swamp certainly has played a role in modifying the minerals deposited in the swamp, which has acted as a reaction vessel within which pyrite and marcasite could form. Under changing physical conditions during burial and compaction, and later, if subjected to erosion and exposure to circulating ground water and air, physical factors become dominant in controlling the chemical transformations that occur.

Perhaps it would have been more precise to discuss the factors which control the mineral content of coal all under only one classification--geochemical factors. In a broad sense geochemistry is concerned with all the changes by which the chemical composition of earth systems are modified. Sedimentation, a geological process, is itself controlled by diastrophic forces which are initiated by major geochemical forces. In every stage of coalification, from the first accumulation of plant debris to the ultimate exposure and oxidation of a coal bed, geochemical transformations are occurring.

However, such broad concepts, unless one is accustomed to thinking in such terms, do not convey to the fuel chemist the idea that the variable mineral content of coal is dependent upon a relatively few fundamental processes. Therefore, an attempt has been made to weave into the discussion of chemical and physical factors the continuous thread of dependence upon geological control--and this, in essence, makes the controls geochemical.

The mineral content of coal is a natural consequence of its mode of deposition and its subsequent geological history, and is not due to capricious causes. It is common knowledge that the mineral content of coal influences its utilization, often in a deleterious manner. Coal preparation as now practiced, can effectively reduce the mineral content of almost any coal. With a better understaanding of how minerals in coal are formed, and how they occur, the technology of coal preparation can be further improved.

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PROPERTIES AND REACTIONS EXHIBITED BY VITRINOID MACERALS FROM BITUMINOUS COALS

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The commercially important bituminous coals are composed in large part of vitrinitic substances. This fact coupled with what has been a somewhat vaguely defined association of these substances with the coking characteristics of coal places a premium value on any specific information concerning the nature and properties of these organic coal components. The data presented and discussed in the following pages represents a portion of the results obtained in the course of a program of research focused upon these materials.

The first phase of the investigation was initiated in 1952 and this dealt with the problem of developing petrographic descriptions of coal seams which would serve to predict the coking properties of any given coal. Preliminary studies brought out the fact that coal is made up of a complex of materials or entities, each possessing different optical properties, and presumably possessing differing chemical characteristics and carbonizing properties. These preliminary studies also demonstrated that the descriptive systems heretofore used were inadequate to allow differentiation of the coal macerals that were important in determining reacting properties. As a starting point, the most detailed of the existing descriptive systems, the one that had evolved out of the work of Stopes (1935) was used to describe a number of coal seams occurring in a single mining area in Kentucky.

The coal seams of this area are all of High Volatile "A" rank, and were very similar in their proximate and ultimate analyses, but great differences were noted when they were carbonized to produce metallurgical coke. This presented the opportunity to determine whether these differences in coking ability could be related to the petrography of the coal. The petrographic evaluations showed that the seams varied in entity composition. In addition, the investigation revealed that the seams varied in that they were differentially banded, that is, each coal seam was made up of many layers of differing composition. These layers of differing composition were called the petrographic divisions of the coal seam. Figure 1 presents a typical petrographic analysis. Note that within this seam there are 22 layers or petrographic divisions each differing in composition from the ones immediately adjacent to it.

From the petrographic data amassed on these seams it became apparent that if sufficient material could be obtained from some of these distinct bands occurring in the subject coals, test samples would be available that ranged in the major component composition from 38 % to 92% vitrinite, 1% to 35% exinite, 5% to 40% micrinite and from essentially none to about 14% fusinite. This material could then be carbonized and subjected to the tests used to evaluate metallurgical coke in order to demonstrate the effect of the petrographic composition of the coals. Several hundred pounds of each of 19 narrow coal bands were hand mined from three coal seams. This material was cut into two parts: one for a petrographic check, and the other was coked in duplicate in a 30 pound test oven and subjected to drop-shatter, tumbler and micro-strength evaluations. The results of these investigations have already been reported (Spackman, Brisse, Berry, 1957). In brief, the conclusions were as follows:

1. That in general the material designated fusinite was detrimental to coke strength if present in large particle size because it served as a locus of fracture points.

2. That the material micrinite was beneficial to coke strength up to a certain concentration. This action was likened to a concrete mixture. Pure cement will not make a strong product (cement = vitrinite); when aggregate is added to the cement - water mixture up to a certain limit, a very strong product results (aggregate = micrinite). Therefore there is, for concrete, an optimum mixture for greatest product strength, likewise these tests indicated that there was also an optimum maceral ratio for maximum coke strength. For the coals initially studied this ratio is on the order of 3 parts vitrinite to one part micrinite.
3. That the material exinite contributed to the bonding capacity of certain coal blends and when present in concentrations of over 10%, materially enhanced the strength of the coke.
4. That the material vitrinite is the prime factor controlling the carbonizing properties of the coals tested. This is in part due to its great predominance in the subject coals. No entire seam investigated contained less than 50% of this material and one had greater than 80% vitrinite. Secondly, this material is one of the substances of the coal that produces its fluid characteristics when heated. Figure 2 presents the expressed relationship between the vitrinite content and the coke strength (reproduced from Spackman, Brisse and Berry, 1957). Notice that there is an optimum amount of this material associated with maximum coke strength and that an excess or deficiency of the material results in a loss of coke strength.

With this correlation in hand it was decided to test further the validity of the inferred relationship by coking samples on a larger scale (500# test oven). If the curve was valid each samples' vitrinite content would cause it to fall on the correlation curve. Figure 3 presents the results of these experiments. Note that four of the five points fall where expected, but the fifth, a known poor coking coal, fell completely off the supposed correlation curve. Re-examination of this fifth sample brought out a very curious fact: the material classed as vitrinite in this coal contained a variety of materials with differing optical properties but under the descriptive system used there was no choice other than to classify them as vitrinite. Re-evaluation of the other four seams showed that this was true to a much lesser degree. Sample 5 was found to contain between 15% and 20% of materials that differed from the typical "vitrinite" which predominated in the other four samples. For the time being the more abundant material was called vitrinite, and when sample 5 was re-analyzed counting only this material as "vitrinite", the point moved to the predicted position as shown on the other graphs in Figure 3.

It would appear then that:

1. The maceral terms as proposed by Stopes do not, in fact, describe the basic entities of coal, rather they include a group of genetically related materials that in actuality differ in optical, physical and chemical properties.
2. Recognizing the variability within any one of Stopes' "macerals" it was suggested that these terms be elevated to a maceral group status because there was a value in retaining the genetic aspects of the classification. This would allow the description of the entities occurring in the group and their designation as macerals (see Spackman, 1958).
3. To facilitate this the following changes are suggested: Stopes' terms have achieved world wide recognition in describing coal materials so in order to avoid confusion, it is suggested that these descriptive names be retained but the suffix changed to "oid" to designate that these represent a group of materials, and, that as the macerals are described, they be named appropriately and use the ending "inite".

For present purposes the macerals comprising any one group are designated by type number until more complete data has been amassed. Table 1 presents the classification as it is presently used.

Table 1

Maceral Groups	Vitrinoids									Micrinoids		Fusinoids		Resinoids			Exinoids		
	Type I	Type II	Type III	Type IV	Type V	Type VI	Type VII	Type VIII	Type IX	Type I	Type II	Type I	Type II	Type I	Type II	Type III	Type I	Type II	Type III

Utilizing this classification system, the next phase of research opened with the sampling of coals of all ranks from widely separated geographical areas. Coals were collected from Utah, Illinois, Pennsylvania, Ohio, West Virginia, Kentucky and Alabama. All of these coals were examined using normal petrographic methods and their entities classified on the basis of their optical properties. This completed, the next step was to be sure that the entities classified by optical means were indeed different in their reactive properties.

To facilitate this, and since the primary interest at the time was the ability to predict any coal's coking potential, a research instrument was assembled to evaluate the thermal properties of the entities. A Leitz 1000° heating stage, a research microscope and a temperature control unit comprise the basic components of the assembly. This apparatus is shown in Figure 4. This heating stage can be brought, at any rate of heat, to any temperature between 0 and 1000° Centigrade. It is so built that a sample can be viewed in transmitted or reflected light while being brought through its heating cycle. A nitrogen atmosphere is maintained in the furnace to stop oxidation of the subject material. All reactions can be biewed as they occur, and to facilitate the recording of the data a time lapse motion picture camera is included in the system. This allows the recording by color motion pictures of the reactions of the various entities as they take place. Figure 5 presents a picture of the control panel associated with this heating stage microscope. The incorporation of a program controller in the system allows the selection of any rate of heat from 3° to 15°C./minute, by setting the desired rate on the upper left timer control. If a period of soaking at any temperature between 100° and 900°C. is desired, the controller can be set to cut out at that temperature, the soak timer (directly below the aforementioned rate controller) can be set to any period of time and will cause the main controller to maintain the desired temperature. At the close of the soaking period the timer will throw the control to the right hand rate controller which will pick up the original rate of heat or any other desired rate. The camera control (left lower center) allows camera speeds of 1 frame every 5 seconds to 8 frames per second. A secondary piece of equipment allows camera speeds up to 32 frames per second. Figure 6 illustrates the type data that can be obtained by microcinephotography. The sequence on the left shows a mass of exinoid material just at its melting point, the next frame shows it in a partially fluid state, the third in a totally fluid state and the fourth shows its residue. The sequence on the right shows the melting and volatilization of one of the resinoids. Note that it is almost completely volatilized in the last frame. After preliminary investigations on several of the important coal macerals to ascertain that they were different in their reacting properties, it was decided to work first with the group of materials occurring most abundantly in the coal. These were the vitrinoids. The suite of coals were thoroughly studied microscopically and the nine most prominent vitrinoids were isolated for detailed property analysis.

The first series of tests involved the heating of specific vitrinoid types at a heating rate of 3°C/min. which is roughly equivalent to the rate of heat used in a commercial coke oven. Figure 7 presents the results of this study. All of the data presented are based on at least five runs in which reproducible results were obtained. Note that the entities studied can be grouped into three categories: Non-Plastic, Semi-Plastic, and Plastic types. The non-plastic vitrinoids, Types I and II, are predominant in occurrence in High Volatile C and B coals and for all intents and purposes are inert at this rate of heat. The semi-plastic vitrinoid, Type IX, is common in occurrence in the low volatile coals but in general its percent occurrence

is low. The plastic materials Types III, IV, V, VI, VII, and VIII are found in varying amounts throughout the bituminous coal range. Based on the coals studied to date, it appears that these nine vitrinoid types appear in the range of bituminous coals as shown in Table 2.

Table 2

Influence of Vitrinoid Type on Rank Designation of Bright Coals

Vitrinoid Composition of Typical Bituminous Coals			Resultant Rank
Predominant Type	Major Types	Minor Types	Designation
I	II	III and IV	High Volatile C
II	I and III	IV, V and VI	High Volatile B
IV	III and V	II, VI and VII	High Volatile A
VII	IV and VIII	III, IV, V, IX	Medium Volatile
VIII	VI and VII	V and IX	Low Volatile

Although all of the vitrinoid types described in Figure 7 exhibit some difference in the manner in which they respond to this heating program, similarities are evident in the case of the plastic varieties. An attempt has been made to emphasize this fact by separating obviously dissimilar materials with horizontal lines.

Figure 8 presents data on an identical study using a heating rate of 12°C per minute, the object being to determine the manner in which each vitrinoid reacts under another set of conditions. One of the most striking differences apparent is that there are no longer vitrinoids which fail to show fluidity when this accelerated heating rate is used. Notice that the capacity to fuse with similar particles is enhanced in every case, also that the parallel lines delineating vitrinoids of similar properties have shifted.

From these studies involving only a change in rate of heat, two major conclusions can be drawn: 1. that the optically distinct vitrinoid types do possess differing thermal properties and can be expected to react differently in certain industrial processes; 2. that an increase in heating ratio elicits a variety of reactions from the vitrinoids investigated.

The next series of tests on these vitrinoids were designed to record the differences, if any, in the reactions exhibited when the entities were subjected to shock heating at 600 and 800°C.

Figure 9 illustrates the extremes in the recorded reactions of this study. In these tests a chip of pure vitrinoid material was photographed before and after exposure to shock heating in a top and side view. The tests shown in Figure 9 illustrate two vitrinoids which exhibited extremes in behavior. One of them, Type II, actually volatilizes with such explosiveness that a loss in volume over that of the original material results. The other material, Type VII, shows a strong swelling to several times the size of the original material. Figure 10 illustrates some of the results obtained in these tests. Note that Type II, when shock heated at 600°C. shows little change in mass; however when shock heated at 800°C. a large portion of the material volatilizes leaving a mass smaller in size than that of the original material. Type III shows an increase in mass at 600° and an even greater expansion at 800°. Type IV displays a strong increase in mass at 600° shock but when exposed to temperatures of 800° the material expands strongly but has a period of contraction before solidification. This is also true of Types VII and VIII. Type VII shows a massive increase in volume when shocked at 600°, this is especially interesting because

coals that are associated with oven pressure problems in the metallurgical coke industry are generally rich in this vitrinoid type. When shocked at 800° Type VII displayed less expansion, perhaps indicating that when dealing with a strongly swelling coal a faster rate of heat will lessen the potential pressure dangers. Type VIII exhibits a behavior pattern similar to Type VII, however, this material swells to a much lesser degree.

Conclusions to be drawn from this test series are, again, that the subject vitrinoid types vary in their reactions and that for certain applications the desired reaction can be enhanced by a greater rate of heat.

The curve previously presented as Figure 2 which related one of the vitrinoids to coke strength showed that the presence of too much or too little of this material would cause a loss in strength. It was also noted that a ratio between this vitrinoid and the micrinoids of approximately 3 to 1 produced the strongest coke. The question then arose as to what amount of material each of the vitrinoid types could assimilate into a coke mass, and what the affect of such an assimilation would be on the strength of the resultant coke.

A series of small tests were performed using pure vitrinoid types and varying amounts of an inorganic inert material. Enough of these pure substances were picked out, with microscopic control, to allow the running of duplicate tests on each of the vitrinoid types using the following proportions (Table 3).

Table 3

Composition of Test Blends

Percent Pure Vitrinoid Type	Percent Inorganic Inert
100	0
90	10
80	20
70	30
60	40
50	50
40	60
30	70
20	80
10	90

The inert substance used was hydrated alumina and the tests consisted of coking the pure and diluted vitrinoid types in small crucibles, in an electric muffle furnace. The evaluation for strength was done on a microhardness tester.

The experimental results on the tests performed on vitrinoid Type II are presented in Figures 11, 12 and 13. Figure 11 consists of photographs of the actual coke buttons produced in the study and the unassimilated inert material. When the pure vitrinoid was coked, violent eruptions of fluid coal took place and in several cases the material produced minor explosions. This continued until 30% inert material was mixed in (refer to photographs). Note also that it is not until after 40% of inert material has been added that any unagglomerated residue appears. Notice also that the apparent stability of the coke mass improves until the amount of inerts added becomes too great to be assimilated. Figure 12 presents cross sections of the coke buttons showing the apparent effect on the coke structure of inert addition. Notice the effect of the violent reaction of this pure vitrinoid on its internal structure and how the structure stabilizes with the addition of inert material. With 80% of inert material in the mix a stable-appearing structure is still in evidence. Figure 13 presents data on the yield of coke of a particular strength. Notice that not until greater than 40% inert

material has been added does the strength drop below that of the pure maceral, in fact at 40% dilution a slight rise in strength is noted.

The test results of vitrinoid Type III are presented in Figures 14, 15 and 16. The coke buttons shown in Figure 14 show that this material can assimilate up to 40% of inerts without loss of the stabilizing effect. In Figure 15 the button cross-sections show this stabilizing effect to a much greater degree than in the case of the results obtained by blending Type II material and Figure 16 presents a set of data which contrast markedly to those presented in Figure 13. Note that greater than 50% inerts were added before the coke strength dropped below that of the pure Type III material and also that there is an impressive gain in strength at the 30% dilution level.

Figures 17, 18 and 19 represent the accumulated data on Type IV. Figure 17 again points out the stabilizing effect of the addition of inert material. Note here that the 50% dilution level has been reached before any unbonded inert material becomes evident. Figure 18 substantiates the points brought out by the previous figure and illustrates the fact that this inert additive tends to stop the fissuring apparent in the blends high in Type IV. Figure 19 presents the strength-yield curve for this type. Note that the inert dilution approaches 60% before the strength drops below that of the pure maceral and there is a sizeable strength increase over a rather large range exhibited by this maceral.

The testing of Type VII brought out several interesting points on the expansion properties. This is especially informative because, as was mentioned before, coals that present problems to the coke oven operator in the form of sticking charges and unsafe pressure on the oven walls often contain large portions of vitrinoid Type VII in their composition. Figure 20, the coke button photographs, illustrate this swelling property. Note that in the picture of the pure maceral the button is the largest and as the inert percentage becomes greater the button size decreases and generally stabilizes in size at about 50% dilution. The fact that this material has the ability of incorporating greater than 50% inert material into the mass is also evident. Figure 21 makes evident one of the factors responsible for this swelling property. Note that in the button cross-section of the 100% Type VII there is a very large center vacuole. This vacuole was made by entrapped gases in the center of the button which were apparently unable to force their way through the viscous surrounding material. These gases then caused the mass to swell and with no exit route the gases in the vacuole were trapped. Notice that as the percentage of inert substances becomes greater, the swelling and the vacuole size diminishes. This tends to show that inert addition either allows the gases to exit through the viscous mass or the viscosity of the fluid vitrinoid Type VII has been lowered to allow normal bubbling off of the gases. Figure 22 again shows a distinctive dilution strength-yield in which over 50% dilution is necessary before the strength is increased approximately 20% over that of the pure maceral. Note the wide range of strength beneficiation.

Vitrinoid Type VIII differs from all other vitrinoid types. Note the frothiness of the buttons (Figure 23) and the projections on the button tops. The frothiness is apparently due to fast coking in which the gases of the mass were trapped in the cell structure. The top projections indicate that the outer button wall was coked and solidified quickly forcing the inner fluid material to erupt through the top of the button. Greater than 50% of inert material can be incorporated into the mass and structure stabilization is brought about by the addition of inert material. The button cross-sections (Figure 24) show that dilution with inert material initially increases swelling and central vacuole development. In effect inert dilution causes the mass to become more viscous thus presenting a barrier to escaping gases. Figure 25 illustrates the strength-yield characteristics of vitrinoid Type VIII.

The tests dealing with the assimilation capacities of these macerals of coal led to many important conclusions. The first and most obvious is that each entity tested displays a differing behavior pattern. Figure 26 compares the two type extremes showing their apparent assimilation potentials. Figure 27 compares five types of vitrinoid by illustrating the button produced by the pure vitrinoid types and the blend of that type with inert material that produced the highest strength. In Figure 28, coke button cross-sections show the structure and vacuole development of the pure materials, and in this figure the blends yielding the highest strength coke and the maximum vacuole development are also depicted.

This research has produced data that shows graphically that these materials differ in at least optical, physical and thermal properties. The data presented here has all been slanted toward establishing the basis for evaluating bituminous coal for use in metallurgical coke production. However, this is not the only application that will come from this type of study. Work is nearing completion on the effect of the vitrinoids on one another. It is important to know the affects of one entity on the other because a coal seam generally has one predominant vitrinoid type and two or three others that occur in quantities large enough to effect the commercial products. Once the critical data are obtained it should be possible to describe the combustion, carbonization, and hydrogenation potential of a coal seam from small samples such as those obtained in exploratory drilling operations. In addition, such information should provide the basis for prescribing more efficient preparation and blending operations. Through these avenues a contribution should be made to increasing the efficiency and effectiveness with which coal is utilized.

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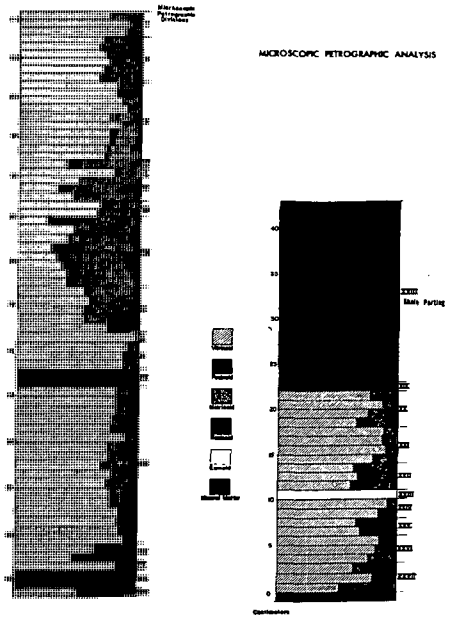
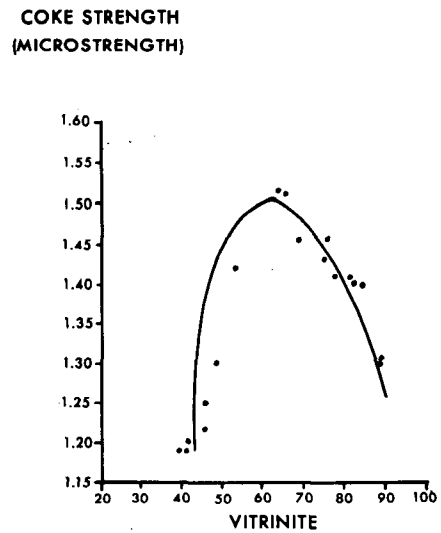


Figure 1



RELATIONSHIP OF VITRINITE CONTENT
TO
COKE STRENGTH

Figure 2

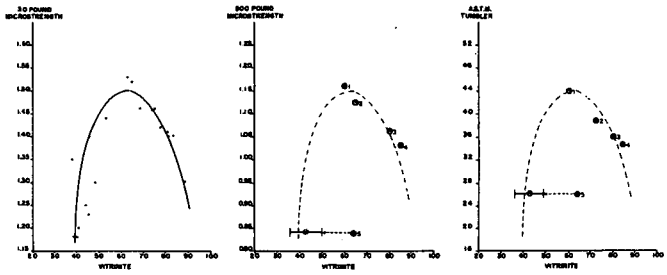


Figure 3

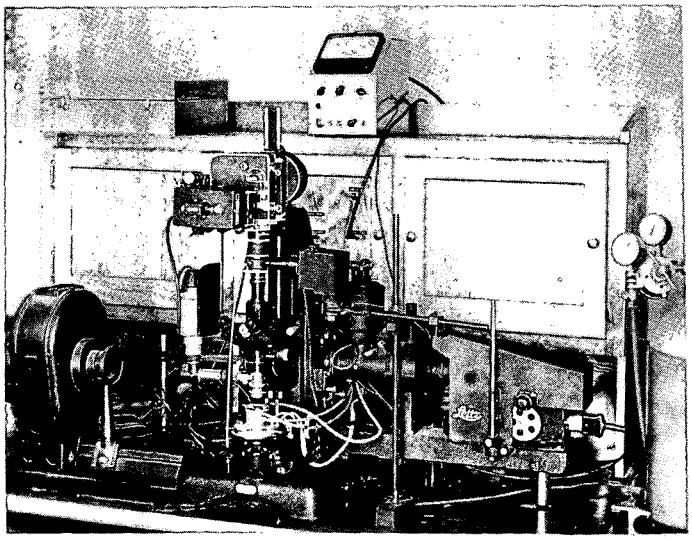


Figure 4

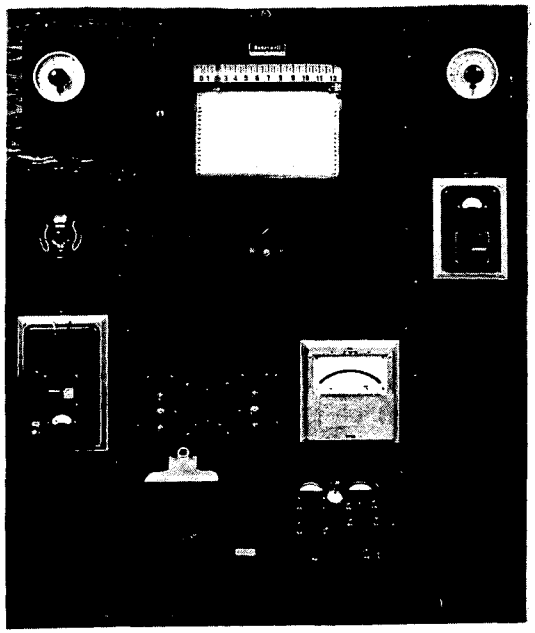


Figure 5

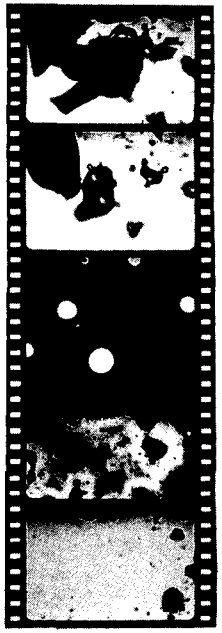


Figure 6

THERMOPLASTIC PROPERTIES
OF
VITRINOIDS AND RELATED SUBSTANCES
(3 C./min.)

		Average Fluid Range (C.)	Average Softening Point (C.)	Average Solidification Point (C.)	Capacity to Fuse with Similar Particles
NON-PLASTIC	TYPE I	None	None	None	None
	TYPE II	None	None	None	None
SEMI-PLASTIC	TYPE IX	Semisolid	453	552	None
PLASTIC	TYPE VIII	75	420	495	Fair
	TYPE V	109	411	520	Good
	TYPE VI	125	426	551	Fair
	TYPE IV	161	409	571	Good
	TYPE III	161	412	573	Poor
	TYPE VII	182	416	598	Poor

Figure 7

THERMOPLASTIC PROPERTIES
OF
VITRINOIDS AND RELATED SUBSTANCES
(12 C./min.)

		Average Fluid Range (C.)	Average Softening Point (C.)	Average Solidification Point (C.)	Capacity to Fuse with Similar Particles
NON-PLASTIC	TYPE I	83	417	500	Poor
	TYPE II	95	412	507	Good
SEMI-PLASTIC	TYPE IX	Semisolid	440	550	Poor
PLASTIC	TYPE V	110	416	526	Excellent
	TYPE VI	124	431	555	Excellent
	TYPE IV	165	406	571	Excellent
	TYPE III	164	407	571	Good
	TYPE VIII	203	447	650	Good
	TYPE VII	220	411	631	Fair

Figure 8

EFFECT OF SHOCK HEATING
on
VITRINOIDS II AND VII

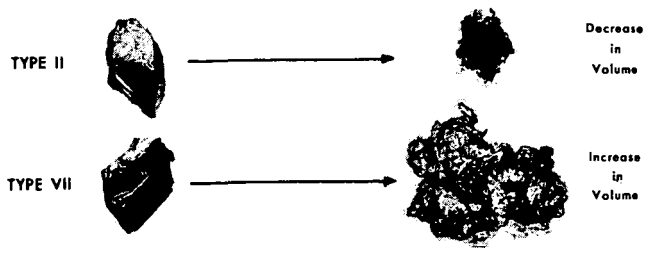


Figure 9

EFFECT OF SHOCK HEATING
ON CERTAIN VITRINOIDS

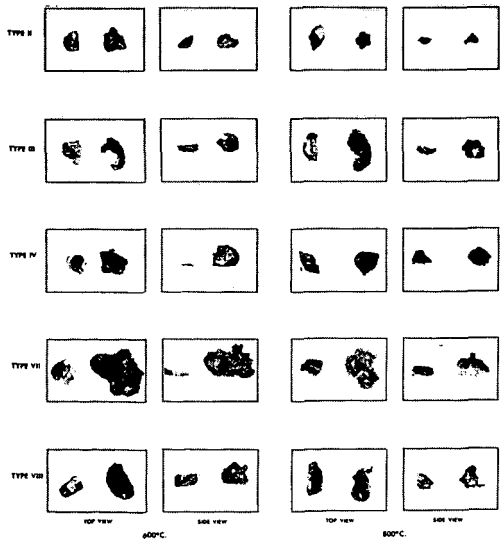
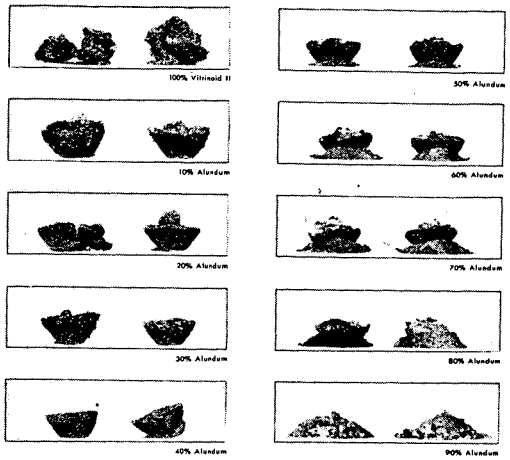


Figure 10



EFFECT OF INERT MATERIAL ON COKE PRODUCED FROM VITRINOID TYPE II

Figure 11

EFFECT OF BLENDING INERT MATERIAL
WITH VITRINOID TYPE II

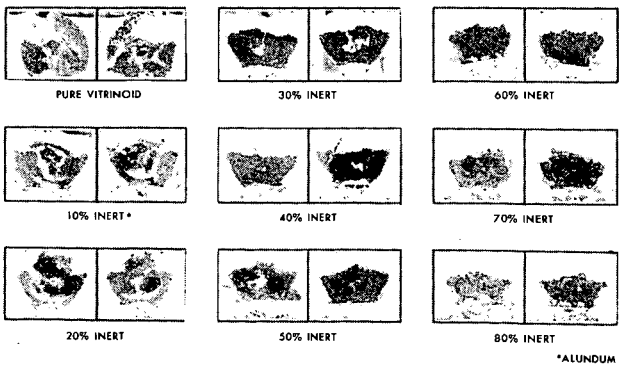
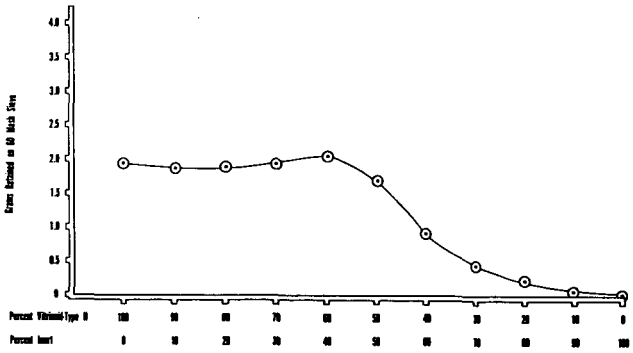
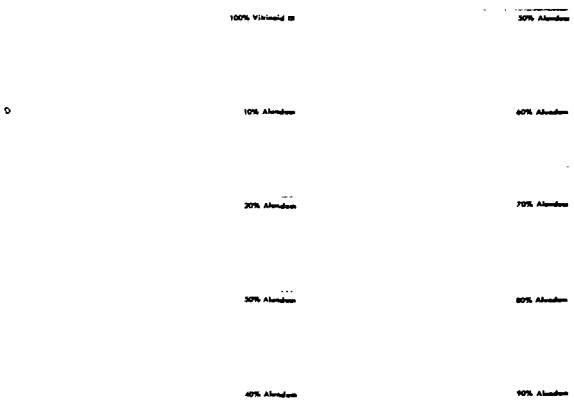


Figure 12



MICROHARDNESS TEST DATA
YIELD OF 60 MESH COKE
DERIVED FROM 4 GRAMS OF VITRINOID TYPE II

Figure 13



EFFECT OF INERT MATERIAL ON COKE PRODUCED FROM VITRINOID TYPE III

Figure 14

EFFECT OF BLENDING INERT MATERIAL WITH VITRINOID TYPE III

PURE VITRINOID

10% INERT*

20% INERT

30% INERT

40% INERT

50% INERT

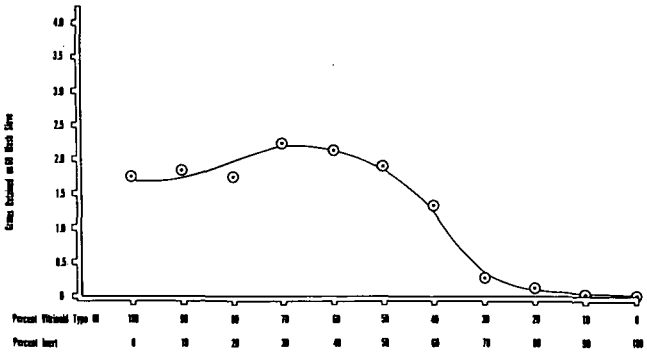
60% INERT

70% INERT

80% INERT

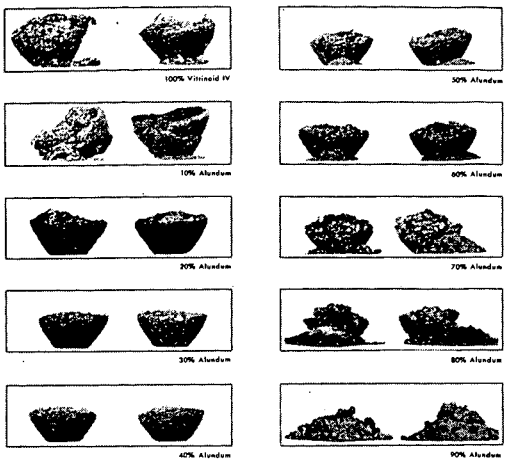
*ALUNDUM

Figure 15



MICROHARDNESS TEST DATA
YIELD OF 60 MESH COKE
DERIVED FROM 4 GRAMS OF VITRINOID TYPE III

Figure 16



EFFECT OF INERT MATERIAL ON COKE PRODUCED FROM VITRINOID TYPE IV

Figure 17

EFFECT OF BLENDING INERT MATERIAL
WITH VITRINOID TYPE IV

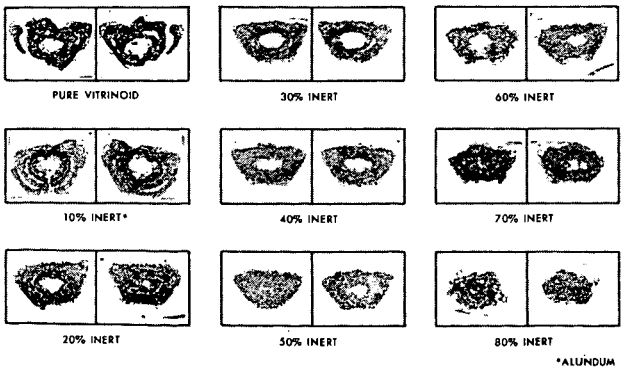
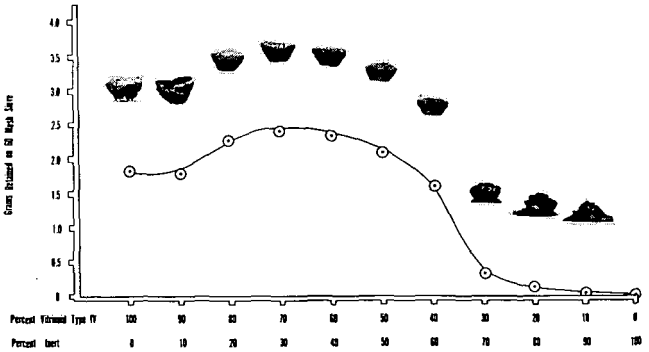
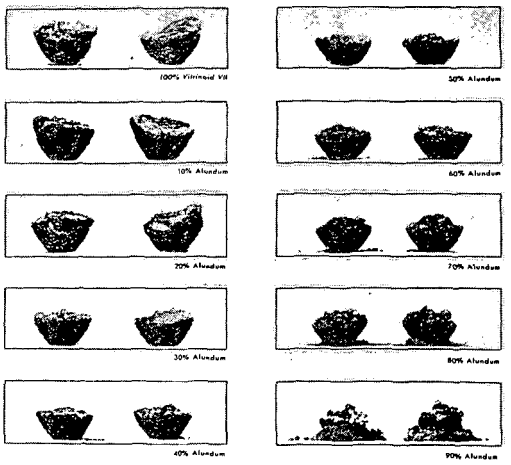


Figure 18



MICROHARDNESS TEST DATA
YIELD OF 60 MESH COKE
DERIVED FROM 4 GRAMS OF VITRINOID TYPE IV

Figure 19



EFFECT OF INERT MATERIAL ON COKE PRODUCED FROM VITRINOID TYPE VII

Figure 20

EFFECT OF BLENDING INERT MATERIAL WITH VITRINOID TYPE VII

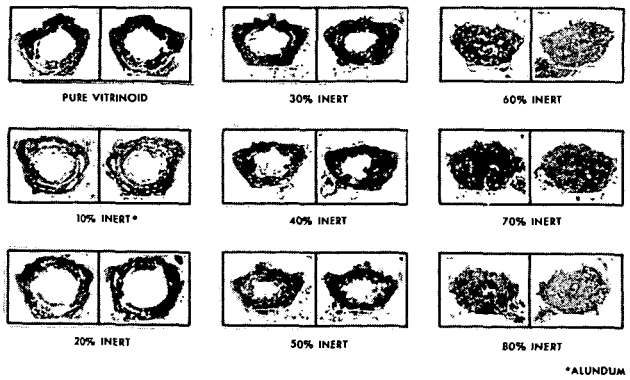
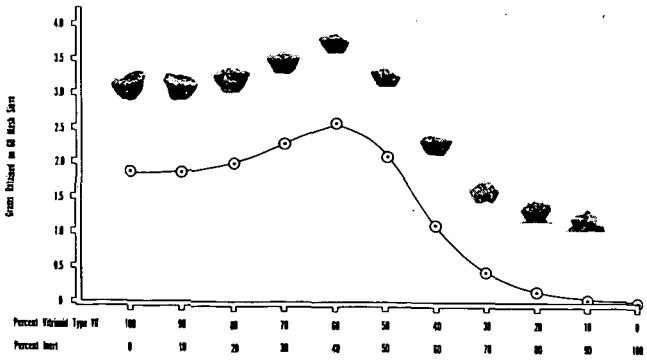
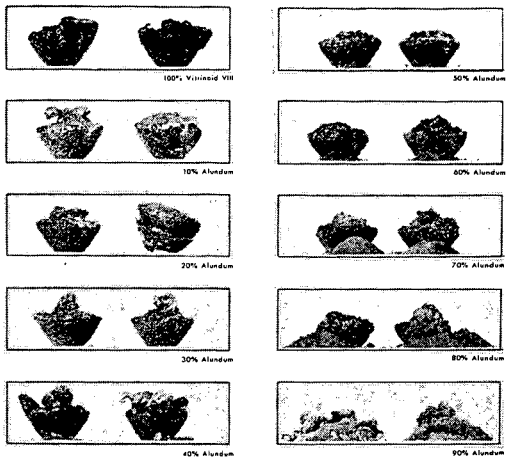


Figure 21



MICROHARDNESS TEST DATA
YIELD OF 60 MESH COKE
DERIVED FROM 4 GRAMS OF VITRINOID TYPE VII

Figure 22



EFFECT OF INERT MATERIAL ON COKE PRODUCED FROM VITRINOID TYPE VIII

Figure 23

EFFECT OF BLENDING INERT MATERIAL
WITH VITRINOID TYPE VIII

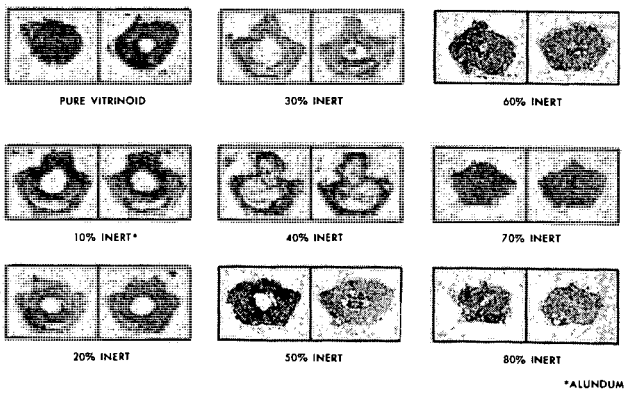
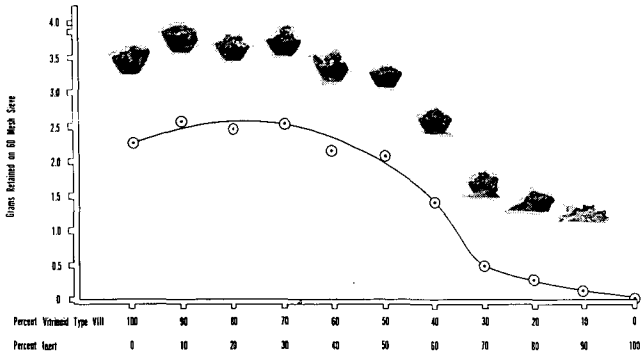
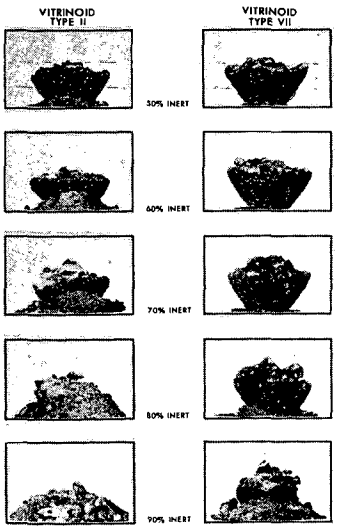


Figure 24



MICROHARDNESS TEST DATA
YIELD OF 60 MESH COKE
DERIVED FROM 4 GRAMS OF VITRINOID TYPE VIII

Figure 25



COMPARISON
of
INERT ASSIMILATING CAPACITIES

Figure 26

COMPARISON OF COKE
DERIVED FROM PURE VITRINOIDS
WITH COKE PRODUCED FROM BEST BLEND

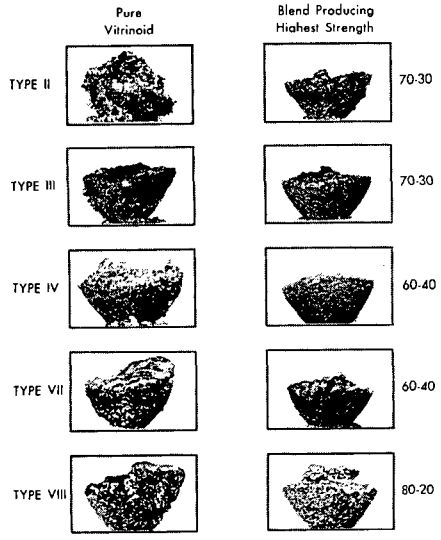


Figure 27

INFLUENCE OF VITRINOID TYPES ON COKE STRUCTURE

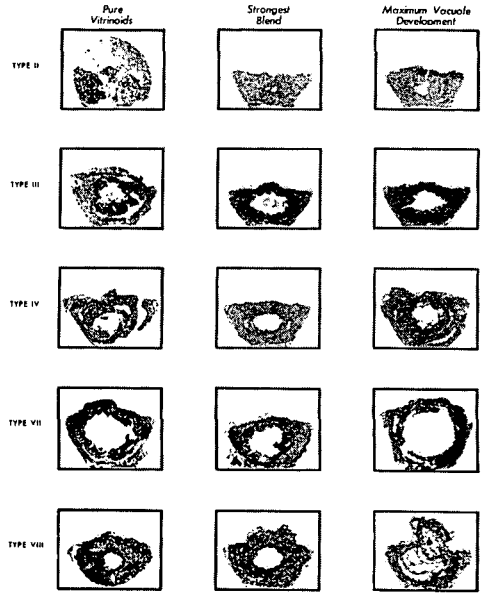


Figure 28

Not for Publication
Presented Before the Division of Gas and Fuel Chemistry
American Chemical Society
Boston, Massachusetts, Meeting, April 5-10, 1959

Some Properties of Cuticle-Derived Components of Coal*

By R. C. Neavel and L. V. Miller

Indiana Geological Survey, Bloomington, Indiana

The chemical and physical characteristics of any coal seam or portion of a seam are determined by the chemical and physical characteristics of the constituent parts called macerals or phyterals. Vitrinite, derived from the cell walls of the contributing plants, predominates in most coals; while micrinite, resinite, exinite, and fusinite make up only minor amounts of most coals. An above average amount of any of these latter four constituents in a coal sample will result in that sample being classed as chemically and physically abnormal when compared to typical coals from the same vicinity.

Among the coal ingredients which normally constitute a minor part of a coal seam, are the remains of plant cuticles (which are classed with the exinites). Cuticle is a wax-like covering on leaves and young twigs, and serves to deter dessication of these succulent tissues. Cutin, the constituent material of cuticles, is formed by the atmospheric condensation and oxidation of fatty acids which migrate to the surface of the plants (Weaver and Clements, 1938). Cuticles are essentially resistant to bacterial and chemical destruction when deposited in swamp conditions and thus are preserved in an essentially unaltered condition in most peat deposits. Van Krevelen and Schuyer (1957, p. 241), as well as other authors, indicate that exines (of which cuticle is one) are less affected by dynamic metamorphism than ligno-cellulosic constituents and thus tend to retain their distinctive identities well into the bituminous rank coals. Thus, in high-volatile bituminous coals, cutinite is chemically distinct from the associated vitrinites. It seems best to refer to cuticular remains in coal as "cutinite," (Stopes, 1935) as they have been altered, if only slightly, from the original cutin.

Legg and Wheeler (1925, 1929) conducted the first modern analyses of present-day and fossil cuticles. By analysing cuticles from Agave (a highly cutinized, semi-tropical plant) Legg and Wheeler determined that cuticle consists of four major components, three of which are respectively soluble in boiling water, alcohol, and cuprammonia solution. The residue, after extracting the above soluble constituents, represents 60 percent of the weight of the original cuticle and was referred to as "cutin," the basic cuticle substance. Ultimate analyses of the dissolved fractions indicated their compositions to be:

Water soluble -	carbon 48.7	hydrogen 6.7	ash 28.8
Alcohol soluble (waxes) -	79.1	13.1	10.8
Cuprammonia soluble (cellulose) -	44.1	6.4	2.0
Cutin residue -	67.1	9.9	2.8

Treatment of the residue (cutin) yielded two semi-liquid acids, the formulae for which Legg and Wheeler calculated to be $C_{26}H_{50}O_6$ and $C_{13}H_{22}O_3$; and two solid acids, one with a melting point of 107-108°C, thought to be phloionic acid, and the other with a melting point of 88-90°C, to which no name was assigned.

* Published by permission of the State Geologist, Indiana Department of Conservation, Geological Survey.

Matic (1955) was "... concerned with the separation, isolation and structure of the acids constituting the ether soluble fraction obtained on saponification of cutin from A. americana L.". Matic succeeded in isolating 5 acids, all of which he named with their respective organic terms. He concluded that "in the light of evidence presented, it is quite clear that the cutin acids reported on previously (Fremy, 1859, 1881, 1885; Legg and Wheeler, 1925, 1929) were not pure compounds, but mixtures with the possible exception of Legg and Wheeler's 'phloionic' acid which was probably impure phloionolic acid ...."

Legg and Wheeler (1929) also analysed cuticles isolated from several coals. Russian Papierkohle samples were treated with NH_4OH to remove the ulmins and the cuticles were then mechanically separated from any remaining undissolved ulmins. Ultimate analyses of the concentrated cutinite indicated: carbon 73.9, hydrogen 11.4, nitrogen 1.1, sulphur 2.1, and ash 13.4 percent. They felt that fossil cuticles (cutinite) contain neither water solubles nor cellulose, although they undoubtedly do contain waxes. Roelofsen (1952) after optically studying cuticles, also concluded that after severe extractions (which we might consider partly analogous to biogentic coal formation) cuticles still contain waxes. Legg and Wheeler (1929) also isolated cuticles from an English durain by oxidizing and subsequently removing the ulmins with NH_4OH. The durain contained; carbon 83.0 and hydrogen 5.5 percent, whereas the isolated cuticles (cutinite) contained; carbon 65.2 and hydrogen 7.4, ash 4.9 percent, and traces of nitrogen and sulphur.

Analyses conducted by Edwards (1947) on hand picked cuticles (cutinite) from pockets in the Yallourn brown coal of Australia, indicate the following composition; carbon 70.4, hydrogen 7.6, nitrogen 0.45, sulphur 0.20, oxygen 21.64, and ash 0.6 percent. The coal from which these cuticles were obtained had a fuel ratio (FC/VM) of about 0.9, while the cuticles had a fuel ratio of about 0.25.

Legg and Wheeler (1929) subjected Agave cutin, Papierkohle cutinite, and durain derived cutinite to destructive distillation in a vacuum apparatus. The results are presented as Table 1. The low distillate yield of the durain cutinite may be partially attributable to the method of obtaining the cuticle, that is, by severe oxidation and treatment with NH_4OH, to remove ulmins. Oxidation is known to reduce tar yields of coals (Schmidt, 1945, p. 666).

Table 1
Distillation of Cutin (from Legg and Wheeler, 1929)

Properties of Oils	Plant Cutin	Papierkohle Cutin	East Kirkby Durain Cutin
First appearance °C	280	265	350
Main evolution °C	300 - 350	300 - 350	350 - 370
Yield percent by weight	60	40	20
Analysis percent			
Saturated Hydrocarbons	38	25	11
Unsaturated Hydrocarbons	trace	33	22
Aromatic Hydrocarbons	16	9	22
Phenolic and Acidic Oils	26	10	1
Oxygenated Compounds	8	16	22
Ether soluble resin	4	3	11
Chloroform soluble pitch	7	3	11

In 1958, a coal seam containing abnormally abundant cuticle derived components was discovered in Indiana. (See Neavel and Guennel, in manuscript). Chemical analyses of cutinite from this "paper coal" were instigated at the Indiana Geological Survey. Mechanical weathering of the paper coal, removed much of the vitrinite in which the cuticles were embedded. Several grams of pure cutinite were concentrated by disaggregation of the coal in water and hand-picking pieces of cutinite. In order to check the results obtained from analysing this sample, several more samples of relatively pure cutinite were obtained by dissolving the weathered vitrinite of the paper coal in a dilute KOH solution. Petrographic analyses of these latter samples indicated that they still contained between 10 and 20 percent vitrinite. Results of their analyses could thus be calculated to a vitrinite-free basis. Analyses of the cutinite were, in most cases, standard coal analyses rather than organic chemical analyses. No attempts were made to determine molecular constituents. The results of the analyses of the cutinite concentrates from Indiana paper coal and the results of analyses conducted by several other investigators on other cutinite concentrates are presented, along with results of several control sample analyses, as table 2. A description of the samples follows:

Sample No.	Description
1	Channel sample of weathered paper coal
2	Grab sample of weathered paper coal - analysed by U. S. Bureau of Mines Laboratory - results courtesy of Dr. J. M. Schopf, United States Geological Survey
3	Coal lying 15 feet below paper coal
4	Coal V sample used for control in retort
5	Pure cutinite - hand-picked from disaggregated paper coal
6,7,8	Cutinite concentrates obtained by treating paper coal with KOH
9	Cutinite from Australian lignite (Edwards, 1947)
10	Cutinite from Russian paper coal (Legg and Wheeler, 1929)
11	Cutinite from durain (Legg and Wheeler, 1929)
12	Cutinite from HVC bituminous coal (Kosanke, 1952)

Table 2 - Analyses of Cutinite and Control Samples

Samp. No.	Sample Description	Moist. AR	Ash Dry	VM DAF	BTU AR	BTU DAF	S. DAF	H. DAF	C. DAF	N. DAF	O. DAF
1	Paper coal	14.3	14.9	66.5	8896	12203	0.62				
2	Paper coal	5.0	25.6	60.2	8690	12280	0.5	7.1	69.6	1.4	21.4
3	Lower coal	14.7	7.7	42.8	11411	14499					
4	Retort control	14.0	7.2	44.4	11360	14232	4.23	5.4	78.9	1.7	9.8
5	Pure cutinite	11.0	10.7	84.7	13320	16730	0.21	8.1	74.7	0.7	16.3
6	Cutinite conc.	5.4	14.9	79.2	11372	14134	0.45	8.2	74.5	1.2	15.6
7	Cutinite conc.	6.7	13.3	77.4	11258	13906	0.62	8.0	74.9	1.3	15.3
8	Cutinite conc.	7.4	11.2	77.1	11510	14050	0.17	7.7	73.4	1.3	17.5
9	Lignite cutinite	6.1	0.6	79.0	NA*	NA	0.20	7.6	70.4	0.45	21.64
10	Russian Paper coal	NA	13.4	NA	NA	NA	2.1	11.4	73.9	1.1	11.4
11	Durain cutinite	NA	4.9	NA	NA	NA	Tr.	7.8	68.5	Tr.	23.3
12	HVC bit.cutinite	17.0	Tr.	NA	NA	NA	NA	6.3	74.5		

*Data not available

The analyses of sample 5 best show the characteristics of cutinite from the Indiana paper coal. The ash content appears to be exceptionally high when cognizance is taken of the fact that there is little, if any, mineral matter in the sample. All, or almost all, of the 10.7 percent dry ash is inherent ash; that is, it is actually a part of the plant tissue. Semi-quantitative spectrographic analyses indicate that over 30 percent of the ash is CaO and less than 5 percent is Al_2O_3. Much of the remainder is probably silica, although the techniques used did not allow its determination.

The amounts, in percent of cutinite ash, of trace and minor elements, determined spectrographically, are (abundances in earth's crust, in parentheses, from Mason, 1952): B - 0.14(0.0003), Cr - 0.066(0.02), Ge - 0.01(0.007), Fe - 0.78(5.0), Pb - 0.01 (0.0016), MN - 0.044(0.1), Mg - trace(2.1), Mo - 0.01(0.0015, Ni - 0.01(0.008), P - 1.0 (0.12), Sn - 0.08(0.004), Ti - 0.11(0.44), V - 0.01(0.015), Zn - 0.059(0.013), and Y - 0.02(0.0028). Ash content and ash properties of any coal ingredient are, however, functions of swamp environment and plant type. The present results, therefore, are not necessarily indicative of ash content and ash properties to be found in all cutinite (note sample 12). The high ash content of the Indiana paper coal does, however, point out the importance of inherent or non-mineral matter ash in certain coal ingredients.

The volatile matter content of cutinite is very high. On the basis of analyses performed by the Indiana Geological Survey during the last 4 years on over 400 samples of Indiana coals, the average volatile matter content of Indiana coal is 47.9 percent (daf). The paper coal cutinite contains almost 85 percent dry, ash-free volatile matter. As samples 6, 7, and 8 are not pure cutinite, their volatile matter contents are somewhat lower than 85 percent. In order to check this figure of 85 percent, the amount of cutinite in samples 6, 7, and 8 was determined. Thin-sections of pelletized portions of these samples were analysed petrographically, and samples 6, 7, and 8 were found to contain, respectively, 82, 84, and 90 percent cutinite; the remainder was vitrinite. No mineral matter was visible although the higher ash content of samples 6 and 7 indicate that they probably contained some adventitious mineral matter.

Vitrinite from coal wherein the cutinite has a volatile matter content of 85 percent, should have a volatile content of about 40 percent. This value was obtained by extrapolating the figures given by Van Krevelen and Schuyer (1957) in their Table X, 1, P. 239. The total dry, ash-free volatile matter of a sample containing vitrinite and exinite is the sum of the volatile matter derived from each of the constituents. Therefore, the following equation was set up: VM% (vitrinite%) + VM% (exinite%) X 100 = Total VM as daf% of sample.

By substituting the respective amounts for vitrinite and exinite determined microscopically, 40 percent for VM of vitrinite, and the respective total VM in each sample one arrives at figures of 88.0, 84.2 and 81.3 percent for the volatile matter content of the exinite in samples 6, 7, and 8 respectively. The average of these three is 84.5 which corresponds quite well with the figure of 84.7 percent determined on pure cutinite (sample 5).

When one realizes that the calorific value of coal is normally inversely proportional to the total volatile matter content, the results of calorimetry of cutinite are somewhat surprising. The figure of 16,780 Btu/lb for sample 5 (daf basis) represents an average of several determinations, and is felt to be fairly accurate. The authors found it somewhat difficult to reconcile the relatively low calorific values for samples 6, 7 and 8 with the calorific value of sample 5 (pure cutinite), even if it is assumed that the vitrinite in samples 6, 7, and 8 has no heating value, which probably is not true. It is probable that the treatment of the samples with KOH affected their heating value, but not their volatile matter yields. The calorific value of cutinite is apparently higher than the calorific value of associated coals subjected to the same metamorphism and consequently of the same "rank." An interesting point raised by this fact is that the coal ingredients containing the most volatile matter (exinite) and the least volatile matter (fusinite) have higher calorific values than vitrinite (which has intermediate volatile matter content) from the same coal.

The present ultimate analyses indicate that cutinite contains a high proportion of hydrogen, which is reflected in the high volatile matter yields. Van Krevelen and Schuyer (1957) have prepared graphs to represent the carbon, hydrogen, and oxygen relationships of typical macerals. Four of these graphs have been reproduced (and extended when necessary) as Plate 1 and the results of the cutinite analyses (including those

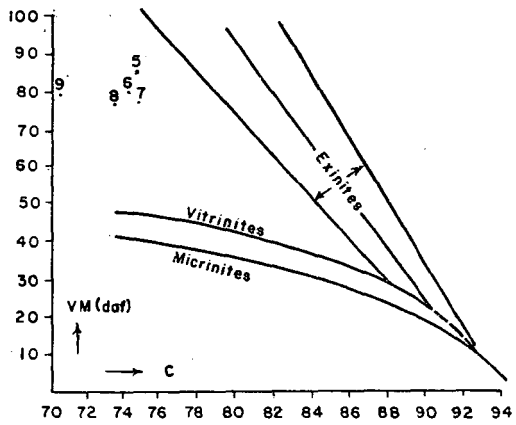


Figure 1

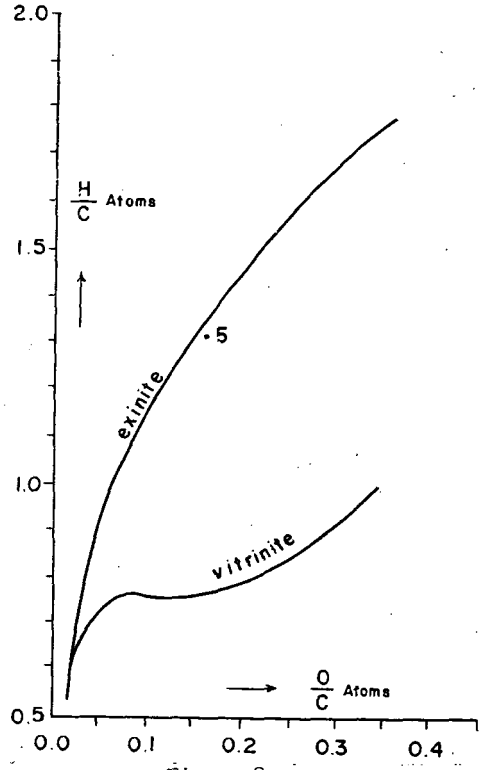


Figure 2

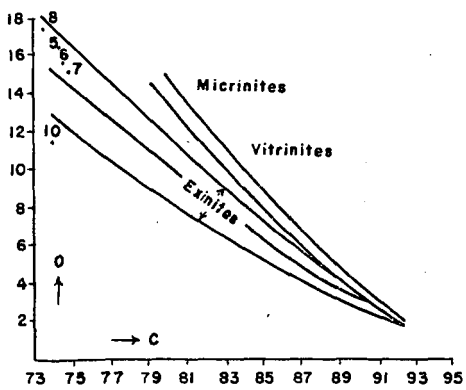


Figure 3

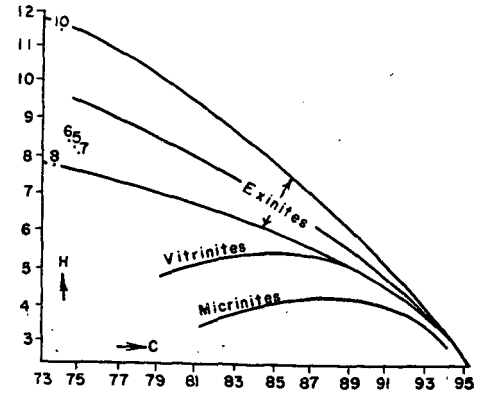


Figure 4

Graphs from Van Krevelen and Schuyer (1957)
Points from present data, Edwards (1947(, and Legg and Wheeler

PLATE 1

of Edwards (1947) and Legg and Wheeler (1929)) are superposed on the graphs. The points are numbered to correspond to the sample numbers in table 2. All of the points fit into the exinite areas except those on fig. 1, which plots volatile matter against carbon. Even sample 5, which is pure cutinite, is well outside the exinite lines, suggesting that the exinite area should curve downward in the lower carbon region, as do the lines for micrinite and vitrinite. Only the point for sample 5 is placed in fig. 2 (which plots the ratio of atomic hydrogen and atomic carbon against the ratio of atomic oxygen and atomic carbon). The fact that the point for sample 5 falls almost on the median line for the exinites tends to substantiate both the graph and our assumption that sample 5 is pure cutinite.

Because coals containing abnormally high proportions of exinite may serve as sources of petroleum substitutes, distillation assays were conducted on the cutinite samples to determine the types of yields which could be expected from the exinite fraction of coals.

The method used to determine distillation yields was patterned after the Fischer-Schraeder low temperature carbonization method with modifications of apparatus to utilize the equipment on hand. A retort 6" long was machined out of a stainless steel rod that was 1" in diameter. The retort chamber was tapered for ease of coke removal and holds a maximum coal charge of 3 grams. The charged retort was connected to the tar distilling flask with a copper tubing which during carbonization was wrapped with a heating tape that reached a temperature of approximately 400°C. A "U" tube containing anhydrous calcium chloride was attached to the tar distilling flask to absorb any water that may have escaped the tar distilling flask. The tar distilling flask was immersed in ice water. The light oil tube attached to the calcium chloride tube was a conventional 100 mm. "U" tube stuffed with glass wool and was immersed to its side arms in dry ice and acetone. During carbonization no attempt was made to measure the volume of gas that was evolved. The first noticeable condensation in the tar distilling flask was between 52° - 80°C. Visible vaporous volatiles were given off from 200° - 260°C and the first drop of tar was noticed at 450°C. In all instances, gas stopped evolving around 760°C. The retort was allowed to reach 950°C and was held at this temperature for 7 minutes. The retort was heated by means of a Hoskins FA120 Furnace which was attached to a temperature controller, permitting temperatures to be controlled with a fair degree of accuracy. This furnace is recommended for volatile determinations by A.S.T.M.D-271. The time consumed for the entire experiment was approximately 1 hour.

The results are shown in Table 3. Sample number 4, a sample of Indiana coal V, was first run as a control or standard sample. Thin-sections of this sample indicate it to be a typical vitrinitic coal with several percent of exinite and several percent of opaque matter. About 11 percent of the dry, ash-free sample was precipitated as tar, ammonia, and light oil. The cutinite concentrates (samples 6, 7, and 8; insufficient material was left of sample 5 to run tar assays) yielded over four times this amount.

Table 3 - Distillation Yields of Cutinite Concentrates

Samp. No.	Char DAF	Tar DAF	Lt. Oil DAF	Gas DAF	Tar Calculated 1	2	3	4
4	66.3	10.5	0.6	21.9	13.2	17.9	14.8	18.0
6	26.5	58.6	0.2	11.3	53.5	45.3	49.4	39.7
7	24.8	53.4	0.5	19.0	50.5	43.5	45.5	38.5
8	22.1	48.2	1.6	23.2	45.5	40.6	43.0	36.3

1 Francis (1954) tar and oil = eH 1.5 x 5.48 where eH is H over 3.6
2 Selvig and Ode (1944) tar = $0.697X + 0.0031X^2 - 6.4$ where X = VM - (1.3 x O)
3 Selvig and Ode (1944) tar (for cannel coals) = 12.3 (H_2 - 4.2)
4. Selvig and Ode (1957) tar = (0.783 x VM) - (0.96 x O) - 7.3

The amount of dry, ash-free char produced averaged about 1.18 times the amount of dry, ash-free fixed carbon in the original sample; meaning that some of the original material driven off as volatile matter in the proximate analyses is retained in the char of the assays. The yields of char shown in Table 3 represent only the organic portion of the char (percentage of ash in char was determined experimentally) as the percentage of the dry, ash-free charge. The yield of tar shown in Table 3 represents distilled volatiles less moisture (from proximate analysis) calculated as percent of dry, ash-free charge.

The calculated tar yields shown in Table 3 were obtained from several formulae suggested by the respective authors as means to estimate tar yields from proximate and ultimate analyses data. Although there appears to be no constant factor relating the yields obtained with those estimated, the general relationship of highest to lowest yields from samples 6 through 8 in both the experimental and calculated results suggests that the experimentally determined yields are probably correct. The experimental yields are, except for sample 4, all higher than the estimated yields, probably as a function of the high final temperature used. It might be noted that the tar yields are apparently inversely related to the amount of petrographically determined cutinite in samples 6, 7 and 8. It is felt that this apparent anomaly is a function of sample treatment, and consequently all of the yields would be even higher if pure, untreated cutinite was utilized.

Summary:

Analyses of the cuticle-derived component (cutinite) of Indiana paper coal which lies in an area containing high-volatile C and high-volatile B bituminous coals indicate that cutinite exhibits the following characteristics:

1. High ash content - analyses of other cutinite samples by other investigators suggest, however, that ash content varies from only a trace to over 16 percent, and is dependent upon swamp environment and plant type.
2. High volatile matter content - The apparent volatile matter content appears to be about 85 percent of the dry, ash-free cutinite.
3. High calorific value - Dry, ash-free cutinite was determined to contain over 16,000 Btu/lb.
4. Carbon, hydrogen and oxygen contents - Ultimate analyses indicate that hydrogen is abundant in pure cutinite, attaining a value of approximately 8 percent. The results of all of the ultimate analyses fall within the "exinite" areas of the graphs prepared by Van Krevelen and Schuyer (1957) to show the characteristics of macerals.
5. Tar, oil and coke assays - Tar yield was exceptionally high, averaging over 50 percent of the dry, ash-free sample.

One of the properties of cutinite is that of yielding high proportions of condensable tars. Gas yields differed little from yields of normal coals of the same rank.

Unquestionably, coal containing a high proportion of cutinite, if it is not associated with equally high proportions of opaque matter, would serve as an ideal raw material for the extraction of tars and oils. Such coals should, wherever possible, be utilized for this purpose.

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THE TRANSITION FROM BITUMINOUS TO ANTHRACITIC COALS

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With reference to thin section techniques and the normal sectioning of coal the following comments have been made: "... the method fails with anthracites and other coals rich in carbon ..." (Seyler, 1925, p. 117) and "anthracite has failed to respond.." (Turner, 1925, p. 127). More recently, Plumstead (1957, p. 12) has stated: "... they can no longer be studied by transmitted light for the anthracite has lost transparency even in the very thinnest sections". These comments are very similar to many others made before and after the dates cited, principally by the European coal petrologists. There is no doubt that anthracite and semianthracites have presented great technological barriers to the thin section workers. Petrologic study of these higher rank coals has been sorely neglected when compared to the wealth of information developed for those coals lower in rank.

Recently, however, a technique has been developed at the Anthracological Laboratories of The Pennsylvania State University for the preparation of creditable thin sections of semianthracite and anthracite. The two most important factors which differ from previous methods used are the mounting medium and the extended preparation time. An epoxy resin (Biggs Bonding Agent R-313) is used and allowed to "cold-set". Allowing the resin to "set" without the use of heat lengthens the curing time but also minimizes the stresses and strains set up due to heating and cooling of the microscope slide, the mounting medium and the coal block. So-called standard techniques are employed for preparation of the coal surface, "cut-off", and removal of excess material from the slide. The mounting of the block (as previously mentioned) and the finishing operations are where variations occur. Fine finishing is carried out on a Belgian hone as would normally be done. After this step, hand finishing with erasers or corks dipped in cerium oxide or red rouge are used to bring the sections to completion. It is this last step that is very tedious and time consuming.

The thin sections of anthracite prepared to date are not of the high quality it is possible to attain when one works with bituminous and other lower rank coal. However it is possible to view many of the organic entities present under transmitted light. The anthrinoids, micrinoids and fusinoids are present and may be studied in considerable detail. Thus far no representatives of the "resinoid" or "exinoid" maceral groups have been encountered in a recognizable form.

Geology and many of the other scientific disciplines owe a great deal to William Morris Davis. His presentation of the concept of "structure-process and stage" is applicable in most fields. With special reference to coal and the evolution of plant materials to form peat, lignite, subbituminous, bituminous and anthracitic coals it is of particular significance. In all coal seams a particular set of constituents exists at each point in this progression. These materials are acted upon by a set of physical and chemical forces which act or have acted for a period of time. Thus we have structure - the materials at hand, process - the forces acting upon these materials, and stage - the time for which these forces have acted and the degree to which the constituents have progressed to produce the subject materials.

The original "structures" we have to work with, the progenitors of all the macerals, are the plant materials deposited in the original coal swamp. It is not the purpose of

this article to trace the evolutionary development of these plant materials through the various coalification stages, but to look more closely at the maceral relationships encountered in the high-volatile, low-volatile and anthracite coals. It seems evident that there are more macerals present in the medium- and low-volatile coals than there are in either those of high-volatile or anthracitic rank. This is at first surprising but evaluation of many hundreds of thin sections makes this apparent.

It has been generally felt that in the coalification series of peat to anthracite, that the degree of complexity of composition decreases with an increase in fixed carbon and a decrease in volatile matter. Overall this is true, but there is an increase in the total number of macerals present when medium- and low-volatile bituminous coals are examined. Figure 1 is an attempt to show this phenomenon diagrammatically. No exact numerical values have been determined for the macerals present in the peat, lignite and subbituminous coals. However they far outnumber those present in coals of higher rank.

The decrease of macerals as one goes from peat to the high-volatile bituminous coals is explained by the fact that certain maceral types present in the early stages of coalification are lost completely during the increase in rank of the coals. Also two or more macerals may combine to form one type higher in the coalification series. The sudden increase in numbers of entities present in the medium- and low-volatile bituminous coals poses certain problems. The series which has been approaching near homogeneity in anthracites and meta-anthracites here deviates in pattern. Why does the general picture of a decrease in numbers suddenly reverse its trend and show an increase, numerically and in complexity, about the medium- and low-volatile bituminous range? This increase in numbers and complexity of the macerals occurs primarily in the vitrinoid and exinoid groups. These substances have resisted change during "process" longer than the others and after the others are somewhat stabilized, they break down to form new constituents. These are recognizable by structure (and texture) and by color. Thermal decomposition data also support these differences in vitrinoids and exinoids (Spackman, Brisse and Berry, 1957).

Within the anthracites thus far examined, three maceral groups have been recognized - the anthrinoids, micrinoids, and fusinoids. There are three principal anthrinoids all of which are opaque in sections of normal thickness. In the exceptionally thin sections used in this study one of these macerals appears as a red to red-brown homogeneous material and the second is dull, drab brown and appears to be very homogeneous. A material which may have been derived from the semi-fusinite in a lower rank "stage" is also present and included in the anthrinoids.

The fusinoids are represented by fusinite only, and this material occurs in masses which appear either lens-shaped or round. Certain of the masses are similar to those which have been identified as sclerotia or sclerotinite by Stach (1934, 1956a, 1956b) and as resin rodlets by Schopf (1939) and Kosanke and Harrison (1957). Micrinite is the only micrinoid encountered so far and it occurs principally as very finely divided stringers of opaque matter in the red anthrinoid.

The use of thin sections in anthracite petrology and petrography is not expected to replace the use of polished surfaces but it has been shown that they should be further employed to gain valuable supplemental data for polished surface work and that they can add greatly to our knowledge of the coalification series and the problems of coal genesis. By looking at coal with the "structure, process and stage" concept always in mind, we can more adequately evaluate this organic sediment.

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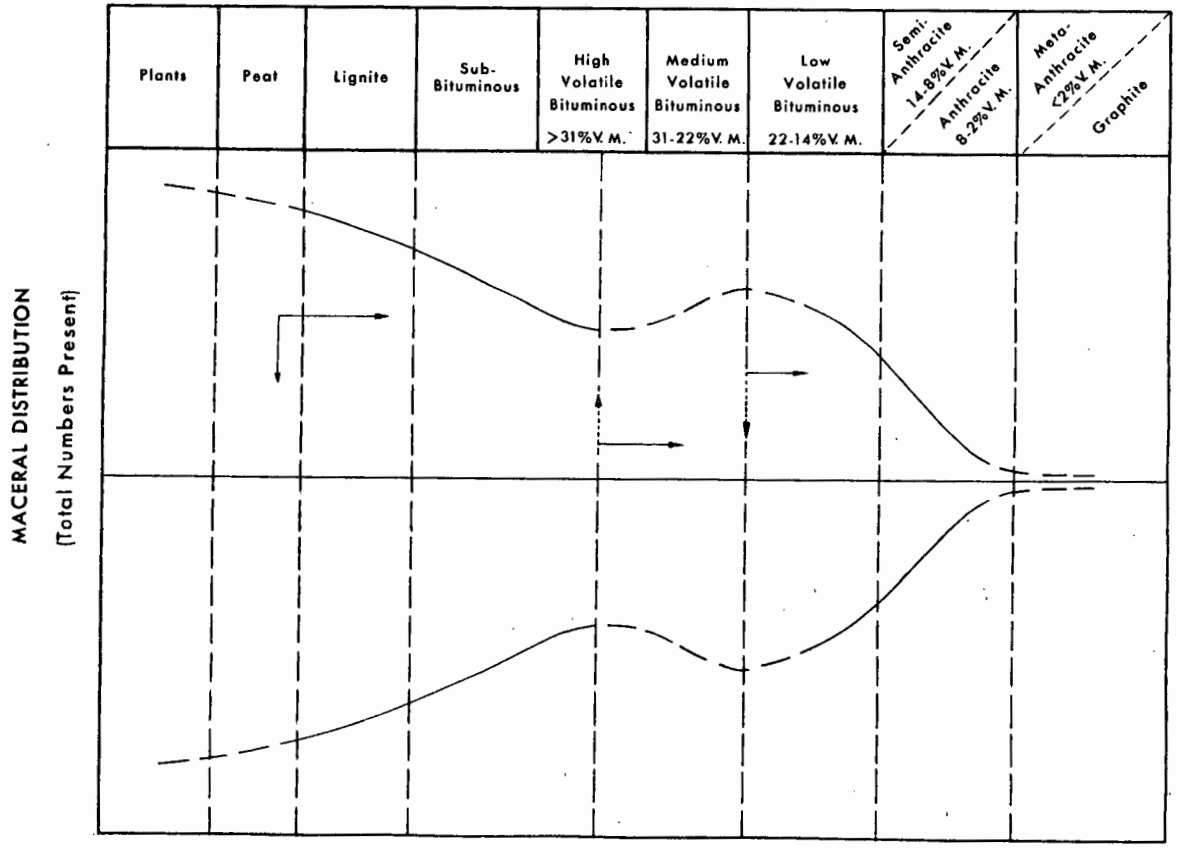

MACERAL CONTENT AND COALIFICATION SERIES

Figure 1

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PROPERTIES AND REACTIONS EXHIBITED BY ANTHRACITE LITHOTYPES UNDER THERMAL STRESS

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Although anthracite is no longer as important a metallurgical fuel as formerly, its chemical and physical properties as well as the advantageous location of the anthracite fields make consideration of its use as a metallurgical fuel imperative. Attempts to use raw anthracite as a fuel for blast furnace and cupola operations have shown it to be less satisfactory than coke. The major limitation in the use of anthracite in the metallurgical industry is its tendency to decrepitate when subjected to extreme temperature gradients. The extent of this decrepitation varies depending upon the heating conditions and the nature of the coal. The decrepitation of anthracite, when subjected to thermal shock, is believed to be caused by several factors including rapid moisture and volatile matter evolution, crystallite growth and differential expansion of anthracite laminations (see Delvaux et al, 1957, Eckerd et al, 1957, and Nelson et al, 1958). Decrepitation is the occurrence of one or a combination of these factors resulting in an internal pressure in excess of that required to overcome the physical strength of the material. The thermal decrepitation, then, is a disintegration of the anthracite when subjected to high temperatures which cause excessive pressure drops during cupola and blast furnace operation resulting in restricted gas and air flow in the stock column. The decrepitation process of anthracite is the total effect resulting from a series of reactions which are dependent upon the physical and chemical properties of the coal, and one grain of anthracite may or may not produce a product of physical strength comparable to another under identical thermal conditions.

An informative review of previous work in this field (Nelson et al, 1958) shows that investigation of anthracite decrepitation has been concerned primarily with the treating of lump coal. However, it is felt that disruption of equal importance occurs when small size particles are involved. This is of significance because of the possible effect of such fracturing on the strength of a metallurgical coke produced with anthracite in the blend. Thus, an investigation was undertaken to determine the behavior of petrographically distinct anthracite particles under thermal stress.

Equipment and Methods of Investigation

To adequately study the decrepitation phenomena of small particles a Leitz 0-1000°C. heating stage was employed. This stage was mounted on a Leitz Panphot microscope which is equipped with optics to allow observation with oblique illumination at 28.5 to 137.5 diameters. Vertical illumination is possible in the 42x to 562.5x range. The objectives giving the first range are most often employed because of their long working distance and therefore they are safer from any deleterious effects of high temperatures. The rate of heating is controlled manually and temperatures are read directly on a "direct-reading" galvanometer. The instrument as used is shown in Plate I. A close-up of the microfurnace is shown as Plate II. A grain of anthracite can be seen in place, through an open window, on a quartz specimen holder. Preliminary examination of anthracite particles showed that all coals studied could be readily shown to consist of four types of particles. These are: 1) a bright particle, having a vitreous luster and exhibiting conchoidal fracture; 2) a dull particle with a matte surface and irregular fracture; 3) a mixture of one and two as more or less alternating bands; and 4) grains having a fibrous, porous structure and appearing like charcoal. For these four lithotypes the terms vitrain,

durain, clarain and fusain have been tentatively employed. Representative grain types are shown on Plate III.

The materials selected for study were taken from the plus 2 inch fraction of channel samples. The seams represented are the middle split of the Mammoth Seam and the Primrose Seam, both from Northumberland County, Pennsylvania, and the Buck Mountain Seam from Schuykill County, Pennsylvania. In the order presented they are referred to as anthracites A, B and C.

Two particle sizes were selected for study, 10 x 14 mesh and 6 x 10 mesh. The anthracites were subjected to the following experimental conditions: 1) gradual heating to temperatures ranging from 500°C. to approximately 1000°C. at varying heating rates; 2) shock heating at temperatures ranging from 300°C. to approximately 1000°C. for varying times and with different particle sizes; and 3) preheating to varying temperatures prior to shock heating.

Effect of Heating Rate on Decrepitation

Investigations were carried out concerning the effect of heating rate on decrepitation. Table 1 shows the relation between the temperature at which decrepitation first visibly occurred and the heating rate. In the absence of a program controller heating rates less than 5°C. per minute were not accurately attainable. These experiments were performed with clarain grains. The maximum temperatures employed were in the range of 920°C. to 960°C. These figures show no significant relation between heating rate and observable decrepitation, although at the higher heating rates the decrepitation did consistently occur initially at a higher temperature.

Table 1

Effect of Heating Rate on the Temperature at Which Decrepitation First Visibly Occurred[1]

Heating Rate (°C./min.)	Temperature at Which Visible Decrepitation First Occurred (°C.)
5	750
10	800
15	600
20	650
40	675
50	800
57	800
70	800
78	(after cooling)

[1]Experiments carried out on the +2" fraction of "Anthracite B"

Most of the work done on the effect of gradual heating was with clarain particles because the other petrographic entities of the anthracite used, vitrain, durain, and fusain, underwent no visible decrepitation whatever when subjected to heating rates varying from 25°C. per minute to 63°C. per minute to maximum temperatures of 940°C. to 980°C. However, while no decrepitation in fusain particles was observed, these particles after treatment were much weaker than before and were very easily crushed.

An attempt was made to correlate change in weight of the particles due to heating with thermal decrepitation. The existence of such a relationship seems reasonable in view of the believed causes of decrepitation, in particular rapid evolution of moisture and volatile matter. These experiments were carried out with clarain particles of "Anthracite B" subjected to heating rates of 5°C. per minute to 78°C. per minute. Figure 1 shows no definite relation between weight change due to heating and heating rate, either with or without segregation according to range of particle size, although a

general decrease in weight loss occurs for increasing heating rates.

A general decrease in friability at low heating rates is in accord with prior investigations (Grace and Jackson, 1954; Jackson and Grace, 1954; Geller et al, 1955) which reasoned that lower heating rates permit sufficient time for the gases to escape without developing critical gas pressures within the coal structure greater than those sufficient to overcome the physical strength of the material. Recent work (Delvaux et al, 1957) has reported an initial rise in friability at low heating rates.

Effect of Shock Heat on Decrepitation

The different petrographic entities studied were subjected to shock heat treatment at temperatures varying from 500°C. to 970°C., the time of shock heat varying from 10 to 15 minutes. Table 2 and Plate IV show the results of this work. Durain and vitrain first demonstrated observable decrepitation when subjected to shock heat at 950°C. Although fusain showed no visible cracking until shock heat at 950°C., the treated product in each case of shock heat at lower temperatures was so powdery and easily crushed that it was concluded that decrepitation had occurred to a great extent. Clarain was the only entity to undergo visible decrepitation at a shock heat temperature below 950°C., doing so at 800°C. The decrepitation which clarain underwent was more immediate and more violent than that of the other entities.

Table 2

Effect of Shock Heat on Visible Decrepitation[1]

Temperature of Shock Heat °C.	Vitrain	Durain	Fusain	Clarain
500	None Visible	None visible	No visible cracking occurred but treated product easily crushed	None visible
600	None visible	None visible	" "	None visible
700	None visible	None visible	" "	None visible
800	None visible	None visible	" "	Grain split in half immediately on placing in furnace
950	Visible cracking and splitting of grain	Visible cracking	Visible cracking	Immediate cracking and splitting occurred

[1]Experiments carried out on the +2" fraction of "Anthracite B"

Plate IV shows petrographic particles before any treatment and the resulting products after subjection to shock heat at various temperatures. These particles were all shock heated for 10 to 15 minutes in a nitrogen atmosphere.

Clarain was selected for more detailed study under thermal shock conditions on the basis of the results presented in the preceeding paragraphs which indicate a more observable decrepitation present in these than in the other particles. Clarain particles within a weight range of 1 to 8 milligrams from Anthracites A, B and C were subjected to shock heat treatment. Figure 2 shows the relation between loss of weight and shock heat temperature. For each series of experiments except Anthracite B(2) the critical temperature (the temperature above which further increases in shock heat temperature produce a significant increase in decrepitation) is in the range of 625°C. to 675°C. Anthracites A and B underwent visible decrepitation in all but a very few experiments on shock heating at 700°C. or greater, while Anthracite A showed almost no observable cracking

even at 900°C. At the higher temperatures of shock heat (700°C. and above) there was a tendency for the light vitrain bands to blend into and become indistinguishable from the dull durain background.

Experiments were run varying the time of shock heat in an attempt to determine whether decrepitation is primarily an immediate phenomenon or one dependent upon time of exposure to heat. While the degree to which a given anthracite will fragment or decrepitate varies depending on the heating conditions and the nature of the coal, clarain particles of "Anthracite B" were chosen because of their tendency to readily undergo decrepitation. Although there is a general disparity of results as shown by Figure 3, the trend shows that at the shock heat temperature employed, 800°C., decrepitation as related to the weight loss is not an entirely immediate effect. Many of the experiments shown in Figure 3 resulted in cracking immediately on placing the clarain grain in the furnace at 800°C., but in several cases no cracks were visible until the entire heating period was completed.

A likely source of the wide difference of percent weight loss in Figure 3 (in particular at 10, 15 and 25 minutes) as well as in the other weight loss calculations is the necessity of working with very small quantities, of the order of 1.5 to 15 milligrams, from which it follows that a difference in weight of 2/10 of one milligram can cause a difference in weight lost of from 13 percent down to 1 percent, depending on the size of the particle examined.

Effect of Particle Size on Decrepitation

As considerable work had been done in the past on the effect of size of anthracite on decrepitation, an investigation was made into the relation between particle size and thermal decrepitation for each of the petrographic entities being studied. Figures 4 and 5 show the relation between loss in weight due to heating and the original particle weight. Although the amount of weight lost increased in each case with the particle size (Figure 4), the percent loss (Figure 5), with the exception of durain, either remained nearly the same or decreased with increasing particle size. These results are contrary to evidence reported by previous workers (Wright et al, 1941; Delvaux et al, 1957; Eckerd and Tenney, 1957; Anthracite Institute) who found that the degree of decrepitation increases with the size of the coal. There are two relevant distinctions between the past work and that carried out in the instant investigation: 1) all past work was performed with lump size coal while this investigation dealt solely with much smaller sized particles; 2) the previous studies were of anthracite as "whole coal", while this work was concerned with the petrographically distinct entities of anthracite.

A concept often used to explain the increased decrepitation of larger sized anthracite is that the increased surface area indicates a less dense structure and hence lesser strength. This would seem to have a minimum of applicability here where, though increased particle size is accompanied by increased surface area, the sizes of all the particles are so small as to render any difference in decrepitation due solely to particle size nominal.

The study of anthracite decrepitation on a petrographic basis causes another distinction to be made. For a given anthracite, though two or even three of the four petrographic entities may show either no change or even a decrease in decrepitation for increased particle size, an increase in decrepitation which the other entity may undergo could be more than sufficient to offset the total decrease of the other entities and cause the anthracite to suffer a net increase in decrepitation with increased particle size. Due to the heterogeneous nature of coal, the decrepitation characteristics of one anthracite need have no necessary relation to those of another anthracite (Figure 2).

This investigation does not purport to show that decrepitation does not increase overall with increasing size of anthracite, but rather that at the smaller level no

increase was noted within the petrographic entities with the exception of durain (Figure 5).

Effect of Preheat Treatment on Decrepitation

Several prior investigations have noted that anthracite which has been subject to gradual heating showed a reduced tendency to decrepitate when subjected to extreme temperature gradients (Miroshnichenko, 1938; Skomorochov, 1938; Clendenin et al, 1945; Erenburg, 1954). Work at The Pennsylvania State University (Delvaux et al, 1957) indicates that a critical heating rate exists for each anthracite which if exceeded results in increased decrepitation. Also indicated is the existence of a critical temperature level. Once this is reached, the rate of heating does not effect decrepitation. Neither the critical heating rate nor the critical temperature has as yet been determined conclusively.

The previous work referred to was carried out with lump size anthracite while the present study was confined to smaller sized petrographic entities of anthracite. Previous experiments had preheated to relatively high temperatures at low heating rates: to 1400°C. at a rate of 1.3°C. per minute (Miroshnichenko, 1938; Skomorochov, 1938), and to 1400°C. at a rate of 5°C. to 6°C. per minute (Erenburg, 1954). In an attempt to reduce the required process time as well as the cost of pretreatment, higher rates of heating to lower ultimate temperatures were investigated.

For these experiments clarain particles of "Anthracite B" were chosen. The particles were subjected to preheat treatment at a uniform heating rate (14°C. per minute) the preheating being carried out to varying temperatures. The particles were then cooled and each subjected to thermal shock at 900°C. The results of these investigations, presented as Table 3 and Plate V, show that preheating the grains to 900°C. prior to shock heat definitely reduced the visible decrepitation to a marked extent. More data is necessary on preheating each of the petrographic entities to different maximum temperatures and particularly at reduced heating rates in order to determine the mode as well as the extent of preheat treatment which will maximize thermal stability. Previous work (Clendenin et al, 1945) has shown that while some coals which had a lower physical stability before thermal treatment showed an increase in strength after the treatment, other coals demonstrated reverse behavior. Other work (Delvaux et al, 1957) has even indicated that none of the supposed causes of decrepitation, volatile matter and moisture evolution, and pore structure, are really useful in determining the degree of decrepitation which anthracite undergoes when subjected to thermal shock, but rather that certain types of coals, aside from these characteristics, are more stable than others. The key to this problem might well be in identifying the decrepitation characteristics of the petrographic entities and determining the tendency of the particular anthracite to decrepitate from the decrepitation characteristics of the petrographic entities and the relative amounts of the various entities present in the coal.

Table 3

Effect of Preheat Treatment on Decrepitation

Maximum Temperature of Preheat Treatment (°C.)	Observations During Preheat Treatment and Upon Thermal Shock
500	No visible decrepitation during preheat. No immediate cracking on shock heat, but after 3-4 minutes of shock heat, visible decrepitation occurred.
600	No visible decrepitation during preheat. Some immediate, and great deal of delayed cracking occurred upon shock heat.

Table 3 (Cont.)

Maximum Temperature of Preheat Treatment (°C.)	Observations During Preheat Treatment and Upon Thermal Shock
700	No visible decrepitation during preheat. On shock heat a great deal of immediate cracking and very little delayed cracking took place.
800	Few small cracks appeared on preheat. No immediate cracking and very little delayed cracking on shock heat.
900	No visible decrepitation occurred either on preheat treatment or on shock heating.

Clarain particles of +2" fraction of "Anthracite B" preheated at rate of 14°C. per minute to varying temperatures, cooled, and subjected to shock heat at 900°C. for 15 minutes.

On the basis of the experiments performed an attempt has been made to rank the petrographic entities in the order of increasing resistance to decrepitation. Work done on the effect of heating rate on decrepitation indicates that fusain and clarain decrepitate to a greater extent than vitrain and durain when subjected to gradual heating.

Visual observation of the particles when subjected to shock heat as well as the resulting product (Table 2) shows that fusain undergoes a greater degree of decrepitation than any of the other entities. Clarain also decrepitates to a greater extent than either vitrain or durain when subjected to shock heat; the cracking occurs at a lower temperature of shock heat and is much more violent than that exhibited by the other lithotypes.

Weight loss studies (Figures 4 and 5) show that fusain undergoes a much greater loss in weight than any of the other particles. Figures 4 and 5 might be interpreted as showing vitrain to be less resistant to decrepitation than clarain, but the results of observing the particles when subjected to gradual heating at varying rates as well as shock heat at different temperatures (Table 2) show that in the overall picture clarain is much less resistant to thermal decrepitation than vitrain.

The classification of the petrographic entities of "Anthracite B" in the order of increasing resistance to thermal decrepitation on the basis of the investigation would be, 1) fusain, 2) clarain, 3) vitrain, 4) durain. More data would be necessary to establish the variation among anthracites of the decrepitation which these entities undergo.

Conclusions

From the work carried out the following conclusions are drawn:

1. A decrease in weight loss accompanies increasing heating rates for the range of heating rates employed (Figure 1).

2. The critical temperature does not vary significantly for the three anthracites studied, being in the range of 625°C. to 675°C. (Figure 2).

3. Decrepitation is not an entirely immediate phenomenon, but tends to increase as the total heating time is increased (Figure 3).

4. Decrepitation, as measured by the weight loss, either decreases to a slight extent or shows no change with increasing particle size for the petrographic entities studied with the exception of durain which shows a slight increase (Figure 5).

5. Preheating the particles prior to shock heat reduced the visible drecrepitation to a marked extent.

6. The studies of the petrographic entities of anthracite indicate a resistance to thermal shock in the increasing order of 1) fusain, 2) clarain, 3) vitrain, 4) durain.

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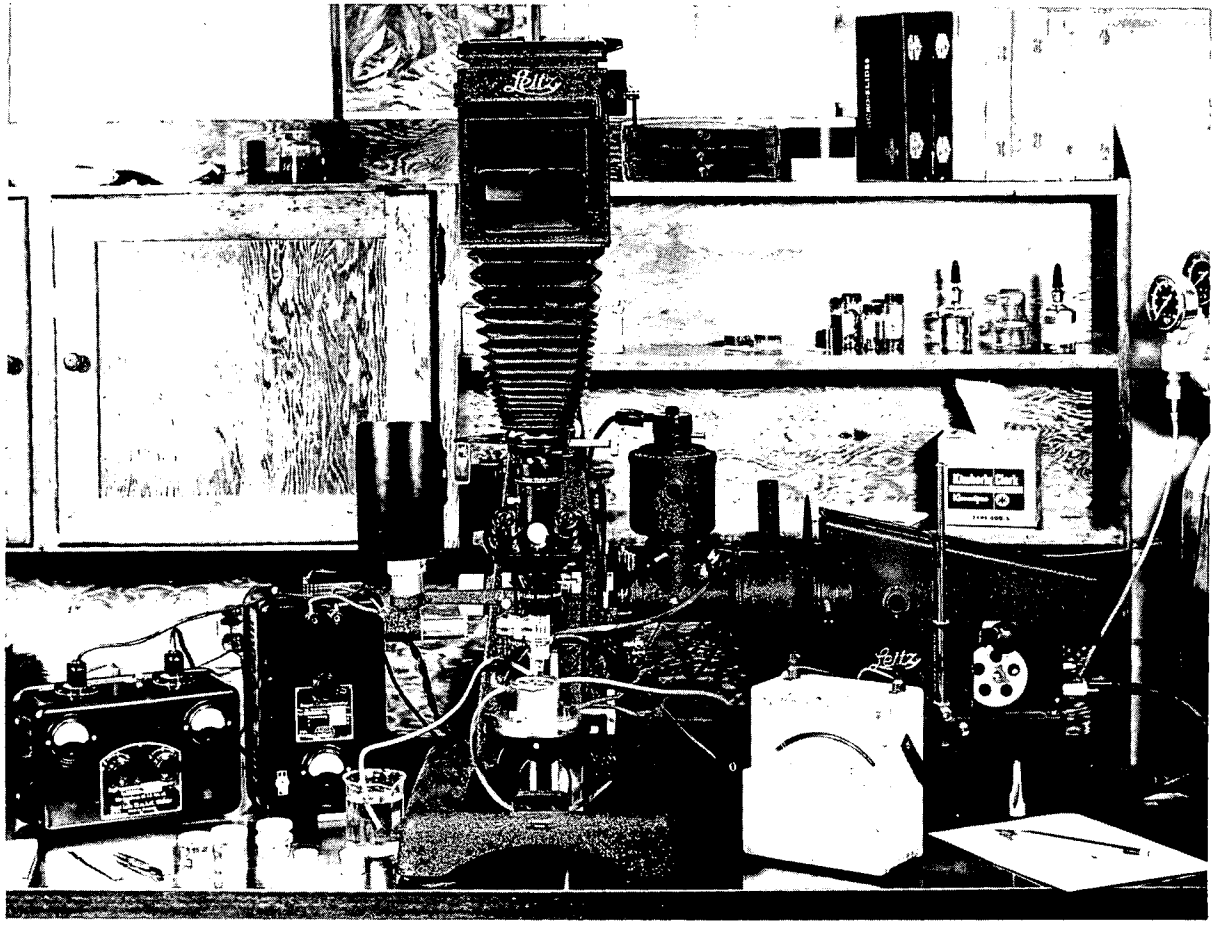


PLATE I

Leitz Panphot with Heating Stage

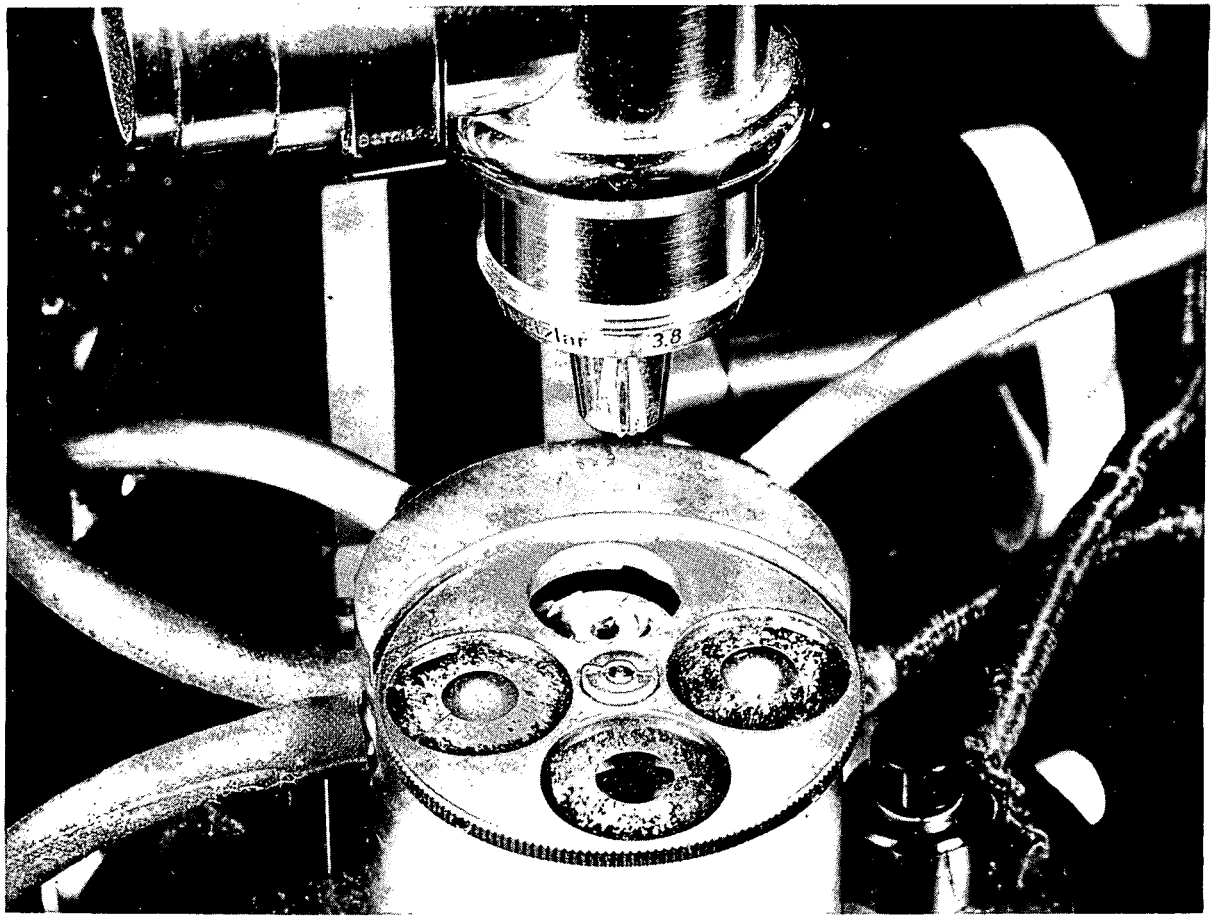


PLATE II

Close-Up of Heating Stage with a Grain of Anthracite in the Micro-Furnace

VITRAIN
Anthracite "B"

CLARAIN
Anthracite "B"

DURAIN
Anthracite "B"

FUSAIN
Anthracite "C"

PLATE III

Types of Petrographically Distinct Particles Investigated

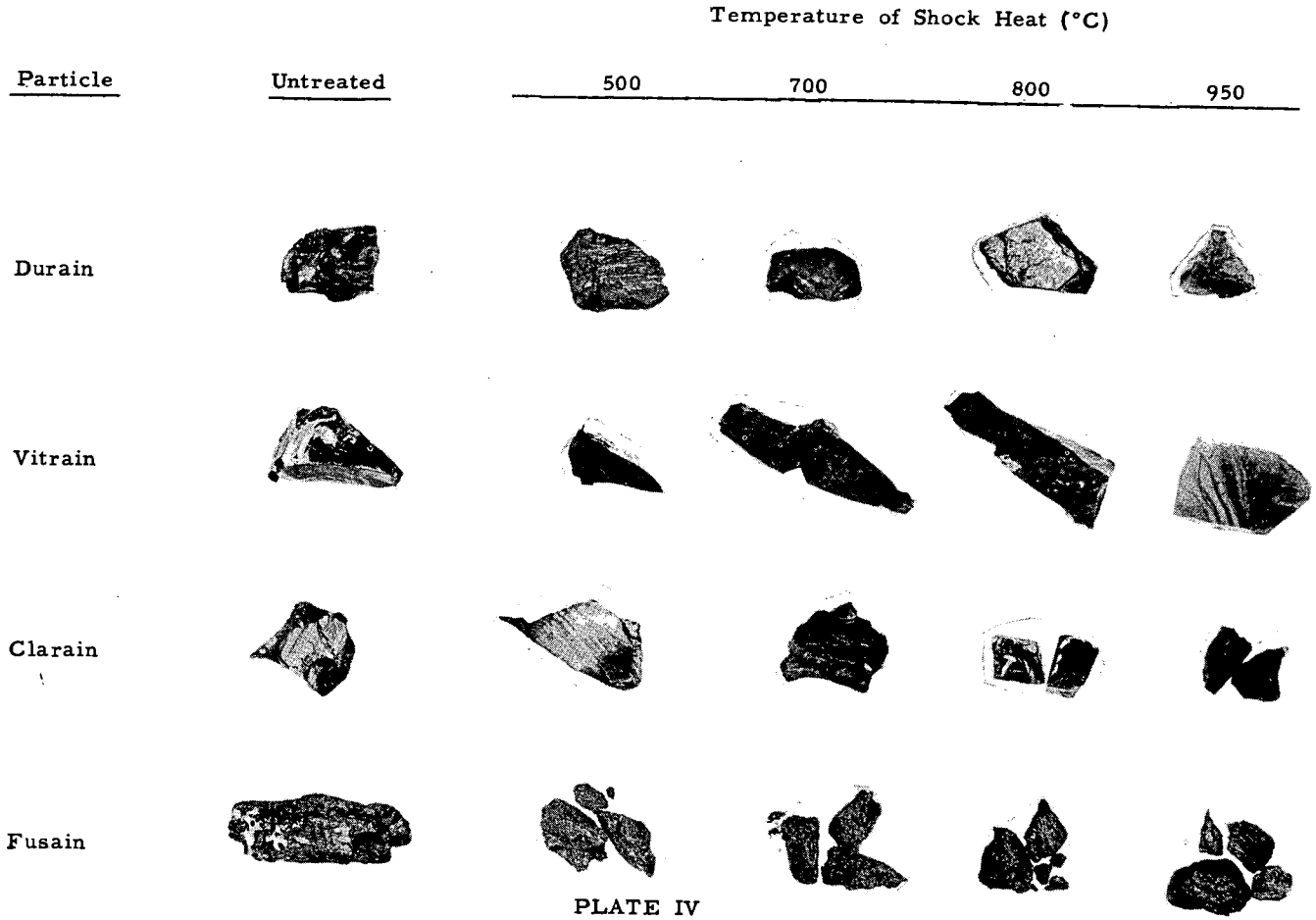


PLATE IV

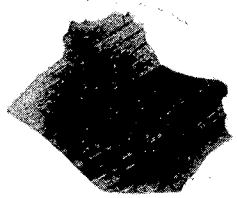
Effect of Shock Heat on Petrographically Distinct Grains of Anthracite

Particles from "Anthracite B" shock heated from 10 to 15 minutes in a nitrogen atmosphere.

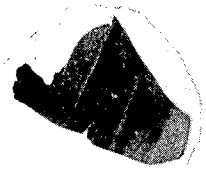
No Preheat Treatment

Preheated to 500°C

Preheated to 600°C



Preheated to 700°C



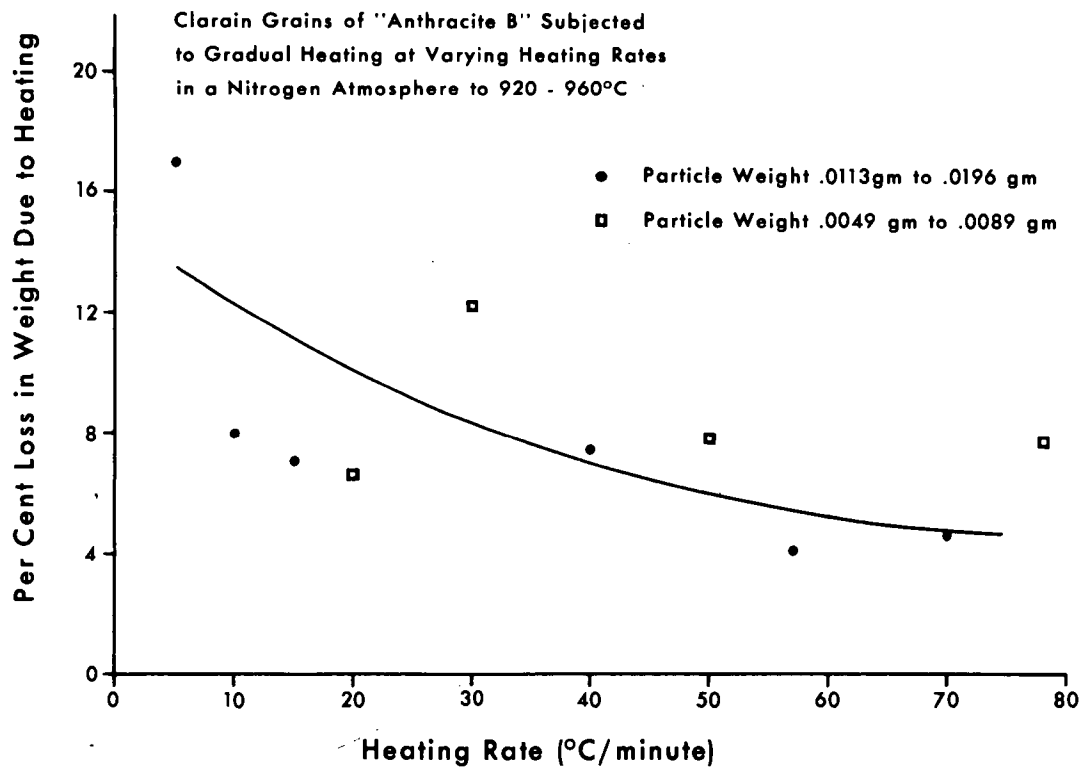
Preheated to 800°C

Preheated to 900°C

PLATE V

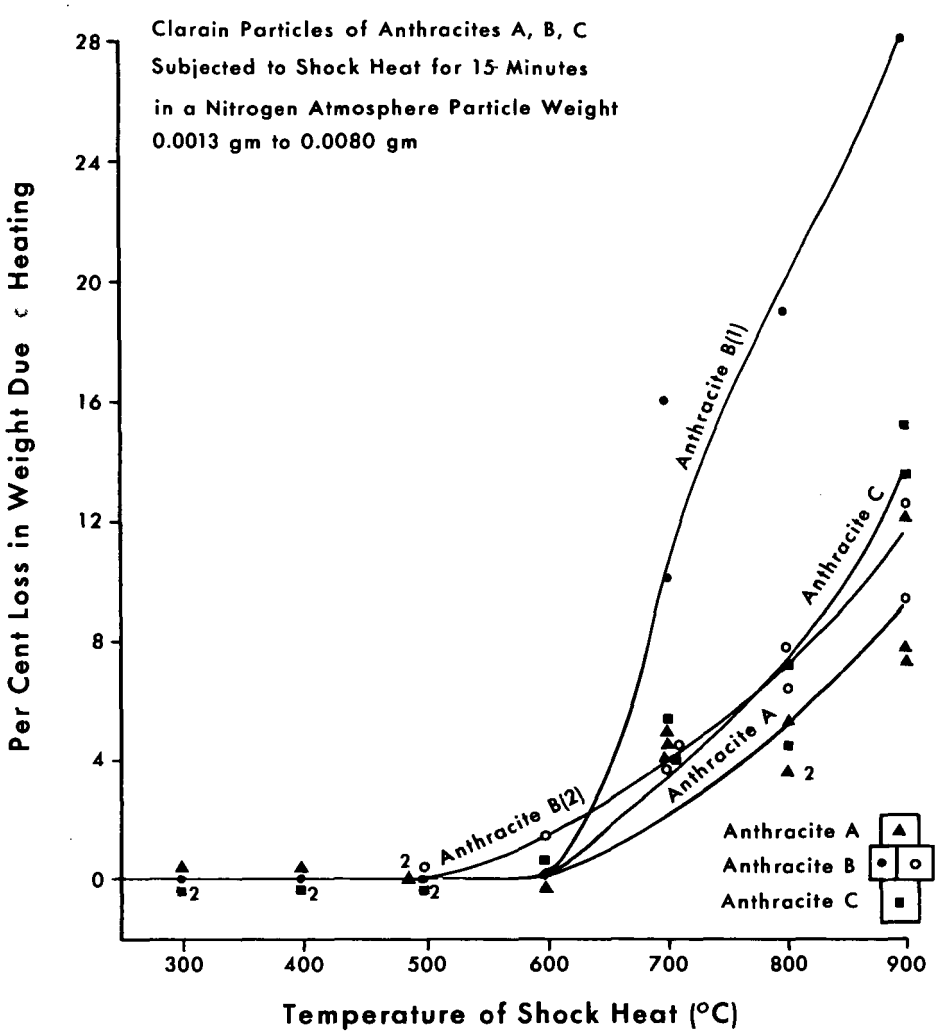
Effect of Preheat Treatment on Thermal Stability of Anthracite Particles

Clarain particles of "Anthracite B" preheated to different temperatures at a heating rate of 14°C per minute, cooled, then shock heated for 15 minutes at 900°C in a nitrogen atmosphere.



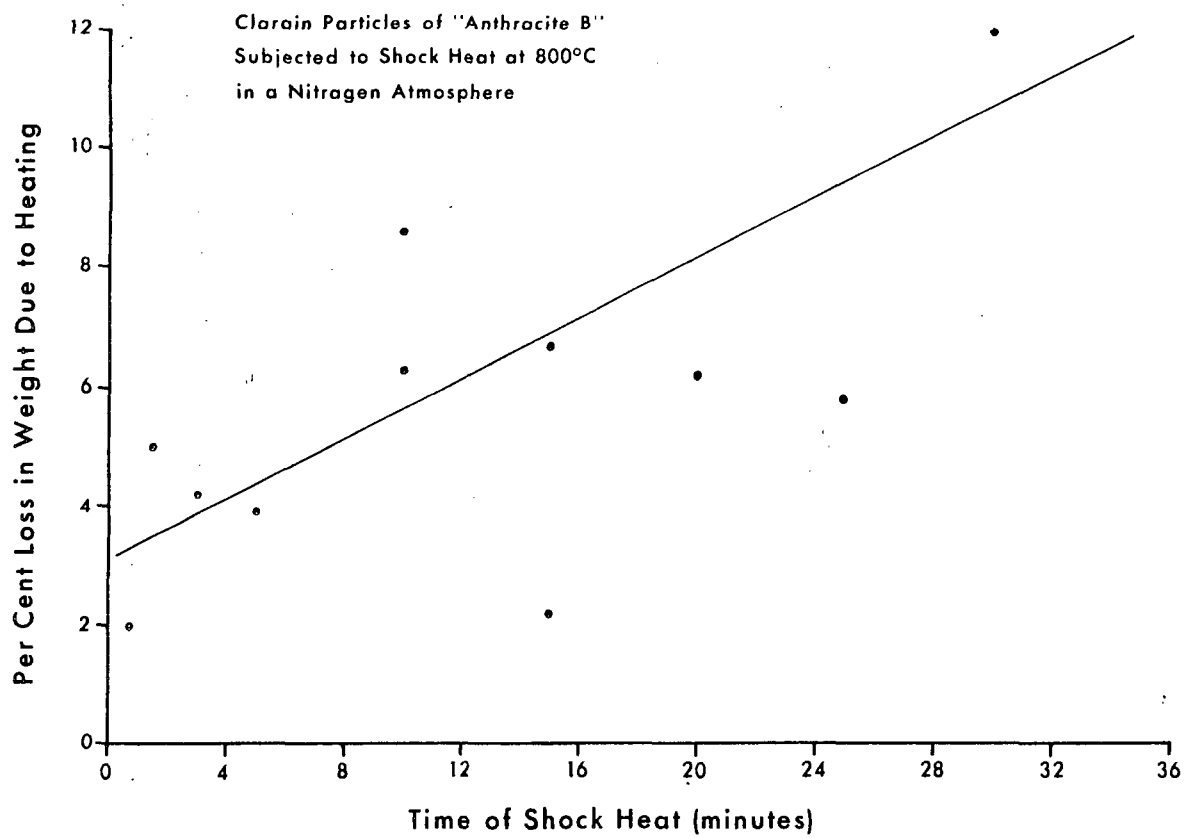
RELATION BETWEEN LOSS IN WEIGHT
AND
HEATING RATE

Figure 1



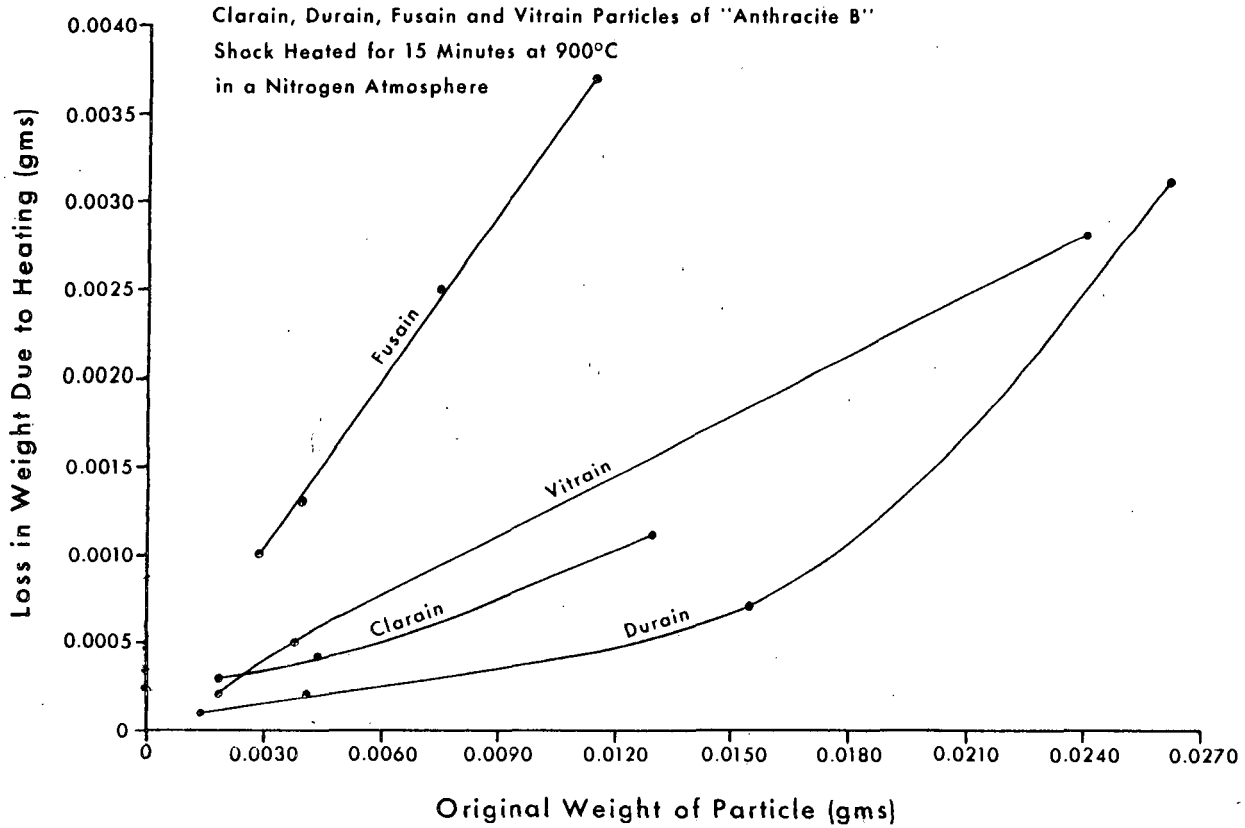
RELATION BETWEEN LOSS IN WEIGHT
AND
SHOCK HEAT TEMPERATURE

Figure 2



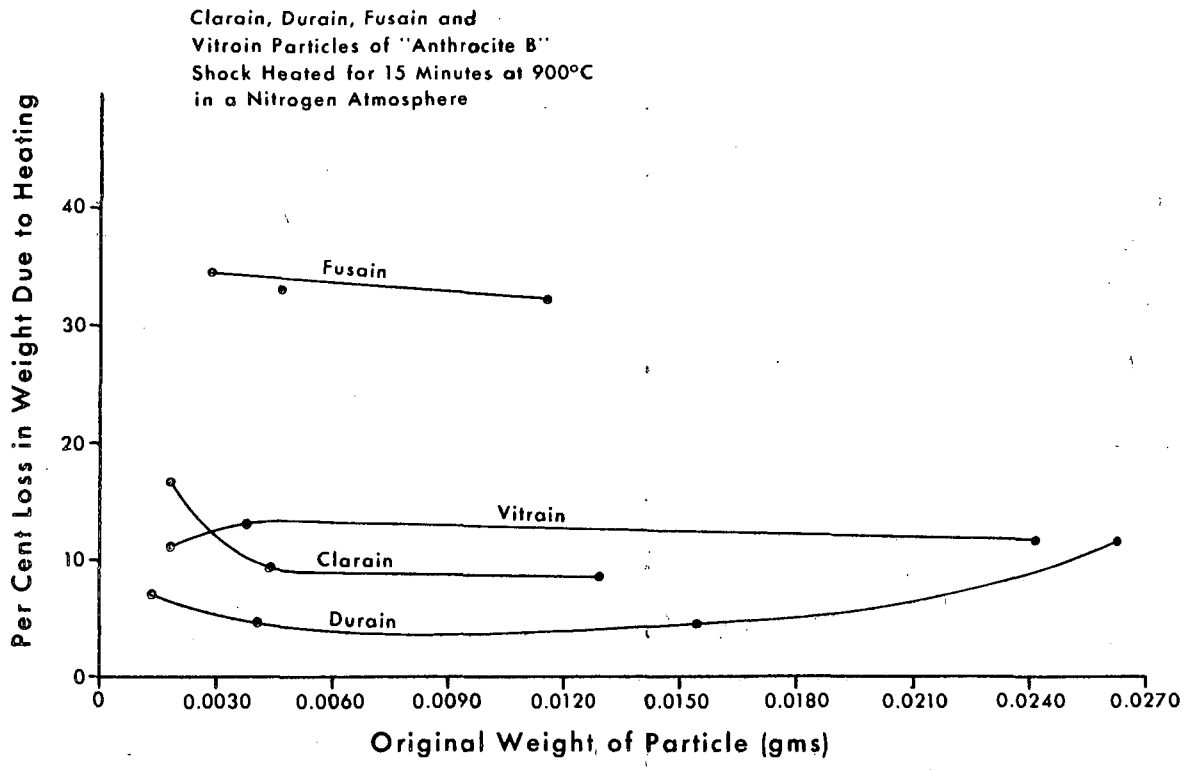
RELATION BETWEEN LOSS IN WEIGHT
AND
TIME OF SHOCK HEAT

Figure 3



RELATION BETWEEN LOSS IN WEIGHT
AND
TIME OF SHOCK HEAT

Figure 4



RELATION BETWEEN LOSS IN WEIGHT
AND
ORIGINAL PARTICLE WEIGHT

Figure 5

PETROGRAPHIC STUDIES OF THE MECHANISM OF COKE FORMATION

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Petrographic studies and small-scale carbonization tests have shown that optically and physically recognizable materials in coal (entities) behave differently under carbonizing conditions and that, although the entities are altered, the association of entities produces an identifiable residue in the coke. In addition, empirical test data have been determined to integrate further these studies with quality-control tests.*

*Complete manuscript not received in time for preprinting.

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EFFECT OF HIGH-CARBON COMPONENTS AND OTHER ADDITIVES UPON CHARACTER OF COKES: LABORATORY SCALE STUDY

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INTRODUCTION

A high percentage of metallurgical coke is produced by blending at least two coals in order to make a coke having the desired physical properties. A number of laboratories, some with pilot plant coking facilities, are conducting investigations in which various coal blends that contain marginal coking coal are being tested. As reserves of coal, now considered as good coking coal, continue to decrease, it will be necessary to know how best to use the marginal coking coals to meet the demands for good metallurgical coke.

Laboratory investigations at the Illinois State Geological Survey have indicated that the petrographic composition of the coal charge definitely affects the coke. One aspect of the laboratory investigation that has been tested on a limited basis in the pilot plant is the alteration of the petrographic composition of the coal charge by increasing the amount of high-carbon coal component fusain. Although direct correlation between the laboratory and pilot plant scale tests was not made, the trends established in tumbler and shatter tests of cokes made in the laboratory were generally the same as those from the larger scale tests, and in each case certain physical properties of the resulting coke were improved with the addition of an optimum amount of fusain.

The present study is concerned with the influence upon the physical properties of coke produced by blending coal with one of the components. These components or additives varied in amounts and size and some additives contained a high percentage of carbon. Laboratory scale coke tests on blends of No. 6 and No. 5 Coals established on optimum coal blend that was used as a "standard blend" to which the high-carbon components were added. Materials added to the "standard blend" are referred to subsequently as additives. Trends established in these laboratory studies in which the petrographic composition of the coal charge was closely controlled provide a basis for pilot scale tests.

PROCEDURES

Coal Samples; Collection and Selection

Channel samples, six inches wide and four inches deep, were cut from fresh coal faces of No. 6 Coal in Jefferson County, and from No. 5 Coal in Saline County. Large bands of mineral matter was removed and the samples were sealed in air-tight cans in the mine to minimize oxidation of the coal.

Previous studies (Marshall et al., 1958) demonstrated that a method of crushing, achieved by progressive screening and crushing to prevent overcrushing of fine size, yielded optimum physical properties in the coke produced from No. 6 and No. 5 coals on a laboratory scale. The same crushing procedure was adapted for the present study. This procedure reduced all the sample to minus 1/8-inch

except for 0.2 or 0.3 percent which consisted predominantly of shale and dull coal.

The resulting sample was considered as standard and had constant size consist as determined by screen analysis. The size analysis of both No. 6 and No. 5 coal is essentially the same.

Additives; Collection and Selection

Additives used in this investigation were fusain, anthracite, coke dust, coke breeze, petroleum coke, minus 48-mesh coal from a preparation plant, black shale and the blend of No. 6 and No. 5 Coals reduced to three size fractions smaller than the standard size fraction.

Lenses of almost pure fusain four to five inches thick were handpicked, dried, and screened through a minus 150-mesh screen without crushing. Hard mineral-bearing fusain was retained on a 20-mesh screen. The screen analysis of the minus 150-mesh fusain demonstrates that the natural breakage of the material is 92.9 percent minus 270-mesh.

Three sized samples of anthracite were prepared, namely: minus 10-mesh, minus 20-mesh, and minus 150-mesh (the latter had approximately the same size consist as the minus 150-mesh fusain, fig. 1). Anthracite was first crushed by duplicating the crushing procedures used for No. 6 and No. 5 coals. The sample was divided into three equal fractions, one for each size fraction. The minus 10-mesh sample was prepared by passing the anthracite three times through the rolls set at 1/8 inch. After each crushing the minus 10-mesh material was screened out to prevent additional crushing of the fine sizes. It was necessary to set the rolls of the crusher at 1/20 inch in the preparation of the minus 20-mesh anthracite, which was also crushed and progressively screened three times. To secure the high percentage of minus 270-mesh material, comparable to that in the fusain, it was necessary alternately to hand grind and screen the anthracite until the desired size consist was reached.

Coke dust and coke breeze for this investigation was taken from the Survey's pilot plant oven. Coke dust was derived from the samples used in tumbler tests and the material was all minus 20-mesh. The minus 150-mesh sample was obtained by hand grinding and progressive screening. Two size fractions, 6 x 10-mesh and minus 10-mesh were screened from the coke breeze. It was necessary to pass the coke breeze through the rolls set at 1/20 inch to obtain the minus 20-mesh coke breeze sample. No minus 150-mesh coke breeze was used in the tests.

The petroleum coke had been previously crushed when furnished to our laboratory. Only the minus 10- and minus 20-mesh fractions were screened from this material for use in coking tests.

The minus 48-mesh coal was added to the coke charge without additional screening in hopes that improvements could be made in the physical properties of coke with minimum preparation.

A sample of black shale was collected from over the No. 5 coal in Fulton County, Illinois, and prepared in the same manner as the anthracite in minus 10-mesh, minus 20-mesh, and minus 150-mesh size fractions.

The minus 10-mesh, minus 20-mesh, and the minus 150-mesh size fractions of the "standard blend" of No. 6 and No. 5 Coals were obtained by first screening the standard size samples to produce the minus 10-mesh size. The oversize was crushed and screened for the minus 20-mesh fraction, and oversize was recrushed to produce the minus 150-mesh size consist.

Petrographic and Shape Examination, Analysis and Assessment

Petrographic analyses of broken coal samples were determined by the point count method. (See Marshall et al., 1958, for methods of sample preparation.)

For this investigation macerals were designated as vitrinite, exinite, semi-fusinite, and inertinite. Vitrinite is a group term which included all vitrain with the lower limit imposed by the resolving power of the microscope, humic degradation matter, resin rodlets, and resins classified as red resins in transmitted light studies. All spore coats, cuticles, and yellow resins were considered as exinite. Semi-fusinite consisted of the material intermediate between vitrinite and fusinite. Under the term inertinite were grouped the macerals known as fusinite, micrinite, and a material that resembled sclerotinite. Visible mineral matter was also determined.

All petrographic analyses were made with an oil objective at a magnification of 320 diameters.

Shape analyses were made with the same microscope but with an optical system using a dry objective which gave a magnification of 128 diameters. Criterion established for the shape analysis placed individual coal particles in one of five categories, equi-dimensional, elongate, rodlike, triangular, and angular.

Chemical Analyses

Proximate analyses were made on all samples. Gieseler fluidity and Free Swelling Index determinations also were made on all samples which developed plasticity.

Coke Production

In an earlier investigation by Marshall et al. (1959), the furnace used for coke production, the charging temperature, rate of heating, final temperature, and the final coking period were investigated thoroughly and reported in detail. For this report a brief discussion of the oven and crucible used, along with optimum coking temperatures, will suffice.

The oven is a Harper Globar type furnace (pl. 1) with thermostatic controls. With the addition of a flue, a series of closely adjustable dampers, and an exhaust system for removal of volatiles, this furnace gave excellent service.

The crucibles were thin-walled alumina, cylindrical, three inches in diameter and approximately six inches in height, in which coal charges of 300 to 400 grams could be coked conveniently. Fireclay covers and bases were used to protect the charge and the crucibles.

Each coke run was made in triplicate, and as the oven would hold nine crucibles, three different coke runs were undertaken each time the furnace was heated. The furnace was charged at a temperature of 842°F (450°C). Temperatures were increased at the rate of 6.5°F per minute (3.6°C. per minute) until it attained 1850°F (1010°C), at which point a constant temperature was maintained for a two-hour period.

Upon removal from the furnace the contents of each crucible were quickly quenched in individual water baths, then removed from the water, placed in individual pans, and dried for two days on the furnace top.

Coke Tests

Two of the methods of testing developed in the previous study by Marshall et al., (1958) were used. These were modifications of ASTM shatter and tumbler procedures in which it was hoped that the results would show trends similar to those shown by the standard methods of testing. Limited tests - three which considered size consist of the coal charge and three in which the amount of fusain was varied - indicated that laboratory test cokes showed physical properties similar to those shown by pilot plant cokes, although the absolute values of shatter and tumbler indices differ in magnitude.

Present day industrial evaluation of the physical properties of coke indicates that blast furnace behavior is more nearly characterized by tumbler tests than by shatter tests. Therefore two samples of each coke run were subjected to the tumbler tests and one to the shatter test.

The tumbler test was made by placing the coke sample in a 1/2 gallon metal can, and rotating the can, end over end, for 40 minutes at the rate of 40 revolutions per minute.

The stability index was measured by the tumbler plus 1-inch percentage, and the resistance to abrasion (hardness) was measured by the tumbler plus 1/4 inch fraction. For this investigation the minus 1/4 inch index was plotted as this reflects more clearly the hardness character of the coke. The plus 1-inch fraction from the shatter test was considered a basis for a shatter index. Percentage data on plus 1/4 and minus 1/4 fractions also have been plotted.

It is realized that the modified shatter and tumbler tests used in this investigation, like the standard ASTM tests, are highly emperical and must not be thought of as giving precise results. Test results which differ by small amounts are probably not significant, and a strict comparative evaluation of cokes on the basis of small differences in shatter and tumbler indices is not intended.

STUDY RESULTS

Effect of Blending No. 6 and No. 5 Coals in Various Amounts

For a standard blend, with which various sizes and amounts of additives were to be combined, Illinois No. 6 and No. 5 Coals were blended. To obtain as nearly an optimum blend as possible, eight mixtures of the standard size fractions of No. 6 and No. 5 Coals were coked.

Coal mixtures in this series varied, in 10 percent increments, from a blend of 90 percent No. 6 Coal and 10 percent No. 5 Coal; to 30 percent No. 6 Coal and 70 percent No. 5 Coal. One run of 100 percent No. 6 Coal also was made. Variations in the physical properties of the resulting coke were not great in this series (fig. 2). In evaluating these data tumbler indices were considered more important than shatter indices. Nevertheless, shatter values were not disregarded, and in some instances, when the tumbler indices of two cokes were essentially equal, the shatter indices were used as the deciding factor as to which coke was the better.

Optimum condition for shatter index was found in the 90 percent No. 6 - 10 percent No. 5 Coal blend with 95.3 percent of the coke larger than 1 inch and 97.0 percent larger than 1/4 inch. The lowest of the tumbler minus 1/4-inch indices 9.5 which is desirable, was produced by the blend of 40 percent No. 6 - 60 percent No. 5 Coal. The highest tumbler plus 1-inch index occurred in the blend of 70 percent

No. 6 - 30 percent No. 5 Coal, which appeared to be optimum of the blends when all tumbler and shatter indices were considered. An additional run using the blend of 70 percent No. 6 - 30 percent No. 5 Coal not only showed the reproducibility of the testing, but also sustained the fact that this blend was the optimum. Therefore in all subsequent coke runs, which included additives, the No. 6 and No. 5 proportions were recalculated so that "standard blend" plus additive totaled 100 percent. All subsequent comparisons relative to the "standard blend" refer to both shatter and tumbler indices obtained in testing coke produced from the blend of 70 percent No. 6 - 30 percent No. 5 Coal.

Petrographic analysis of No. 6 and No. 5 Coals was essentially the same (fig. 2). The maximum variation of two percent was found in the exinite; 8.3 percent in No. 6 Coal and 6.3 percent in No. 5 Coal.

Results of screen analysis of the standard samples of No. 6 and No. 5 Coals showed that the breakage produced very nearly the same size consist in both coals.

Chemical analysis of both No. 6 and No. 5 coal samples were made. Gieseler fluidity for both coals is low; No. 6 coal had a maximum fluidity of 3 dial divisions per minute and the No. 5 coal had 29 dial divisions per minute.

Effect of Fusain Additive

Recent studies, both laboratory and pilot plant, have indicated that addition of fusain in an optimum amount to the coal generally improves the physical properties of the resulting coke. In this investigation five, ten, fifteen and twenty percent minus 150 mesh fusain was mixed with the standard 70-30 blend of No. 6 and No. 5 coals.

For reasons undetermined the tumbler plus 1 inch index decreased below that of the "standard blend" with addition of 5 percent minus 150 mesh fusain, but rose to an optimum high of 90.2 when 10 percent fusain was added. The tumbler minus 1/4 inch responded accordingly with an optimum low of 9.4 with 10 percent added fusain. The shatter plus 1 inch rose to its optimum of 95.1 with addition of 5 percent minus 150 mesh fusain and declined steadily thereafter. As fusain has no fusion properties of its own, when an excessive amount is present which cannot be incorporated by the vitrinite and other macerals in the softening period of carbonization, weaker areas occur within the coke. This is strikingly demonstrated as 15 percent fusain is added to the coal charge. With the addition of 20 percent fusain, all indices of the resulting coke deteriorated.

As natural breakage of relatively pure fusain produces a size of minus 150-mesh it is impossible to obtain larger sizes for blending. Larger sizes result from mineralization of the fusain. A 20 x 150-mesh size fusain was obtained and blended with the "standard blend," but this fusain was highly mineralized.

Effect of Anthracite Additive

Blending of anthracite with coal for production of metallurgical coke is not new, but results vary, and, therefore, during this investigation, the effect of amount and size of the anthracite blended with Illinois coals was studied. As previously stated three sized samples of anthracite were prepared, namely minus 150-mesh, minus 20-mesh, and minus 10-mesh. Each size was blended with the "standard blend" in amounts of 5, 10, 15, and 20 percent.

Addition of minus 150-mesh anthracite to the "standard blend" produced cokes whose shatter and tumbler indices were not as good as those of the "standard blend." It was interesting to note that addition of 5 percent minus 150-mesh anthracite had an effect similar to that of adding the same quantity of fusain. The tumbler plus 1-inch and minus 1/4-mesh as well as the shatter plus 1-inch indices indicated a coke of poorer quality than that produced from the "standard blend" alone. The blending of 10 percent minus 150-mesh anthracite produced an improvement, but not to the same extent as that with the fusain blend. Addition of 15 and 20 percent minus 150-mesh anthracite resulted in cokes whose indices decreased greatly.

When the minus 20-mesh sample of anthracite was blended the effect on coke values was different. All tumbler indices improved with the blending of 5 percent of this anthracite and addition of 10 percent produced one of the best cokes made from any blend which included only coal and high-carbon components. The tumbler plus 1-inch index rose to 90.6 and tumbler minus 1/4-inch index fell to 8.4. The tumbler plus 1-inch dropped to 84.7 when 15 percent was added, but instead of continuing to decline as in previous tests with minus 150-mesh anthracite and fusain, this index rose to 86.6 or 1.4 above the "standard blend" for this index. The tumbler minus 1/4-inch index also rose, instead of declining, to 12.6 or 1 above that of the standard blend." All shatter test indices declined slightly.

Shatter and tumbler indices derived from cokes produced from blends of minus 10-mesh anthracite gave results similar to those produced from blends of minus 20-mesh anthracite. Optimum results were obtained with the blending of 10 percent minus 10-mesh anthracite, but the amount of the tumbler plus 1-inch coke was not as great, nor the amount of tumbler minus 1/4-inch coke as small in this optimum as corresponding values obtained with the minus 20-mesh anthracite.

Effect of Coke Dust Additives

Coke dust was acquired from coke used in the tumbler test apparatus at the pilot plant of the Survey and consequently all coke dust was smaller than 20-mesh.

Five percent minus 150-mesh coke dust mixed with the "standard blend" improved the tumbler indices of the resulting coke, but all coke qualities declined as additional minus 150-mesh coke dust was added.

As in anthracite, optimum results were obtained with coke dust by blending the minus 20-mesh material with the "standard blend." The blend of 5 percent minus 20-mesh coke dust resulted in a slight increase in the tumbler index for plus 1-inch, but all other indices were the same or showed a slight decline from the "standard blend." All tumbler values increased to an optimum with the blend of 10 percent minus 20-mesh coke dust, and all indices declined with additional coke dust. Coke dust minus 20-mesh and anthracite minus 20-mesh gave essentially the same optimum results in the 10 percent blend.

Effect of Coke Breeze Additives

Of the three size fractions of coke breeze added, minus 20-mesh, minus 10-mesh, and 6 x 10-mesh, none produced coke having all physical properties better or equivalent to the "standard blend" cokes. The tumbler indices of cokes produced from the blend containing minus 20-mesh coke breeze remained relatively high through the 10 percent blend, but the 1-inch index plunged from 79.9 to 58.4 when 15 percent coke breeze was added.

Optimum coke from this series was produced from blends with 5 percent minus 10-mesh coke breeze; the index for tumbler plus 1-inch increased slightly, giving a higher value than the "standard blend," but all other indices declined. With 10 percent

minus 10-mesh breeze the tumbler plus 1 inch dropped from 86.4 to 79.9; with 15 percent breeze this index decreased to 58.4.

Drastic deterioration in coke character was produced by mixing the "standard blend" with 6 x 10 mesh coke breeze. Although the coke remained in one piece upon being discharged from the crucible, and the shrinkage appeared to be slight, the tumbler + 1 inch index was only 40 and the shatter + 1 inch index was only 60.4. Blending of 10 percent 6 x 10 coke breeze caused a further drop in tumbler + 1 inch index to 16 and in the shatter + 1-inch index to 47.6.

Effect of Petroleum Coke Additive

A blend containing 5 percent minus 10-mesh petroleum coke produced optimum coke characteristics in this series. The indices for tumbler plus 1-inch and tumbler minus 1/4 inch were generally comparable with coke produced from 10 percent minus 10-mesh anthracite, (fig. 3), and both were superior to coke produced from the "standard blend." All indices remained relatively high in the petroleum coke blends, both minus 10-mesh (fig. 3) and minus 20-mesh (fig. 4) and did not show the large declines as observed with the coke breeze additive.

Effect of "Fine Coal" Additive

To compare the relative effect on coke of reduced sizes of the coal itself and the relatively high-carbon additives, a sample of the 70 percent No. 6 Coal -30 percent No. 5 Coal was reduced to sizes comparable to those of the high-carbon components, minus 150-mesh, minus 20-mesh and minus 10-mesh size fractions and substituted for them in coal blends for laboratory tests. Physical properties of cokes obtained from blending fine coal with the "standard blend" were closely related to the physical properties of cokes produced by blending various percentages of No. 6 and No. 5 Coals, except for two tests. In these the tumbler indices showed an improvement when 5 and 10 percent of the minus 20-mesh fine coal was used; an increase in inertinite occured in this minus 20-mesh fraction.

Black Shale Additive

In hopes of finding some other natural substance to replace the high-carbon components, black petroliferous shale from above the No. 5 Coal was obtained from a strip mine in western Illinois. A high-ash content was expected but a low total sulfur was hoped for. Analysis shows an ash of 60.2 percent and a total sulfur of 1.52 percent on the "as received" basis. The black shale was prepared in three size fractions, minus 150-, minus 20- and minus 10-mesh, and amounts of 2.5, 5, 7.5, and 10 percent were blended with the "standard blend' of No. 6 and No. 5 Coals. None of the cokes produced from mixtures of minus 150-mesh black shale or minus 10-mesh black shale with the "standard blend" had tumbler and shatter indices equal to those of the "standard blend" when coked alone.

The only black shale size fraction that produced a better coke than that of the "standard blend" was the minus 20-mesh size blended in the amount of 5 percent.

Effect of Minus 48-mesh Coal

Minus 48-mesh coal had previously been considered as a source of a high concentration of fusain. Unfortunately, petrographic analyses of this material

exhibited an inertinite (includes fusain) content of only 13.2 percent. The remaining 86.5 percent was composed of 79.6 percent vitrinite, 3.4 percent exinite and 3.8 percent visible mineral matter.

Tumbler and shatter indices of the coke produced by blending this minus 48-mesh coal were deleterious except for the 5 percent blend. In this coke the indices for tumbler plus 1-inch, shatter plus 1/4-inch, and the shatter minus 1/4-inch showed a slight improvement. Although this trend was slight it warrants additional consideration in future testing.

Effect of "Resin" or "Asphaltine" Additive

The previous study by Marshall et al. (1958) demonstrated that a benzene soluble, petroleum ether insoluble, extract of coal tar pitch (termed "resin" or "asphaltene"), when added to a blend of coal and fusain, markedly improved the quality of laboratory cokes produced.

For this latest investigation "resin" was added to those mixtures of additives and "standard blend" which gave optimum coke results. In blends not containing "resin" calculations were made so that the "standard blend" plus the additive equaled 100 percent. In these tests the same calculations were used and 5 percent additional "resin" was added to this blend. The results of these tests are shown in figure 5. Parenthesis around the run number indicates that the coke quality of that run is better than coke produced with the "standard blend."

Run 25A demonstrates that coke quality is improved by addition of "resin" to the "standard blend," but a decided increase in coke quality is produced when 10 percent minus 150-mesh fusain is included in the blend (Run 25B). Tumbler index plus 1-inch increased from 85.2 for the "standard blend" to 93.5 and the index for tumbler minus 1/4-inch decreased from 11.9 to 6.3. Additional fusain in the blend caused deterioration of all cokes, as shown in Figure 5.

Twenty percent minus 20-mesh anthracite was needed in the "resin" and "standard blend" mixture for the optimum coke in the anthracite series (Run 26F). The tumbler index for plus 1-inch was 91.7 and for minus 1/4-inch was 8.3. Addition of 5 percent resin to optimum blends of coke dust or petroleum coke was detrimental, and coke qualities declined below those of the coke produced from the "standard blend."

FACTORS WHICH POSSIBLY AFFECT COKING RESULTS WHEN ADDITIVES ARE USED

Nature of the Additive

A few of the factors that can possibly affect the quality of coke produced by the addition of high-carbon components are considered. The nature of the additive is obviously an important factor. A totally inert substance does not shrink but expands slightly upon heating, and therefore the shrinkage of the mixture is reduced and thus fracturing is reduced. From this, it can be concluded that the temperature at which maximum expansion occurs is important because if maximum expansion occurs after resolidification of the main mass, fractures will form that will weaken the coke. A study of the possible different expansion temperature of high-carbon components used in this investigation was not investigated but should be considered.

The ability of the surface of the additive to absorb the fluid products derived from heating the coal will affect the coking capacity of the charge. It is probable that this ability varies in the additives used in this investigation.

Shape of Individual Particles of Additive

An attempt to evaluate the effect of the shape of individual particles upon coke character did not produce a clean-cut correlation, but two observations were made. The shapes adopted for this classification, as previously mentioned, were equidimension, elongate, rod-like, triangular, and angular. In all shape analyses, the majority of particles were classified as either elongate or rod-like.

The shape of particles in the minus 150-mesh fusain was predominantly rod-like, 79.6 percent, and this component produced the optimum coke, as compared to other additives, in the same size range. Considering only this size fraction, the fusain had a larger surface area than the other additives. Figure 3 shows that most additives produce optimum coke from the minus 20-mesh size. It may be possible that an optimum surface area for an individual particle is necessary for an optimum coke.

The second observation resulted from the comparison of the shape analysis of the coke dust and coke breeze. In the latter, which produced an inferior coke, the percentage of angular particles were higher, 15.8 percent as compared to 3.8 percent for the coke dust.

Amount of Additive

A direct relation between the amount of the additive and coke quality is shown in figures 3, 4, and 6, which show optimum coke indices for each additive in each particular size category. For some components the variation of 5 percent produces marked changes in shatter and tumbler indices (see fusain column in fig. 6). Anthracite in the minus 10-mesh fraction (fig. 3) and coke dust in the minus 20-mesh fraction (fig. 4) demonstrate variations with somewhat less magnitude. Marked deteriorations are produced when the minus 20-mesh and minus 10-mesh fractions of coke breeze are increased from 10 to 15 percent. Marked deteriorations are also shown for black shale minus 150-mesh, anthracite minus 150-mesh, and fusain minus 150-mesh when the amount of each component was increased from 10 to 15 percent.

Particle Size of Additive

The effect of the particle size of the additive upon coke is clearly seen by combined study of figures 3, 4, and 6. Each figure represents coke data produced by blending various amounts of the additives of different size range with the "standard blend." Parentheses have been placed around the percentage figure, at the bottom of each chart, to identify those blends which produced cokes having better physical properties than the coke produced from the "standard blend" alone. These are referred to as "improved cokes."

Only fusain in the minus 150-mesh size range produced improved coke, but three blends of minus 10-mesh material, two anthracite, and one petroleum coke produced this improved coke. Seven blends of minus 20-mesh material, coke dust 10 and 15 percent, anthracite 5 and 10 percent, fine coal 5 and 10 percent, and black shale 5 percent produced improved coke.

The amount of additive, the size of its particles, and the nature of the material appear to be interrelated. For anthracite, 10 percent additive is required for the optimum coke in each size range tested, and in each produced an improved coke. Blends containing 5 percent additives were optimum for black shale and petroleum coke in all size fractions tested, and of these only the black shale minus 20-mesh and petroleum coke minus 10-mesh gave improved cokes. For fine coal, optimum coke was obtained with 5 percent minus 20-mesh and 5 percent minus 150-mesh material added, but in the minus 10-mesh material 15 percent additive was necessary for the most favorable coke indices. Two blends, the minus 20-mesh fraction in 5 and 10 percent amounts produced an improved coke. Five percent minus 10-mesh coke breeze was optimum in this series, but for the minus 20-mesh fraction no amount proved to be optimum for any one blend, as both 5 and 10 percent additive gave about the same over-all results. When coke dust was used as an additive, 10 percent of the minus 20-mesh size consist was optimum and produced an improved coke, but in the minus 150-mesh size consist only 5 percent additive was needed for the optimum coke.

Variation in the Size Consist

An attempt was made to correlate the amount of additive needed, for an optimum coke, with the distribution of the size of the material within each size consist prepared, but it was not possible to make direct correlations using available information.

Blends that Produced an Improved Coke

Figures 7 and 8 show physical properties of 16 improved cokes produced from blends of various additives and the "standard blend" of No. 6 and No. 5 Coals. All additives tested are represented here except coke breeze and minus 48-mesh coal. The best cokes, as evaluated by laboratory shatter and tumbler tests, resulted from blends of coal, anthracite, or fusain, and "resin." Coke derived from coal and coke dust, anthracite, or fusain had physical properties almost as good as those mentioned above. These figures also demonstrate the effect of size and amount of additive upon the coke produced.

CONCLUSION

Physical properties of coke produced from Illinois coals, on a laboratory scale, can be improved by altering the petrographic composition with the addition of high-carbon and other components. Character of the coke produced from these blends depends upon a number of factors among which are the petrographic composition and size of the coal. The surface character, expansion characteristics, chemical composition, amount, particle size, and possibly the shape of the material added are factors that also should be considered.

It has been shown that a certain amount of additive is needed to produce optimum coke indices with each size fraction of additive, but this amount may be different for the different size fractions of the same additive and may vary for different materials added.

From these data we can conclude that blending additives with a coal charge to produce optimum coke is not a haphazard process. Many factors must be considered and each evaluated for optimum conditions to obtain the most favorable shatter and tumbler indices in a coke produced from any one blend.

A logical continuation of this investigation would be on a pilot scale to determine if tendencies as indicated on the laboratory scale would hold true in tests on the larger scale. It is recognized that certain problems exist, such as securing a homogeneous mixture in a 700-pound charge if the sizes of the coal and the additive vary greatly. Preventing segregation in handling the mixture and charging the furnace is important.

Acknowledgments

The author greatly appreciated the cooperation shown by the companies that furnished the coals and other components that were blended with the coal in this laboratory coking investigation. The column sample from the No. 5 Coal was obtained from the Sahara Coal Company's Mine No. 16 Saline County, Illinois. Coal samples and fusain were taken from the No. 6 Coal of the Freeman Coal Mining Corporation's Orient No. 3 mine in Jefferson County, Illinois. Anthracite was furnished by the Glen Alden Corporation, Hudson Coal Company, and Jeddo - Highland Coal Company. The Great Lakes Carbon Company supplied the petroleum coke for the investigation.

The author is indebted to G. H. Yohe, Head of Coal Chemistry Section of the Geochemical Group, Illinois State Geological Survey, who prepared the "resin" extract from the coal tar pitch.

To other members of the Geological Survey who assisted in many ways throughout the investigation, I offer my sincere thanks.

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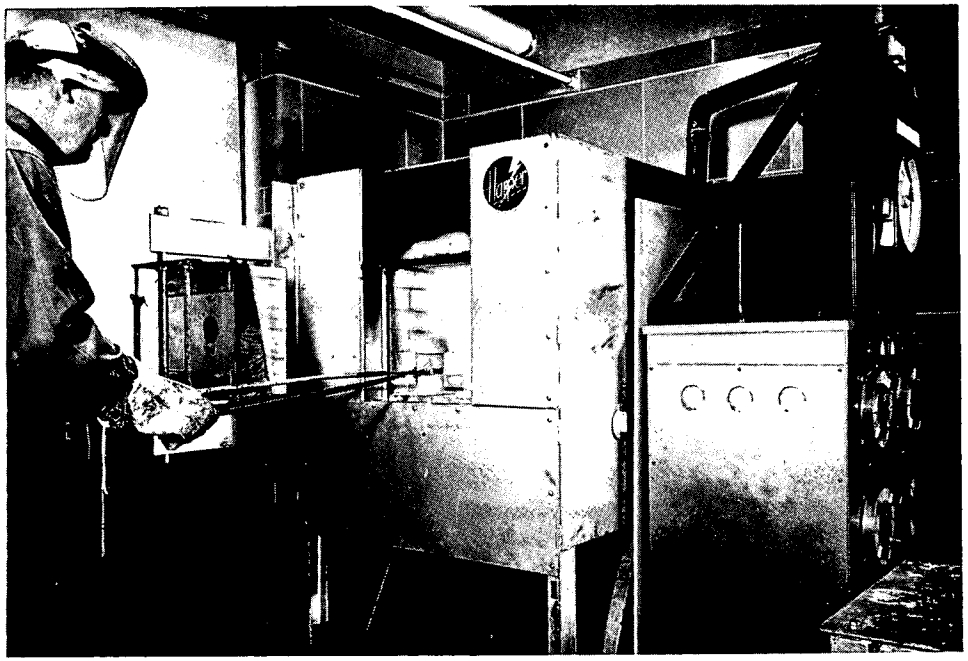


Plate 1. - Charging alumina crucible with fireclay cover and base into furnace used for laboratory coking tests.

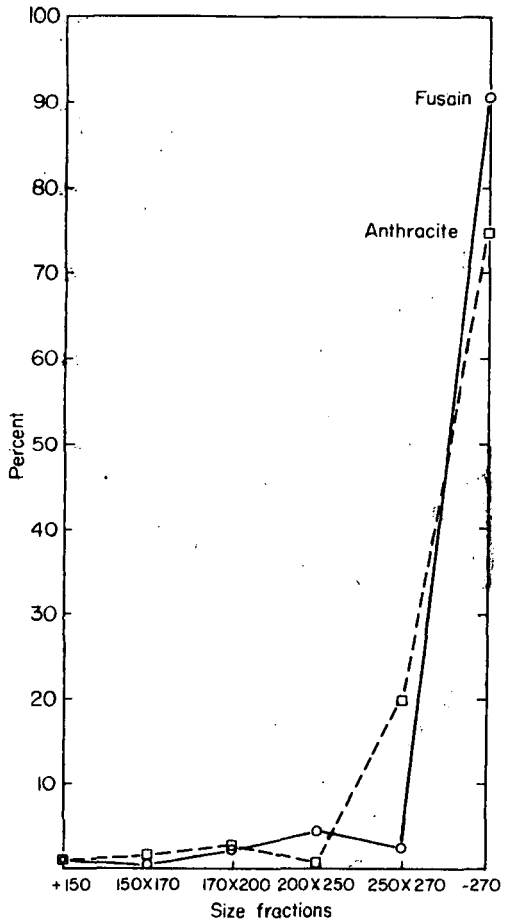


Fig. 1. - Screen analysis of minus 150 mash fusain and anthracite

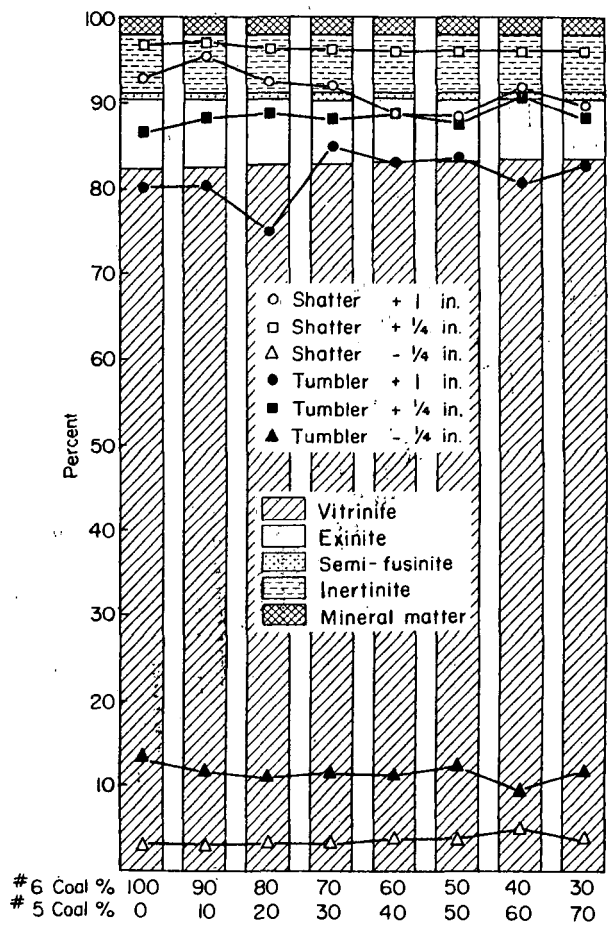


Fig. 2. - Petrographic analysis and character of coke produced from different blends of No. 6 and No. 5 Coals of standard size consist.

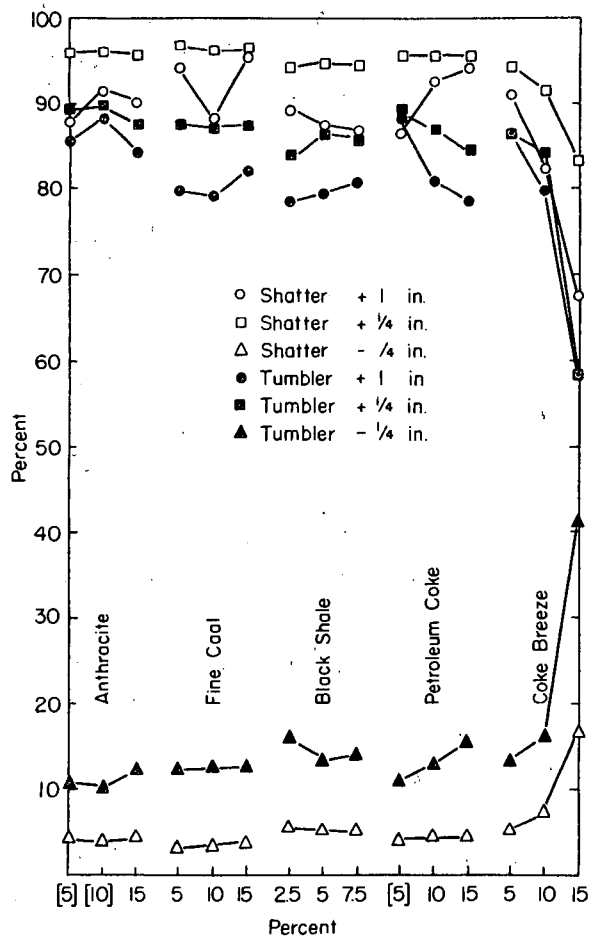


Fig. 3. - Comparison of coke character and the amount of minus 10 mesh material used in blends of different additives.

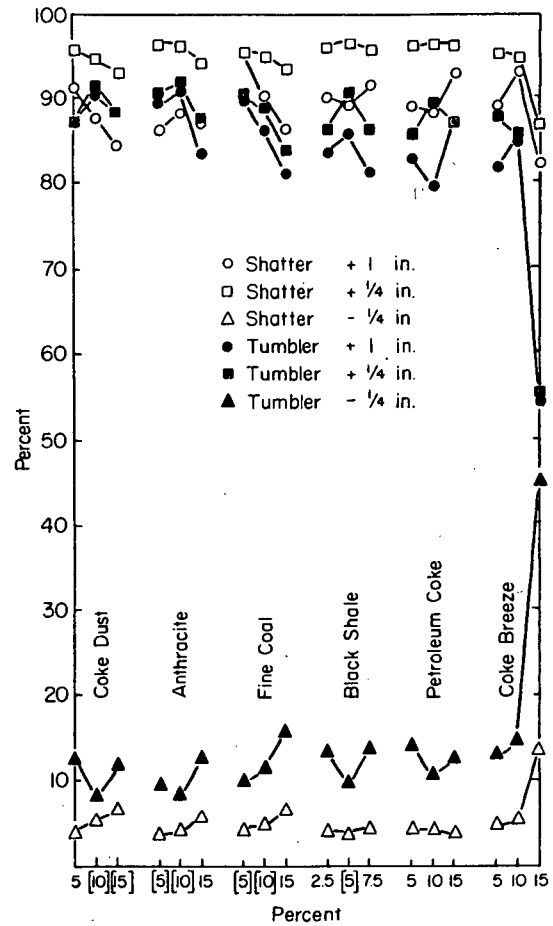
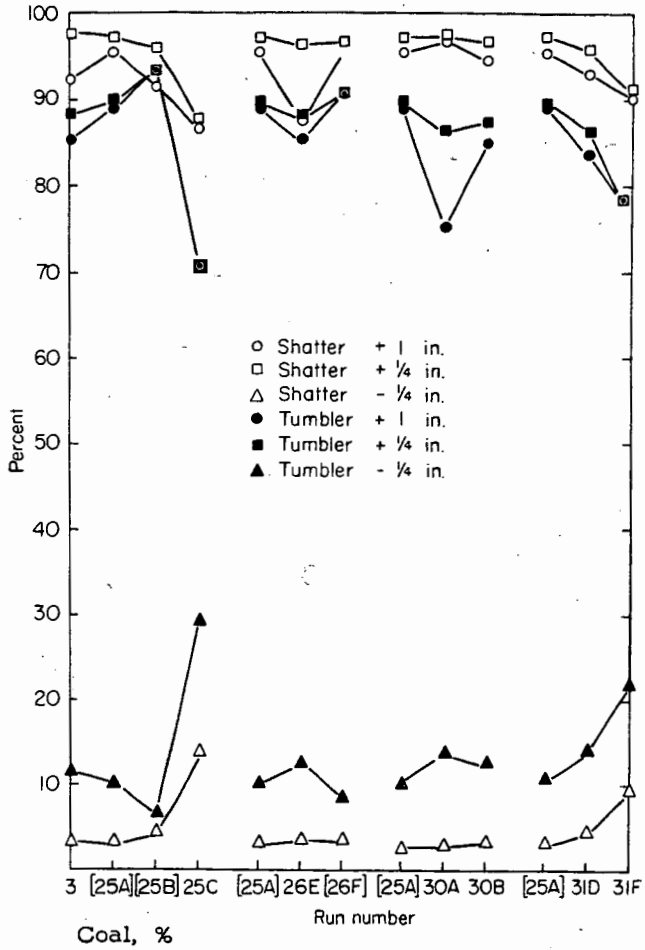


Fig. 4. - Comparison of coke character and the amount of minus 20 mesh material used in blends of different additives.



Run	Coal, % No. 6	No. 5	Additives	%	Others	%
3	70	30				
25A	70	30			"Resin"	5
25B	63	27	Fusain (-150M)	10	"Resin"	5
25C	56	24	Fusain (-150M)	20	"Resin"	5
26E	63	27	Anthracite (-20M)	10	"Resin"	5
26F	56	24	Anthracite (-20M)	20	"Resin"	5
30A	63	27	Petroleum Coke (-10M)	10	"Resin"	5
30B	56	24	Petroleum Coke (-10M)	20	"Resin"	5
31D	63	27	Coke Dust (-20M)	10	"Resin"	5
31F	63	27	Fusain (-150M)	10	Coal Tar	5

Fig. 5. - Character of coke produced by blends containing five percent "resin" and various amounts of high carbon components.

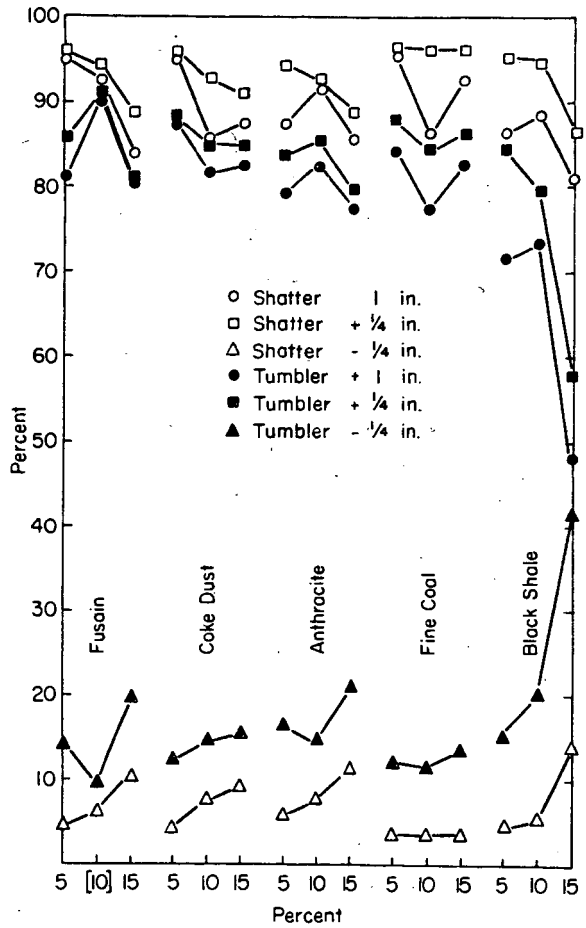
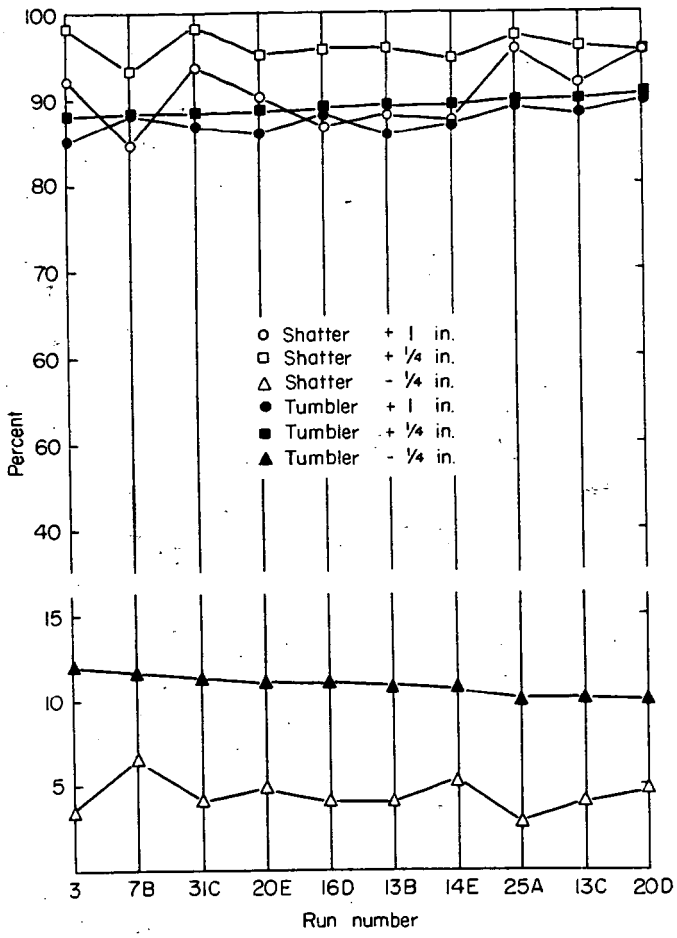
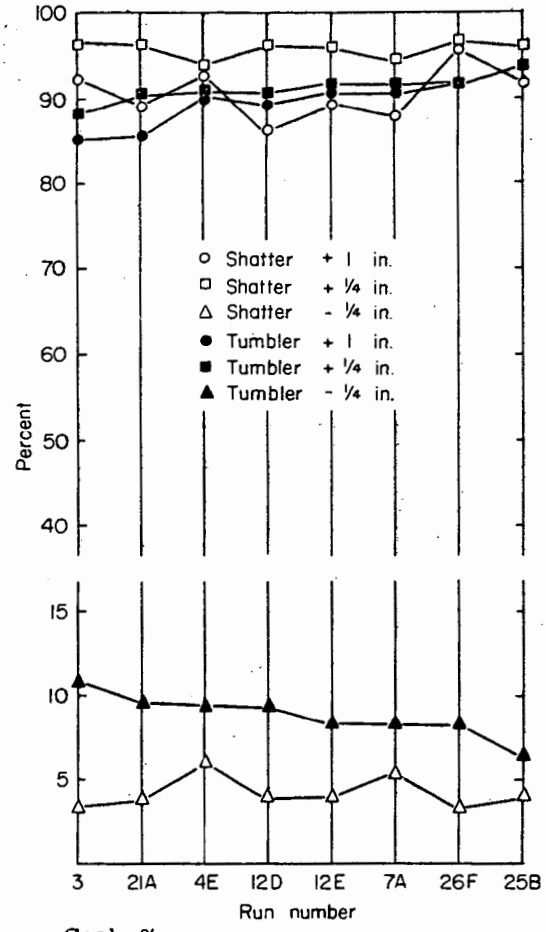


Fig. 6. - Comparison of coke character and the amount of the minus 150 mesh material used in blends of different additives.



Run	Coal, % No. 6	No. 5	Additives	%	Others	%
3	70	30				
7B	59.5	25.5	Coke Dust (-20M)	15		
31F	63	27	Fusain (-150M)	10	Coal Tar	5
20E	63	27	"Fine Coal" (-20M)	10		
16D	66.5	28.5	Petroleum Coke (-10M)	5		
13B	66.5	28.5	Anthracite (-10M)	5		
14E	56	24	Anthracite (-10M)	20		
25A	70	30			"Resin",	5
13C	63	27	Anthracite (-10M)	10		
20D	66.5	28.5	"Fine Coal" (-20M)	5		

Fig. 7. - Coke character produced by various sizes and amounts of different additives. All cokes are superior to those produced from "standard blend" alone.



Run	Coal, % No. 6	No. 5	Additives	%	Others	%
3	70	30				
21A	66.5	28.5	Black Shale (-20M)	5		
4E	63	27	Fusain (-150M)	10		
12D	66.5	28.5	Anthracite (-20M)	5		
12E	63	27	Anthracite (-20M)	10		
7A	63	27	Coke Dust (-20M)	10		
26F	56	24	Anthracite (-20M)	20	"Resin"	5
25B	63	27	Fusain (-150M)	10	"Resin"	5

Fig. 8. - Coke character produced by various sizes and amounts of different additives. All cokes are superior to those produced from "standard blend" alone.

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Properties of Chars Produced from Wyoming Coals

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Scope and Objectives of Work

During the past years, a certain demand for low volatile solid fuel has been developed in the Middle United States. As a blend for the carbonization of high volatile coking coal available locally, low volatile bituminous coal has to be shipped in over great distances. The taconite industry in Minnesota has to ship in anthracite for sintering fuel, and the demand for metallurgical processes might well increase greatly with the development of the iron ore resources of Wyoming. There is also a considerable tonnage required for the reduction of phosphate to elemental phosphorus.

There are vast reserves of coals available locally (4), and these coals no doubt will in time be utilized for their solid carbon, especially as it is known that in such processing a large amount of tar can be recovered.

The work discussed here was undertaken in order to throw more light on the properties of chars which can be produced from Wyoming bituminous and subbituminous coals. Chars were produced at varying carbonization temperatures, and their properties, as well as the properties of the coals from which they were derived, were compared with the properties of by-product coke produced in the West as well as that produced from blended Pittsburgh Seam coal.

It appeared desirable to get comparative data on the reactivity of these materials. In order to test their reactivity with oxygen, their free combustibility in air was measured. To test their reactivity with carbon dioxide, they were exposed to a stream of CO_2 at 950°C and at lower temperatures. In order to obtain a measure of their electrical conductivity, the electrical resistivity was measured. To test the mechanical strength, the Hardgrove grindability index was determined. To obtain information on their relative porosity and surface characteristics, the density was measured by displacement with mercury and with methanol, also their heat of wetting in methanol. To show the changes caused in their crystallographic structure by carbonization, they were examined by X-ray diffraction.

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Coals and Chars Examined

With a few exceptions, the coals of Wyoming range from High Volatile C Bituminous to Subbituminous C. Three coals were selected for examination: D. O. Clark, Superior is a High Volatile C Bituminous coal; Elkol, Kemmerer, is a Subbituminous B coal; and Wyodak, Gillette, is a Subbituminous C coal. The proximate and ultimate analyses, also the heating values of these coals and the atomic hydrogen to carbon ratios, are compiled in Table I.

Coal samples were supplied by the operators in the fall of 1956. Mr. William Ross, Manager of the Gillette Resource Development Corporation, supplied the Wyodak coal; Mr. G. E. Sorensen, President of the Kemmerer Coal Company, supplied the Elkol coal; and Mr. V. O. Murray, President of the Union Pacific Coal Company, supplied the D. O. Clark coal.

The coal was carbonized in a horizontal stainless steel retort in batches of about 250 grams each. This apparatus was previously described by Prostel and Rice (16). The coal was crushed to pass US No. 13 screen, and the retort placed in an electrically heated muffle furnace. The furnace temperature was increased at the rate of 5°C per minute.

The moisture shown in Table I was determined on air-dry coal. No record was kept of the temperature and the atmospheric pressure when the moisture determination was performed. Barometric pressure at the laboratory averages close to 23" Hg, and the humidity varies mostly between 10 and 20 percent.

The sulfur reported was determined from the calorimeter bomb washings, precipitated and weighed as barium sulfate. It appears from examining the analysis of some of the ashes that the sulfur is present largely as sulfate. As the sulfur in the ash was not determined, it had to be estimated for the calculation of the oxygen or nitrogen plus oxygen respectively. The small amount of combustible sulfur, of course, was burned and absorbed with the carbon dioxide, and is reported as carbon in the ultimate analyses.

Electrical Resistance

Two kinds of electrical resistance were obtained. First: particles between No. 12 and No. 30 screens were subjected to a pressure of 0.34 kg/cm^2 after being dried for 20 hours at 100 to 110°C. Sample height varied between 0.8 and 1.3 cm. Accuracy was ± 5 percent. Second: particles passing No. 200 screen were dried in the same way and then subjected to 3,000 kg/cm^2 pressure. Sample height, in this case, varied between 0.5 and 1.2 cm, and the results did not differ by more than 2 percent.

It is well known that the specific resistance decreases with the pressure applied (2) (21). Measurements were taken at a variety of pressures up to 3,270 kg/cm^2. As determined by Davis and Auvil (2), the specific resistance decreased with increasing pressure but at a progressively slower rate. The pressure of 3,000 kg/cm^2 was finally chosen for the tests as a reasonable compromise between minimum resistance and test accuracy on the one hand and pressure applied to the sample on the other hand.

Table II gives the specific electrical resistances determined at the two pressures. The respective values for cokes appear in Table III.

Table I. Analyses of Coals, Chars and Cokes

Mine	Product	H_2O Airdry %	1.) VM %	1.) FC %	1.) Ash %	1.) Heating Value Btu/lb	1.) H_2 %	2.) C %	1.) N_2 %	1.) O_2 %	1.) S %	Atomic Ratio H/C
Wyodak	Subc-Coal	5.7	42.3	47.7	10.0	11,340	4.5	66.3	1.1	18.1	1.0	0.81
"	500°C-Char	0.8	17.2	69.0	13.8	12,300	2.7	65.0	18.5		1.0	0.50
"	600°C "	0.3	12.0	73.4	14.6	12,300	2.3	77.6	5.5		1.0	0.36
"	700°C "	0.4	7.9	76.4	15.7	12,300	1.6	77.3	5.4		1.1	0.25
"	800°C "	0.4	4.4	80.0	15.6	12,280	1.1	83.3	0.0		1.4	0.16
"	900°C "	0.1	2.9	81.0	16.1	12,210	0.8	83.1	0.0		1.4	0.12
"	950°C "	0.3	2.1	81.6	16.3	12,400	0.5	83.2	0.0		1.4	0.07
Elkol	Subb-Coal	3.6	43.0	54.5	2.5	12,580	5.0	72.6	1.5	17.8	0.8	0.83
"	500°C-Char	0.3	17.2	79.0	3.8	13,500	3.2	83.1	9.6		0.6	0.46
"	600°C "	0.4	9.5	86.2	4.3	14,170	2.6	87.3	5.7		0.5	0.36
"	700°C "	0.4	4.5	91.1	4.4	14,090	1.6	91.0	3.0		0.4	0.21
"	800°C "	0.5	2.2	93.5	4.3	13,710	1.0	91.9	2.8		0.4	0.13
"	900°C "	0.7	1.5	94.0	4.5	13,680	0.8	92.3	2.4		0.4	0.09
"	950°C "	0.3	2.0	93.5	4.5	13,660	0.5	92.7	2.3		0.4	0.06
D. O. Clark	Hvcb-Coal	1.1	39.9	55.7	4.4	13,330	5.5	73.9	1.6	13.9	1.0	0.89
"	500°C-Char	0.3	15.0	79.7	5.3	13,520	3.2	82.9	8.2		0.8	0.46
"	600°C "	0.3	8.6	85.3	6.1	13,830	2.3	85.3	6.1		0.7	0.32
"	700°C "	0.2	3.7	89.4	6.9	13,560	1.7	87.3	3.9		0.7	0.23
"	800°C "	0.3	2.4	90.7	6.9	13,330	0.8	89.0	3.2		0.6	0.11
"	900°C "	0.3	1.6	91.6	6.8	13,280	0.7	89.9	2.6		0.5	0.09
"	950°C "	0.2	1.5	91.1	7.4	13,270	0.6	90.2	1.8		0.5	0.08
Pittsb. Seam Rocky Mtn. Region	Typical Blast Furnace Cokes	0.4	0.5	90.4	9.1	11,810	0.3	88.9	1.7		0.5	0.04
		0.3	1.4	86.2	12.4	12,040	0.4	85.8	1.4		0.4	0.06
		0.3	0.6	88.5	10.9	11,140	0.2	87.3	1.6		0.6	0.03

1.) On moisture free basis
Subc - Subbituminous C
Subb - Subbituminous B
Hvcb - High Volatile C Bituminous

2.) May include small amounts of sulfur

Table II. Specific Electrical Resistance in ohms per cm cube

Coal or Char	Wyodak		Elkol		D. O. Clark	
	at 3,000 kg/cm Pressure	at 0.34 kg/cm Pressure	at 3,000 kg/cm Pressure	at 0.34 kg/cm Pressure	at 3,000 kg/cm Pressure	at 0.34 kg/cm Pressure
Airdry Coal	10^8 +	10^8 +	4.3×10^8	10^8 +	1.4×10^8	10^8 +
500°C Char	3.17×10^7	6.3×10^6	1.17×10^6	10^8 +	3.09×10^7	2.5×10^7
600°C Char	4.57×10^4	5.2×10^5	1.30×10^5	1.7×10^6	6.81×10^4	5.4×10^2
700°C Char	5.12	3.46×10^2	5.26	3.88×10^2	5.80	5.24×10
800°C Char	2.06×10^{-1}	1.65×10	1.64×10^{-1}	1.28×10	1.32×10^{-1}	1.28×10
900°C Char	7.06×10^{-2}	4.45	7.28×10^{-2}	5.02	4.69×10^{-2}	4.05
950°C Char	4.16×10^{-2}	3.28	5.08×10^{-2}	3.55	4.71×10^{-2}	3.08

Table III. Specific Electrical Resistance of Cokes
ohms/cm Cube

Sample	Specific Elec. Resistance at 3,000 kg/cm Pressure	Specific Elec. Resistance at 0.34 kg /cm Pressure
A	0.0414	1.13
B	0.0106	1.13
C	0.0129	1.79

As will be seen from Table II, the resistance at high pressure decreases sharply with increasing carbonization temperatures to between 700 and 800°C, then decreases gradually until it reaches a value in the order of 10^{-2} ohms per cm cube. This change in resistance is consistent with changes taking place in the coal constituents as carbonization proceeds. Non-crystalline constituents are decomposing and more crystalline bodies are forming in the residual char. The resistance at low pressure shows a similar tendency of variation with carbonization temperature.

Mechanical Strength

The mechanical strength was determined by the Hardgrove grindability test, following the procedure described in ASTM designation D 409-51.

The results of this test as shown in Figure 1 reveal a similar tendency of change in resistance to mechanical grinding for the three series of samples as a function of carbonization temperature. It is easily understood that the straight increase in mechanical strength (decrease in grindability index) between 600 and 950°C is due to the increasing development of crystallographic units, also by the increasing compactness of residual solids which will be shown by a sharp increase in density in the corresponding temperature range. The tendency of the curves below 600°C seems harder to explain. Some coals, Wyodak for example, show a decreasing grindability with decreasing moisture content, as has been demonstrated by comparative grindability tests with this coal at varying moisture percentages (17). This tendency apparently is prevalent also in the early stages of carbonization, or at least in that temperature range in which absorbed gases are expelled. At somewhat higher temperature (possibly much below 500°C) an increasing decomposition of the coal substance seems to weaken the residual solid whereas above 600°C the structure of the residue changes increasingly, and crystallization becomes dominant.

Reactivity

Reactivity with oxygen in air was measured by Newall's method (15). The sample was crushed to pass No. 200 screen, and was dried for one hour at a temperature between 100 and 110°C. The propagation of the zone of combustion was measured over a 5 cm course. Results of these tests are shown in Table IV. Combustibility of the chars from the lowest rank coal (Wyodak) could be maintained up to the 800°C char. Combustibility of the chars from the Elkol coal could be maintained only to the 500°C char. Combustibility could not be maintained with any of the chars from the highest rank coal (D. O. Clark).

Table IV. Free Combustion in Air

Sample	Rate of Combustion, mm/min Wyodak	Elkol	D. O. Clark
Airdry Coal	3.2	2.8	3.3
500° Char	5.2	2.3	---
600° "	5.4	---	---
700° "	4.9	---	---
800° "	2.1	---	---
900° "	---	---	---
950° "	---	---	---

The reactivity with carbon dioxide was determined in the apparatus illustrated in Figure 2. The sample ground to pass No. 12 screen and retained on No. 30, was dried at a temperature between 100 and 110°C for two hours, and then placed into the furnace. The furnace heat was regulated to the desired temperature and the air was eliminated from the apparatus by a sufficient flow of carbon dioxide before starting the test. In accordance with the report of Müller and Jandl (14), the evolution of carbon monoxide was rapid in the initial stages of the reaction, but within 20 minutes gradually approached a constant rate. Readings of the flowmeters were taken at two-minute intervals in the equilibrium state, and an average of at least ten readings for each flowmeter were obtained.

The ratio of the volume of carbon monoxide evolved to the volume of carbon dioxide introduced per time unit expressed in percent was termed reactivity. According to Shinmura (18), the amount of carbon dioxide reacted is affected by the duration of contact of the coke sample with the gas. For this reason, the height of the sample was held in all cases at 5.0 cm. The reactivity of all chars was determined at 950°C, the reactivity of 950°C chars was also determined at 700, 800, and 900°C. The reproducibility of the results was $\pm$ 3 percent or better.

The difference in physical structure and chemical activity of coals and chars will result in differences in combustibility in air and reactivity with carbon dioxide because these reactions of solids with gases are controlled by both the physical and chemical characteristics of the solids (3). Recent physical investigations indicate that some structural irregularity and in consequence a high chemical activity may be expected in chars carbonized at temperatures between 500 and 600°C (20) (8).

Figure 3 shows the reactivity of the chars with carbon dioxide determined at 950°C. It should be noted that all samples carbonized primarily at temperatures between 500°C and 900° were carbonized again rapidly when the samples were put into the furnace preheated to 950°C. Therefore, the reactivities shown in Figure 3 must have been influenced by this second rapid heat treatment.

The almost unchanged reactivity values for Elkol and Wyodak chars prepared at temperatures from 500 to 950°C imply that these low rank coals yield rather uniform solid residues without regard for the rate of heat increase at which they are carbonized. On the other hand, the chars from D. O. Clark coal which is of higher rank show progressively lower reactivity to CO_2, which indicates

that the rate of heat increase in carbonization is very important for chars from such coal. When the coal is carbonized at a comparatively slow rate of temperature rise as in the case of the 950°C char, the reactivity is comparatively low. The 500°C char, on the other hand, which has been carbonized rapidly above 500°C in the reactivity furnace shows a much higher reactivity. This difference in behavior between the different coals may be due to the difference in the nature of the cracking products from the primary tars which deposit on the surfaces of the chars.

For purposes of comparison, the reactivity values of coke breezes were also determined. The reactivity of D. O. Clark chars seems to approach the values of blast furnace cokes shown in Table V but the chars from subbituminous coals have a much higher reactivity.

The reactivity of chars produced primarily at 950°C was further investigated by determining the variation of reactivity at lower temperatures in comparison with the results for coke breezes in order to compute the apparent activation energy of the carbon - carbon dioxide reaction. Specific results appear in Table V. The apparent activation energy was calculated according to Arrhenius' equation. Activation energy values clearly show that the 950°C chars from the three Wyoming coals react with carbon dioxide in the order: Wyodak, Elkol, and D. O. Clark.

Table V. Variation of Reactivity with Temperature and Activation Energy

Coal	Carbonization Temperature °C	Reactivity Determined at °C 700	800	900	950	Activation Energy, kcal/mole
Wyodak	950	6.9	56.8	128.8	146.0	28
Elkol	950	3.0	23.0	122.2	143.0	35
D. O. Clark	950	0.8	6.0	39.9	58.5	42
Coke A	---	0.0	5.5	21.8	46.3	34
Coke B	---	0.0	2.0	14.8	22.5	43
Coke C	---	0.0	3.8	22.5	34.5	38

The reactivity would be influenced by various factors, as internal surface, chemical reactivity of surface, development of crystallographic units, content and nature of inorganic constituents. The size of the crystallites and the heats of wetting described below are referred to as some of the reasons for the difference in reactivity of these chars.

Density

The density of the samples was determined with two replacement liquids. The methanol density approaches a true density while a density by mercury replacement gives a means of estimating voids or porosity by comparing the two density values on a given char.

The density was determined by replacement with methanol in a density bottle of 25 ml capacity fitted with a thermometer and ground glass stopper. One and one-half to two grams of sample, ground to pass a US No. 200 screen and dried at 100 to 110°C for at least one hour was weighed in the pyknometer and immersed in purified methanol. After standing for two hours, it was gradually evacuated to 40 mm of mercury and held there for several hours with gentle boiling of

the liquid. The pyknometer was then completely filled with methanol and the bottle placed in a water bath at 30°C ± 0.2°C. The experimental error of the density determination was ± 0.5 percent or less.

The density bottle used for replacement with mercury is shown in Figure 4 (19). Samples were ground to pass a US No. 12 screen and to be retained on a No. 30 screen, then dried for at least two hours before they were weighed into the density bottle. The sample weight ranged from 0.2 to 0.4 grams. Mercury was drawn into the bottle by suction at a temperature slightly below 30°C. The sample floated on the mercury and was drawn tightly against the fritted glass filter where air was replaced by the mercury. The bottle was then immersed in a water bath at 30°C ± 0.2°C for about one hour, dried and weighed. The accuracy of the method was ± 3 percent or better.

Figure 5 shows the changes in density values with carbonization temperatures as obtained by displacement of methanol and of mercury and the porosity calculated from these two density values. The values for the three blast furnace cokes used as reference samples are given in Table VI.

Table VI. Density and Porosity of Cokes

Sample	Methanol Density g /cc	Mercury Density g /cc	Porosity %
A	2.062	1.47	28.7
B	1.896	1.48	21.9
C	1.950	1.41	27.7

The methanol density curves for all three series of chars are roughly similar whereas the mercury density of Elkol chars rises to a higher maximum than either of the others. This results in a lower porosity for the Elkol chars than for chars from the other two coals.

There is a steady rise in methanol and mercury density as carbonization progresses to 800 or 900°C, after which there is a consistent drop. Loss in volatile matter and consequent shrinkage in all cases at the lower carbonization temperatures leads to higher density until the maximum is reached in each case where structural changes result in closing pores which exclude the displacing liquids giving, consequently, lower densities (5). It is interesting, however, to note that the density measured by mercury displacement in the samples between No. 12 and No. 30 screens showed a similar maximum at almost the same range of temperatures. This fact tends to support the theory that the structure of these chars is rather homogeneous, and that only the state of orientation, perhaps even a faint turbostatic orientation of the ultimate crystallographic units determines the macroscopic structure, as Blayden (1) and Inouye (10) have suggested for blast furnace cokes.

From the curves in Figure 5 it is also apparent that the porosity of the coal decreases with increase in rank in the order: Wyodak, Elkol, and D. O. Clark. While the porosity of the chars also decreases from Wyodak to Elkol, the porosity of the D. O. Clark chars is considerably higher. Something must have happened in the carbonization process at a temperature lower than 500°C which decreased the mercury density and thus increased the porosity beyond what would be expected from the coal structure. Below 500°C, all coking coals pass through the plastic stage, and D. O. Clark coal has a faint tendency to

coke. The thermoplastic products of carbonization then may develop into sponge-like material which is permeable to methanol but not permeable to mercury, and which is responsible for the lowered mercury density and the increased porosity.

The very high crest in porosity in the case of D. O. Clark, with the sudden drop-off, results from the lag of mercury density changes behind the changes in methanol density. No doubt the methanol molecule finds entry to pores and fissures earlier in the progress of their appearance during carbonization than does mercury.

The maximum densities in the 800 to 900°C temperature range may be compared to similar maxima reported by Franklin (5) and by Honda, Ouichi and Hirose (7) in the cases of carbonization of high rank bituminous coals and of cellulose and glucose. The temperature discrepancy may possible be ascribed to a difference in the structure of the present coals from the substances studied by these workers or it may be at least partially due to differing carbonization conditions. One of the present authors, Inouye, has recognized (11) that the density maximum appears only in the case of chars produced from non-caking young coals and for anthracite. This property apparently influences the behavior of chars from these sources during further heat treatment at higher temperatures and during activation.

Heat of Wetting

The heat of wetting was employed as a comparative measure of internal surface area, with the assumption that heat evolved by wetting a unit area is identical from carbon to carbon as suggested by Maggs (13).

Maggs estimates that the methanol molecule will occupy 16^2 Å in a monolayer distribution. A mean figure of roughly 0.1 calorie per square meter of surface area is estimated in the case of methanol wetting a carbon surface, thus the surface area in square meters may be estimated at ten times the magnitude of the heat of wetting in calories per gram.

Apparatus and procedure followed closely the proposals of Griffith and Hirst (6). The apparatus as used is shown in Figure 6. The sample was ground to pass No. 200 screen and dried at 100 to 110°C for 20 hours. The results shown in Table VII indicate that the 950°C chars from Elkol and D. O. Clark coals have internal surface areas of an order similar to coke breeze while the Wyodak char carbonized at 950°C embraces highly developed internal surfaces.

Table VII. Heat of Wetting Data

Sample	Carbonization Temperature °C	Heat of Wetting with Methanol, cal/g(dry)
Wyodak Char	950	2.69
Elkol Char	950	0.38
D. O. Clark Char	950	0.37
Coke A	---	0.29
Coke B	---	0.34
Coke C	---	0.23

X-Ray Diffraction

The qualitative comparison of the ultimate crystallite size revealed by X-ray diffraction was carried out by means of a GE-XRD3 unit, according to the following conditions: The samples were irradiated by copper K Alpha radiation, produced at 36 kv and 16 ma, filtered by nickel foil. Samples had been ground by mortar and pestle to pass a No. 200 screen, and de-ashed repeatedly with 20 percent hydrochloric acid and 48 percent hydrofluoric acid. The diffraction patterns were recorded at a scanning speed of two degrees per minute. The reading was calibrated by the scaler system. The incoherent background scattering was reduced on the chart, and the apparent half-intensity widths were obtained for (002) and (10) bands. The instrumental correction was applied by the Klug-Alexander's procedure (12). The crystallite dimensions for (002) and (10) bands were calculated by means of Scherrer's and Warren's formulae, respectively.

The crystallite dimensions revealed by X-ray diffraction are shown in Figure 7. The lattice parameters were also obtained, but they did not show any considerable changes throughout all samples examined, namely, 2.1-2.2 Å for (10) band and 3.4-3.5 Å for (002) band. As shown in Figure 7, the variation of crystallite size in (002) does not seem to be significant. Inouye has suggested (9), (10) that the variation of crystallite size in the (10), or a-axis direction, which will reflect the average size of ultimate units composing the coke or char, controls predominatingly the physical structure of the product and hence, in various cases, a qualitative interpretation can be given by a-axis dimensions to differences in internal structure, such as mechanical strength and some chemical properties.

It is recognized that the a-axis dimension increases in the temperature range from 700 to 950°C for D. O. Clark and Wyodak, while the crystallites of chars from Elkol develop less noticeably with carbonization. Comparing this result with the variations of density and electrical resistance described above, it appears that the properties of chars are much influenced by other factors such as the state of agglomeration or crystallites, and possibly three-dimensional networks developed in chars carbonized at higher temperatures than 800°C. In particular, the subbituminous coals have extremely complicated structures in their original state and their behavior during the course of carbonization would not be interpreted simply as one might hope for bituminous coals. It is interesting, however, to compare the curve of crystallite size growth of D. O. Clark, a bituminous coal, in Figure 7 with that of reactivity in Figure 3, because it is shown that the tendency of variation is about the reverse, namely, the chars with larger values of crystallite size have lower reactivity as suggested formerly for blast furnace cokes based on other properties (10). Table VIII gives the crystallite dimensions of three reference coke breezes.

Table VIII. Crystallite Dimensions of Coke Breezes

Sample	Crystallite Dimensions, Å (002)	(10)
A	18.2	42.3
B	20.5	43.4
C	21.6	46.9

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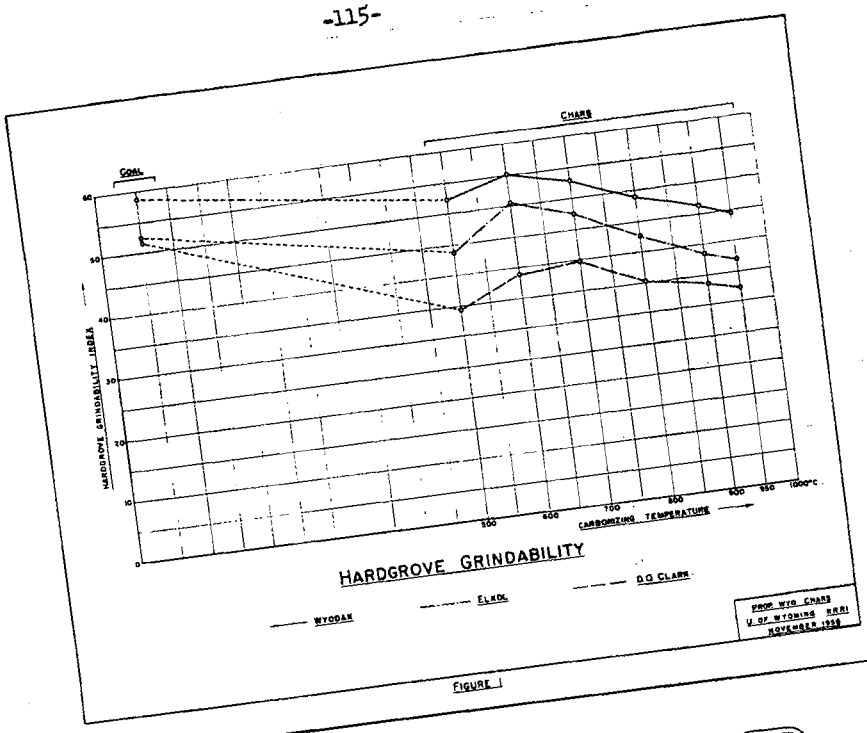
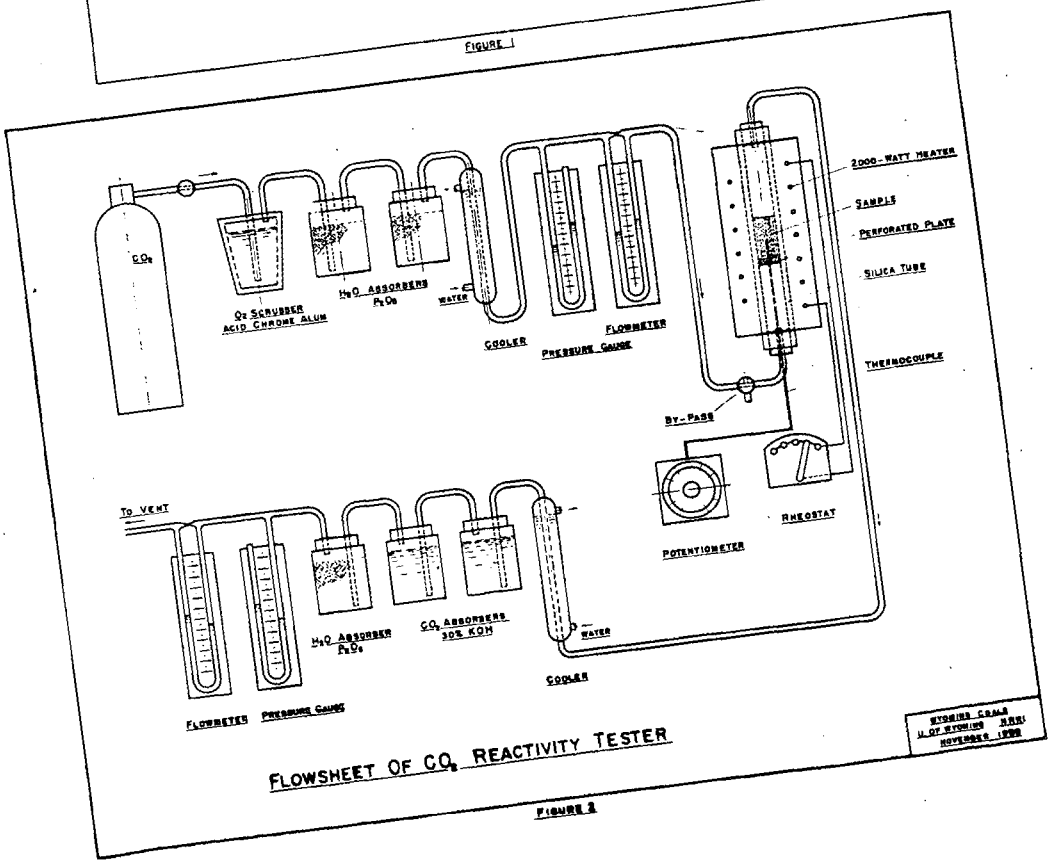
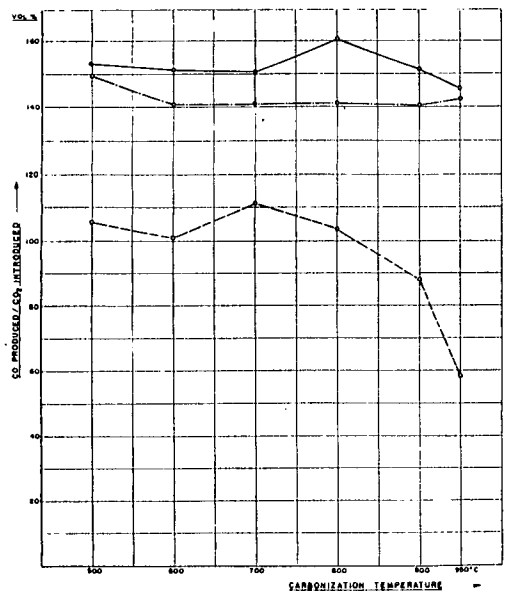


FIGURE 1



FLOWSHEET OF CO_2 REACTIVITY TESTER

FIGURE 2

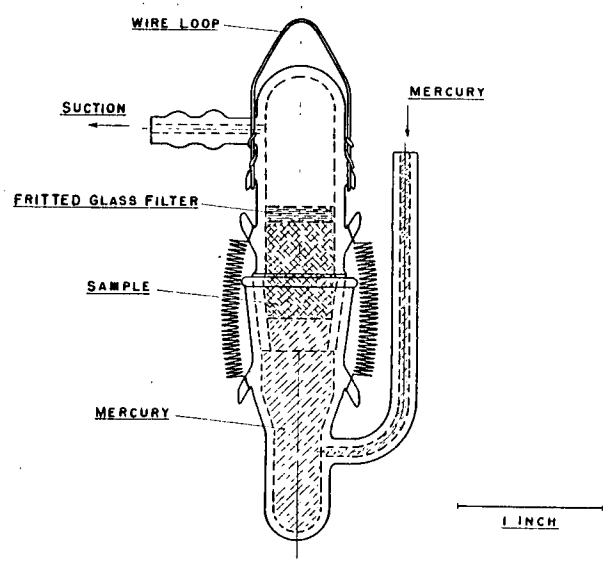


REACTIVITY OF CHARS WITH CO_2 AT 950°C

—— WYODAK —·— ELKOL ---- DOCLARK

PROP. WYO. CHARS
U. OF WYOMING NRRI
DECEMBER 1959

FIGURE 3



DENSITY BOTTLE
FOR MERCURY DISPLACEMENT

PROP. WYO. CHARS
U. OF WYOMING NRRI
OCTOBER 1959

FIGURE 4

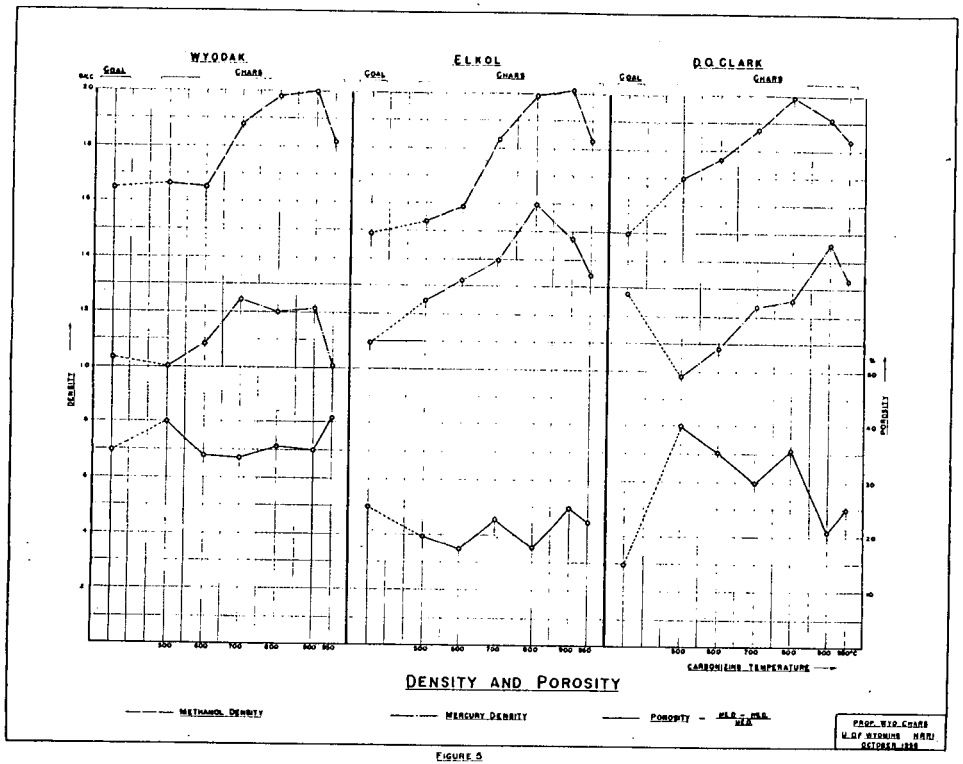

WYODAK
ELKOL
D.O. CLARK
COAL
CHARS
DENSITY
POROSITY
CARBONIZING TEMPERATURE
DENSITY AND POROSITY
METHANOL DENSITY
MERCURY DENSITY
POROSITY
PROF. WYO. CHARS
U OF WYOMING NARU
OCTOBER 1958

FIGURE 5

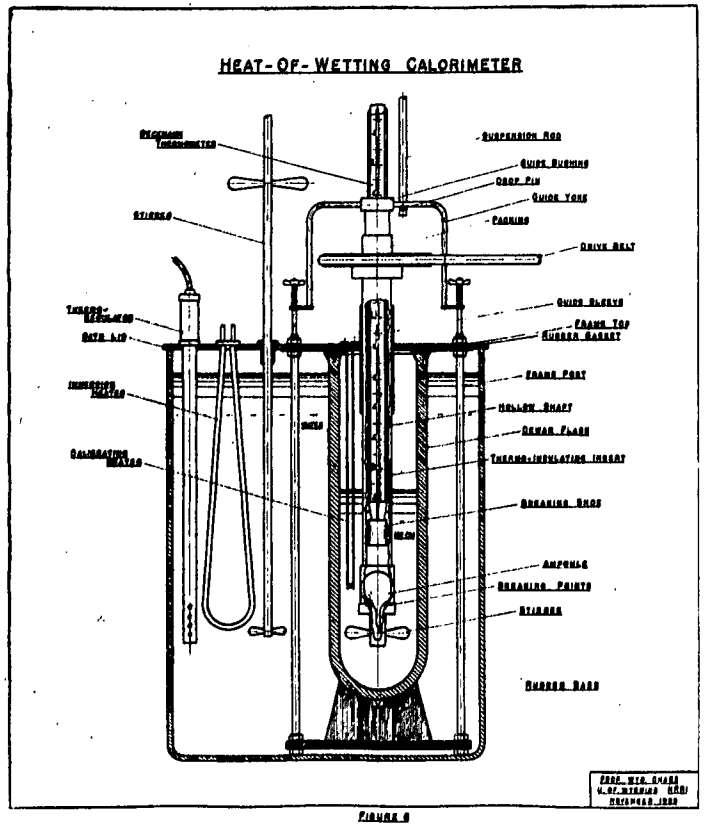


FIGURE 6

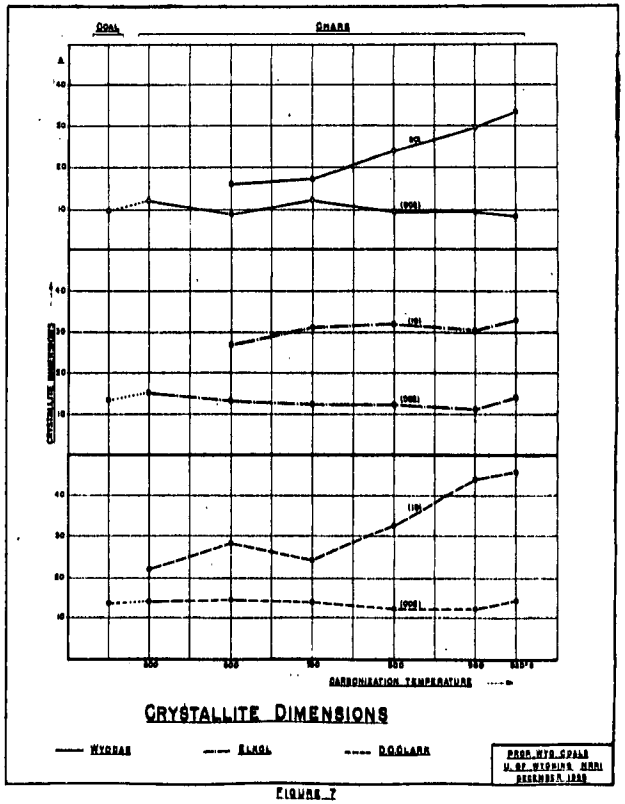


FIGURE 7

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American Chemical Society
Boston, Massachusetts, Meeting, April 5-10, 1959

Desulfurization of Low Temperature Char
I - Rate and Total Inhibition Data in Batch Systems

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INTRODUCTION

The desulfurization of char with hydrogen and hydrogen steam mixtures[1)] was described in a previous publication. The data were obtained in a batch system and the role of hydrogen sulfide in inhibiting the rate of the desulfurization process was discussed.

The char used in the earlier work was produced from a Pittsburgh Seam coal in the Disco process, a commercial rotary kiln, low temperature carbonization process. These data are now extended to chars produced from a number of other Pittsburgh Seam coals in a fifty ton per day fluidized low temperature carbonization pilot plant.

Data were obtained both in very shallow beds where the role of hydrogen sulfide inhibition is very small and also in deep batch beds where inhibition of the desulfurization rate is quite large.

It is well known from earlier work by Powell[2)] and Huff[3)] that the reaction of hydrogen sulfide-hydrogen mixtures with carbonaceous materials is reversible. High ratios of hydrogen-hydrogen sulfide cause sulfur removal from the chars while at low ratios sulfur is deposited on the chars. Powell[2)] showed that a characteristic isotherm could be developed for materials such as sugar char and coke by passing hydrogen very slowly over the material under investigation and measuring the hydrogen sulfide evolved.

Powell[2)], however, showed that this was not a true equilibrium process since the isotherms depended to some extent on the prior thermal history and origin of the carbonaceous material.

We have developed similar isotherms by a different technique than was used by Powell for the low temperature chars used in this investigation. These isotherms were developed under conditions of time and temperature similar to those that would be employed in an actual desulfurization process. They, therefore, represent the hydrogen-hydrogen sulfide ratio as a function of the sulfur content of the char which corresponds to complete inhibition of the desulfurization process.

These total inhibition isotherms provide a useful tool for interpretation of the hydrogen sulfide inhibition observed in the present work as well as some of our earlier published data. They also provide a basis for estimation of the minimum hydrogen circulation requirements in possible commercial processes.

EXPERIMENTAL

Raw Materials

The chars used in this work were all produced in Consolidation Coals fifty ton per day fluidized low temperature carbonization pilot plant at 900-950°F. The coals from which the chars were prepared were all Pittsburgh Seam coals from three different mines. These were the Arkwright and Montour 10 mines of Consolidation Coal Company and the Alexander mine of the Valley Champ Coal Company. The sulfur content of the chars varied over the range of 1.3 to 4.5 weight percent. The analysis of the feed chars is given in Table I.

The investigations were of three types and were carried out in three different kinds of equipment and by three different procedures.

Total Inhibition Data

The method used by Powell in determining the total inhibition isotherms suffers from the major deficiency that there is no assurance that equilibrium was achieved.

The data reported here were obtained by a more standard equilibrium method. Chars of several sulfur contents were contacted with H_2S-H_2 mixtures of several concentrations. Each run was of sufficient duration to obtain a reasonable approach to equilibrium.

A single series of experiments with a constant gas composition caused sulfiding of the lower sulfur chars and desulfurization of the higher sulfur chars. The sulfur content corresponding to total inhibition was thus bracketed by approaching it from both directions.

The chars employed for developing a particular isotherm covered a range of sulfur values. They were prepared by desulfurization of the standard nitrogen pretreated char with hydrogen. The pretreatment and desulfurization temperature were always the same as that for which the isotherm was developed.

The equipment used in this study is shown in Figure 1. The reactor was a 22 mm ID Vycor tube about 20" long with a standard taper joint at the upper end for the take-off tube and thermowell assembly.

A mixture of hydrogen sulfide and hydrogen was made up and stored in the gas mixture bomb. It was analyzed for hydrogen sulfide by passing a portion of it after drying with anhydrone through a Nesbit bottle containing Ascarite and measuring the volume of residual hydrogen passed. The hydrogen sulfide content was obtained from the weight gain of the Ascarite. The analysis was made before and after a run and the average used for the calculations.

A ten-gram char sample was used for an actual run. The Vycor reactor was brought up to temperature with nitrogen passing through the char

bed. The nitrogen was replaced with the hydrogen sulfide - hydrogen mixture after the temperature was lined out. The reactor was operated as a fluidized bed using a superficial velocity of 0.4 feet per second. The treatment of the char was continued generally for a period of from 2-4 hours. The residue char was analyzed for total and sulfide sulfur. The observed sulfur level of the char was then associated as near equilibrium with the gas composition used.

Total sulfur was determined by the Eschka[4] method while sulfide sulfur was determined by the evolution[4] method.

All the data obtained in runs of this type are not reproduced. The data from which the 1350°F isotherm is derived are given in Table II.

The isotherms at 1350°F developed from these data for the Arkwright and Alexander Mine chars are shown in Figure 2 while 1100 and 1600°F isotherms for Arkwright char are given in Figure 3. The experimental points shown are distinguished by arrows pointing to the left or right. The left arrow designates the lowest sulfur value reached in a series of desulfurization runs at the gas composition used. A right arrow similarly designates the highest sulfur value reached in a corresponding series of sulfiding experiments.

Deep Bed Runs

The procedure used in these runs was similar to that described in our earlier gasification[5] and desulfurization[1] studies. The main difference was the use of a 4-inch internal diameter pressure balanced reactor instead of the 1-1/2-inch diameter Uniloy reactor described previously[5].

All runs were made at 1600°F and 6 atmospheres pressure using 35-100 mesh Arkwright I char. The runs were made using a batch fluid bed fluidized with pure hydrogen at 0.2 ft. per second. The char was introduced into the reactor when the latter reached 950°F. The char was fluidized in nitrogen and preheated to 1600°F. The pretreatment in nitrogen was continued for one hour after 1600°F was reached. The reactor was pressurized to 6 atmospheres and the hydrogen turned on.

A series of 9 runs was made with hydrogen treatment times of 30, 60 and 120 minutes and initial bed weights of 430, 860 and 1720 grams.

The loss in bed weight and in sulfur due to the nitrogen pretreatment was determined by separate experiments. The average analysis of the pretreated Arkwright char is given in Table I.

No analyses other than proximate and ultimate of bed residues were made in this series of runs. Some typical analyses of the bed residues are given in Table III.

The complete summary of run conditions and of the sulfur analyses of the solid residues are given in Table IV.

Shallow Bed Runs

The aim of these runs was to obtain differential data, i.e., the rate of desulfurization in pure hydrogen and in the absence of any significant concentration of hydrogen sulfide.

The runs were made using a batch fluid bed. The 1-1/2-inch diameter Uniloy reactor system formerly employed was used in this work. The char bed was, however, contained in a stainless steel liner which was lifted out of the reactor at the end of each run.

One important change in procedure was made. The initial pretreatment used previously for one hour in nitrogen before desulfurization was eliminated. This was accomplished by preheating the reactor to desulfurization temperature in a hydrogen atmosphere before admitting the char. A ten-gram char sample was usually used although all the work with the Alexander char as well as some with the other chars was made with a five-gram sample. The weighed char sample was charged, the reactor sealed and brought to full pressure and temperature as quickly as possible. This process took between four to ten minutes. The small char bed was fluidized with hydrogen at a velocity of 0.4 feet per second for one hour after full pressure was reached. The reactor was quickly depressurized, purged with nitrogen and the bed residue removed cooled in nitrogen and recovered for weighing and analysis. The only analyses made were the sulfur content of the bed residues.

Three different chars of widely different sulfur content whose analyses are given in Table I were used in this work. Each char was treated at five different temperatures from 1000 to 1600°F inclusive and at three pressures, i.e., 1, 3 and 6 atmospheres absolute.

The total hydrogen used in these runs per lb. of char treated varied from about 140-280 SCF depending on whether a five or ten-gram bed was used in the runs at 1 atmosphere to about 600-1200 SCF in the six atmosphere runs. A pair of runs were made at 1450°F and 1600°F and 1 atmosphere where the hydrogen rate was increased by a factor of three, i.e., from about 140 to 400 SCF/lb. The sulfur content of the residue at 1450°F, i.e., 0.66 weight percent, was unaffected by this increase in hydrogen-char ratio while at 1600°F a decrease from 0.72 to 0.58 weight percent was noted. It is clear, therefore, that the data approaches that which would be obtained in a true differential reactor.

The sulfur levels of the treated chars are presented graphically in Figures 6, 7 and 8.

Interpretation of Results

Total Inhibition Data

The data of Figures 2 and 3 show the position of the sulfide plateau in the correct place as reported by Powell[2] and is in accord with the equilibrium data of Alcock and Richardson[6]. The plateau corresponds to the equilibrium in the reduction of iron sulfide, i.e.,

$$FeS + H_2 = H_2S + Fe$$

The amount of organic sulfur "locked" below the sulfide plateau is also in general agreement with Powell's[2] data for coke. No distinction can be made from our data, however, between the forms of organic sulfur as discussed by Powell, i.e., solid solution and adsorbed sulfur. The comparison between the data for Arkwright char and Alexander Mine char given in Figure 2 shows that in the latter case the curve does not go through the origin. The reason for this is that the Alexander char contains about 0.25 weight percent of sulfide sulfur in the form of calcium sulfide which is substantially irreducible.

The total inhibition data for the organic sulfur on a moisture and ash-free basis for Arkwright char is given in Figure 4. A comparison is also made with Powell's data for sugar char. It is seen that the inhibition of the organic sulfur removal like that of the sulfide sulfur becomes more marked as the temperature is lowered. Powell's data for sugar char is similar to that of the coal derived chars but is far from identical. It may thus be concluded that the total inhibition isotherms are not universal but depend on the nature of the char. The Alexander Mine data also show differences when plotted on a moisture and ash-free basis. The removal of the organic sulfur from this char appears to be more highly inhibited than removal from the Arkwright char. The data are not plotted, however, since the analytical data did not provide in this case as clear a distinction between the sulfide and organic sulfur.

Deep Bed Runs

Under conditions where the rate of desulfurization is rapid, the total inhibition isotherms conservatively determine the amount of desulfurization that can be achieved rather than the desulfurization kinetics. The result is conservative since the total inhibition isotherms are representative for chars that have received several hours of thermal pretreatment at the temperature in question. Powell's data as well as some of our own experience suggests that the sulfur is somewhat more labile in the raw char.

Consider, for example, desulfurization in an isothermal batch fluidized bed. In the limiting totally inhibited case, the gas leaving the bed will be in equilibrium with the solids in the bed at any instant. The equilibrium conditions may be developed mathematically in terms of the total inhibition isotherms by forcing a sulfur balance between the sulfur in the gas and in the solid. By this procedure we find

$$\int_0^{\eta_H} \frac{d\eta_H}{1-\alpha\eta_H} = \int_S^{S_0} \frac{dS}{32f(S)-\alpha S} \qquad 1)$$

$$\text{or} \quad \frac{1}{\alpha}\ln\left(\frac{1}{1-\alpha\eta_H}\right) = \int_S^{S_0} \frac{dS}{32f(S)-\alpha S} \qquad 2)$$

The quantities involved in equations 1) and 2) are defined in the appendix. Equation 2) may be further simplified if the devolatilization or loss in weight of the char due to passage of hydrogen through the bed can be neglected, i.e., $\alpha = 0$. In this case equation 2) reduces to

$$\eta_H = \frac{1}{32}\int_S^{S_0} \frac{dS}{f(S)} \qquad 3)$$

Where one is interested only in relatively high sulfur levels, i.e., above about 1.2-1.3 weight percent sulfur for the Arkwright case it is a sufficiently good approximation to treat $f(s)$ as a linear function, i.e.,

$$f(s) = k\left(S - S_i\right) \qquad 4)$$

Using equation 4) equations 2) and 3) reduce to the simplified equations 5) and 6) respectively

$$\log\left(\frac{1}{1-\alpha n_H}\right) = \frac{\alpha}{(32k-\alpha)} \log\left[\frac{(32k-\alpha)S_0 - 32kS_i}{(32k-\alpha)S - 32kS_i}\right] \qquad 5)$$

$$n_H = \frac{1}{32k} \ln\left(\frac{S_0 - S_i}{S - S_i}\right) \qquad 6)$$

The above equations can be used to determine the "maximum" amount of desulfurization that can be achieved in batch fluidized beds. The first rather remarkable result worth noting is the rather high degree of desulfurization that was achieved in the batch desulfurization of the feed char. The desulfurization from 1.96 to 1.43 weight percent sulfur was accomplished simply by devolatilization in a stream of nitrogen at 1600°F. Results to be reported in a companion paper show that under these conditions the yield of devolatilized char is 88.7 weight percent of the feed char while the amount of hydrogen evolved is about 2.6 SCF per pound of feed char, i.e., $\alpha = 16.2$. Based on the assumption that all of the hydrogen was evolved at 1600°F and using equation 5), one calculates that the sulfur content of the devolatilized char should be 1.35 weight percent as against the observed value of 1.43 weight percent. It is thus obvious that very close to equilibrium conditions are maintained during devolatilization of the char in spite of the very low average partial pressure of hydrogen. The extraordinary lability of the sulfur in low temperature char is thus emphasized.

The degree of desulfurization obtained is also clearly greater than is achieved in the devolatilization of coal in a coke oven. The reason for this can be traced again back to the total inhibition isotherm. The staging effect obtained by batch desulfurization in a fluidized bed is now absent since the coke sees on the average a gas corresponding in sulfur content to the whole coke oven gas. For example, if the Arkwright char were equilibriated with the whole devolatilization product gas the sulfur content of the product char would rise from 1.43 to 1.65 weight percent.

After the char is devolatilized, further weight loss in the hydrogen treatment in deep beds is rather minor. This is clear from the data given in Table IV. As a good approximation it is possible to assume $\alpha = 0$ in

establishing the equilibrium desulfurization curves for devolatilized chars. It is also necessary to assume that the total inhibition isotherms are independent of the pressure. This assumption seems reasonable but has not been proven experimentally.

Curves which are shown in Figure 5 have thus been developed by application of equation 3) which show the minimum amount of hydrogen required for desulfurization of char in batch fluidized beds. Curves are shown for operation at both 1600°F and 1350°F.

The experimental data from the deep bed runs are shown for comparison. It is seen that for beds larger than 430 grams the results are determined largely by equilibrium and not by kinetics. This is true at least under the operating conditions used, i.e., 6 atmospheres pressure at 1600°F.

Some of our prior published data using hydrogen-steam mixtures for char desulfurization was treated in the same way. A comparison of the sulfur values observed with those calculated on the above equilibrium basis is given in Table V. The same results are apparent, i.e., at partial pressures of hydrogen above 1.5 atmospheres and for beds larger than 70 grams that the desulfurization is equilibrium controlled. The steam under these conditions thus plays the role of an inert diluent with respect to desulfurization.

Shallow Bed Runs

It is clear that for shallow char beds, kinetics and not equilibrium determines the amount of desulfurization. Thus, from Figure 5, it is clear that the hydrogen to char ratio used in our shallow bed runs, i.e., greater than 140 SCF per pound would be sufficient to achieve very much lower sulfur values than are apparent from the results shown in Figure 6.

All the results with the three different chars are plotted on a percentage sulfur elimination basis in Figure 9. It is thus seen that the sulfur elimination achieved in shallow beds, is as a first approximation, a function only of the conditions employed and independent of the sulfur content of the feed char.

The sulfur elimination shown is the percentage of the total sulfur in the feed char that is rejected and thus takes account of the measured weight loss of the chars during the desulfurization treatment.

The above correlation is consistent with the assumption that sulfur elimination is roughly a first order reaction independent of the sulfur level of the feed char, i.e.,

$$-\frac{dS}{dt} = k\, p_{H_2}^{a}\, S \qquad 7)$$

Equation 7) in integrated form may be written

$$\ln\left(\frac{1}{1-\beta}\right) = k\, p_{H_2}^{a}\, t \qquad 8)$$

Where β is the fraction sulfur eliminated. The data cannot be used to obtain reliable values of the rate constant k and the reaction order a since only one time was investigated. It is clear from the data, however, that the value of a is less than one, i.e., the reaction is less than first order with respect to hydrogen pressure.

APPENDIX

Definition of Mathematical Terms

S_0 = Initial Total Sulfur Content of Char Weight Percent.

S = Final Sulfur Content of Char.

S_i = Intercept for Linear Approximation $f(S) = k(S - S_i)$

n_s = Total Mols Hydrogen Sulfide in Gas x 100 Per Lb. Char Fed.

n_H = Mols Hydrogen Passed Per Lb. Char.

α = Lbs. of Char Devolatilized Per Mol of Hydrogen Passed.

$f(S)$ = Total Inhibition Isotherm, i.e., Sulfur Content of Char Versus $\frac{n_s}{n_H}$

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Table I

ANALYSIS OF FEED CHARS (DRY BASIS)

	Arkwright I[1]				
	Raw	Pretreated[3]	Raw Arkwright II[2]	Raw Montour 10	Raw Alexander Mine
H	2.99	0.68	3.22	3.34	3.25
C	77.69	84.70	78.29	80.46	70.46
N	1.74	1.27	1.72	1.79	1.25
O	4.93	0.68	5.01	6.56	5.89
S	1.96	1.43	2.53	1.33	4.51
Ash	10.69	11.24	9.23	6.52	14.64
Sulfide S	0.13	0.39	0.39	-	-

1) Feed char to deep bed desulfurization runs.

2) Feed char to shallow bed and total inhibition experiments.

3) Pretreated at 1600°F for one hour in nitrogen.

Table II

TABULATED DATA FOR CHAR-H_2S REACTION AT 1350°F

All feeds were produced at 1350°F from Arkwright Char II

All runs made with 10 gms of char; gas rate was 1.2 SCFH

Run No.	Gas Comp. (% H_2S in H_2)	% Sulfur in Feed Char			% Sulfur in Residue Char			Time of Treatment
		Organic MAF	Sulfide Dry	Total Dry	Organic MAF	Sulfide Dry	Total Dry	
74	0.11	0.33	0.07	0.37	0.36	0.07	0.39	249 min
75	0.15	0.33	0.07	0.37	0.52	0.40	0.86	234
86	0.17	1.33	0.13	1.31	0.91	0.35	1.16	211
73	0.20	0.33	0.07	0.37	0.70	0.32	0.94	196
79	0.26	0.55	0.19	0.68	0.72	0.46	1.09	226
70	0.27	1.33	0.13	1.31	1.06	0.29	1.24	201
68	0.53	0.33	0.07	0.37	1.04	0.40	1.32	226
69	0.54	1.33	0.13	1.31	1.18	0.37	1.41	236
78	0.53	1.84	0.31	1.96	0.98	0.51	1.38	215
67	1.06	0.33	0.07	0.37	1.20	0.33	1.40	151
71	1.05	1.33	0.13	1.31	1.43	0.35	1.62	156
77	1.03	1.84	0.31	1.96	1.28	0.40	1.53	158
66	2.05	0.33	0.07	0.37	1.69	0.34	1.84	171
72	2.07	1.33	0.13	1.31	1.70	0.24	1.76	179
76	2.07	1.84	0.31	1.96	1.58	0.41	1.82	176
85	3.04	1.84	0.31	1.96	1.90	0.33	2.03	136

Table III

ANALYSIS OF SOME TYPICAL BED RESIDUES FROM DEEP BED DESULFURIZATION AT 1600°F, 6 Atm. H_2

Wt. of Feed, gm	430[1)]	860[1)]	1720[2)]
H	0.98	0.79	0.49
C	85.25	85.45	85.49
N	1.09	1.00	1.11
O	0.85	0.50	0.43
S	0.42	0.33	0.89
Ash	11.41	11.93	11.59

1) 60 Minutes treatment time.

2) 30 Minutes treatment time.

Table IV

SUMMARY OF DATA FROM DEEP BED DESULFURIZATION RUNS

Conditions: Pressure 6 Atm. Abs. Temperature 1600°F
Inlet H_2 Rate 97.7 SCFH @ 70°F

Raw Feed Charged, gms	Bed Weight Grams: After Drying and Pretreatment, gms	Bed Weight Grams: Final	Hydrogen Treatment Time	Approx. Vol. H_2/Lb. Char SCF/Lb.	Sulfur Content of Residue: Organic	Sulfur Content of Residue: Sulfide	Sulfur Content of Residue: Total
500	430	416	30	50	0.34	0.14	0.50
500	430	411	60	100	0.29	0.13	0.42
500	430	405	120	200	0.12	0.07	0.19
1000	860	835	30	25	0.38	0.18	0.56
1000	860	822	60	50	0.23	0.10	0.33
1000	860	812	120	100	0.14	0.09	0.23
2000	1720	1671	30	12	0.47	0.42	0.89
2000	1720	1650	60	25	0.31	0.24	0.55
2000	1720	1633	120	50	0.21	0.12	0.33

Table V

APPROACH TO EQUILIBRIUM IN THE REMOVAL
OF ORGANIC SULFUR FROM DISCO CHAR
USING 25% H_2-75% H_2O FOR DESULFURIZATION AT 1600°F

Initial Bed Weight, gms	Press. Atms. Abs.	Desulf. Time Mins.	Calculated % H_2S in Effluent Hydrogen	Residue Organic S Content %	
				Experimental	Equilibrium
20.8	1	81	0.17	0.80	0.40
38.8	1	93	0.29	0.93	0.61
80.8	1	109	0.43	1.01	0.79
34.5	6	37	0.12	0.49	0.28
69.5	6	22	0.39	0.97	0.76
69.7	6	48	0.17	0.54	0.40
107	6	25	0.49	0.95	0.86
107	6	57	0.25	0.58	0.54

Figure 1

FLOW DIAGRAM OF EXPERIMENTAL EQUIPMENT

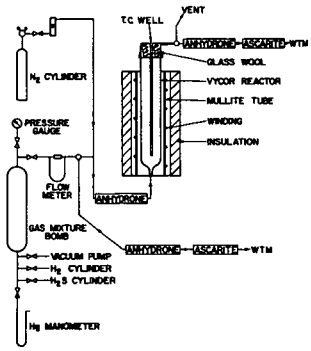


FIGURE 2
TOTAL INHIBITION DATA AT 1350°F

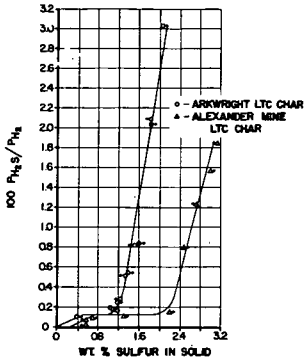


FIGURE 3
TOTAL INHIBITION DATA ARKWRIGHT LTC CHAR

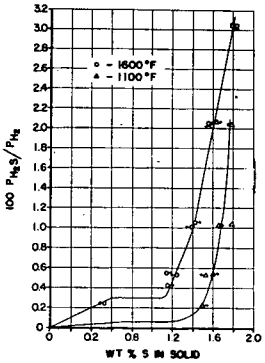


FIGURE 4
TOTAL INHIBITION DATA FOR ORGANIC SULFUR

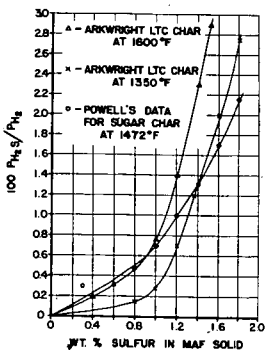


FIGURE 5
EQUILIBRIUM CURVE FOR BATCH DESULFURIZATION COMPARISON WITH EXPERIMENTAL DATA

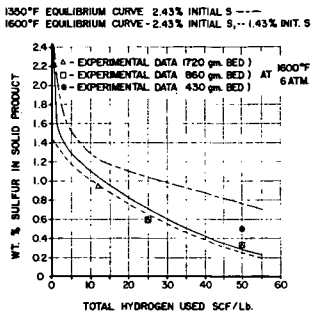


FIGURE 6
SHALLOW BED DESULFURIZATION OF ARKWRIGHT CHAR

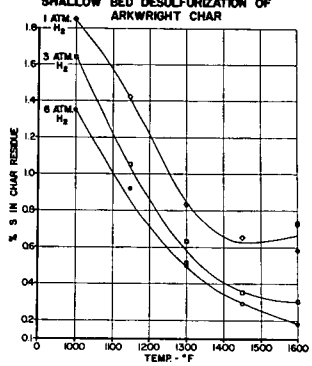


FIGURE 7
SHALLOW BED DESULFURIZATION OF MONTOUR-10 CHAR

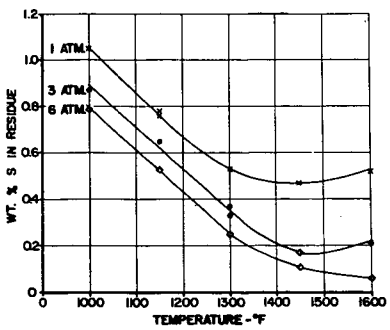


FIGURE 8
DIFFERENTIAL DESULFURIZATION OF MOUNDSVILLE LTC CHAR

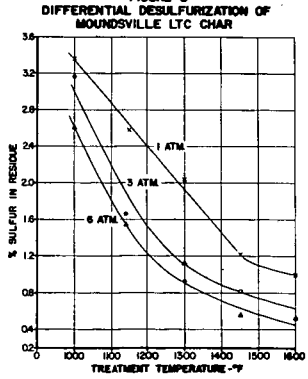
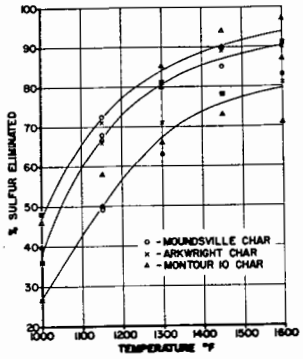


FIGURE 9
SULFUR ELIMINATION OF THREE
DIFFERENT LTC CHARS



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Desulfurization of Low Temperature Char
II - Rate Data in A Continuous System

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INTRODUCTION

The desulfurization of low temperature char in batch fluidized systems was presented in previous publications[1]. Commercial application of the process would most likely require the use of a continuous processing technique. The assessment of the commercial potentialities of the process therefore requires that experimental data be obtained in a system which is operated continuously both with respect to the solids and the gas.

Such data have now been obtained in a continuous bench scale fluidized unit both using fresh hydrogen and recycle gas for desulfurization and are presented here. Inhibition by the hydrogen sulfide product was found to control the amount of desulfurization achieved. The results in this sense are similar to those reported previously in deep batch beds[2]. The data are interpreted in terms of the total inhibition isotherms discussed previously.

Subsidiary data of interest are also presented relative to the rate of production of methane by direct hydrogenation of char and to the yield of hydrogen produced by the devolatilization of char.

Prior data are available on the production of methane by hydrogenation of char by Dent[3] and others[4,5]. None of the published data were obtained, however, in a continuous system.

EXPERIMENTAL

Raw Material

A low temperature char produced by the fluidized carbonization of a Pittsburgh Seam coal at 950°F was used in this work. It was the same Arkwright char[2] previously used in our batch work. An average analysis of the feed char is given in Table VI. The char was fed without prior drying. The moisture and elemental analysis was determined for the feed char to each run. These analyses varied somewhat from run to run and each individual analysis was used in determining the elementary balances for the corresponding run. Only an average analysis with the exception of the sulfur content is given for the sake of brevity. One run was made, No. 58, with a char which had previously been desulfurized to 1.47 percent sulfur.

Equipment

The runs were all made in a continuous bench scale fluidized reactor system. The equipment had been designed to study gasification reactions at

temperatures up to 1800°F and pressures up to 50 atmospheres. The details of the equipment are quite complex and for brevity will largely be eliminated from the discussion here. A simplified flow diagram is shown in Figure 1.

The char was fed from a pressurized hopper by a rubber roll feeder. The feed rate is regulated by a variable speed drive which turns the feeder shaft. A pressure equalizing line equalizes the pressure between the feed hopper and the discharge from the rolls.

The solids are picked up with the process gas, i.e., either fresh hydrogen or recycle gas and transported into the fluidized reactor.

The hydrogen was passed through a purifying train for removal of oxygen and moisture which consisted of a nickel-alumina catalyst chamber and a silica gel tower in series. These are not shown. The hydrogen was then metered into the reaction system by means of a rotameter. The recycle gas runs were conducted by recycling the product gas, after removal of hydrogen sulfide, with a Gast rotary pump enclosed within a pressure housing. The hydrogen sulfide was removed by passing through a catalyst tube packed with 1/8-inch pellets of a sulfur acceptor containing 80% Cu-10% V-10% Cr. The preparation and regeneration of this material was carried out according to the procedure recommended by the U. S. Bureau of Mines[8].

The fluidizing vessel was a 4-inch diameter cast Duralloy (28% Cr-4% Ni) tube approximately 55 inches long with a 60 degree cone bottom. It was supported by means of a ring joint flange to an upper section which was attached to the top flange. This particular alloy was found to be quite resistant to attack by hydrogen sulfide.

The reactor tube was surrounded by a concentric furnace which contained four independently controlled heater circuits. The reactor tube was maintained in pressure balance with the furnace jacket which were both enclosed in a large water jacketed pressure vessel.

The pressure bearing walls were held at 450°F by controlling the steam pressure and water level in the jacket.

The inlet line to the reactor tube passes through a packing gland at the bottom of the shell vessel and thus seals the furnace zone from the reaction zone. Pressure balance was maintained across the reactor by using a Kendall gas relay to feed nitrogen to the furnace zone. Purge nitrogen was also fed at a metered rate through the top reactor flange to purge the dead space above the bed level. This was replaced with recycle gas in the recycle gas runs.

The fluidized bed level was controlled by an adjustable J-tube which entered through a packing gland in the top flange. The solid and gaseous reaction products left the reactor through the J-tube and into a 1-1/2" internal diameter cyclone. The solids knocked out of the gas in this cyclone flow by gravity to either of two char receivers selected by the char diversion valve mounted above them. The partially cleaned gas passed on to either of two 1/2" internal diameter cyclones each of which were mounted inside a fines receiver. A fines diversion valve was placed upstream for switching from one receiver to another. Final cleanup of the exit gas from the fines receiver was accomplished by the dust filter which was packed with a Fiberglas blanket material.

The filtered gas is cooled and the moisture condensed. A liquid letdown valve allows removal of the condensate.

Excess gas was throttled through a back pressure control valve and through a water bubbler to the wet test meter. This valve automatically controlled the system pressure. Part of the exhaust gas stream could be by-passed around the bubbler and through the thermal conductivity cell.

The fresh hydrogen runs were conducted on a once-through basis with respect to gas. After temperature and pressure in the reactor had lined out, the char feed was started and continued long enough to fill the reactor and pass three additional inventories through the reactor. The material balance was initiated by switching the char and fines solid products from the lineout pots to the material balance pots. After the material balance period, the unit was switched back to the lineout catch pots and shut down immediately by cutting of both the feed char and gas.

The bed of char remaining was drained from the reactor and determined as the inventory weight. The weight of char fed was determined by difference between the amount charged and the amount left in the feed hopper after the run. The residence time was calculated by comparison of the product rate to char inventory weight.

Gas samples were taken during the material balance period of the run. Triplicate bottles were used for a gravimetric[7] analysis for carbon dioxide and total carbon and hydrogen content, infrared analysis for methane, ethane and carbon monoxide and a Tutweiler analysis for hydrogen sulfide.

Moisture yields were determined by the difference between the condensate yield and the moisture in the feed char after allowing for uncondensed moisture in the gas.

Ultimate analyses were obtained on the product and feed chars.

The recycle gas runs were conducted in a similar fashion. The unit was started in operation with the system full of hydrogen. The lineout period in these runs was continued until the outlet gas composition reached a steady value as indicated by the thermal conductivity cell. Adjustment of the recycle gas rotameter reading was effected during the lineout period to compensate for changes in gas density.

The operating data for the fresh hydrogen and recycle gas runs are given in Tables I and II. The material and elementary balances and yields for the fresh hydrogen runs are given in Table III. A negative figure indicates a deficiency in the product as compared with the feed. The yield figures are given as determined with the exception of the char yield which is forced to give a 100 percent weight balance. Char yield is omitted where the discrepancy in the weight balance was greater than 3 percent. The gas and solids analyses are omitted for the sake of brevity.

Table IV gives the corresponding data for the recycle gas runs. All the yields in this case are forced, i.e., the char yield is adjusted to give a 100 percent closure of the weight balance while simultaneously the liquor and product gas rates were adjusted to obtain closures around the oxygen and hydrogen balances, respectively.

Tables V and VI give the product gas and char analyses for the recycle gas runs. The gas analysis is recorded as determined with the exception of the nitrogen content which was forced to give a nitrogen balance.

INTERPRETATION OF RESULTS

Discussion in Terms of Total Inhibition Isotherms

The conditions which correspond to total inhibition of the desulfurization process have been given in the previous paper[2] in the form of the corresponding isotherms. These were used to determine the hydrogen circulation requirements in batch fluidized systems. The isotherms may also be used directly to determine the "equilibrium" sulfur reduction that would be obtained in a single stage continuous fluidized system.

The hydrogen circulation requirements calculated in this manner are shown as a function of the sulfur level of the product char in Figure 2. Curves are shown for three different treatment temperatures, i.e., 1100°F, 1350°F and 1600°F. The hydrogen requirements are given in terms of standard cubic feet per pound of dry feed char measured at 70°F. The curves are based on the use of an Arkwright char feed which has an initial sulfur content of 2.45 weight percent.

The hydrogen requirements are considerably larger than those given previously for the batch system. This is because of the absence of the staging effect characteristic of the batch system. Staging in a continuous system may be effected by separately devolatilizing the char and then using a multi-stage countercurrent hydrogen treatment system for desulfurization.

The devolatilization reduces the sulfur of the feed char from 2.4 to 1.9 weight percent without the addition of external hydrogen. Calculated curves giving the hydrogen recirculation requirements for multi-stage systems of the above type at 1600°F are also shown in Figure 2. The curve for the ideal countercurrent system corresponds to the lowest hydrogen requirements even where a very large number of stages are used.

The method of calculation was a graphical one and similar to that used in conventional countercurrent adsorption calculations.

All of our experimental data were obtained in a single stage fluidized system. Some of our experimental points are shown for comparison with the calculated curves in Figure 2. Also a comparison is made in case of all the runs of the observed hydrogen sulfide to hydrogen ratio in the product gas with the ratio that corresponds to an "equilibrium" condition. These data are given in columns 10 and 11 of Tables I and II.

It is noted that only under the very mildest conditions used was the amount of desulfurization less than corresponds to "equilibrium", i.e., at hydrogen partial pressures of one atmosphere or less or at temperatures below 1350°F and residence times of the order of 20 minutes or less.

It is also seen that under the more severe conditions, i.e., at hydrogen partial pressures above about 3 atmospheres that the amount of desulfurization achieved was greater than corresponds to "equilibrium". Thus at the most severe conditions employed, i.e., total pressure 11 atmospheres, 28 minutes residence time and 1600°F the amount of desulfurization achieved was better than could be obtained under "equilibrium" conditions even if the char was devolatilized in a separate stage before desulfurization.

It is apparent from this violation of the "equilibrium" desulfurization concept that the sulfur in the raw char is in a more labile condition both in

the thermodynamic and kinetic sense than after the char had been thermally treated for several hours. The experimental data upon which the total inhibition isotherms are based unavoidably involved thermal treatment of the char for several hours. This undoubtedly causes a transformation of the sulfur to a more stable form. Such a phenomenon was previously noted by Powell[8] who ascribed it to a transition from the absorbed to solid solution states.

It is clear, from the above, that the hydrogen circulation requirements as given in Figure 2 are conservative and that better results can be obtained in practice at least under relatively severe operating conditions.

It is probable, however, that the equilibrium curves of Figure 2 would adequately predict the hydrogen requirements for the production of lower sulfur chars of the order of 0.6 weight percent or better. This is indicated by the results of Run No. 58. Here a char that had been previously desulfurized to 1.47 weight percent sulfur was further desulfurized at 1600°F and 6 atmospheres to produce a product char of 0.62 weight percent sulfur. The amount of desulfurization achieved corresponded quite closely to the "equilibrium" condition. These same experimental conditions were sufficiently severe, however, to produce a greater than "equilibrium" amount of desulfurization with the normal high sulfur feed char.

Kinetics of Desulfurization Process

The above data suggests that the net rate of desulfurization is determined by the competition between two processes, namely, the thermal fixation of the sulfur to produce a more stable form and its rate or removal by hydrogen while still in the labile form.

Since thermal fixation occurs more rapidly the higher the temperature it would not be surprising to find an optimum temperature for maximum desulfurization. Some of the differential rate data presented in the previous paper[2], i.e., Figures 6 and 7 suggests the possibility of an optimum rate at about 1450°F for desulfurization at low pressures of the order of one atmosphere.

The present data are not very suitable for kinetic interpretation since "equilibrium" conditions or better were achieved in most of the runs. An empirical approach to the question of the relative desulfurization rates at 1350 and 1600°F was therefore used.

The desulfurization efficiency is shown in Figure 3 as a function of an empirical severity factor. The desulfurization efficiency is defined as the ratio of the hydrogen sulfide concentration observed in the exit gas to that which would be obtained if "equilibrium" were achieved. The severity factor is rather arbitrarily defined as the partial pressure of hydrogen in the exit gas multiplied by the square root of the solids residence time.

These data illustrate the point discussed earlier that equilibrium conditions or better were achieved in most of our runs.

The bulk of the data were at the two temperatures of 1350°F and 1600°F, respectively. A statistical analysis of the data at these two temperature levels was made to discern whether any difference in desulfurization ease could be noted. A best straight line was drawn through the origin in

both cases by the method of least squares. The lines were forced through the origin for physical reasons since it is obvious that the desulfurization efficiency should be zero when the severity factor is zero.

A difference in slope between the 1350°F and 1600°F data is apparent. The analysis of variance was applied to these data to determine whether this difference in slope is a real effect or simply a result of the random scattering of the data. The t-test outlined by Youden[9] was applied and a value for t equal to 2.1 was obtained. Since the system has 16 degrees of freedom, a probability equal to 0.95 is found that the difference in slopes is real.

It is therefore concluded that less severe operating conditions are required to achieve equilibrium or better desulfurization at 1350°F than at 1600°F.

This is in accord with the above discussion on relative rates of thermal fixation and removal of sulfur.

Methane Yields and Approach to Equilibrium

The data are potentially of commercial interest to the problem of producing pipeline gas by partial hydrogenation of char at low pressures. It is of interest first of all to examine the data to determine how much methane is produced relative to the graphite hydrogen equilibrium.

The equilibrium constants $K = P_{H_2}^2/P_{CH_4}$ in the effluent gas from the 1350°F fresh hydrogen runs all, with the exception of Run 57, fall within the range of 19 to 53. Since the equilibrium constant is 10 at this temperature, it is clear that the methane content of all the fresh hydrogen runs at 1350°F fall short of the graphite equilibrium value.

Figure 4 shows the approach to the graphite equilibrium in the fresh hydrogen runs at 1600°F. In this case it is seen that the methane content of the gas is greater than the equilibrium value at pressures below 4 atmospheres. Even at the highest pressure studied, i.e., at eleven atmospheres the methane concentration approaches within 65 percent of the equilibrium value.

The high methane yield in relationship to the graphite equilibrium can be ascribed to the selective hydrogenation of the volatile matter of the char as was proposed previously by Dent[3]. Such a process would not be controlled by the graphite equilibrium.

The approach to graphite equilibrium in the recycle gas runs is illustrated in Figure 5. It is seen that the methane concentration at all temperatures studies is well in excess of the graphite equilibrium value. The methane in these runs is produced by thermal decomposition of the char volatile matter. The methane yield in such a process would also obviously not be controlled by the graphite equilibrium.

An examination of the data for the fresh hydrogen runs shows that the methane yield, everything else being equal, increases with the operating pressure. A somewhat higher yield on the average is obtained at 1350°F than at 1600°F.

The yield of methane in the fresh hydrogen runs is always greater than in the recycle runs even at low pressures. At 11 atmospheres the yield of methane is approximately 3.5 times greater in the fresh hydrogen runs.

Reaction Rate Constants

An earlier study[5] gave quite extensive information on the rate of hydrogenation of devolatilized char. It would be of interest to compare the present data on raw char with the previous data.

The data at 1600°F could be more easily compared since there are earlier data at the same temperature. Unfortunately, the close approach to methane equilibrium makes a kinetic analysis of these data relatively meaningless.

This problem does not exist with the 1350°F data and the rate constants are shown as a function of the amount of methane produced in Figure 6.

The rate constants are calculated on the assumption that the reaction rate is first order with respect to hydrogen pressure. It is also assumed that the gas in the fluid bed is perfectly mixed, i.e., the outlet partial pressure of hydrogen controls the reaction rate. Also in calculating the rate the yield of methane produced by devolatilization was subtracted from the observed methane yield.

For comparison purposes the rate constants for devolatilized char at the lowest temperature investigated, i.e., 1500°F, is shown.

It is seen that it is not possible to correlate all the experimental points over the whole pressure range. All the points at 3.0 atmospheres pressure lie approximately on a straight line. The line illustrates the rapid decrease in rate to a value more in line with that of devolatilized char as the amount of char hydrogenated to methane increases.

The higher pressure points are insufficient in number to point up any definite trends. However, the first order rate constants, at the same level of methane yield definitely increase with pressure. It may be conjectured, therefore, that the period of abnormally high hydrogenation rate extends to higher methane yields as the pressure is increased. This would have to be confirmed by more experimental data, however.

Gas Yields in Char Devolatilization

The devolatilization of char could conceivably be of commercial interest from the point of view of hydrogen production. It is noted in Table V, for example, that the gas produced by devolatilization at 1600°F contains better than 70 percent hydrogen or better than 80 percent of hydrogen plus carbon monoxide.

The yields of these gases as well as the hydrogen concentration increases rapidly with the temperature. The yield-temperature relationship is shown in Figure 7.

The relative constancy of the liquor yield and the increased yield of carbon monoxide with increasing temperature can be assumed to show increasing direct gasification with temperature of the char by the water vapor present in the system.

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Table I

Fresh Hydrogen Runs

Operating Data

Run No.	Dry Char Feed Rate Lbs./Hr.	Temp, °F	Press. Atm.	P_{H_2} Atm.	Inlet H_2/Char SCF/Lb.	Res. Time Min.	% Sulfur in Char Feed	% Sulfur in Char Product	P_{H_2S}/P_{H_2} x 100) Obs. in Exit Gas	P_{H_2S}/P_{H_2} x 100) Equil.
54	7.26	1202	3.01	2.41	12.7	11	2.47	1.72	0.50	1.55
55	7.29	1202	3.01	2.34	12.6	23	2.43	1.69	0.89	1.34
51	6.91	1206	3.01	2.40	13.6	36	2.33	1.61	0.82	0.86
14	3.87	1350	1.28	1.08	15.2	21	2.46	1.60	0.87	1.24
16	3.73	1361	1.21	1.04	15.6	78	2.45	1.43	0.71	0.66
23	6.01	1348	1.40	0.99	5.9	47	2.52	1.72	1.44	1.72
19	5.32	1348	3.00	2.48	16.2	20	2.47	1.40	0.68	0.64
18	5.16	1358	3.00	2.43	16.8	40	2.45	1.42	0.69	0.65
39	5.97	1345	3.01	2.36	14.5	54	2.40	1.47	0.88	0.88
40	3.34	1358	3.00	2.66	35.8	58	2.54	1.31	0.43	0.42
57	7.07	1342	6.06	4.59	20.2	44	2.33	1.24	0.91	0.28
59	11.61	1350	11.17	8.6	22.6	26	2.43	1.23	0.8(est)	0.28
12	2.13	1600	1.05	0.87	14.4	50	2.46	1.51	0.95	1.52
42	3.30	1592	1.38	1.19	15.3	64	2.43	1.55	0.64	1.72
32	5.96	1601	2.98	2.50	15.1	16	2.41	1.51	0.69	1.52
29	5.92	1599	3.00	2.51	15.4	57	2.52	1.28	1.02	0.68
11	5.83	1591	3.01	2.74	23.9	44	2.46	1.21	0.71	0.48
31	7.93	1611	5.99	4.79	15.1	46	2.44	1.19	0.87	0.44
56	8.31	1590	6.07	4.71	14.8	51	2.50	1.19	0.88	0.44
58	3.64	1601	6.07	5.45	50.1	53	1.47	0.62	0.27	0.30
41	12.62	1601	11.16	8.48	15.9	28	2.45	1.12	0.68	0.30
60	12.75	1597	11.18	7.86	16.1	28	2.40	1.09	1.00	0.30

Table II

Recycle Gas Runs

Operating Data

Run No.	Dry Char Feed Rate Lbs./Hr.	Temp., °F	Press. Atm.	P_{H_2} Atm.	Gas Rate Total Recycle	SCF/Lb. Char Hydrogen Recycle	Res. Time Min.	% Sulfur Feed	% Sulfur Product	% H_2S in H_2 Obs. in Exit Gas	% H_2S in H_2 Equil.
27	3.69	1099	3.00	0.74	25.7	6.7	44	2.34	1.90	1.00	2.62
25	3.90	1330	1.34	0.72	14.6	8.5	52	2.50	1.76	1.07	1.73
38	1.60	1348	1.37	0.70	28.9	16.0	48	2.45	1.47	0.79	0.73
26	3.82	1345	3.01	1.38	26.3	12.8	52	2.37	1.48	1.07	0.76
33	1.70	1599	1.39	1.02	24.4	18.8	52	2.40	1.56	0.62	1.80
34	3.71	1594	3.01	2.12	23.7	17.3	57	2.44	1.28	1.03	0.60
36	5.49	1606	6.04	3.91	24.3	16.7	64	2.47	1.32	1.11	0.72

Table III

Yields and Material Balances -- Fresh Hydrogen Runs

Run No.	Balances Percent Closure				Yields -Wt.% Feed Char Dry			
	Total	Sulfur	Carbon	Hydrogen	Char	CH_4	CO	H_2O
54	-0.6	-15.3	-2.2	-7.4	87.9	2.8	2.4	2.3
55	+3.5	+3.3	-1.7	-4.8	-	3.5	3.3	2.3
51	+0.9	-7.6	-2.4	-7.4	87.2	4.0	2.8	1.8
14	-1.0	-1.1	-3.2	-2.0	87.0	2.7	3.7	4.1
16	-0.3	-6.6	-0.3	+0.5	87.4	3.8	3.1	2.8
23	-1.4	-8.6	-2.1	-6.5	88.5	3.7	3.2	2.3
19	-	-	-	-	-	4.6	2.3	3.3
18	-0.3	-1.6	-0.4	-0.9	85.5	6.0	2.6	3.3
39	-3.1	-2.8	-3.7	-4.6	-	6.4	2.4	3.4
40	-1.0	-8.2	-1.3	-3.5	84.1	7.0	4.7	2.9
57	+4.2	+3.0	+0.3	-6.5	-	8.5	4.7	3.4
59	-2.4	-8.5	-3.0	-	79.4	9.9	4.5	5.1
12	+2.6	+9.8	+4.9	-3.9	-	-	-	-
42	-2.7	-6.3	-0.4	-7.0	86.9	3.1	5.8	-
32	-1.3	-3.5	-2.9	+3.2	84.6	3.2	2.7	-
29	-3.3	+0.7	-2.6	-4.1	-	5.3	4.3	2.0
11	-3.0	+0.0	-1.3	-0.6	-	5.4	4.3	0.7
31	-0.5	-10.8	-0.7	-0.8	81.5	7.1	5.4	2.5
56	-3.7	-18.8	-8.4	-2.1	-	6.7	6.6	4.8
58	+7.3	-11.1	+2.8	-3.9	-	8.8	9.2	1.8
41	+2.1	-23.9	-1.7	-13.5	77.1	6.7	6.9	2.6
60	+30.8	+3.9	+31.5	-3.8	-	8.6	7.2	3.5

Table IV

Yields and Material Balances

Recycle Gas Runs

Run No.	Balances Percent Closure				Wt.% Yield		
	Total	Sulfur	Carbon	Hydrogen	Gas	Liquor	Solid
27	-3.6	-0.8	-2.6	+0.1	2.4	3.4	93.6
25	-6.9	-4.1	-4.6	-11.1	6.6	3.1	89.6
38	-0.4	+1.3	-0.7	+12.1	7.6	2.6	89.3
26	-6.3	+4.4	-6.0	+0.1	7.2	3.1	88.4
33	-13.1	-1.6	-11.8	-3.8	7.1	3.4	88.7
34	-6.2	+8.8	-5.9	-8.6	8.0	3.0	87.5
36	-0.9	+21.3	-1.7	-5.8	-	-	-

Table V

Gas Analysis and Yields

Recycle Gas Runs

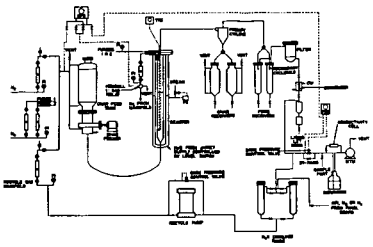
Run No.	Gas Yield SCF/Lb.	Dry Gas Analysis						
		H_2S	CO_2	CO	CH_4	C_2H_6	N_2	H_2
27	0.64	0.26	11.7	16.6	43.7	0.4	1.9	25.5
25	2.51	0.63	3.6	11.6	24.3	0.3	2.2	57.4
38	2.72	0.44	3.5	14.7	24.7	-	2.9	53.8
26	2.42	0.52	2.3	14.8	32.0	0.3	2.7	47.4
33	3.94	0.48	1.4	10.1	10.6	-	2.4	75.0
34	4.06	0.75	0.8	12.9	11.8	-	2.5	71.3

Table VI

Solids Analysis - Recycle Gas Runs

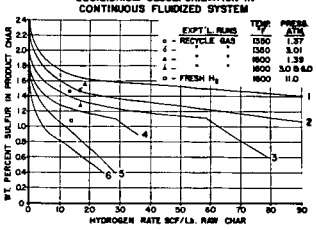
Run No.	Ultimate Analysis (Dry Basis)					Sulfide Plus Pyritic Sulfur	Ash	Moisture
	H	C	N	O	S			
Average Feed Char	3.10	78.08	1.76	5.69	2.44	0.63	8.93	4.0
Product Chars								
27	2.72	82.07	1.77	1.93	1.90	0.18	9.61	
25	1.55	85.31	1.52	-0.17	1.75	0.23	10.04	
38	1.42	84.49	1.34	1.36	1.47	0.24	9.78	
26	1.90	85.11	1.45	-0.34	1.48	0.25	10.40	
33	1.06	85.57	1.21	-0.07	1.56	0.33	10.53	
34	0.78	85.15	1.15	0.98	1.28	0.38	10.66	

Figure 1



FLOW DIAGRAM OF CHAR DESULFURIZATION UNIT

FIGURE 2
EQUILIBRIUM DESULFURIZATION IN
CONTINUOUS FLUIDIZED SYSTEM



1 - 1100 °F - SINGLE STAGE
2 - 1350 °F - SINGLE STAGE
3 - 1500 °F - SINGLE STAGE
4 - 1500 °F - DEVOLATILIZATION PLUS 1 STAGE
5 - 1500 °F - DEVOLATILIZATION PLUS 2 COUNTERCURRENT STAGES
6 - 1500 °F - IDEAL COUNTERCURRENT

FIGURE 3
VARIATION OF
DESULFURIZATION EFFICIENCY
WITH SEVERITY OF TREATMENT

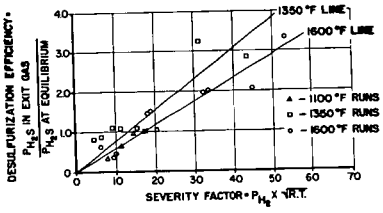


FIGURE 4
APPROACH TO METHANE EQUILIBRIUM
IN FRESH HYDROGEN RUNS

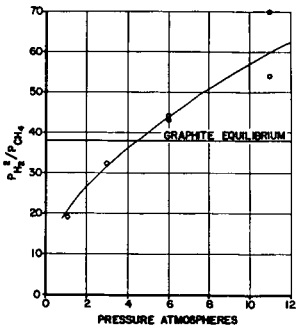


FIGURE 5
APPROACH TO METHANE EQUILIBRIUM
IN RECYCLE GAS RUNS

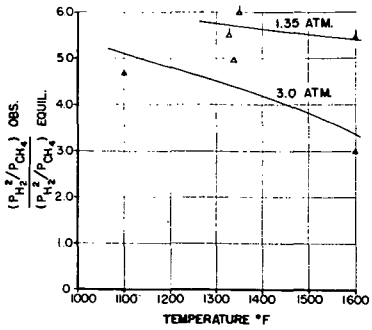


FIGURE 6
FIRST ORDER
REACTION RATE CONSTANTS FOR HYDROGENATION
OF FRESH AND DEVOLATILIZED CHARS

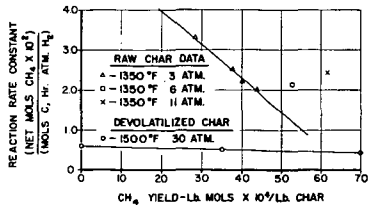
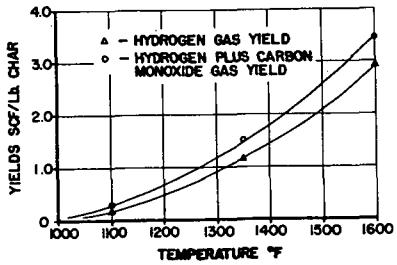


FIGURE 7
HYDROGEN YIELDS FROM CHAR
DEVOLATILIZATION



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ETHYLENE AND AROMATICS BY THE CARBONIZATION OF LIGNITE

By

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The Dow Chemical Company, Midland, Michigan

The work reported in this paper was carried out in an effort to determine the feasibility of manufacturing ethylene and aromatics by the carbonization of lignite. These raw materials are of great importance to the chemical industry and we can look forward to a future of dwindling supplies and increased prices for the crude oil which is now used for their manufacture. Since it was the aim of this research to produce maximum yields of ethylene and aromatics, the carbonization was not carried out in the usual manner. The central idea was to retort the lignite under conditions that will yield a maximum of volatile products and then thermally crack these volatile products under conditions which would produce a maximum yield of ethylene and aromatic hydrocarbons. This entails a low-temperature carbonization of the lignite immediately followed by a high temperature cracking of the volatile products. Preliminary experiments showed that it was very important that the carbonization products be cracked without being first allowed to condense. If the low-temperature tar is allowed to condense, subsequent thermal treatment will produce much greater amounts of residue and smaller amounts of the desired products.

After some preliminary experiments had been made in order to determine approximately the optimum conditions using a sample of Texas Sandow lignite, a series of more carefully planned experiments were made to more precisely determine the effect of the reaction conditions and to compare Texas lignite with North Dakota lignite in this process. All of the carbonization runs were made in a batch-type retort. The temperature of the retort was raised to a maximum of 800° and two cracking temperatures were used, 600° and 800°. Two lengths of cracking zone, 18 inches and 36 inches, were used so that the effect of retention time could be evaluated in addition to the effects of the retorting and cracking temperatures.

Equipment. - The equipment was arranged as indicated in Figure 1. The evolved volatile matter passed from the retort through the cracking zone into the collection train, which consisted of a water-jacketed receiver, spiral condenser, electrostatic precipitator, and another spiral condenser. From there the gas passed through a cotton trap to remove any uncondensed fog and mist, through a dry ice-acetone trap to condense low boiling constituents and finally through a wet-test gas meter used to measure the volume of evolved gas. This train is similar to that used in the Modified Distillation Assay Apparatus described in the Bureau of Mines Report 4954. (1)

(1) V. F. Parry, W. S. Landers, E. O. Wagner, J. B. Goodman, and G. C. Lammers, Bureau of Mines Report of Investigations 4954, (1953).

FIGURE I

LIGNITE CARBONIZATION APPARATUS

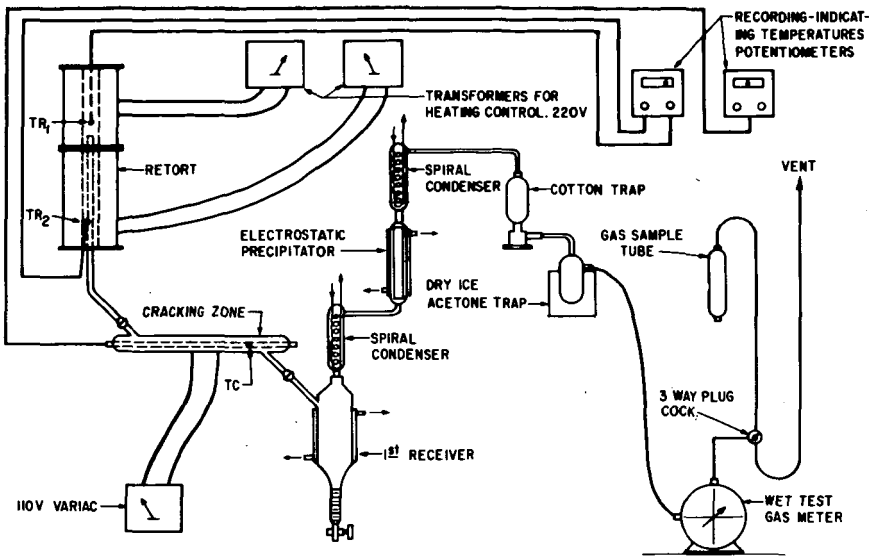
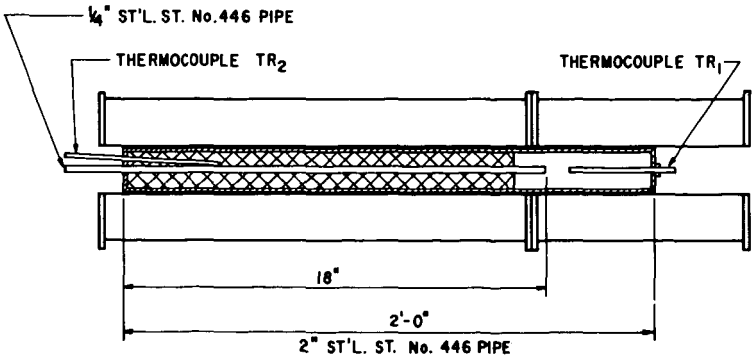


FIGURE 2

CROSS SECTION OF RETORT



The retort used for these carbonization runs consisted of a 2 inch 466 stainless steel pipe 24 inches in length. (Figure 2) Extending from the bottom of the retort to within 6 inches of the top was a 1/4 inch stainless steel pipe, used as an exit for all the volatile matter. A 1 inch stainless steel plug fitted with a thermowell (TR_1) was used at the top of the retort for the introduction of the lignite charge and for the removal of the char. A second thermowell (TR_2) was provided through the bottom of the retort the innermost point being welded to the 1/4 inch pipe. Heat for the retort was provided by electric furnaces controlled with variacs. The temperatures were measured with thermocouples, and recorded on electronic recorders.

Two cracking zones were fabricated of 31 mm. O. D. "Vycor" brand tubing, so that "L" in Figure 3 was 18 inches and 36 inches respectively. A concentric 9 mm. O. D. "Vycor" tube ran through the entire length of the cracking tube. This arrangement allowed a thermocouple to be placed inside the tube and the cracking temperature (TC) to be recorded for any point in the tube. It was recorded continuously on a single line recording-indicating temperature potentiometer. The thermocouple was placed inside the 9 mm. tube so that the temperature was measured at a point 2/3 of the distance from the entrance of the cracking zone to the exit. The cracking zone was heated with "Nichrome V Alloy" resistance tape wound directly on the tubing and the electric current controlled by means of a variac.

Some difficulty was experienced in the the condensation of the fog and mist during the preliminary experiments. Ice-water condensers proved to be ineffective in most instances so a small electrostatic precipitator was made. It consisted of four parallel 12 inch lengths of 3/4 inch O. D. stainless steel tubing in water-jacketed "Pyrex" brand glass housings. Suspended coaxially in the tubes were No. 31 platinum wires which were connected to a negative D. C. potential of 3 kv. The stainless steel tube was connected to ground.

Lignite Used. - The lignites used in these investigations were samples of Texas and North Dakota lignites. The Texas lignite was obtained from Bastrop County and the North Dakota lignite obtained from the Truax-Traer Coal Company, Minot, North Dakota. The samples were obtained in sealed drums in an "as mined" state and were of 3 inch particle size.

The lignite was dried overnight at 100° in a vacuum oven at 3 to 5 mm. pressure. During this operation the Texas lignite lost 29.3% while the North Dakota lignite lost 31.1 of its weight. The dried lignite was then crushed and the crushed material separated into fractions based on particle size. For the carbonization runs, the fraction was used that passed 3-1/2 mesh screen and remained in 10 mesh screen.

FIGURE 3

CRACKING ZONE

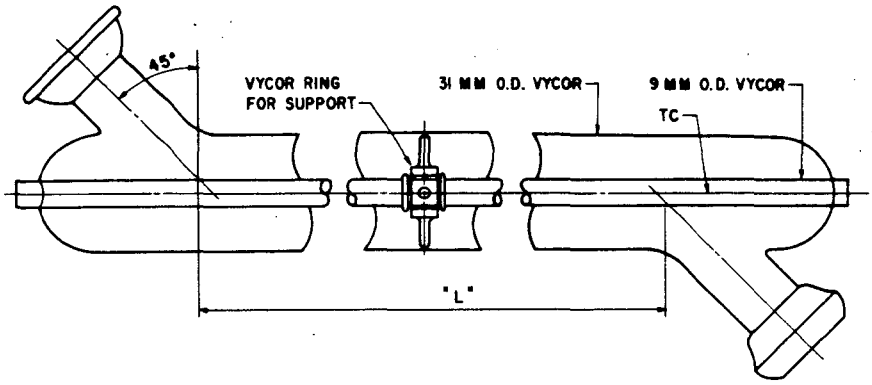


FIGURE 4

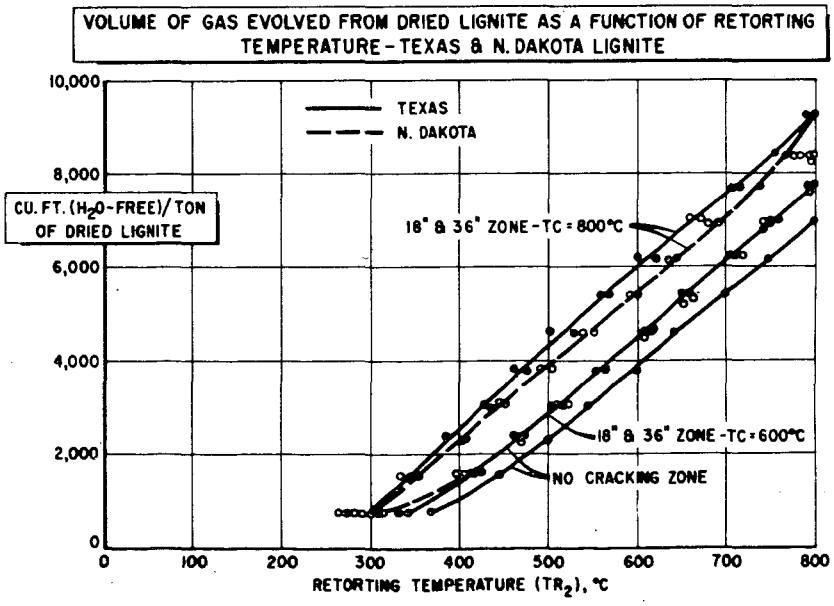


TABLE I

ANALYSIS OF RAW LIGNITES

Proximate Analysis	Weight Per Cent	
	Texas	North Dakota
Moisture	34.0	35.2
Net Volatile	31.6	45.1
Fixed Carbon	24.7	14.2
Ash	10.6	5.5
	100.9	100.0
Ultimate Analysis		
Ash	10.6	5.5
Hydrogen	5.2	6.5
Carbon	41.2	40.4
Nitrogen	0.8	0.7
Oxygen	41.5	46.5
Sulfur	0.9	0.5
	100.2	100.1

TABLE II

ANALYSIS OF DRIED LIGNITES

Proximate Analysis	Weight Per Cent	
	Texas	North Dakota
Moisture	10.0	10.8
Net Volatile	41.5	39.6
Fixed Carbon	36.3	42.3
Ash	12.4	7.3
	100.2	100.0
Ultimate Analysis		
Ash	12.4	7.3
Hydrogen	5.7	5.1
Carbon	56.8	56.7
Nitrogen	0.9	0.9
Oxygen	23.2	29.4
Sulfur	1.0	0.6
	100.0	100.0

It should be noted that during the drying operation, some volatile, carbon-containing material was removed from the lignite.

PROCEDURE

Dried lignite (500 grams) was charged into the retort and the cracking zone temperature brought up to the predetermined level. Ice water was circulated through the condensers and the water jackets. When the cracking zone temperature reached this predetermined point, the temperatures of the retort was slowly and uniformly raised to a maximum of 800°. About 70 minutes was required for TR_2 to increase from 300° to 800°. Electric current to the retort furnaces was controlled manually in such a manner that TR_1 equaled TR_2. When the retort temperature reached 800°, it was stabilized at this point and maintained there for another hour. After this length of time no further gas evolution was observed. All heat was then turned off, the cold trap was removed from the dry ice-acetone bath and allowed to come to room temperature, and the ice water was removed from the condensers and jackets. Steam was then passed through the condensers and jackets thus forcing any material collected on the condensers and precipitator to run back into the receiver. The volume of water and oil was estimated in the graduated section of the receiver and the contents of the dry ice-acetone trap were poured into the first receiver and the weight of all materials in the first receiver was determined. The cotton trap was weighed to check the efficiency of the electrostatic precipitator and any gain in weight was added to the weight of the water plus heavy oil. For those runs designated "no cracking zone", the cracking zone was eliminated entirely and the retort attached directly to the first receiver.

The contents of the first receiver were steam distilled and the non-aqueous layer of the distillate separated and designated as the "steam distillable oil". The residual oil and tar was designated "heavy oil". Samples of the steam distillable oil were examined by means of infrared and mass spectroscopy and samples of the heavy oil examined by means of infrared spectroscopy. The volume of the gas produced was measured with the wet-test gas meter. Samples of the evolved gas were taken every 12 liters and analyzed for their components by mass spectrometry. The weight of the char was determined by weighing the contents of the retort after the run had been completed.

RESULTS

Complete material balances for the runs are given in Table III. Very accurate determinations of the yields of the various gases, the light oils, and char were made but only the total of heavy oil and water was determined in most cases because of the difficulty encountered in separating them. The yields of heavy oil, however, were only of secondary importance since the major emphasis in this work was on the yields of ethylene and benzene.

Analysis of the products obtained in these carbonization runs makes it possible to evaluate the effect of retorting and cracking temperatures and retention times on the yields of the various products. Since all the volatile matter passed through the cracking zone, the volume and composition of the evolved oil and gases were affected by both the retorting and cracking temperatures and retention times. The char, of course, was affected only by the retorting temperature.

TABLE III

MATERIAL BALANCES ON THE CARBONIZATIONS

(Yields of lbs. per ton of Dried Lignite)

Lignite	North Dakota					Texas				
Cracking Temperature		600°		800°			600°		800°	
Zone Length	None	18"	36"	18"	36"	None	18"	36"	18"	36"
Ethylene	3.6	6.0	7.8	20.0	23.9	5.2	13.6	14.7	39.6	44.2
Propylene	0.3	2.7	5.4	8.9	1.0	3.6	12.4	13.8	14.4	108.7
Methane	67.6	67.6	71.5	82.9	89.7	64.4	76.0	82.7	100.1	108.7
Ethane	7.9	9.6	8.9	6.4	0	8.8	13.2	15.7	9.3	5.9
Hydrogen	16.3	15.9	15.6	16.8	17.3	12.8	15.2	14.3	16.6	16.9
Carbon Monoxide	101.7	95.7	102.6	106.7	117.3	79.6	87.2	87.4	109.1	114.1
Carbon Dioxide	198.6	196.6	198.0	218.9	205.2	155.6	146.0	155.5	149.0	167.0
Hydrogen Sulfide	2.2	2.2	2.2	3.2	2.5	6.0	7.2	7.2	7.2	7.8
Total Gases	396.2	396.3	412.0	463.8	456.9	336.0	369.6	391.3	445.2	472.9
Light Oil	26.1	24.2	22.7	15.4	11.5	52.4	38.1	49.0	17.8	37.8
Heavy Oil and Water	562	551	519	500	484	408	420	426	435	376
Char	1032	1028	1024	1028	1028	1096	1092	1096	1096	1096
TOTAL	2016	2000	1978	2007	1980	1992	1920	1962	1994	1983

Gas Volume. - The volume of evolved gas is approximately a linear function of the retorting temperature. (Figure 4) When higher cracking temperatures are employed, more gas is obtained due to the conversion of some of the oil to gaseous products. So fas as the volume of gases is concerned, there is little difference between Texas and North Dakota lignite.

Gas Composition. - The composition of the gas evolved varies widely as the retort temperature passes through the temperature range from room temperature to 800°C. The effect of the retorting temperature on the instantaneous composition of the gas is quite pronounced, but since a cumulative gas composition would be obtained under the conditions of commercial carbonization, this effect would be much less. The major components of the evolved gas are: ethylene, propylene, methane, ethane, hydrogen, carbon monoxide, carbon dioxide, and hydrogen sulfide. These comprise at least 98% of the gas produced. The effects of the retorting and cracking temperatures on the proportions of each of these gases will be discussed in the order that they are listed above.

Ethylene.- Of all the gaseous products, ethylene is the most valuable. The proportion of this gas shows a maximum at about 400°C. and drops very abruptly when the retort temperature exceeds 500°C. (Figure 5) This latter retort temperature coincides with the point where no further oil is collected in the fore part of the collection train. The retort temperature has a very marked effect of the amount of ethylene obtained although the retention time does not seem to be particularly important. A good deal more ethylene was obtained at a cracking temperature of 800°C. than was obtained at 600°C. Texas and North Dakota lignite behave similarly, but Texas produces almost twice as much ethylene as does North Dakota lignite.

Propylene. - The proportion of propylene in the evolved gas shows a well defined maximum at retort temperatures of approximately 450°C. (Figure 6) The proportion of propylene, contrary to that of ethylene, decreases as the cracking temperature is increased from 600°C. to 800°C. As was the case with ethylene, Texas lignite produces much more propylene than does North Dakota. lignite.

Methane. - The production of methane in the evolved gas is a maximum at a retort temperature of approximately 500°C. (Figure 7) More methane is obtained from Texas lignite using a cracking temperature of 800°C. than is obtained with a cracking temperature of 600°C. while the reverse is true with North Dakota lignite. Retention time, however, does not seem very important in this case. Somewhat more of this gas is produced from Texas lignite than is produced from North Dakota lignite.

Ethane. - The maximum evolution of this gas occurs at a retort temperature of about 450°C. and its production is favored by low cracking temperatures. (Figure 8) At the higher cracking temperatures, much of the ethane that is produced in the retort is converted to ethylene. In the case of this gas, too, more is obtained from Texas than from North Dakota lignite.

FIGURE 5

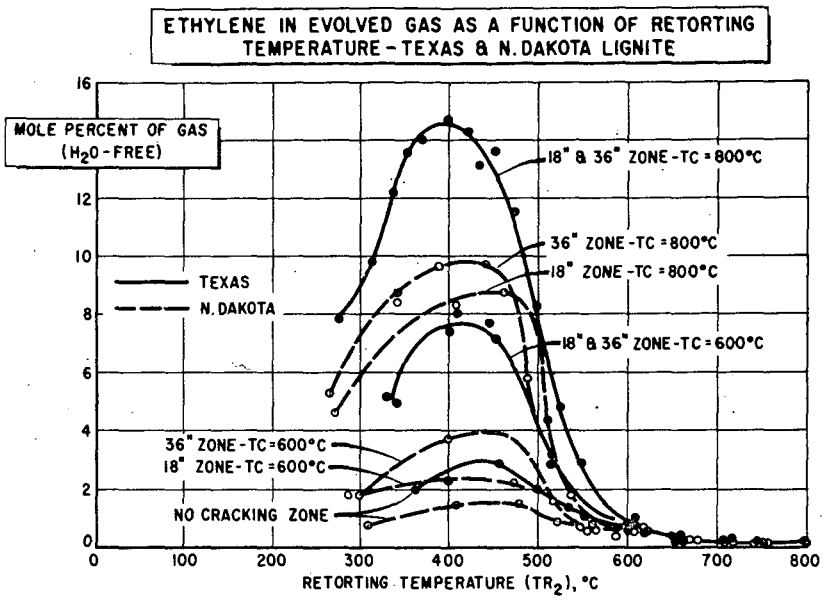


FIGURE 6

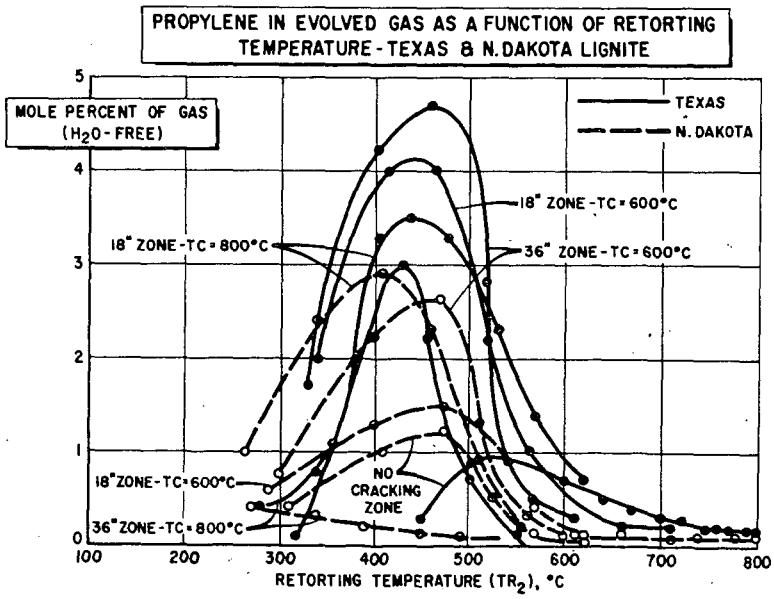


FIGURE 7

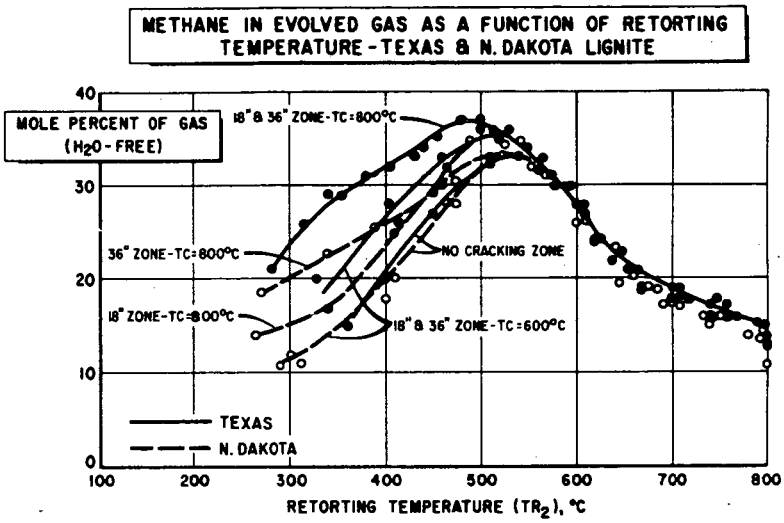
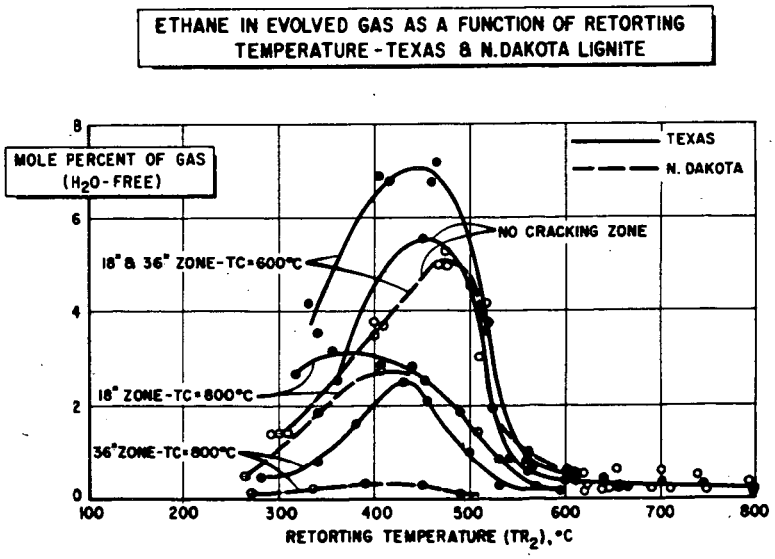


FIGURE 8



Hydrogen. - The evolution of this gas is different from that of the hydrocarbon gases in that it continues to increase with retort temperature to the highest retort temperatures investigated. (Figure 9) Below a retort temperature of 500°C., its production is favored by high cracking temperatures and the longer retention time, conditions which would be expected to favor the conversion of saturated to unsaturated hydrocarbons. The production of this gas was almost identical from both lignites.

Carbon Monoxide. - As the retort temperature is increased the proportion of carbon monoxide in the evolved gas shows a minimum at 540° and a well defined maximum at 670°C. at all cracking temperatures and retention times. (Figure 10) The production of this gas is almost completely insensitive to the cracking conditions. Texas and North Dakota lignites behave very similarly although slightly more carbon monoxide is obtained from North Dakota lignite at retort temperatures below 600°C.

Carbon Dioxide. - Less of this gas is evolved as the retort temperature is raised until essentially none is evolved at retort temperatures in excess of 730°C. (Figure 11) The proportion of carbon dioxide in the evolved gases below a retort temperature of 550°C. is lower at the higher cracking temperatures although this is due entirely to the greater amount of total gas produced under these conditions. More carbon dioxide is obtained from North Dakota lignite than is obtained from Texas lignite.

Hydrogen Sulfide. - Only rather small amounts of this gas are obtained and almost all of it below a retort temperature of 600°C. (Figure 12) While the proportion of this gas in the evolved gas is affected by the cracking conditions in the case of the Texas lignite, it is not in the case of the North Dakota lignite. Approximately twice as much hydrogen sulfide is also obtained from the Texas lignite.

Liquid Products. - Since the liquid products were determined only at the end of the run, little can be said about the effect of retorting temperature on their amount and composition but it was noticed that all the evolution of oil occurred between retort temperatures of 250°C. and 550°C. The effect of cracking temperature and retention time, however, was determined.

Light Oil. - Less light oil is obtained at the higher cracking temperatures. (Figure 13) The retention time had little effect on the amount produced from North Dakota lignite but significantly more was produced from Texas lignite at the longer retention time. At the longer retention time, approximately twice as much light oil was produced from Texas lignite than was produced from North Dakota lignite.

The components of the steam distillable oil obtained at the lower cracking temperatures were mainly saturated aliphatic hydrocarbons, while at the higher cracking temperatures, the components were benzene, toluene, naphthalene, aliphatic substituted naphthalenes, mixed alkyl benzenes, and some phenolics and polynuclear aromatic hydrocarbons of the lower molecular weights. (Table IV)

FIGURE 9

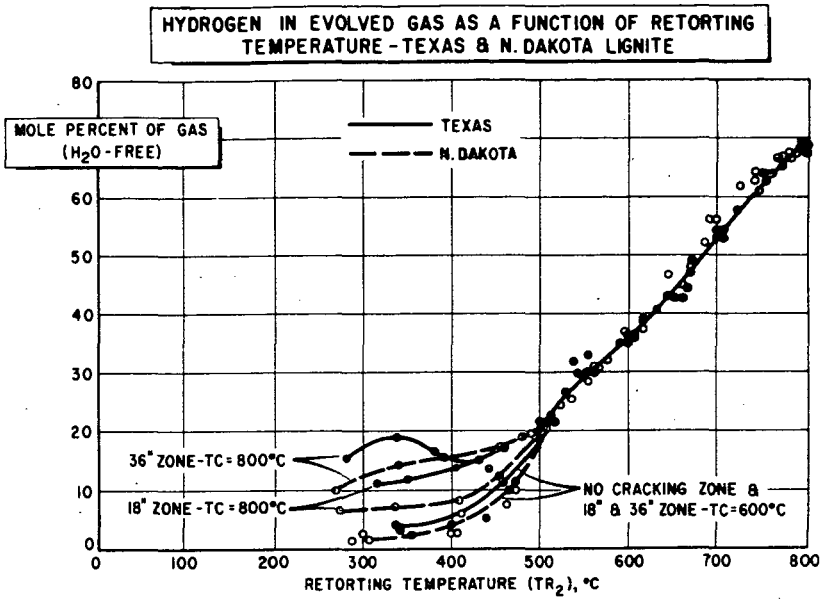


FIGURE 10

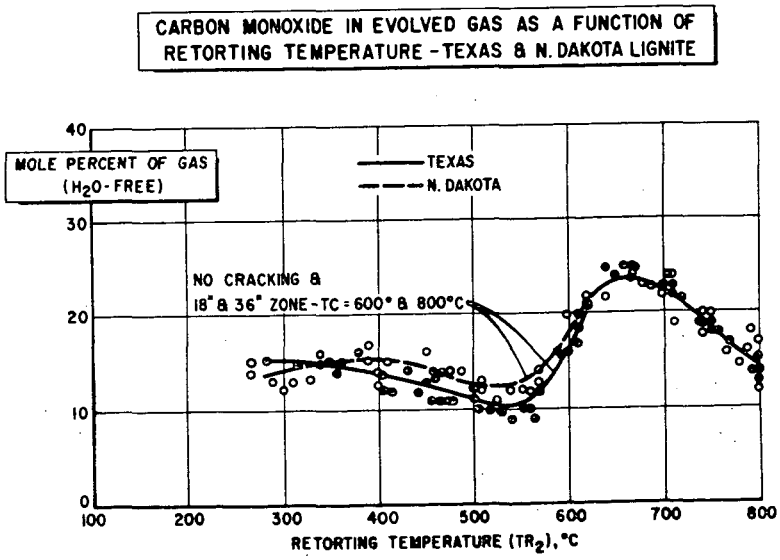


FIGURE 11

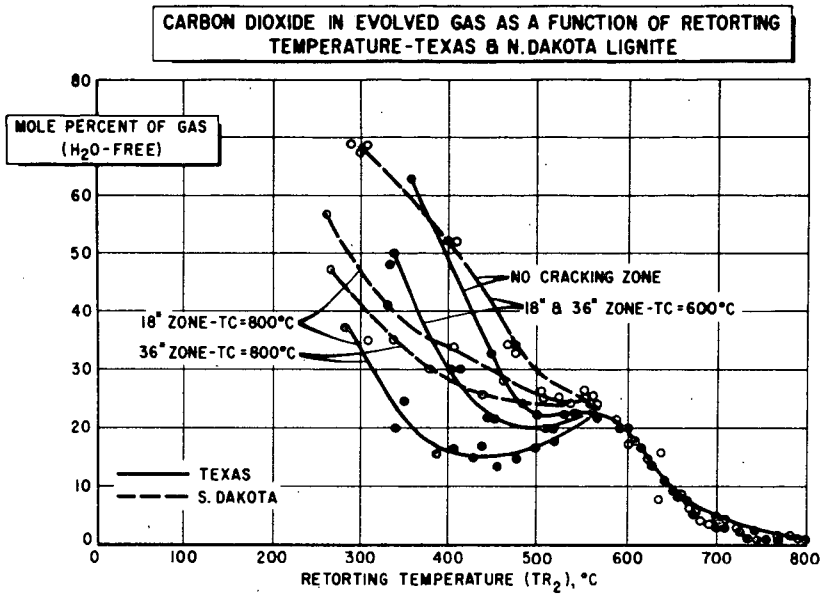


FIGURE 12

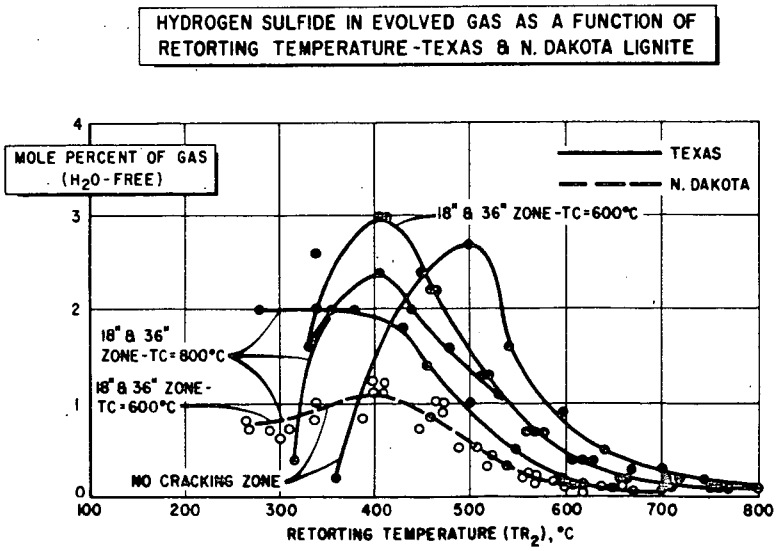


FIGURE 13

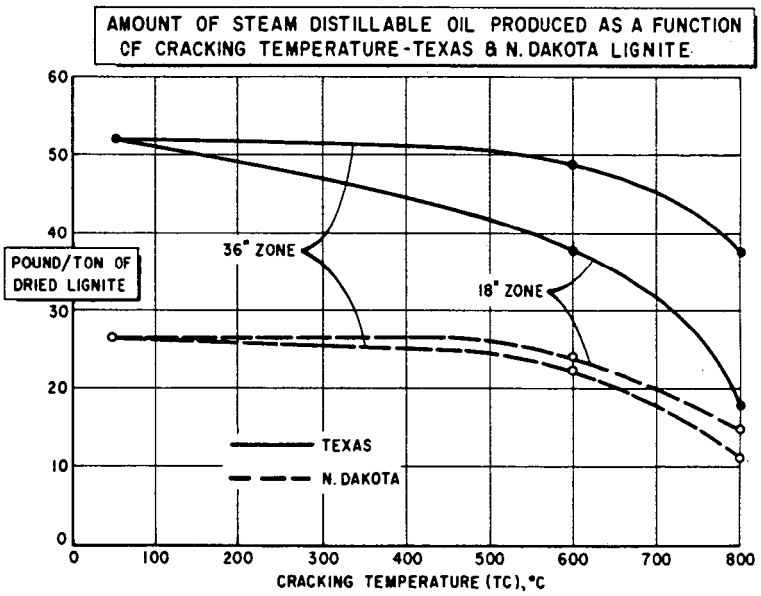

AMOUNT OF STEAM DISTILLABLE OIL PRODUCED AS A FUNCTION OF CRACKING TEMPERATURE-TEXAS & N. DAKOTA LIGNITE
POUND/TON OF DRIED LIGNITE
60
50
40
30
20
10
0
36" ZONE
18" ZONE
TEXAS
N. DAKOTA
0
100
200
300
400
500
600
700
800
CRACKING TEMPERATURE (TC), °C

TABLE IV

EFFECT OF CRACKING CONDITIONS ON THE COMPOSITION
AND YIELDS OF LIGHT OIL
(Yields in lbs. per Ton of Dried Lignite)

Lignite	North Dakota					Texas				
Cracking Temperature		600°		800°			600°		800°	
Zone Length	None	18"	36"	18"	36"	None	18"	36"	18"	36"
Benzene	0	0	0.2	0.2	0.6	0.5	0.4	1.0	0.2	6.0
Toluene	0	0.2	0.7	0.9	0.7	1.0	1.1	1.5	1.2	4.9
Xylene and/or ethylbenzene	1.0	1.0	1.4	1.2	0.3	1.6	2.3	2.0	1.4	2.3
Mass 120 (C_3 benzene)*	1.0	1.0	0.9	0.6	0.1	1.0	1.5	1.5	0.4	0.4
Mass 134 (C_4 benzene)	1.0	0.7	0.7	0.3	0.3	1.0	0.8	1.0	0.4	1.1
Styrene	0.1	0.07	0.2	0.6	0.6	0.2	0.4	0.5	0.9	1.9
Naphthalene	0.3	0.2	0.2	0.6	1.4	0.5	0.8	0.5	1.1	3.0
Methylnaphthalene	0.3	0.2	0.2	0.5	0.2	0.2	0.4	0.5	0.5	1.1
Indene	0.3	0.2	0.2	0.8	0.6	0.2	0.8	0.5	1.2	1.9
Mass 118	0.3	0.2	0.5	0.9	0.3	0.5	1.1	0.5	1.1	0.7
Other components	21.7	20.3	17.5	8.9	6.3	45.6	28.6	39.6	9.4	14.4
TOTAL	26.0	24.1	22.7	15.5	11.4	52.3	38.2	49.1	17.8	37.7

*This notation designates a benzene ring substituted with three saturated, carbons, i.e. methyl ethyl benzene, propyl benzene, and/or mesitylene.

Heavy Oil. - As expected, the amount of heavy oil obtained decreases as the cracking conditions become more severe due to the conversion of some of this material to light oils and volatile hydrocarbon gases. The infrared spectra indicates that the heavy oil obtained using the lower cracking temperatures was composed of saturated aliphatic hydrocarbons of high molecular weights with little of the aromatic hydrocarbons present. Heavy oils obtained using higher cracking temperatures, however, were primarily polynuclear aromatic hydrocarbons of the higher molecular weights with some phenolic components present.

Char. - Retorting, of course, converts part of the lignite into volatile products so that less char is obtained as the retorting temperature is raised. The char, however, has a significantly greater calorific value than did the original dried lignite.

TABLE V

YIELDS OF CHAR OBTAINED FROM TEXAS AND NORTH DAKOTA LIGNITES

	Retorting Temperature	
	550°C.	800°C.
Texas Lignite	1220	1100
North Dakota Lignite	1160	1020

- Yields in lbs. per ton of dried lignite.

TABLE VI

CHAR ANALYSES

Texas Lignite

Proximate Analysis	550°C.	800°C.
Moisture	0.0	0.0
Net Volatile	11.4	3.6
Fixed Carbon	68.7	72.2
Ash	20.0	23.7
	100.1%	100.0%
Ultimate Analysis		
Ash	20.0	23.7
Hydrogen	2.7	0.9
Carbon	72.3	73.3
Nitrogen	1.3	0.9
Oxygen	2.8	0.2
Sulfur	0.9	0.9
	100.0%	99.9%
Calorific Value	12,035 BTU/lb.	11,443 BTU/lb.

TABLE VI (Cont'd)

North Dakota Lignite

Proximate Analysis		
Moisture	0.0	0.0
Net Volatile	14.8	4.0
Fixed Carbon	72.8	82.3
Ash	12.4	13.8
	100.0%	100.1%
Ultimate Analysis		
Ash	12.4	13.8
Hydrogen	2.9	1.3
Carbon	78.0	73.4
Nitrogen	1.3	0.9
Oxygen	4.9	0.2
Sulfur	0.5	0.5
	100.0%	100.1%
Calorific Value	12,571 BTU/lb.	12,608 BTU/lb.

CONCLUSION

Ethylene and aromatics have been obtained by means of a low-temperature carbonization of lignite immediately followed by a thermal cracking of the volatile products. Texas Sandow lignite was found to be much superior to North Dakota lignite in this process and produced almost twice as much ethylene and about ten times as much benzene. Of the conditions evaluated, the best results were obtained when using retorting temperatures only up to 550°C., a cracking temperature of 800°C., and a cracking zone length of thirty-six inches. This was the longest cracking zone length investigated and its use resulted in an "average" retention time of about 1.5 seconds. Of course, these "optimum" conditions would probably be altered somewhat with a large commercial unit. An estimate, however, can be made of the preformance of a large unit on a basis of the experimental results reported here. This estimate is given in Table VII.

TABLE VII

YIELDS OBTAINED FROM TEXAS SANDOW LIGNITE

Conditions: Retort temperature - up to 550°C.
Cracking zone - 36 inches, 800°C.

Yields in lbs. per ton of Dried Lignite

GASES	
Ethylene	40.0
Propylene	7.6
Methane	70.5
Ethane	4.9
Hydrogen	5.6
Carbon Monoxide	56.1
Carbon Dioxide	-126.0
Hydrogen Sulfide	7.2
TOTAL	318
LIQUIDS	
Benzene	6.0
Toluene	4.9
Xylene and/or ethylbenzene	2.3
Mass 120 (C_3 benzene)	0.4
Mass 134 (C_4 benzene)	1.1
Styrene	1.9
Naphthalene	3.0
Methylnaphthalene	1.1
Indene	0.7
Mass 118	0.7
Other Components	14.4
TOTAL LIGHT OIL	37.7
TOTAL HEAVY OIL	~44
CHAR	
Weight	1,220
Calorific Value	12,035 BTU/lb.

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Reactions of a Bituminous Coal with Sulfuric Acid

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INTRODUCTION

Bituminous coals react with concentrated sulfuric acid producing useful ion-exchange materials (1,2). The reaction involves oxidation and sulfonation introducing carboxyl and sulfonic acid groups, but otherwise, little is known about the chemical changes that occur in the coal substance (3). Because sulfuric acid is less oxidizing at moderate temperatures than many of the oxidizing reagents that have been used in coal constitution research [nitric acid for example (4)], and has strong cleavage action on ether linkages, the use of this reagent in studying the constitution of coals should be particularly elucidating.

EXPERIMENTAL

The coal selected for study is from the Pittsburgh seam in western Pennsylvania. An analysis is given in Table I. When the coal, ground to minus 200 mesh, and 96.7% sulfuric acid are mixed at -10°C. or below, no observable reaction occurs, but at 0°C. or higher, the temperature of the mixture rises slightly and sulfur dioxide is evolved. The coal has a large absorptive power for sulfuric acid and it requires several times its weight to obtain a fluid mixture. With a ratio of 12 to 1, the coal disperses freely and increases the viscosity of the acid noticeably. The dispersion cannot be filtered through a coarse fritted glass filter using an aspirator pump. Bubbles of sulfur dioxide rise to the surface, but break with difficulty. After reacting for several hours, an undispersed solid product begins to collect on the surface of the acid. It the mixture is now placed in a refrigerator for a time, the liquid sets to a gel. On warming to room temperature, and when stirred, the gel reverts to the original liquid state.

The dispersing action of concentrated sulfuric acid on the coal can be domonstrated in another way. A 1-cm. cube of coal, dried at 100°C. for 2 hours and placed in the acid at 25°C., immediately begins to undergo disintegration. If the process is aided by stirring, the coal can be dispersed readily in this way. When the coal-acid dispersions are diluted with water, flocculation occurs and filtration can be accomplished. The product, after thorough washing, dries to a relatively hard granular mass. At higher reaction temperatures, the product is actually harder than at lower temperatures.

Standard Sulfonation Procedure:--Twenty grams of minus 60-mesh coal are placed in a 1-l., 3-neck flask fitted with a mercury-sealed stirrer, a thermometer, and a delivery tube for removing the sulfur dioxide. Then, 400 g. of 96.7% sulfuric acid are added to the coal and the stirrer started. Temperature of the mixture is maintained by an electric heating mantle regulated by a transformer.

At the end of the heating period the reaction mixture is cooled and poured on ice. The product is filtered through fritted glass and washed repeatedly until 50 ml. of the wash water titrated less than 1 ml. of 0.1 N sodium hydroxide. The product is dried for 12 hours at 100°C., and again washed with water. This removes additional sulfuric acid. No doubt the samples still retain small amounts of uncombined acid, because they give 0.5% to 2.0% sulfate sulfur, and 0.5% to 1.0% more pyritic sulfur than the original coal, when analyzed by the standard A.S.T.M. method for coals.

Analysis:--Carbon and hydrogen analyses listed in Table II are macro determinations, and the nitrogens are macro Kjeldahls. The sulfur values given in Tables II and III are standard A.S.T.M. determinations of sulfur in coals. The total carbon lost by sulfuric acid treatment, given in Table II, is the difference between the per cent of the original carbon left in the product, calculated from its weight and per cent carbon, and 100%. The surface areas were obtained by the B.E.T. method using nitrogen (5).

DISCUSSION

Yields of product coal obtained at different temperatures from 25° to 150°C. vary from 115% to 125%. From the data given in Table II, it appears that at low temperatures, 25° to 50°C., several days of treatment are required to obtain the maximum yield of 120% to 125%. Only one day is needed at 100° to 110°C. When the reaction is continued beyond the time of maximum yield, 115% to 117% yields result. At this level the product becomes resistant to further loss by continued treatment. Greater precision of the yields would have been obtained had the reaction temperature been maintained more closely. At times the temperature varied by as much as 10°C. because of line voltage variations.

The composition of the products is remarkably constant, both at a given reaction temperature and for a range of temperatures from 25° to 150°C. Table II shows that the per cent carbon of the original coal falls from 82.3% to about 61.6% ±2% under these conditions. A considerable part of this decrease in carbon content is caused by the increased weight of product, but at the same time about 13.3% ±3% of the original carbon of the coal is eliminated, partly by oxidation to carbon dioxide.

The hydrogen content of the coal falls much more than the carbon percentage-wise--from 5.6% to about 2.6% ±ca.1%, if the hydrogen analyses of the 50°C. products in Table II, which seem to be out-of-line, are excluded. This loss of hydrogen is similar to that observed when like coals are oxidized by nitric acid (4) or air (6), and may be accounted for by oxidation because of the evolution of sulfur dioxide. A low atomic hydrogen-carbon ratio of the products of about 0.4 shows that their structure must be that of a polynuclear aromatic, or more likely, quinoid type (7).

The nitrogen analyses in Table II show that almost all of the nitrogen of the original coal is retained in the products, keeping in mind that the latter weigh about 120% of the coal. If the structure of the products is essentially polynuclear or quinoid in character, it follows that the nitrogen atoms of the coal are present in ring structures, substituting for carbon atoms, and thus surviving the oxidative conversion of the rings to the final product.

Also included in Table II are data on the per cent of organic sulfur in the products. This non-sulfatic, non-pyritic sulfur would include organic sulfur of the original coal, although some may have been removed by the sulfuric acid treatment. The data show that a significantly constant amount of sulfur is introduced regardless of the conditions of treatment. Slightly larger amounts are introduced under milder conditions, that is, lower temperatures. At 25°C. the per cent of sulfur decreases with longer reaction times, suggesting that certain structures in the raw coal, such as hydroxyl groups, react but are subsequently oxidized with the loss of the sulfur-containing group. The fact that increasing the temperature of treatment does not introduce additional sulfur groups suggests that the structure of the product is not reactive toward sulfuric acid. This also favors the polynuclear quinoid structure (7) rather than aromatic.

The main sulfur-introducing reaction proceeds readily at 25°C. and to a greater extent than at 150°C. This temperature effect is typical of addition reactions, although it is possible that easily sulfonated structures, such as phenolics, are sulfonated similtaneously. This would inhibit further sulfonation in the immediate vicinity of the sulfonic acid group introduced. A likely structure for the addition-type of reaction would be unsaturated rings which, following the addition of the acid, could indergo oxidation to aromatic or quinoid structures and thus incorporate the sulfur-bearing group into the oxidation-resistant product. The sulfonated phenolics would also be expected to be oxidized to quinoid structures subsequently.

Considering the dispersing action of concentrated sulfuric acid on the coal and the fact that some 13% of the carbon is removed, an examination of some of the physical properties of the product is of importance. Of particular importance for ion exchangers is large surface area. Surface areas of the products obtained under various conditions show that both temperature and time of treatment increase the area markedly, Table II. At 25°C. surface areas are smaller than the original coal, which suggests that the treatment actually seals off pores. At higher temperatures, increased areas indicate increased dispersion and development of new surfaces.

A particularly attractive hypothesis to account for the observed dispersive action of sulfuric acid and increased surface areas is that the acid molecules force their way between the coal lamella (8) during the process of dispersion. This would account for the difficulty of filtering, the gelling on cooling, and the increased surface areas on removing the acid. However, the interlayer spacing of the crystallites of the products actually decrease with increasing surface area. Thus the d-spacing of the raw coal decreases from 3.93A. to 3.66A. when the coal is treated at 110°C. for 1 day and to 3.52A.

after 8 days; meanwhile the surface area increases from 2.7 m^2/g. to 4.5 m^2/g., then to 183 m^2/g. These results indicate that the lamella draw together rather than separate during the acid treatment. Crystallite heights of the raw coal and the 110°C. products are all 7-8A., indicating that the crystallites are but two lamella thick on the average (9).

The action of concentrated sulfuric acid on the mineral matter of the coal is also significant. At 25° to 50°C. the ash content of the coal falls from 8.2% to about 5.5%, see Table III. This is mainly caused by the extraction of soluble sulfates by the acid and subsequent washing. The sulfate sulfur is undoubtedly adsorbed sulfuric acid displaced by hydrochloric acid in the A.S.T.M. procedure. Similarly the cold dilute nitric acid used to determine pyritic sulfur displaces additional sulfuric acid, giving values for pyritic sulfur greater than in the original coal.

The pyrite is attacked by the hot sulfuric acid beginning at 100°C. and completely at 110° to 150°C. This results in a noticeable drop in the percentage of pyritic sulfur and of ash at these temperatures, Table III. The remaining "pyritic sulfur" is believed to be adsorbed sulfuric acid removed by the dilute nitric acid treatment.

In general low "sulfate sulfur" (less than 1.0%) seems to predict that the product will have a large surface area (Table III). No proof is available but it seems to be possible that a high degree of dispersion in sulfuric acid, which leads to a large surface area, might result in a product from which the adsorbed sulfuric acid might be desorbed more easily, on the basis that originally small pores are converted to large ones.

SUMMARY

A high-volatile A bituminous coal reacts with concentrated sulfuric acid, in the range of 25° to 150°C., with the loss of about 13% of its carbon partly as carbon dioxide. Over 50% of the hydrogen is removed, but nearly all of the nitrogen remains. About 5% sulfur is introduced. The composition of the product indicates that it has a polynuclear quinoid type of structure. The crystallites are two lamella high on the average, as in the raw coal, and their interlayer spacing is about that of many chars and carbons. Maximum surface area is developed by prolonged treatment at higher temperatures.

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TABLE I

ANALYSIS OF THE COAL

Constituent	As Received	D.A.F. Basis
Moisture	2.01%	-
Ash	8.04	-
Vol. Matter	36.44	40.51
Carbon	74.02	82.29
Hydrogen	5.29	5.63
Nitrogen	1.16	1.28
Sulfur	2.26	2.51
Cal. Value	13,192 Btu	-

TABLE III

ANALYSIS OF THE PRODUCTS

Conditions of Sulfonation		Analysis, Dry Basis, %				
Temp., °C.	Time, days	Ash	Total S	Sulfate S	Pyrite S	Org. S
Raw Coal		8.2	2.5	0.2	1.0	1.3
25	5	5.9	9.2	1.5	1.8	5.9
	10	5.8	9.4	1.6	1.2	6.6
	20	5.7	9.2	1.8	1.8	5.6
	31	6.3	8.4	1.2	1.9	5.3
50	1	5.9	8.4	1.9	1.8	4.7
	3	5.7	8.6	1.6	2.0	5.0
	5	5.5	9.0	2.4	1.5	5.1
	8	5.4	8.4	1.7	1.7	5.0
100	1	5.4	8.2	1.6	1.2	5.4
	2	5.3	7.2	1.3	1.2	4.7
	5	4.9	7.0	1.2	1.0	4.8
	8	4.9	6.4	0.7	0.8	4.9
110	1	4.8	7.8	2.1	0.9	4.8
	3	4.5	6.1	0.7	0.7	4.7
	8	6.7[a]	5.7	0.6	0.2	4.9
150	1	4.5	6.3	1.1	0.3	4.9
	3	4.3	5.8	0.5	0.5	4.8

[a] The ash content of a duplicate run was 4.5%

TABLE II

SULFONATION DATA

Conditions of Sulfonation		Yield	Analysis, Dry Ash-Free Basis, %				Total C Lost	Surface Area
Temp., °C.	Time, days	%	C	H	N	Org. S	on Treatment, %	$m^2/g.$
Raw Coal		-	82.3	5.6	1.3	1.3	-	2.7
25	5	116	63.6	3.5	1.0	6.2	11.2	2.3[a]
	10	117	62.8	2.0	1.0	6.4	13.2	0.002[a]
	20	120	63.1	2.1	0.9	5.9	10.5	0.12[a]
	31	116	63.8	2.6	1.0	5.7	10.4	1.5
50	1	119	62.0	6.5	0.9	5.0	11.6	3.1
	3	117	61.5	5.6	0.9	5.4	13.5	16.
	5	125	59.7	3.1	0.9	5.4	11.6	-
	8	122	60.7	3.6	0.9	5.2	10.1	54.
100	1	120	61.4	2.6	0.9	5.7	13.5	7.2
	2	116	61.0	4.6	0.8	5.0	13.9	101.
	5	117	60.6	3.1	0.9	5.0	12.7	-
	8	115	62.1	2.6	0.9	5.2	12.7	222.
110	1	123	59.6	2.6	0.9	5.0	12.3	4.5
	3	115	61.2	2.6	0.9	4.9	13.2	158.
	8	116	60.8	2.0	0.9	5.3	16.5	183.
150	1	115	61.3	3.3	1.0	5.1	16.2	178.
	3	117	62.8	2.6	1.0	5.0	13.8	272.

[a] These surface areas were very kindly made by J.R. Malone

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Reduction of Coal by Lithium-Ethylenediamine. Studies on a Series of Vitrains.

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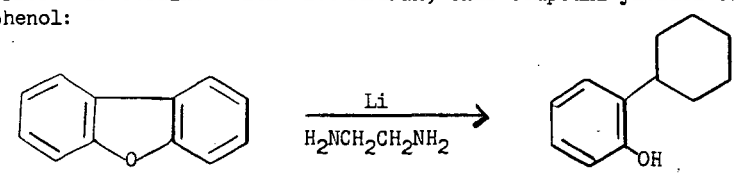
In an earlier report from this laboratory,1/ it was demonstrated that coals are reduced by lithium in ethylenediamine.2/ We now wish to present a more detailed study of the reduction of seven low-ash vitrains of varying ranks, and to describe the reduction of a graphite.

The reductions were carried out under closely controlled conditions, since it is known3/ that the amount of hydrogen added to a vitrain is to some extent a function of the experimental procedure. The starting materials are described in Table I. The analytical data on the starting materials and on the products of reduction are given in Table II. In Table III the analytical data for the starting and reduced materials are corrected to an ash-, sulfur-, and ethylenediamine-free basis. Table III also gives the amount of hydrogen added to the starting materials, expressed both as grams of hydrogen added per 100 g. of starting material and as atoms of hydrogen added per 100 carbon atoms in the starting material.

Figure 1 gives the hydrogen added as a function of carbon content. While the curve needs further definition, its general shape seems clear. The hydrogen uptake is low for lower rank coals, rises rapidly with increasing rank, reaches a maximum at about 90 percent carbon, and then falls sharply. A series of experiments with various polynuclear compounds leads to the formulation of a reasonable explanation of these results.

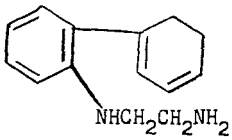
Several pure organic compounds were reduced with lithium in ethylenediamine (according to the usual procedure2/); these were chosen because they contained certain structures known to be present in coal.

Diphenyl ether underwent cleavage of the ether linkage; the product was mainly phenol (83 percent), but small amounts of benzene (1 percent), cyclohexene (3 percent), cyclohexane and cyclohexanone were formed. It is significant that phenol was the major product although excess lithium was used; it is evident that the aromatic ring in phenol is not reduced easily by lithium-ethylenediamine. Further evidence for this effect was obtained with dibenzofuran; this compound yielded chiefly o-cyclohexylphenol:



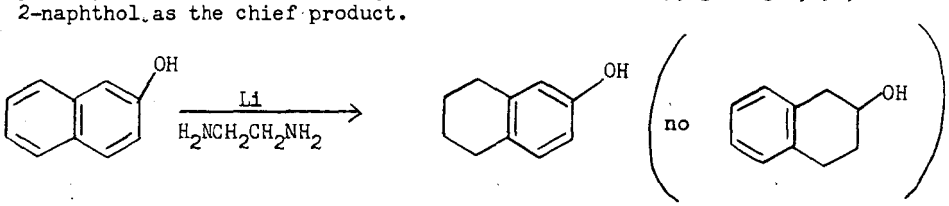
Dibenzofuran o-Cyclohexylphenol

Again, the phenolic part of the molecule is resistant to reduction while the unsubstituted ring reduces easily. Another product formed in small amount was a solid material with the empirical composition $C_{14}H_{19}N_2Cl$; low-voltage mass spectrometric analysis of this material showed that the molecular weight corresponded to a monomer of this empirical formula. This may be the hydrochloride of an amine with a structure such as:



Although the structure is uncertain, this does suggest that ethylenediamine may add to coal by replacing certain oxygen functions with an $-NHCH_2CH_2NH_2$ side chain.

2-Naphthol was treated with lithium-ethylenediamine in the usual way; as expected, the unsubstituted ring was reduced most easily, giving 5,6,7,8-tetrahydro-2-naphthol as the chief product.



None of the secondary alcohol which would result from the reduction of the phenolic ring was found in the reaction products.

These examples show that the presence of a phenolic group on a benzene ring inhibits the reduction of that ring by the lithium-ethylenediamine system. This inhibition may be due to the formation of a lithium salt of the phenol which is then protected from further attack, or to the development of a negative charge on the phenol. Since reductions in metal-amine systems proceed by the addition of electrons, the negative charge would prevent the further addition of electrons to the ring.

On the other hand, it was possible to show that large polynuclear molecules, with no phenolic substituent, are reduced quantitatively by lithium-ethylenediamine. Coronene was reduced almost completely to the perhydro compound, as shown in Figure 5.

The shape of the curve in Figure 1 may now be explained, to some extent at least, in the following manner. Lower rank vitrains are relatively soluble in ethylenediamine, so that they are readily attacked by the reducing system. However, they contain fairly large amounts of oxygen, which is present almost entirely as either ether or hydroxyl; it is known[2] that these groups are relatively resistant to lithium reduction. The higher rank vitrains are less soluble, and thus less amenable to the reagent; but they contain only a small amount of oxygen. The higher rank vitrains also contain many more aromatic structures than the low rank. In the course of the reduction, the soluble, low rank vitrains have added

hydrogen to their aromatic rings, giving cyclohexane or cyclohexene structures; in these vitrains, however, part of the lithium is consumed by attack on oxygen functions and by reaction with the solvent. Vitrains of higher rank also add hydrogen to aromatic structures; since they have more aromatic structures and fewer oxygenated groups, they offer more opportunity for addition of hydrogen. With the very highest rank vitrains, the insolubility of the material tends to overcome the large number of reducible structures, so that the hydrogen uptake decreases. The maximum in the curve is therefore quite reasonable. Further experiments with other vitrains will define the curve more clearly. It should be pointed out that since coal is not a pure compound, two vitrains of the same carbon content may have quite different structures; hence, a certain scatter in the experimental points is to be expected.

Given, Lupton, and Peover[4] have recently reduced a series of whole coals with lithium-ethylamine. The report of their work is quite brief, and exact experimental details are not known. Without further details, it is not possible to put the results of Given and the present results on a strictly comparable basis. However, it appears that lithium-ethylenediamine is more effective than lithium-ethylamine, especially for high rank materials.

Van Krevelen[5] has given a comprehensive discussion of the value of the atomic H/C versus O/C diagram, both in the study of coals and in the study of the changes which take place in coals upon chemical treatment. In most of the vitrain reductions reported here, the analytical results indicate that the reduced sample is higher in both hydrogen and oxygen than is the starting material; reduction has increased the numerical values of both the H/C and O/C ratios. Such a change can best be explained by a combination of hydrogenation and hydration. The exact pathway by which hydrogen is added is not certain;[2] presumably lithium atoms add to the unsaturated structures, and are then replaced by hydrogen atoms, which probably come from the amino groups of ethylenediamine.

In figure 2, each of the vitrains reduced is plotted on the H/C versus O/C diagram. They show the changes which can be attributed to hydrogenation and dehydration, as discussed above.

We have determined pyridine solubility at room temperature for six of the reduced vitrains. Figure 3 and Table IV show the solubilities of the starting and reduced materials. Vitrains in the 82-85 percent carbon range are moderately soluble; reduction causes a moderate increase in solubility. Probably this is due largely to the addition of hydrogen to aromatic rings, since hydroaromatic structures are generally more soluble than the corresponding aromatic molecules. Vitrains in the range of 89-90 percent carbon are of very limited pyridine solubility, because the molecules are fairly large and contain a number of aromatic rings; on reduction, considerable conversion to hydroaromatic structures takes place with a great increase in solubility. A 91 percent carbon vitrain is insoluble both before and after reduction. Here, the platelet size has increased to such a degree that even the highly reduced hydroaromatic types of structures are too large to be soluble.

A typical infrared spectrum is shown in figure 4. The reduced materials show increased C-H absorption at 3.5 μ, decreased absorption at 6.2 μ, and decreased absorption in the three bands at 11.5, 12.3, and 13.3 μ.

The ultraviolet spectra of the reduced materials show decreased absorption. Table V shows the change in extinction coefficient (K) for four of the vitrains; although the data are only semiquantitative, the large changes in K, particularly

for the Pocahontas vitrain, indicate a decrease in aromatic structures. Electron paramagnetic resonance measurements show that reduction causes a marked decrease in the number of free radicals. Table VI shows the change in free radical content of the vitrains after reduction. This data is consistent with a large decrease in aromatic structures.

Examination of scattered X-ray intensities of the reduced vitrains[6] revealed that extensive changes had occurred in the arrangement of carbon atoms. The most apparent major change was in the (002) reflections, the most prominent part of the vitrain patterns. At first glance at the intensity curves, one might presume that a new band has appeared in the angular range corresponding to spacings of 4 to 5 Å, in place of the (002) band at 3.6 Å. This change in the intensity patterns as a result of reduction can be considered mainly a displacement of the (002) band assuming that carbon atoms in the hydrogenated layers are now slightly displaced from planar positions forming buckled layers.

A striking result of the lithium reduction of vitrains is the great reduction in sulfur content, as can be seen from Table II. It is possible that this may be of value in desulfurizing coals on a large scale. Some indication of the way in which sulfur is eliminated was obtained by treating dibenzothiophene with lithium-ethylenediamine; the products are shown in Figure 6. It appears likely that the first attack on dibenzothiophene results in the splitting of a carbon-sulfur bond to give a substituted thiophenol; the unsubstituted ring is then reduced. As with phenols, the sulfhydryl group protects the ring to which it is attached.

In order to determine whether the lithium reduction proceeds to completion under our arbitrary conditions, a large batch of Bruceton vitrain was reduced. Some of this material was then reduced a second time and then a third time. Table VII gives the analytical data for these samples. It can be seen that the reduction on a large scale did not give as large a hydrogen pickup as the small scale reductions, and that the second and third reductions give little or no additional hydrogen uptake. The infrared spectra also showed essentially no changes. The X-ray diffraction patterns, however, did show that the second and third reductions caused further alteration in the vitrain structure. The nature of these changes is not known at the present time.

The reduced Bruceton vitrain was submitted to the Fischer-Schrader low temperature carbonization assay. The results are given in Table VIII. It can be seen that the reduced material forms less coke and more tar than does the starting vitrain. This is probably a reflection of the higher hydrogen content of the reduced vitrain. Table VIII also gives the ASTM free swelling index, and the composition of the coke formed.

Using 3 gram samples, the largest amount of reduction was achieved with the Pocahontas vitrain (44 atoms of hydrogen per 100 carbon atoms in the starting material - see Table III). We have observed that scaling down of the reaction results in greater reduction of the vitrain. Thus, when a one gram sample of Pocahontas vitrain was reduced (one third of the amounts of lithium and ethylenediamine used), 56 atoms of hydrogen were added per 100 carbon atoms in the starting vitrain. One may conclude that over half the carbon atoms in this particular vitrain are involved in carbon-carbon double bonds.

Experimental Procedures

a. Reductions

All operations described below were conducted under nitrogen in a dry box, or were rapidly performed with minimum exposure to air. In general, all grinding, crushing, and screening operations were performed in the dry box. Vitrains were crushed to -6 mesh and stored under nitrogen. Portions of approximately 8 grams were removed and ground to -60 mesh in a mortar and pestle. Grinding was continued overnight in a small ball mill (sometimes a steel mill, but usually a small borundum mill). The ball mill and its contents were given a brief drying (60° and 1 mm. for 1-2 hours) to facilitate screening through a 325 mesh sieve. Approximately 6 grams of -325 mesh material was dried to constant weight at 60° and 1 mm. All dryings in the vacuum oven were terminated by admitting nitrogen and quickly closing the containers as soon as the oven door was opened.

The apparatus consisted of a 500 ml. 3-neck flask with two vertical necks and one side-neck at an angle of 20°. A thermometer was inserted through the 20° angle neck. The center neck was fitted with a mercury-sealed double Hershberg tantalum wire stirrer. The third neck carried an adapter with two condensers, a short stoppered one through which the lithium was added, and a larger spiral condenser, with a mercury-sealed gas inlet tube. Three grams of vitrain prepared as above was quickly weighed in a weighing bottle. The apparatus was flushed with prepurified nitrogen (prepurified nitrogen was used throughout, except for the oxygen-free water dispenser, where ordinary nitrogen (0.2 percent oxygen) was used). Fifty ml. of ethylenediamine was added and the stirrer started. The vitrain was then added, followed by 100 ml. of ethylenediamine. This procedure insured complete dispersion of the vitrain and precluded formation of lumps of agglomerated material. The temperature was raised to 90° and addition of lithium begun. A total of 6.8 grams of lithium was added in the course of 3 hours while the temperature was maintained at 90-100°. Stirring was continued for 1 hour at 90-100°. The reaction mixture was then cooled in an ice bath and approximately 250 ml. of water was added with vigorous stirring. (All water used was boiled and then stored and dispensed under nitrogen.) The mixture was then diluted to approximately 3200 ml. and transferred to 235 ml. polyethylene bottles, centrifuged for 15 minutes at 2500 r.p.m. and 25° and allowed to stand overnight. The clear supernatant solution was decanted and discarded. The residue was transferred to a 1 liter erlenmeyer flask and heated on a wax bath at 125-135° in a stream of nitrogen to dryness. Drying was continued in a vacuum oven at 60° and 1 mm. This operation, by removing ethylenediamine and agglomerating the vitrain, facilitates the final washing with water. The dried residue was ground to -40 mesh and transferred to polyethylene centrifuge bottles. Repeated washing and centrifugation were continued until the washings had a pH of 8 (test paper). This required 7-10 centrifugations. The alkali-free residue was transferred to a 250 ml. erlenmeyer flask and dried in a wax bath at 125° in a stream of nitrogen. Drying was continued in a vacuum oven. The sample was then ground (small stainless steel mill) and screened to pass 325 mesh. It was then dried to constant weight at 60° and 1 mm. For analysis, the starting vitrain was dried again at the same time.

It should be noted that duplicate experiments checked quite closely.

Recoveries were much better than is indicated by the percent recovery figures in Table II. Manipulations in the dry box result in considerable loss. Presumably the recovery might be based on recovery in the 250 ml. erlenmeyer flask, since the

final removal from the flask, grinding, and sieving account for considerable loss. However, the weight in the 250 ml. flask is not recorded since complete dryness is not possible with a sample of large particle size.

b. Solubility Determinations

All samples were redried for 1 hour at 60° and 1 mm. One hundred mg. samples were weighed and transferred to 45 ml. glass-stoppered test tubes with the aid of 15 ml. of dry pyridine. The stoppers were fastened in place with rubber bands, and the test tubes were shaken on a mechanical shaker for 1 hour. The mixtures were then filtered onto 15 ml. fritted-glass filter crucibles (medium porosity). The residues were washed 3 times with 5 ml. portions of pyridine. This was found sufficient to insure that the last washing was colorless. The crucibles were dried to constant weight (95° and 1 mm.). This required 1 to 3 hours. The percent solubility reported was obtained by subtracting the weight percent of residue from 100.

c. Large scale reduction of Bruceton vitrain

Approximately 400 grams of Bruceton vitrain were ground to pass through 325 mesh and then dried at 60° and 1 mm. Four portions of the above material were reduced by lithium in ethylenediamine.

Vitrain (68 grams) was added to 3400 ml. of ethylenediamine in a 5-liter flask. The resulting slurry was stirred and heated to 90-100° before gradual addition of a total of 153 grams of lithium wire. The addition of lithium required 12 hours. The rate of addition was determined by hydrogen evolution as observed in a mercury bubbler. After addition of lithium, the mixture was stirred and heated at 90-100° for another hour. The reaction mixture was cooled in ice water and decomposed by the addition of one liter of water. This slurry was then diluted to a final volume of approximately 18 liters. The slurry was allowed to stand from one to four days; during this time the clear supernatant liquid was decanted and discarded. The residue was then centrifuged at 2700 r.p.m. in 250 ml. polyethylene bottles. The clear supernatant liquid was again decanted and discarded. The residue was transferred to a 1.5-liter erlenmeyer flask which was heated to 125-135° in a wax bath while a current of nitrogen was passed in; this treatment was continued until the product was almost dry. The drying was continued at 60° and 1 ml. in a vacuum oven. This drying operation was intended to agglomerate the recovered anthraxylon and facilitate further washing and removal of lithium salts. The dried residue was ground to pass through 40 mesh and then washed with water and centrifuged repeatedly until the washings were almost colorless and the pH was about 9. This required about ten washings. The residue was again freed of most of the moisture by heating to 125-135° in a stream of nitrogen. The product was ground to pass 100 mesh and drying was then completed at 60° and 1 mm.

Four batches of anthraxylon were reduced in this manner. The percentage recovered in each of the four batches was 89.2, 81.1, 85.1, and 77.8 percent.

It should be noted that the procedure for the last batch differed slightly in that lithium was added to the reaction mixture maintained at 95-105° instead of the usual 90-100°.

The products were submitted for infrared analysis by the potassium bromide pellet technique. The spectra of the four batches were sufficiently similar to each other and to previous reductions of Bruceton anthraxylon to justify mixing them to

make one large sample. The batches were combined, ground to pass 325 mesh, and again dried at 60° and 1 ml. A total of 228 grams of reduced Bruceton anthraxylon was produced.

The material described above is called the first reduction in Table VII. Twelve grams of this material was reduced again in a similar manner; this is the second reduction in Table VII, 8.33 g. being recovered. For the third reduction, 8.04 g. was reduced, 6.11 g. being recovered.

This work was carried out as part of a cooperative agreement between the Bureau of Mines and the Union Carbide Corporation.

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Table I.- Vitrain samples used in 3-gram runs

Run No.	
7R-80	Rock Springs Nos. 7, 7½, 9, and 15 coal beds, Superior, Sweetwater County, Wyoming.
7R-76	Bruceton, Pittsburgh Bed, Allegheny County, Penna.
7R-69	Pond Creek Bed, Majestic Mines, Pike County, Kentucky.
7R-73	Powellton Bed, Elk Creek No. 1 Mine, Logan County, W. Va.
7R-71	Sewell Bed, Marianna Mine, Wyoming County, W. Va.
7R-75	Pocahontas No. 3 Bed, Stephenson, Wyoming County, W. Va.
7R-72	Anthracite, Dorrance Mine, Lehigh Valley Coal Company, Luzerne County, Penna.
7R-79	Madagascar flaky graphite.

Table II.- Microanalysis of vitrains before and after reduction (dried at 60°C and 1 millimeter)

Name	Number*	Carbon	Hydrogen	Nitrogen	Sulfur	Ash	Oxygen (diff.)	Percent recovery
Rock Springs	80	76.25	5.76	2.04	0.87	0.86	14.22	
	80A	72.78	7.21	5.20	0.33	2.00	12.48	40.3
Bruceton	76	80.65	5.42	0.96	1.13	2.27	9.57	
	76A	75.73	6.93	3.81	0.29	2.82	10.42	69.9
Pond Creek	69	82.63	5.15	1.15	0.69	2.25	8.13	
	69A	77.35	7.24	3.05	0.23	2.19	9.94	61.5
Powellton	73	83.63	5.00	1.59	0.46	1.52	7.80	
	73A	79.15	6.58	2.95	0.15	1.94	9.23	76.1
Sewell	71	87.29	5.03	0.97	0.63	2.31	3.77	
	71A	81.42	7.33	2.34	0.19	2.66	6.06	64.3
Pocahontas	75	87.66	4.35	1.49	0.58	2.42	3.50	
	75A	82.04	7.46	2.09	0.12	3.65	4.64	85.5
Anthracite	72	89.02	2.55	1.08	0.60	2.31	4.44	
	72A	81.70	4.93	1.91	0.07	1.96	9.43	71.7
Graphite	79	98.93	0.24	0.18	0.00	0.00	0.65	
	79A	85.76	2.96	3.92	0.00	0.00	7.36	104.0

* A indicates reduced material.

Table III.- Microanalyses of vitrains before and after reduction
(Moisture, ash, sulfur, and ethylenediamine-free basis)

Name	No.*	Carbon	Hydrogen	Nitrogen	Oxygen (diff.)	Grams hydrogen added per 100 g. starting MASF vitrain	Grams water added per 100 g. starting MASF vitrain	Atoms hydrogen added per 100 carbon atoms	Molecules water added per 100 carbon atoms
Rock Springs	80	77.58	5.86	2.08	14.48				
	80A	77.22	6.91	(2.08)	13.79	1.16	-0.69	17.7	-0.6
Bruceton	76	83.46	5.61	1.81	9.12				
	76A	80.05	6.84	(1.81)	11.30	1.18	3.08	16.9	2.5
Pond Creek	69	85.12	5.30	1.18	8.40				
	69A	81.00	7.07	(1.18)	10.75	1.75	3.33	24.5	2.6
Powellton	73	85.32	5.10	1.61	7.97				
	73A	82.13	6.50	(1.61)	9.75	1.37	2.51	19.2	2.0
Sewell	71	89.94	5.18	1.00	3.88				
	71A	85.20	7.35	(1.00)	6.46	2.20	3.36	29.1	2.5
Pocahontas	75	90.37	4.47	1.54	3.62				
	75A	85.89	7.67	(1.54)	4.90	3.40	1.82	44.8	1.3
Anthracite	72	91.68	2.62	1.11	4.59				
	72A	84.21	4.87	(1.11)	9.81	1.90	6.97	24.7	5.1
Graphite	79	98.93	0.24	0.18	0.65				
	79A	89.77	2.04	(0.18)	8.01	0.98	9.22	11.8	6.2

* A indicates reduced material.

Table IV.- Solubility of reduced anthraxylons in pyridine
at room temperature

	% C (maf)	% Soluble, untreated	% Soluble, reduced	% Increase in solubility
Bruceton	82.50	21.4	30.7	43
Pond Creek	84.53	13.2	38.1	113
Powellton	84.88	20.9	36.6	75
Sewell	89.38	2.5	90.9	3636
Pocahontas	89.85	3.9	62.5	1502
Anthracite	91.16	0	0	0

Table V.- Ultraviolet absorption of vitrains

Name	No.	% C	Specific extinction coefficient K (liters/g. cm.) at 4000 A original	reduced	K reduced / K original
Bruceton	76A	82.50	10.1	8.0	79
Powellton	73A	84.88	12.9	5.3	41
Sewell	71A	89.38	13.5	6.8	50
Pocahontas	75A	89.85	26.9	4.6	17

Table VI.- Free radical content of vitrains

Name	No.	% C	Free radical concentration (arbitrary units) original	reduced
Harmatten	70A	77.20	112600	54500
Bruceton	76A	82.50	207000	89300
Powellton	73A	84.88	270000	77200
Sewell	71A	89.38	635000	72000
Anthracite	72A	91.16	2400000	2186000

Table VII.- Repeated reduction of Bruceton vitrain

Run No.	Treatment	C	H	N	S	O (diff.)	Li
		(Ash and ethylenediamine-free basis)					
7R-60	Starting material	81.52	5.32	1.13	1.05	10.99	trace
7R-60F	First reduction	79.08	6.03	(1.13)	0.30	13.46	0.30
7R-65	Second reduction	75.14	6.09	(1.13)	0.08	17.56	-
7R-67	Third reduction	79.60	5.92	(1.13)	0.05	13.30	0.23

Table VIII.- Fischer-Schrader low temperature carbonization assay (500° C.) and ASTM free-swelling index (823° C.)

	Bruceton vitrain 7R-60	Reduced Bruceton vitrain 7R-60-F
Coke	78.3	63.5
Tar	10.9	22.2
Water	6.8	9.4
Light oil	0.51	0.77
Gas	3.5	4.1
F.S.I.	7½	5½
Coke, percent	70.2	52.4
Composition of coke		
C	84.54	83.35
H	3.64	3.64
N	1.81	3.77
S	0.83	0.21
Ash	2.69	3.87

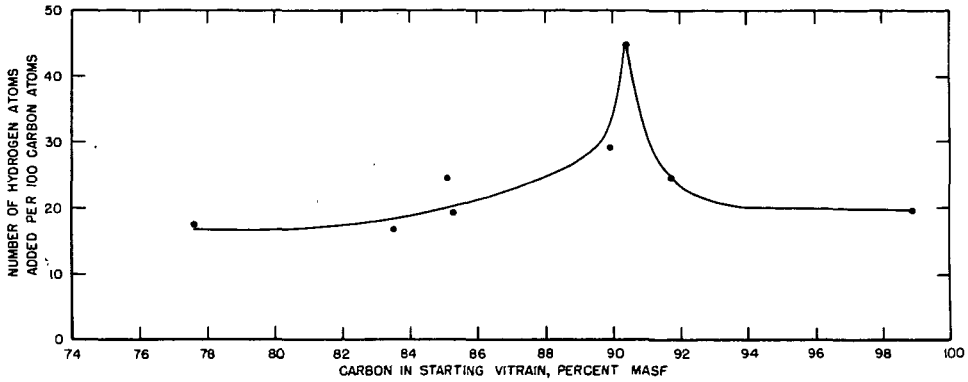

Figure 1.-Hydrogen uptake of vitrains.

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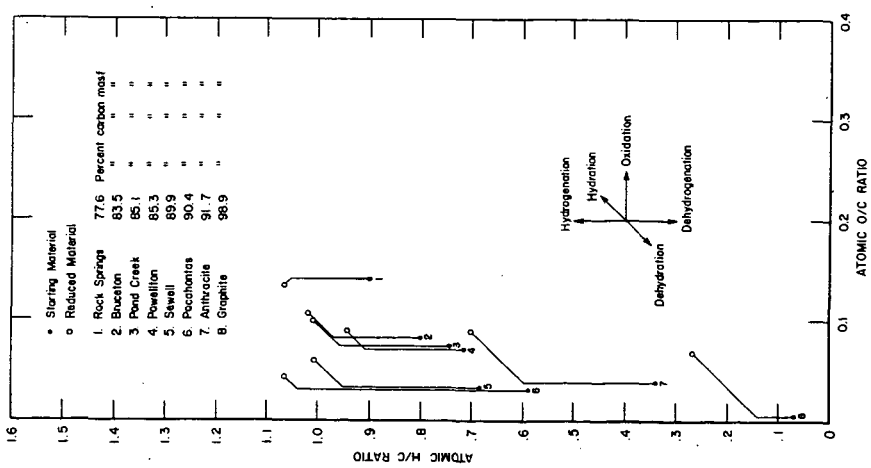

Figure 2.-H/C vs. O/C diagram for vitrains.

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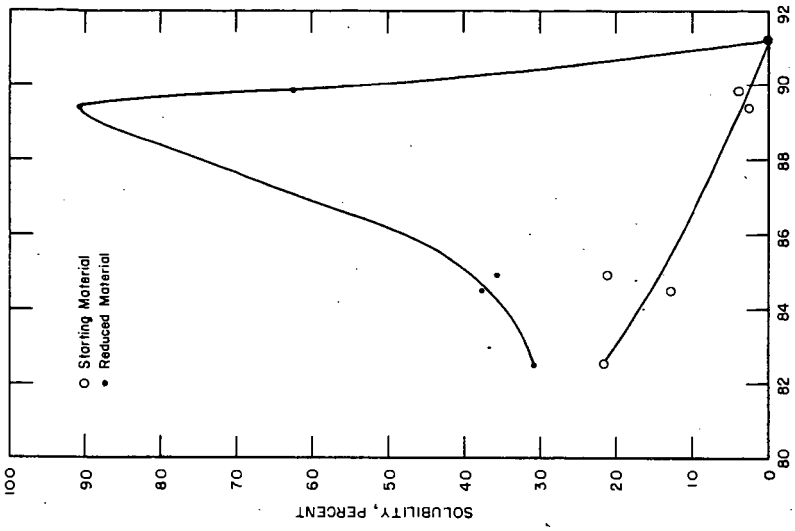

Figure 3 - Solubility of vitrains in pyridine at room temperature.

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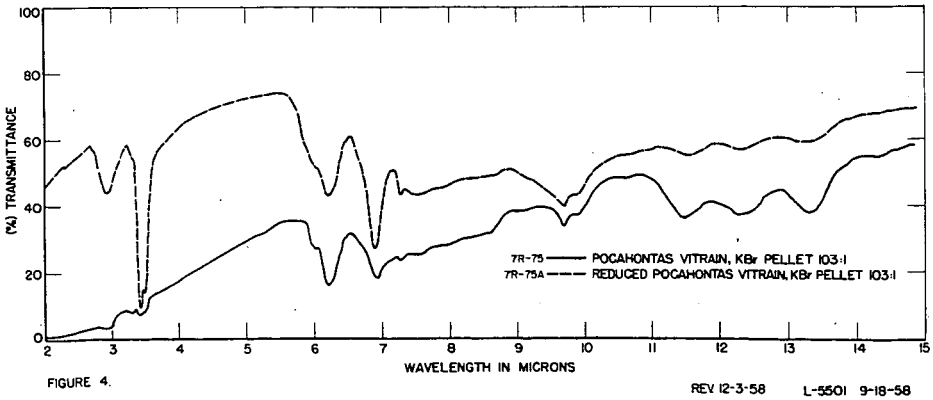

FIGURE 4.

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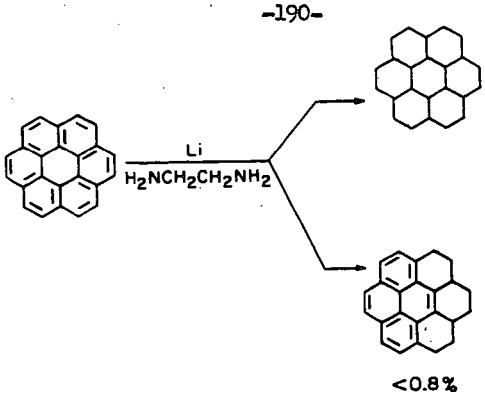

FIGURE 5.- REDUCTION OF CORONENE

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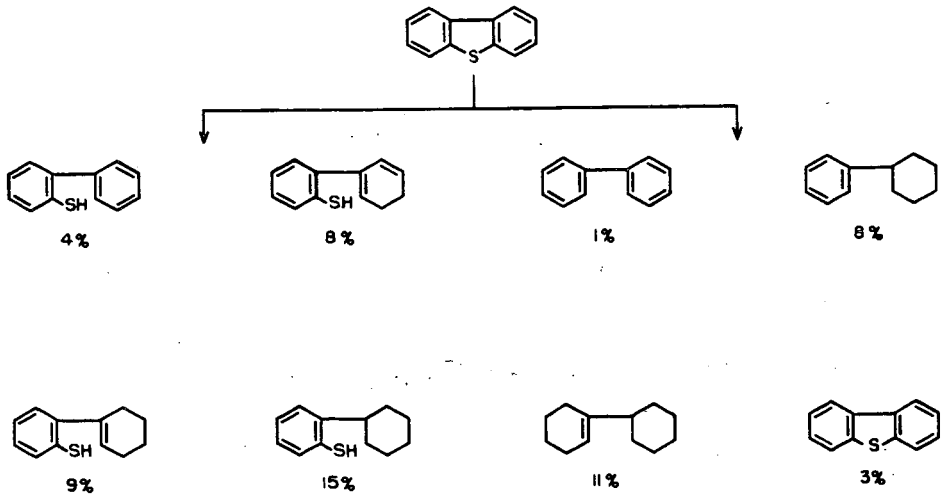

FIGURE 6.

L-5528