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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 CO₂ 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/cm² 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/cm² 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/cm². 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/cm² 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 ₂ O | | VM | | FC | | Ash | | Heating Value | | H ₂ | | C | | N ₂ | | O ₂ | | S | | Atomic Ratio H/C |
|-------------------|---------------------|------------------|------|------|------|--------|-----|--------|------|---------------|------|----------------|---|---|---|----------------|---|----------------|---|---|---|------------------|
| | | Airdry % | % | % | % | % | % | Btu/lb | % | % | % | % | % | % | % | % | % | % | % | % | % | |
| 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 | 73.0 | 13.8 | 12,300 | 2.7 | 65.0 | 18.5 | 1.0 | 0.50 | | | | | | | | | | | |
| " | 600°C " | 0.3 | 12.0 | 69.4 | 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 | Typical | 0.4 | 0.5 | 90.4 | 9.1 | 11,810 | 0.3 | 88.9 | 1.7 | 0.5 | 0.04 | | | | | | | | | | | |
| Rocky Mtn. Region | Blast Furnace Cokes | 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 | 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 | 3.5 |
| 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 CO₂, 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 breeze 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 breeze 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 | | | | Activation Energy, kcal/mole |
|-------------|------------------------------|-----------------------------|------|-------|-------|------------------------------|
| | | 700 | 800 | 900 | 950 | |
| 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 pycnometer 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 pycnometer was then completely filled with methanol and the bottle placed in a water bath at $30^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$. 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 $30^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ 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, Quichi and Hirose (7) in the cases of carbonization of high rank bituminous coals and of cellulose and glucose. The temperature discrepancy may possibly 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 Meggs (13).

Meggs estimates that the methanol molecule will occupy 16^2 \AA 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-XRD5 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 ccke 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 breeze.

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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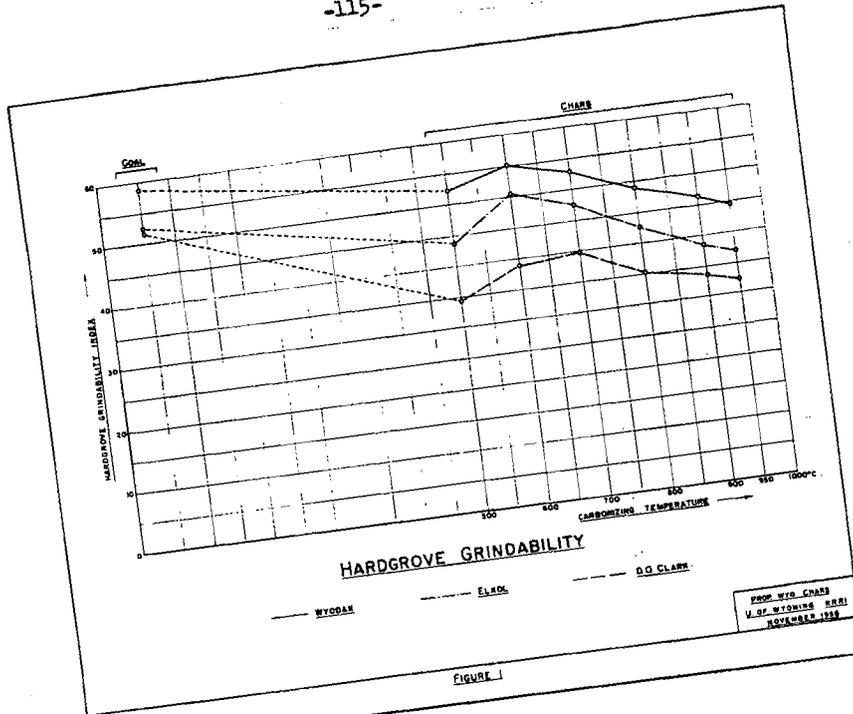


FIGURE 1

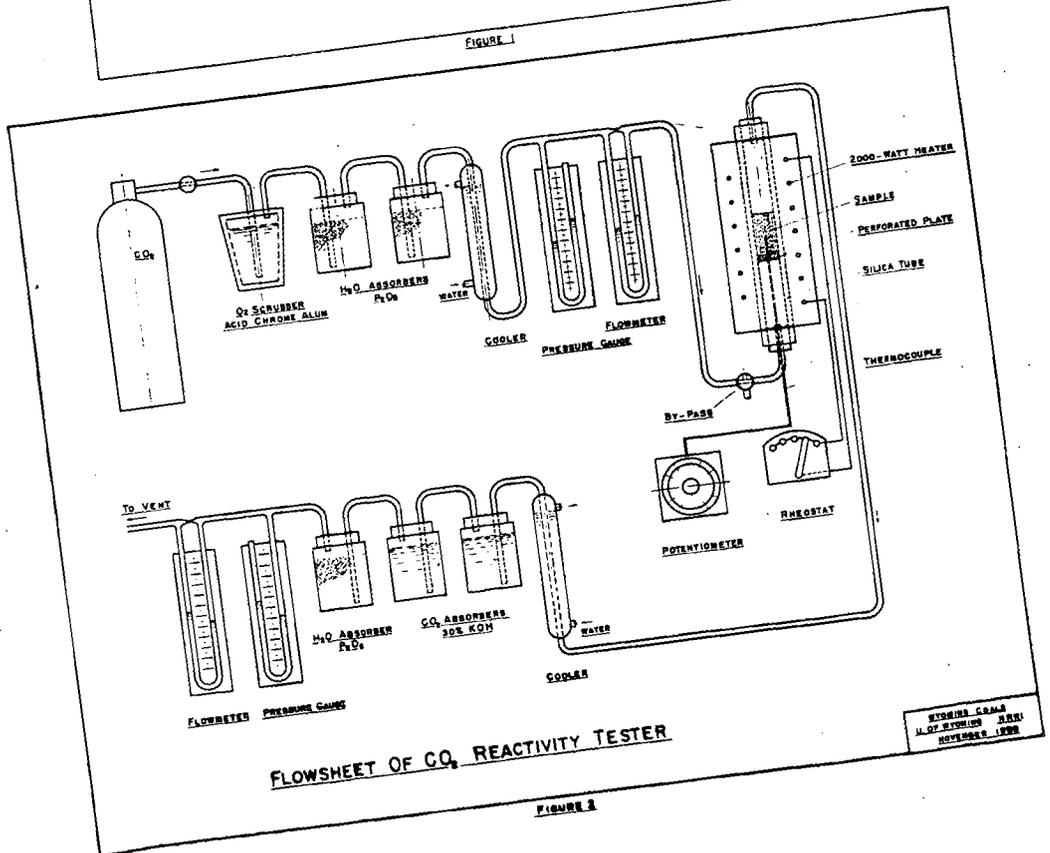
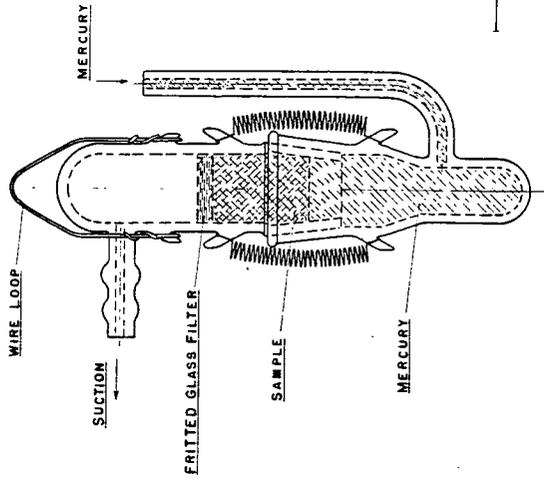


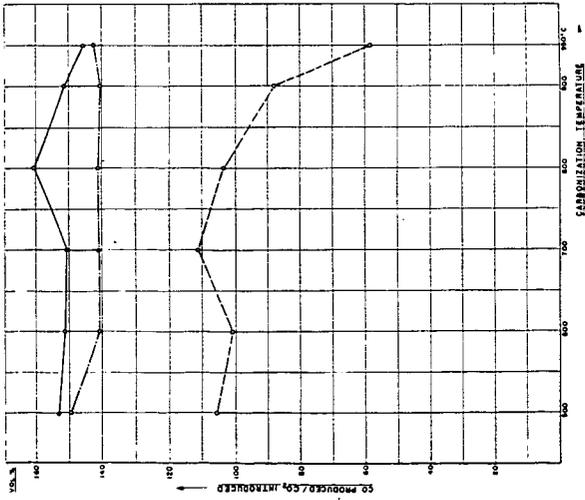
FIGURE 2



DENSITY BOTTLE
FOR MERCURY DISPLACEMENT

PROP. WYO. CHARS
U. OF WYOMING NRI
OCTOBER 1938

FIGURE 4



REACTIVITY OF CHARS WITH CO₂ AT 950°C

— WOODS - - - ELVOS ···· O.C. CLARK

PROP. WYO. CHARS
U. OF WYOMING NRI
MARCH 1938

FIGURE 3

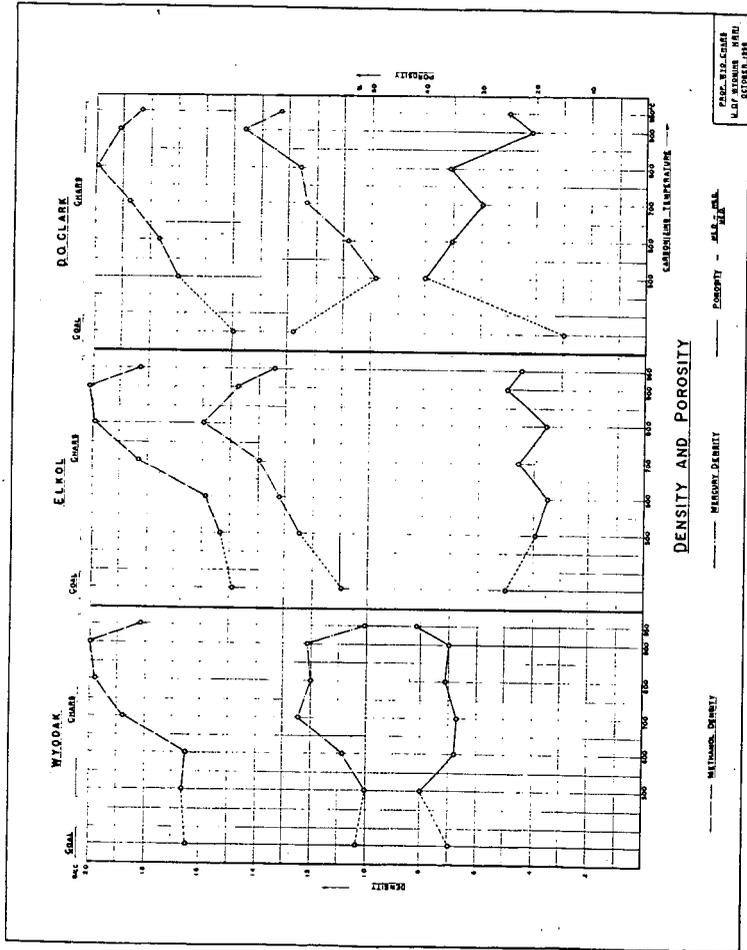


FIGURE 5

