COAL AND CHAR TRANSFORMATION IN HYDROGASIFICATION — LIGNITE TO LOW-VOLATILE BITUMINOUS COAL

David M. Mason

Institute of Gas Technology
3424 S. State Street
Chicago, Illinois 60616

In a previous paper we discussed the behavior of a high-volatile A bituminous coal from the Pittsburgh No. 8 seam in the hydrogasification process (5). This study of the petrographic and physical properties of the coal and chars at different stages of the process had two objectives:

1. To find out as much as possible about what happens to the coal and how it behaves in the process.

2. To develop a correlation between the petrographic properties of the coals and their suitability for hydrogasification.

In the present paper the investigation has been extended to coal ranks ranging from lignite to low-volatile bituminous.

As noted previously, bituminous coal is treated in three successive stages:

1. Pretreatment with air at about 800°F to destroy the agglomerating power of the coal.

2. First-stage hydrogasification at 1200°-1300°F with pretreated coal as the feed.

3. Second-stage hydrogasification at 1700°-2000°F with first-stage residue as the feed.

However, in the present work the hydrogasification processing method was different from that previously reported. In that study, the first and second stages were conducted separately in different moving-bed runs. This time the two stages were combined in a single operation. The first stage was limited to a period of a few seconds while the pretreated coal dropped in free fall through the rising gas in the upper 9 ft of the reactor tube. The second-stage hydrogasification occurred in a fluid bed in the lower 3-4 ft of the reactor tube. With this processing regime it was not possible to obtain samples of char between the two stages. Most of the char residues investigated here were from runs in which the hydrogen fed was 25-30% of the stoichiometric amount required for complete gasification, and the steam comprised 50% of the steam-hydrogen mixture.

The sources and ranks of the coals processed are shown in Table 1. Work is continuing on two or three other coals.

Our petrographic methods have been described previously (5). The only change is that a 40X Achromat objective was used for both maceral analysis and reflectance determination. Surface areas were determined by Numec Instruments and Controls Corporation with carbon dioxide adsorption at 198°K.

Table 1. COAL SOURCES AND RANKS

Seam	Mine	County and State	Rank
Pocahontas No. 4	Stotesbury No. 10	McDowell County, West Virginia	Low-volatile bituminous
Sewell Seam (Lower Kittanning)	Lochgelly	Fayette County, West Virginia	Medium-volatile bituminous
Pittsburgh No. 8	Ireland	Marshall County, West Virginia	High-volatile A bituminous
W. Va. No. 5 Block	Kanawha	Randolph County, West Virginia	High-volatile A bituminous
Ohio No. 6	Broken Arrow	Coshocton County, Ohio	High-volatile B bituminous
Indiana No. 6	Minnehaha	Sullivan County, Indiana	High-volatile C bituminous
Illinois No. 6	Crown	Montgomery County, Illinois	High-volatile C bituminous
Colorado Subbituminous	Eagle	Weld County, Colorado	B subbituminous
N. Dakota Lignite	Glenharold	Mercer County, North Dakota	A lignite

HIGH-VOLATILE BITUMINOUS COALS

The high-volatile bituminous coals ranged in rank from an Illinois No. 6 high-volatile C coal with a mean maximum vitrinite reflectance of 0.45% to a West Virginia No. 5 Block high-volatile A coal with a mean maximum vitrinite reflectance of 0.81%. All of these coals required pretreatment of about the same severity. The effect of pretreatment on any of these coals is not noticeably different from that described previously for the Pittsburgh No. 8 coal – mainly inflation to cenospheres, disappearance of most of the exinite, development of a high-reflectance skin differing in thickness from particle to particle (Figure 1), and a varying lesser increase in reflectance (over that of the coal) in the interior of the particles. Particle structure appears quite similar, although perhaps quantitative determinations of cell wall thickness and vesicle size would show differences.

Several different types of particle structures are found in the char residues after hydrogasification (Figure 2). A fine-textured foam structure is prevalent in the residue from the highest rank coal (West Virginia No. 5 Block) but becomes less frequent with decreasing rank until it is virtually absent in the residue from the Illinois No. 6 coal (Figure 3). Otherwise, the residue particles from the different high-volatile bituminous coals appear quite similar in form. Also, there is little difference in reflectance; the mean reflectance of the residue from the lowest rank coal (Illinois No. 6) does not differ significantly from that of the Pittsburgh No. 8 (Table 2).

Table 2. REFLECTANCE OF HYDROGASIFICATION RESIDUES

Coal	Pittsburgh No. 8	Illinois No. 6	Colorado Subbituminous	N. Dakota Lignite
Run No.	HT-126	HT-155	HT-184	HT-139
Reflectance in Oil, %	Distribution of Reflectance Readings, %			
0-0.9	--	--	--	6.3
1.0-1.9	--	0.4	2.6	19.8
2.0-2.9	2.2	1.3	22.6	47.8
3.0-3.9	22.7	17.1	59.1	20.7
4.0-4.9	48.4	62.8	12.2	4.5
5.0-5.9	22.9	16.2	3.5	0.9
6.0-6.9	3.0	1.3	--	--
7.0-7.9	0.8	0.8	--	--
8.0-8.9	--	0.4	--	--
No. of Readings	362	234	115	111
Avg Reflectance in Oil, %	4.49	4.45	3.36	2.44
Standard Deviation, %	0.80	0.71	0.70	0.90

There is some difference in the anisotropy of the particles. The residue from the Illinois No. 6 coal exhibits very little anisotropy when observed with crossed polars. Less than half of the particles show any anisotropy, and these only in small areas (Figure 4a). Anistropy of the residue increases with coal rank. Thus in the residue from the West Virginia No. 5 Block coal most of the particles show at least a little anisotropy, while some, especially those with the foam structure, are predominantly anisotropic except for the pretreatment skin (Figure 4b). The greater degree of anisotropy and the greater prevalence of foam structure in the residue from the higher rank coals indicates that a greater degree of fluidity is attained in the interior of these particles when the coal is rapidly heated in the hydrogasification reactor.

Surface areas of 503 and 463 sq m/g were obtained on the residues from Pittsburgh No. 8 and Illinois No. 6 coals, respectively. The surface area of the original Pittsburgh No. 8 coal was 131 sq m/g; that of the Illinois No. 6 coal may have been somewhat higher, but was not measured. After pretreatment the Pittsburgh No. 8 coal had a surface area of 148 sq m/g. Thus most of the increase in the surface area occurred during hydrogasification.

Very few differences were evident in processing characteristics among the high-volatile bituminous coals, in either pretreatment or hydrogasification. However, our data indicate that the pretreatment yield increases with the rank of the vitrinite. This is shown in Table 3, where the coals are listed in order of increasing vitrinite reflectance. Yields were calculated by two methods for runs from which the char was either free-flowing or only very lightly caked in a laboratory agglomeration test (2). In one method the yield of moisture- and ash-free coal was calculated from the measured total char yield and the feed and product analyses. (Runs in which the material balance recovery was less than 85 or greater than 100% were excluded.) In the other method, the yield was calculated from the proximate analyses of feed and product, with the assumption that the amount of fixed carbon did not change. A similar calculation based on ash content is sometimes used, but is distrusted here because of the tendency for dense, high-ash particles to accumulate in the pretreatment fluid bed.

The yields from the second method are consistently less than those from the pilot plant data, but both show a trend of increasing yield with rank. The yield, no doubt, also depends on maceral composition because the yield from inertinite is expected to be greater than that from vitrinite, while that from exinite is expected to be much less. The two higher rank coals have, on the average, more of both exinite and inertinite than the two low rank coals. Because the higher exinite content counterbalances the higher inertinite content, it appears that the higher average yield of the two higher rank coals can be attributed entirely to the higher ranks of their vitrinites.

<u>HIGH-RANK BITUMINOUS COALS</u>

The pretreated Pocahontas No. 4 coal showed the usual development of oxidized pretreatment skin, but very little or no vesicle formation (Figure 5) and no significant loss of volatile matter. The pretreatment skin extends into many cracks. Many additional fine cracks were present in many particles. A high rate of attrition was observed in the pretreatment processing, which we attributed to the development of these cracks.

Table 3. YIELDS FROM PRETREATMENT OF HIGH-VOLATILE BITUMINOUS COALS

Coal	Reflectance,[a] %	Maceral Content, Vol %		No. of Pretreatment Runs	Yield of Pretreated Coal, % MAF	
		Exinite	Inertinite[b]		From Pilot Plant Data[c]	From Proximate Analysis[d]
Illinois No. 6	0.45	3	11	7	78.8	82.65
Indiana No. 6	0.48	4	6	6	80.8	80.0
Ohio No. 6	0.53	6	14	2	78.8	83.4
Pittsburgh No. 8	0.68	3	13	6	82.9	89.4
W. Va. No. 5 Block	0.81	10	21	3	82.1	84.7

a. Mean maximum reflectance of vitrinite in oil.

b. Including semifusinite.

c. Two runs on Illinois coal and two runs on Pittsburgh seam coal were excluded because of poor material balances.

d. Fixed carbon assumed to remain unchanged.

Pretreatment of the Sewell seam coal, which is on the borderline between medium- and low-volatile rank, did result in vesicle formation (Figure 6), although not to as great an extent as in the high-volatile coals. Fine cracks were also observed in the pretreated particles of this coal, and a high rate of attrition occurred in the pretreatment processing.

Hydrogasification of these two coals was difficult because the reactor plugged with agglomerating coal particles. To investigate this, agglomerated particles of residue from the Pocahontas coal were examined petrographically. With crossed polars, the pretreatment skin was readily identified. Particles without skins and the interiors of particles with skin were anisotropic and had a foam structure. Agglutination or cementing of particles was done by this foam material only. It was obvious (Figure 7) that the foam material was supplied not only by the particles that had undergone little or no pretreatment, but also by particles with holes or breaks in the skin. It appears that the pretreatment skin can be broken and the contents discharged to the outside of the particle as a result of the simultaneous development of pressure and fluidity in the interior of the particles.

Only a small fraction of the residue from the Pocahontas coal – , probably that derived from inertinite – does not have a foam structure. The residue from the Sewell coal also has a large amount of foam structure, but has an appreciable, perhaps predominant, amount of material with vesicular structure similar to that of the residue from high-volatile bituminous coals. This can be attributed to the greater amount of devolatilization that occurred in the pretreatment of the Sewell coal. Some particles of the residue from the latter coal display the discharge of foam material from the inside of the particle that was observed in the residue from Pocahontas coal. However, the smaller proportion of foam structure in the Sewell residue indicates that its agglomerating tendency should be appreciably less than that of the Pocahontas residue.

SUBBITUMINOUS COAL AND LIGNITE

The residues from lignite and subbituminous coal hydrogasified without pretreatment have a different type of pore structure (Figures 8 and 9). The pores are typically lenticular in cross section rather than rounded, but rounding and expansion of the pores in some areas indicate the development of a greater degree of plasticity in some entire particles and parts of others. More of this pore expansion seems to have occurred in the lignite than in the subbituminous coal. This pore expansion is probably caused by the greater fluidity conferred by the presence of exinite or resinite or both (1,4); these are somewhat more plentiful in the lignite than in the subbituminous sample.

Average reflectance of these residues is substantially less than that of residues from the bituminous coals (Table 2), with that from lignite being least. The surface area of the residue from the lignite, 4[illegible] sq m/g, is in the range of the values obtained in the residues from the high-volatile bituminous coals.

CONCLUSIONS

Petrographic study of the feed coals and chars at different stages of processing has been fruitful in several ways. The detection of contamination of a nonagglomerating coal by a coking coal explained some anomalous processing results, although the examination was not early enough to avoid their occurrence. Agglomeration of pretreated high rank bituminous coals was shown to result from the discharge of fluid material from the interior of pretreated particles as well as from the fluidity of the few particles that escaped pretreatment. Lack of anisotropy in the residue chars from lignite, subbituminous coal, and pretreated high-volatile C coal indicated that little or no fluidity developed in these coals, and accounts for the successful processing of lignite and subbituminous coal without pretreatment. Increasing amounts of anisotropy, indicating development of fluidity, were observed in chars from the higher rank bituminous coals. Increased anisotropy and a very different char particle structure were found when a high-volatile A bituminous coal was fed without pretreatment (5). These differences in structure may become important if process development makes it possible to feed the coal without pretreatment. Because graphitization at higher temperature occurs only when the char has passed through a fluid stage with resulting anisotropy (3), the degree of anisotropy or lack of it may indicate differences in the electrical characteristics of the char; this may affect its behavior in the electrothermal gasification process for production of hydrogen.

With respect to the second objective of our work — the development of a correlation between the petrographic properties of a coal and its suitability for hydrogasification — we find:

1. Exinite is largely lost in pretreatment and, therefore, is of value only if the coal can be processed without pretreatment.

2. High-reflectance inertinite is believed to behave as an unreactive diluent in at least the first stage of the hydrogasification process. We have no information on the degree of activity of semifusinite.

3. Very little difference was evident in the processing characteristics of the high-volatile bituminous coals in either pretreatment or in hydrogasification. The yield of coal from pretreatment increased with rank of the vitrinite; 3 - 6% increase in yield was noted when the reflectance-in-oil of the vitrinite increased from an average of 0.46% for two high-volatile C coals to an average of 0.74% for two high-volatile A coals.

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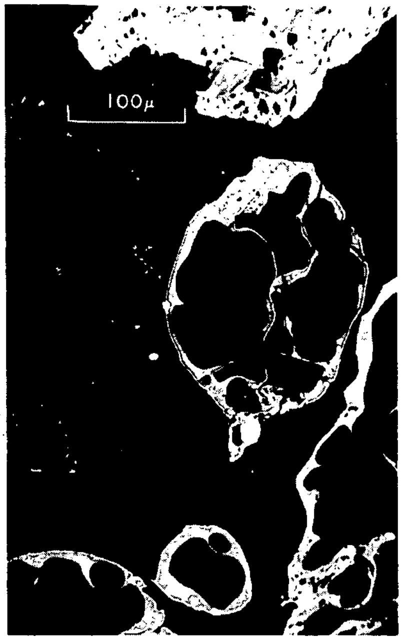


Figure 1. PRETREATED ILLINOIS No. 6 COAL

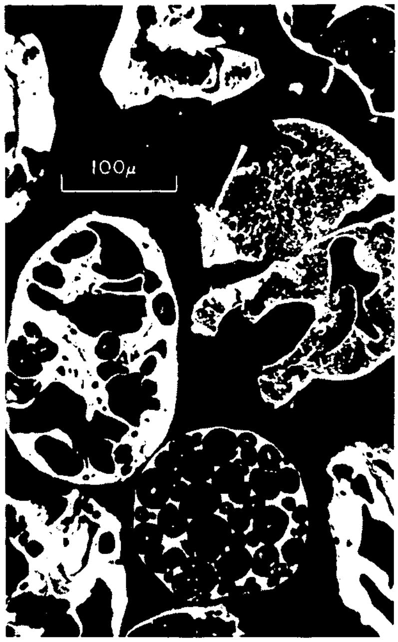
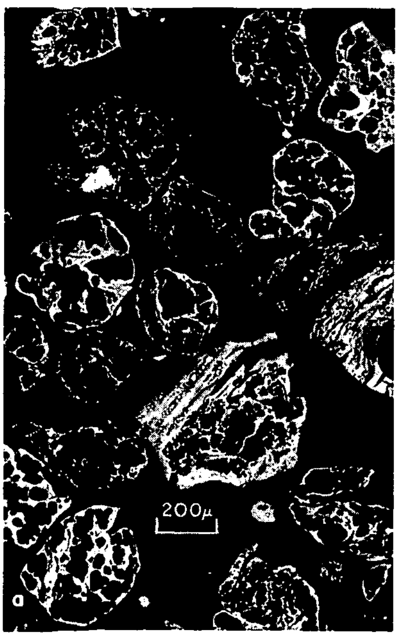


Figure 2. TYPES OF CHAR STRUCTURE IN RESIDUE FROM W.VA. NO. 5 BLOCK COAL



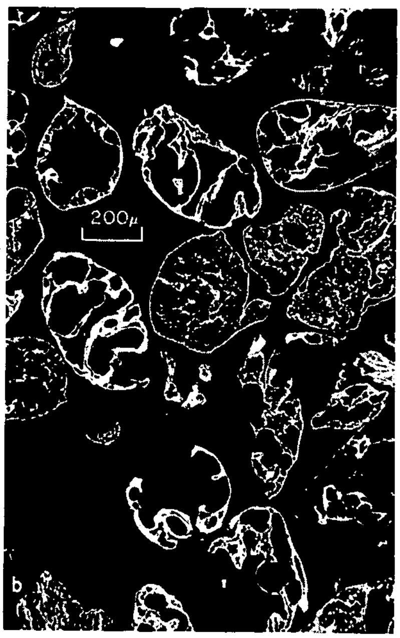


Figure 3. RESIDUE CHARS FROM a) ILLINOIS NO. 6 COAL AND b) W. VA. NO. 5 BLOCK COAL

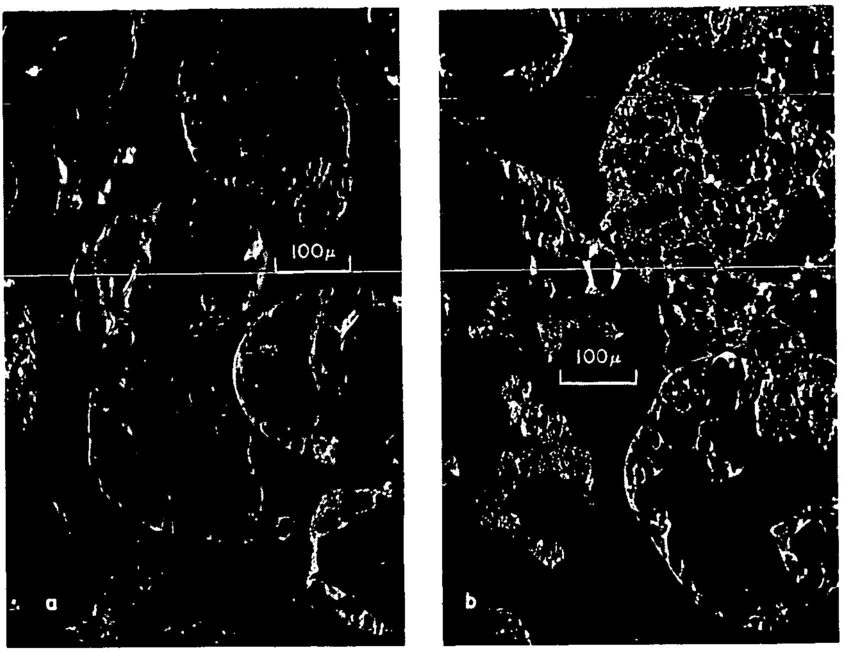


Figure 4. ANISOTROPY OF RESIDUE CHARS OBSERVED WITH CROSSED POLARS. a) FROM ILLINOIS NO. 6 AND b) FROM W. VA. NO. 5 BLOCK COAL

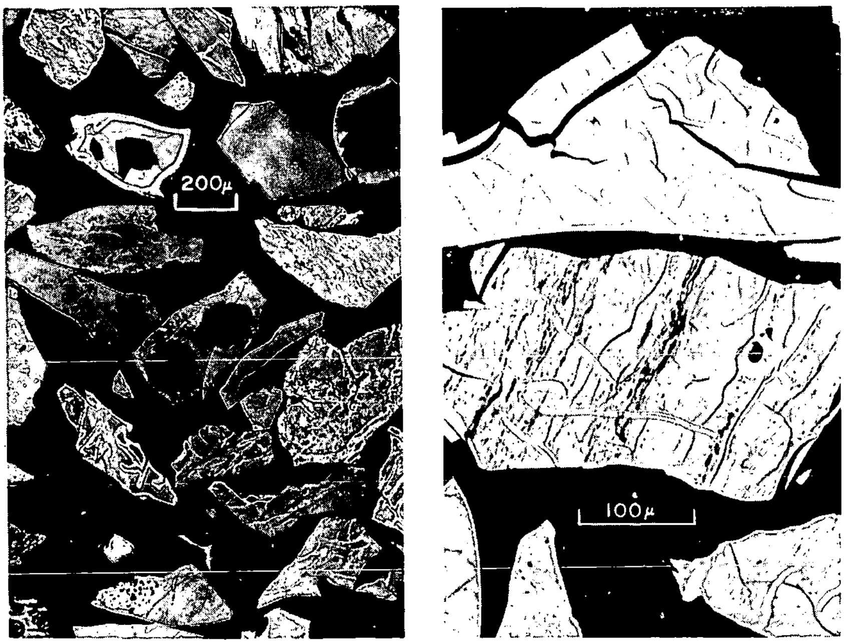


Figure 5. PRETREATED POCAHONTAS NO. 4 COAL

Figure 6. PRETREATED SEWELL SEAM COAL

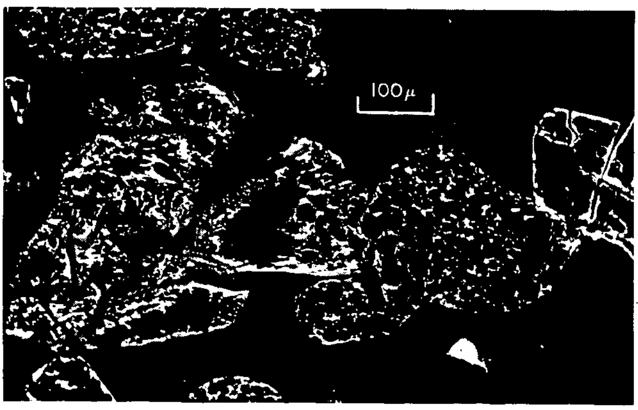


Figure 7. RESIDUE CHAR FROM POCAHONTAS No. 4 COAL OBSERVED WITH CROSSED POLARS

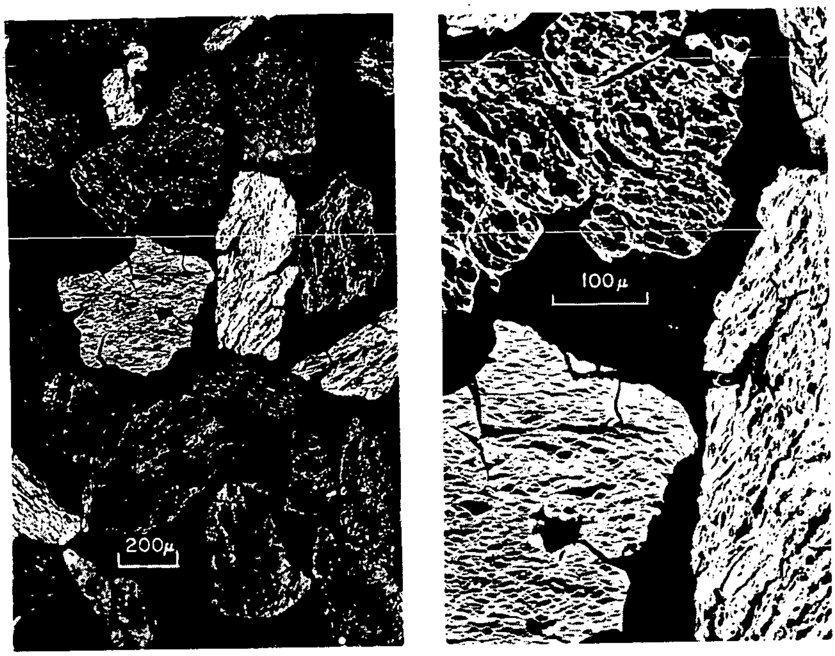


Figure 8. RESIDUE CHAR FROM NORTH DAKOTA LIGNITE

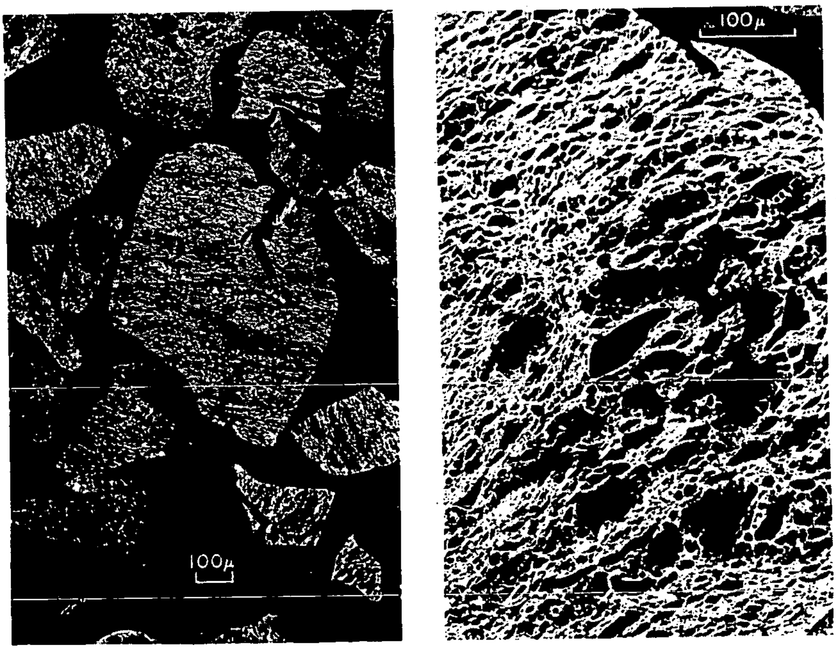


Figure 9. RESIDUE CHAR FROM COLORADO SUBBITUMINOUS