Destruction of the Caking Quality of Bituminous Coal in a Fixed Bed

S. J. Gasior, A. J. Forney, and J. H. Field

U. S. Bureau of Mines, 4800 Forbes Avenue
Pittsburgh 13, Pennsylvania

INTRODUCTION

Production of a high-Btu pipeline gas from coal appears to have great potential for consuming coal in large quantities. Fixed-bed pressure gasification with steam and oxygen is highly attractive for the production of high-Btu gas because a gas with a high methane content is made with comparatively low oxygen requirements. However, strongly caking coals cannot be gasified efficiently in a fixed bed because they agglomerate and fuse when heated through their plastic range. This would render a fixed-bed gasifier inoperable. Most coals found in the East and Midwest, where the largest markets for pipeline gas exist, are highly caking.

Numerous commercial processes[1, 2, 3] have produced a noncaking fuel from bituminous coal for many years; however, each was developed for a specific purpose other than for fixed-bed gasification, and was not particularly suited as a preliminary to gasification. Consequently an experimental pilot plant program was initiated by the Bureau of Mines to develop a process for pretreating a caking bituminous coal specifically for fixed-bed gasification. Based upon the general knowledge that thermal or oxidative treatment or a combination of the two destroys the caking property of coal, a process was envisioned which would utilize the above. An integrated pretreatment and gasification scheme appeared advantageous whereby all or part of the feed gases to be fed to the gasifier, or the hot, raw product gas could be used in the pretreatment, and the volatile matter evolved during pretreatment could be returned as fuel to the gasifier.

Use of thermal pretreatment in an oxidizing atmosphere for treating a highly caking coal of granular or small lump size in a fixed bed presented difficult problems. To make particles of this size nonagglomerating, the treatment would have to be drastic enough not only to affect the surface, but also the interior. Furthermore, because the coal expands on heating, compaction in a fixed bed would be difficult to avoid.

Therefore, the purpose of this investigation was first to determine whether the caking properties could be destroyed sufficiently in a fixed bed, and secondly to determine the conditions requiring the minimum time and effecting the minimum loss of coal. The criterion of successful pretreatment would be that the pretreatment could be completed without agglomeration, and that after pretreatment the coal would not agglomerate in a hydrogen-rich atmosphere at conditions of temperature and pressure similar to those in a fixed-bed gasifier.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

Description of Apparatus

The schematic flow diagram of the pilot plant for coal pretreatment given in figure 1 consists primarily of a gas heater and a vessel in which the coal can be heated and exposed to various atmospheres at controlled rates. The vessel is a 4-foot long, 3-1/2-inch diameter schedule 80 pipe made from 347 stainless steel. It is shown in figure 2. A ring joint blind flange served as a charge port and closure at the top of the vessel. The bed of coal was supported by a perforated stainless steel plate located 2 inches above the bottom of the vessel as shown in figure 3. During all pretreatment tests the coal was always heated externally by electric heaters and internally by the pretreating gas. The gas was heated by passing it through a coiled tube located in an electric furnace.

Gases flow normally up through the coal and out of the top of the vessel; however, several tests were performed with gases flowing down through the bed. Either nitrogen, carbon dioxide, or steam, or a mixture of these gases was satisfactory for pretreatment. In the remainder of this report the term "inert gas" is used to represent any of these gases. In some steps oxygen was also required, and this is specified in the procedure.

Temperatures of the bed were measured by thermocouples inserted in thermowells located in the center and at the periphery of the pretreater vessel. Thermocouples were adjustable and normally measured the temperature of the top, center, and bottom of the bed. The thermowells entered the bottom of the vessel and extended within one foot of the top flange. A differential pressure instrument measured and recorded the pressure drop across the fixed bed of coal. Temperature, pressure, and flow control are provided for at the panel shown in figure 4.

Procedure

The following steps of pretreatment destroyed the caking property of a bituminous coal in a fixed bed,

1. Coal, from 1/8- to 1-1/2-inch size, was heated from ambient temperature to its initial softening temperature as rapidly as possible with an inert gas. This temperature varies with the type or rank of coal, and usually is higher than the softening temperature indicated by the Giesler Plastometer Test (ASTM D-1812-60T).

2. Coal was held at softening temperature for about 1 to 3 hours with an inert gas containing about one volume percent of oxygen. About 17 percent of the volatile matter was removed during this step.

3. Coal was heated through its plastic range in about 1/2 to 1 hour with a superficial linear gas velocity that varied from 0.6 to 12 feet per second, depending upon the pressure and the oxygen content of the inert gas. An additional 33 percent of the volatile matter was removed, leaving about 50 percent of the original volatiles in the pretreated char.

As an alternate to steps 2 and 3, the coal could be effectively pretreated by gradually heating through its plastic range in about 3 hours. A pretreatment was considered successful after the coal was heated through its plastic range without agglomeration in a fixed bed. The char so produced flowed as freely as the original coal.

Testing of Chars and Coals

An arbitrary test was devised in which chars produced by pretreatment were exposed in a fixed bed to hydrogen or hydrogen-rich atmospheres for 1 hour at 400 psig and 600° C. The hydrogen-rich atmospheres contained nigrogen, steam, carbon dioxide, and carbon monoxide. These tests simulated gas compositions and conditions which would be found in a coal gasifier. Chars produced from coals heated through their plastic range without caking in a fixed bed never caked during these tests, indicating a strong probability that a char so produced would not cake in an actual gasifier. Coals not heated through their plastic range invariably caked during the hydrogen test.

Free swelling index (FSI) ASTM Test D-720-57 values of about 1.5 or less, which is usually indicative of a noncaking coal, were recorded for all chars made from coals pretreated through their plastic range. Chars with FSI values were used as a guide in estimating the caking property of chars produced during pretreatment. The ultimate and proximate analyses of coals tested and chars produced were performed according to ASTM procedure D-271-48.

Material

High-volatile A bituminous (hvab) coal from the Pittsburgh seam, one of the most strongly caking coals, was used in most of the pretreatment tests. Hvab coals from Sewickley, Upper Freeport, and Taggart seams, in addition to a high-volatile (hvbb) coal from the Illinois No. 6 seam and a low-volatile bituminous (lvb) coal from the Pocahontas No. 4 seam, were also tested and successfully pretreated. Analyses of coals tested are shown in table 1.

RESULTS

An example describing a successful pretreatment is as follows: A Pittsburgh seam coal was heated with steam, at atmospheric pressure, containing about 1 percent oxygen and flowing at a superficial velocity of 3 feet per second, to its initial softening temperature of 360°-370° C and maintained at that temperature for 3 hours. It was then heated through its plastic range of 370° to 430° C in about 1/2 hour with the same gas at the same velocity and pressure. The treatment was terminated with nitrogen

TABLE 1.- Source, analysis, free swelling index, rank, and heating value of coals tested

County, bed, mine	Proximate, percent				Ultimate, percent					Heating value, Btu (dry basis)	Free swelling index	Rank 1/
	Moisture	Volatile matter	Fixed carbon	Ash	H	C	N	O	S			
Illinois												
Franklin Illinois #6 Old Ben #21	8.0	35.4	50.0	6.6	5.5	70.6	1.7	14.7	0.9	13,550	4.5	hvbb
Pennsylvania												
Allegheny Pittsburgh Federal Bureau Mines, Experimental	2.5	35.6	54.3	7.6	5.3	75.8	1.5	8.2	1.6	13,960	8.5	hvab
Butler Upper Freeport Coal Hollow #2	1.7	35.3	55.9	7.1	5.3	76.9	1.5	7.9	1.3	14,020	8.0	hvab
Virginia												
Wise Taggart Dixiana	1.4	33.8	62.3	2.5	5.3	82.8	1.5	7.2	0.7	14,980	8.5	hvab
West Virginia												
McDowell Pocahontas #4 Bartley #1	2.7	14.8	76.5	6.0	4.4	83.3	1.3	4.5	0.5	14,660	6.5	lvb
Monongalia Sewickley Christopher #5	1.1	36.7	50.9	11.3	5.1	73.3	1.5	6.2	2.6	13,400	8.0	hvab

1/ American Society of Testing Materials, Standard Specifications for Classification of Coals by Rank: ASTM Designation D-388-38 ASA M20.1-1938.

cooling the char to less than 100° C in about 1/2 hour. An inert gas containing nitrogen and carbon dioxide was also used to cool the pretreated coal during other tests. A free flowing char was produced with a FSI indicative of noncaking coal. The treated coal expanded about 50 percent above its original volume.

Heating coal with this same gas through its plastic range in 3 hours also produced free flowing char. Replacing steam with nitrogen or nitrogen plus carbon dioxide or a combination of all three gases plus a small cmount of oxygen destroyed the caking property of coal in a fixed bed as effectively as the steam-oxygen mixture.

Heating coal, as described previously, with a gas containing 0.2 percent oxygen plus 11 to 40 percent hydrogen and the remainder nitrogen, carbon dioxide, and steam produced a solid mass of char with no evidence of pretreatment. This was an attempt to pretreat coal with a gas similar in composition to a gas produced in a coal gasifier.

The pretreatment technique developed in a 6-inch bed depth at atmospheric pressure with gas flowing up through the bed also proved effective in an 18-inch bed depth with the gas flowing up or down. The bed expanded less during the tests with the gas flowing down; however, the char produced was free flowing and showed no evidence of fusion.

Pretreatment at pressures of 50, 150, and 300 psig in a 6-inch bed depth also was effective. Char produced at elevated pressures normally exhibited less expansion than that made at atmospheric pressure.

The caking quality of hvab coal from the Sewickley, Upper Freeport, and Taggart seams was as effectively destroyed as the Pittsburgh seam coal. Of the four hvab coals tested, Pittsburgh and Upper Freeport seams required about 180 minutes of treatment at 360° to 430° C as compared to about 190 and 200 minutes, respectively, for the Taggart and Sewickley seams. The volatile matter of all hvab coals decreased during pretreatment from about 36 to 20 percent. Pretreatment of the hvbb coal from the Illinois No. 6 seam with a high inherent moisture content of about 8 percent was relatively easy, requiring only 80 minutes at 360° to 430° C. A low-volatile bituminous (lvb) coal from the Pocahontas No. 4 seam containing about 15 percent volatile matter was successfully pretreated at its plastic range of 470° to 510° C in about 2 hours with steam plus oxygen. The volatile matter content decreased from 15 to 9 percent during pretreatment. Analyses of chars produced from these coals during typical pretreatment are shown in table 2.

Expansion of coal during pretreatment was related to gas velocity and pressure. Low velocities or high pressures produced less expansion. Coals with high volatile matter content appeared to expand more. Pretreatment appeared more difficult for hvab coals with a low oxygen content.

Pretreatment at gas velocities approaching fluidization velocities of about 13 feet per second appeared easier and required about 2 hours at 360° to 430° C as compared to 3 hours at a velocity of 3 feet per second. At high gas velocities, the oxygen concentrations in the pretreating gas were varied

TABLE 2.- Analysis, free swelling index and heating value of chars produced during pretreatment with steam containing 1 to 3 volume percent oxygen at atmospheric pressure

Char prepared from bed	Proximate, percent				Ultimate, percent				
	Moisture	Volatile matter	Fixed carbon	Ash	H	C	N	O	S
Illinois #6	0.7	23.3	66.4	9.6	4.3	75.2	1.9	8.1	0.9
Pittsburgh	.3	20.9	71.9	6.9	4.1	78.9	1.7	7.4	1.0
Upper Freeport	.5	22.6	66.8	10.1	4.2	76.0	1.7	6.6	1.4
Taggart	.2	23.1	73.2	3.5	4.4	83.6	1.6	6.3	0.6
Pocahontas #4	.8	8.9	81.8	8.5	3.1	82.8	1.3	3.8	.5
Sewickley	.6	22.1	62.9	14.4	4.0	71.8	1.6	6.4	1.8

Char prepared from bed	Heating value, Btu (dry basis)	Free swelling index	Maximum pretreatment, temp., °C
Illinois #6	13,220	NC 1/	430
Pittsburgh	13,580	NC	430
Upper Freeport	13,300	1.0	430
Taggart	14,560	1.5	430
Pocahontas #4	13,830	NC	510
Sewickley	12,460	1.5	430

1/ NC = Noncaking.

from 0.5 to 4.0 percent with good results, whereas at gas velocities of 3.0 feet per second, oxygen content was limited to a range of about 1.0 to 3.0 percent. Low oxygen concentration in the gas is desirable because it allows for close control of the temperature. In tests with oxygen concentrations above 5 percent, temperature control was difficult because of excessive localized combustion.

Figure 5 shows a typical raw coal used plus a char from a successful pretreatment, and the same char after exposing it to a hydrogen flow at 400 psig and 600° C for 1 hour in a fixed bed. There was no evidence of fusion and the char flowed as freely as raw coal. All chars produced during successful pretreatment and subjected to this test did not fuse, or show any evidence of fusion.

Char produced in the manner described from a Pittsburgh seam coal was successfully gasified in a bench-scale, fixed-bed reactor with steam at 800° C and atmospheric pressure at the Bureau of Mines Coal Research Center in Morgantown, W. Va. There was no evidence of caking during gasification, and the results indicate that the char is quite reactive. Even mildly caking coals agglomerated in similar tests.

Tests performed by the Direct Coal-Conversion group at the Bureau of Mines Coal Research Center in Bruceton, Pa., in bench-scale equipment show that the same char as above could be hydrogenated at 3,000 psig and 750° C in free-falling bed without agglomerating. The char was crushed to a 30 x 50 U.S. Tyler mesh size for the hydrogenation tests.

DISCUSSION OF RESULTS

Results from tests performed at conditions other than those outlined in the procedure for successful pretreatment indicate the need for close adherence to the procedure. Several of these tests are described: Coal particles heated directly through their plastic range with inert gas in a fixed bed fused into a solid mass as shown in figure 6. Coal particles heated slowly through their plastic range with a gas containing 11 to 40 percent hydrogen plus 0.2 percent oxygen and the remainder nitrogen, carbon dioxide, and steam, also fused into a solid mass similar to the one shown in figure 6. This test was an attempt to pretreat coal with a gas which was similar in composition to a gas produced in a coal gasifier.

Coal heated at its softening temperature of 360° to 370° C with inert gas plus oxygen for 3 to 8 hours, and not heated through the plastic range, also fused upon subsequent exposure to hydrogen at 400 psig and 600° C; however, as shown in figure 7, there was some evidence of pretreatment since discrete coal-char particles were discernible in the fused mass.

Investigators[4, 5] have shown that oxygen was necessary for the reduction or destruction of the caking quality of coal in fluidized or moving fixed beds; however, evidence of complete and relatively rapid destruction of the caking property of coal in a stationary fixed bed was lacking. Consequently, the techniques as previously described were developed using small amounts of oxygen and a controlled heating cycle to destroy the caking quality of coal in a fixed bed. The role that oxygen plays in helping to destroy the caking property of coal in a fixed bed is not precisely known. However, it is theorized that the "sticky" matter which is normally formed when coal is heated through its softening and plastic range is oxidized to a "nonsticky" material.

The apparent differences in pretreatment time for the coal tested can also be attributed to oxidation. According to Radmacher[6] the rate of oxidation; that is, "the rate of decaking", is generally dependent on the oxygen content of the coal. On the other hand, Schmidt[7] reports that a lvb coal with a low oxygen content was also relatively sensitive to oxidation. This appears to confirm our findings since the hvbb coal from the Illinois No. 6 seam, having the highest oxygen content of about 9.0 percent, required a minimum pretreatment time of about 80 minutes. A pretreatment time of about 120 minutes was required for the lvb coal from the Pocahontas No. 4 seam, which contained about 2.4 percent oxygen.

Pretreatment time for the hvab coals generally was related to the oxygen content. The Pittsburgh and Upper Freeport coals, having an oxygen content of about 7.0 percent, required about 180 minutes of pretreatment, followed by about 190 minutes for the Taggart seam and 200 minutes for the Sewickley seam. Both Taggart and Sewickley seams had a slightly lower oxygen content of about 6.0 percent. The slight difference in pretreatment time for these two coals could be attributed to the differences in volatile matter content, since the Taggart seam had a volatile matter content of about 35 percent compared to 42 percent for the Sewickley seam.

Chars produced from hvab and hvbb coals containing a volatile matter content of 20 percent or less always had a FSI indicative of a noncaking coal. On the other hand, even after it was heated at temperatures that destroyed the caking quality of hvab coals, a lvb coal with a volatile matter content of about 16 percent maintained a FSI of about 5.0 that is indicative of a good caking coal. This would indicate that the caking quality of a coal or char was not directly dependent upon the quantity of volatile matter it contained.

To get an insight into what was occurring to the volatile matter content and FSI of a coal during pretreatment, a series of tests was performed at different maximum temperatures. Each test of the series was performed with a 600-gram batch of Pittsburgh seam coal treated with steam plus 1 percent oxygen at atmospheric pressure at a gas velocity of 3 feet per second. Each batch was heated directly to 360° C in 25 minutes. After reaching 360° C, each individual batch of coal was heated to a designated temperature at 10° C intervals from 360° to 430° C. The coal was heated at a rate of 10° C per 25 minutes. Each test was concluded by rapid cooling with nitrogen as previously described.

Analysis of char taken at 10° C intervals during the gradual heating of a Pittsburgh seam coal through its plastic range indicates little change in the FSI from 360° to 400° C. Heating to 410°, 420°, and 430° C effected a rapid decline in the FSI of the coal-char to 4.5, 2.5, and 1.5, respectively. As shown in figure 8, the volatile matter content of the coal rapidly decreased, following the same pattern as the FSI for every 10° C increase above 400° C. Each 10° C increase was accompanied by an increase in pretreatment time of 25 minutes; thus devolatilization was a function of both temperature and time.

The pretreatment technique developed offers promise, from an economic standpoint, as part of an integrated coal pretreatment and high pressure steam-oxygen-coal gasification process. The pretreatment can be performed at gasification pressure and part or all of the steam and a small part of the oxygen fed to the gasifier can be used as in the pretreatment. Furthermore, the gases and tars produced in pretreatment can be fed directly to the gasifier as fuel. Not only would this conserve energy, it would solve the effluent or off-gas problem from the pretreater. It is also conceivable that the pretreater vessels could serve as feed lock-hoppers for the pressure gasifiers, thus decreasing the net capital investment of the pretreatment.

CONCLUSIONS

A pilot plant study has shown that the caking property of a bituminous coal can be eliminated by pretreatment in a fixed bed. The caking quality of hvab, hvbb, and lvb coals was destroyed either by prolonged heating at the softening temperature followed by rapid heating through the plastic range with an inert gas containing a small amount of oxygen or by rapid initial heating followed by prolonged heating through the plastic range.

There was some variation in the conditions required for treating each coal, but generally hvab coals required about 180 minutes of pretreatment as compared to about 80 minutes for the hvbb coals. The chars produced did not cake when exposed to a hydrogen atmosphere at 600° C and 400 psig, indicating their suitability for use in fixed-bed gasification. The FSI served as a guide to indicate that the coal was no longer agglomerating. For most chars there was no agglomeration when the FSI declined to about 1.5 or lower.

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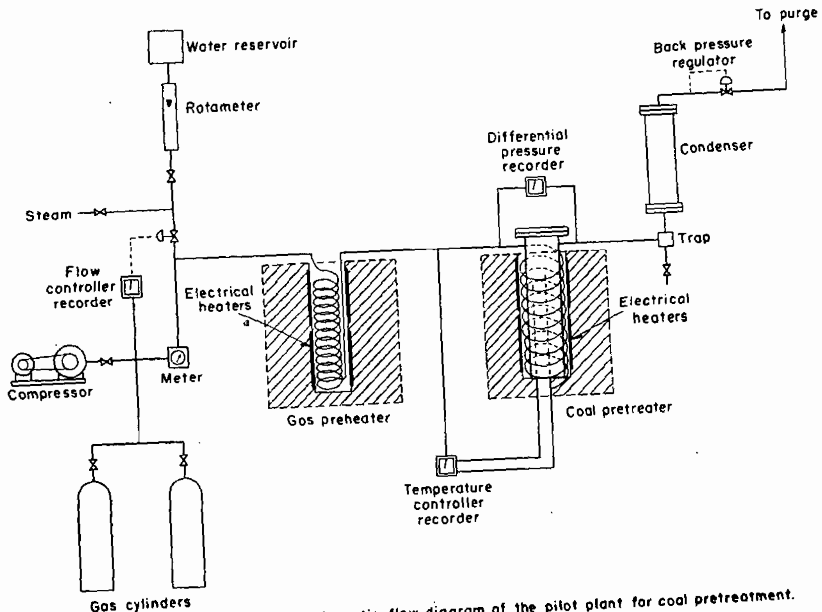

Figure 1.–Schematic flow diagram of the pilot plant for coal pretreatment.

Figure 2

A View of the Vessel in Which the Coal is Pretreated.

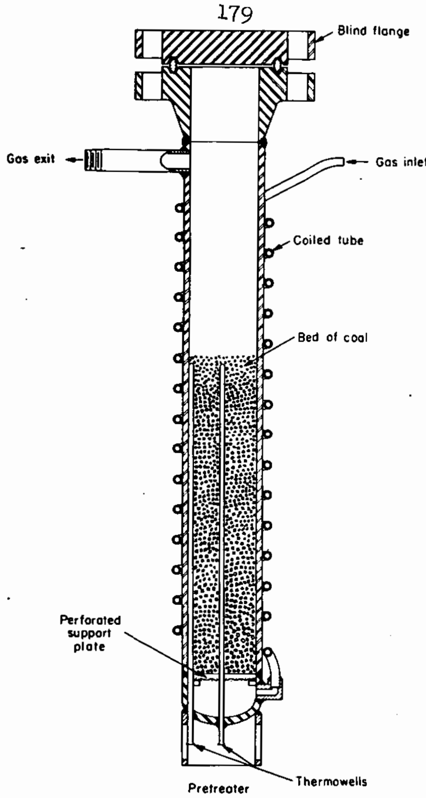

Figure 3.—Cross-sectional view of the coal pretreater vessel.

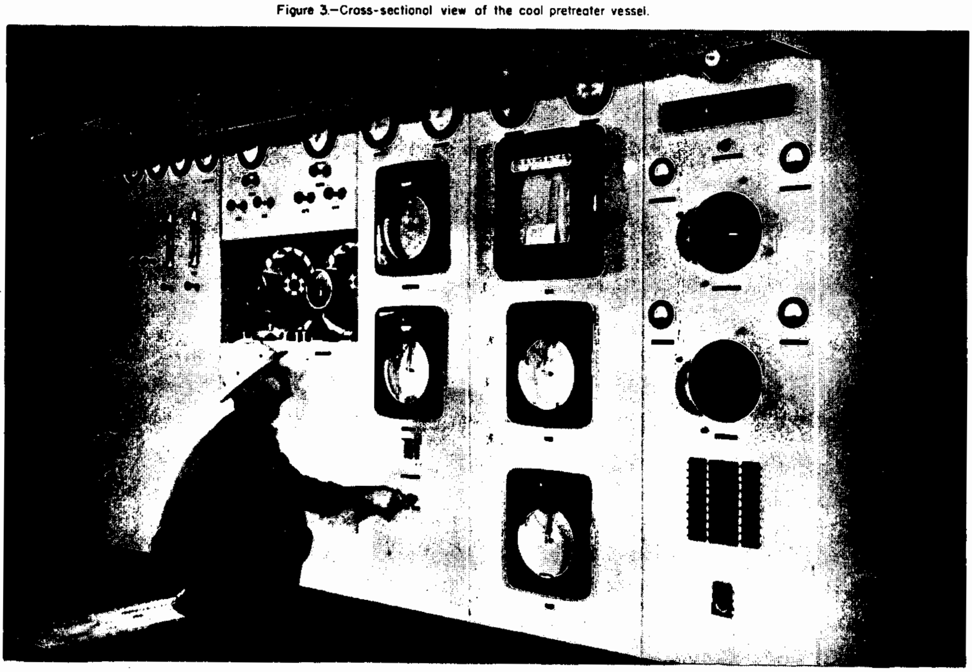

Figure 4. A view of the control panel for the coal pretreating pilot plant.

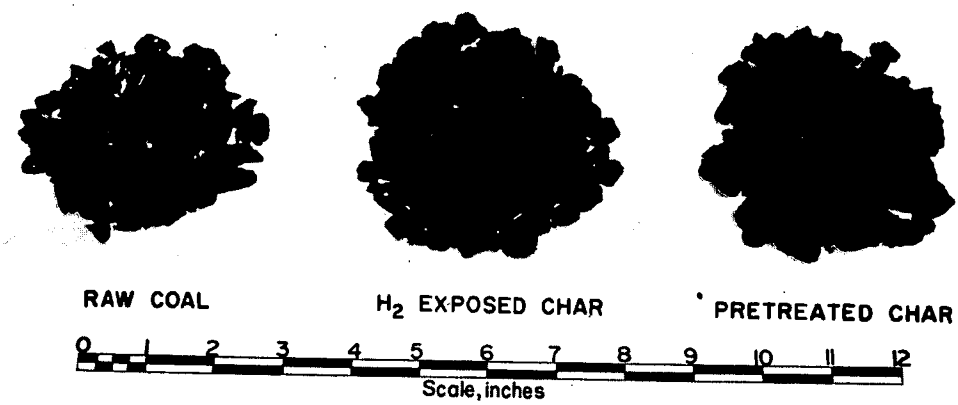

Figure 5. Raw coal used plus char from a typical pretreatment at 430 C and the same char exposed to hydrogen for 1 hour at 600 C and 400 psig.

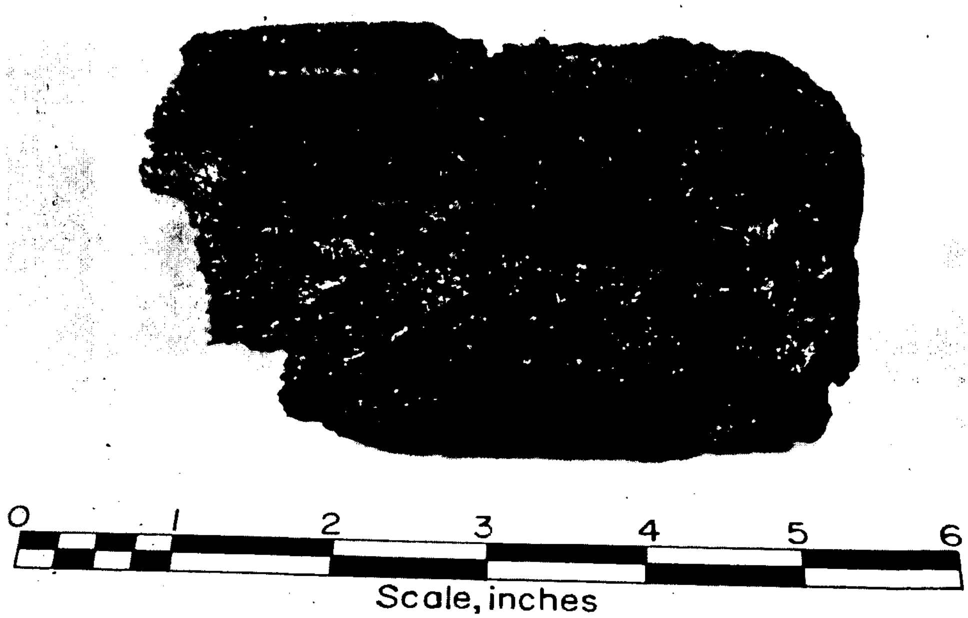

Figure 6. Solid mass of char made from coal with no pretreatment.

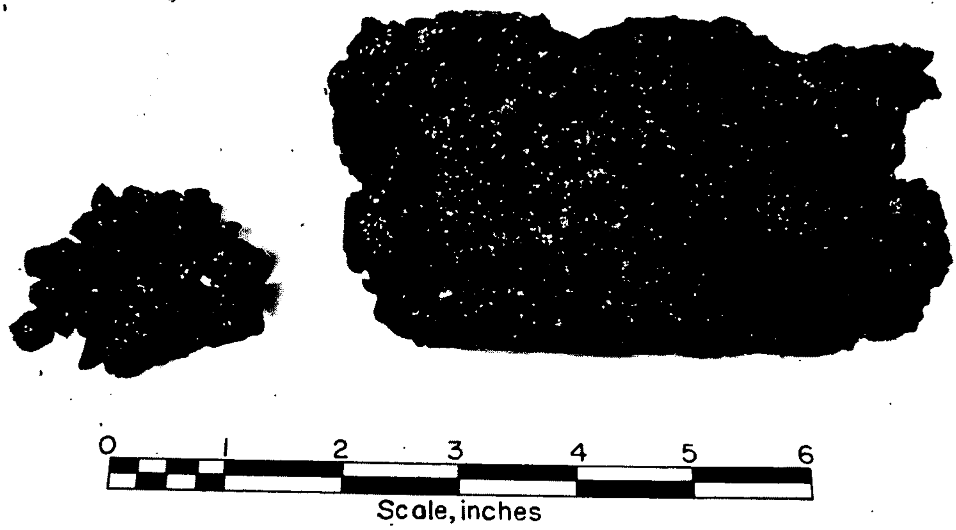

Figure 7. Mass of char containing discrete coal-char particles made from coal with some pretreatment.

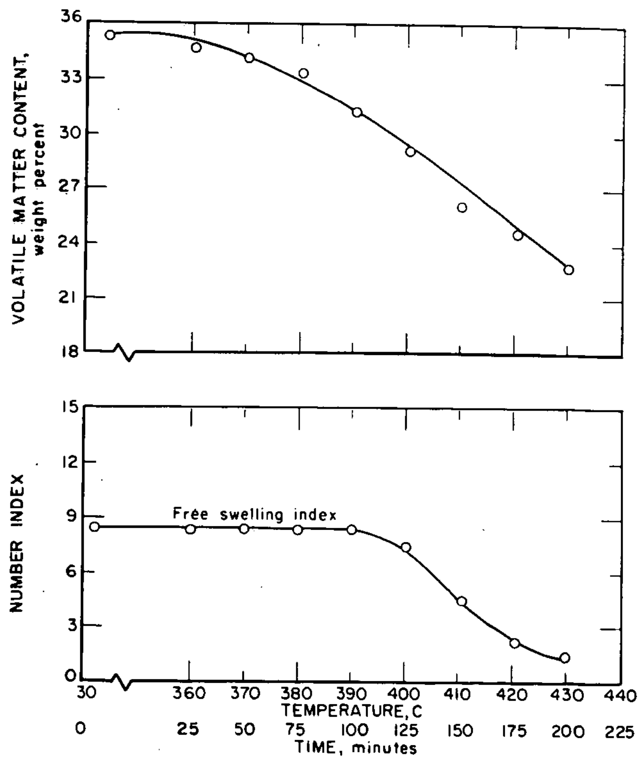

Figure 8.—Effect of temperature and pretreatment time on the free swelling index and volatile matter content of a Pittsburgh seam coal.