The Destruction of the Caking Properties of Coal By Pretreatment in a Fluidized Bed

A. J. Forney, R. F. Kenny, S. J. Gasior, and J. H. Field

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

INTRODUCTION

Gasification of coal to make a synthesis gas that can be converted to fluid fuels is a means of supplementing the country's liquid and gaseous fuel supplies while at the same time increasing the market for coal. A large market for these fuels exists near the eastern coal-fields, but, unfortunately, eastern coals do not readily yield to gasification in commercial fixed-bed and fluidized-bed gasifiers. They become plastic and agglomerate when heated to the gasification temperature, the permeability of the bed to gas is reduced, and objectionable channeling occurs. The Bureau of Mines is investigating methods of pretreating coals to destroy their caking properties in order to overcome these obstacles to gasification. The ultimate objective is to develop a low cost process. The first phase of the work consisted of pretreatment studies in a fluidized bed using various fluidizing gases and operating conditions. The studies were conducted with strongly caking coals, typical of those in the East. The results of the study and the operating requirements necessary to destroy the caking properties of the selected coals are reported.

Other research has been done on methods to destroy the caking properties of these coals. Chanabasappa and Linden[1/] pretreated coal to make a char for hydrogasification. They operated at 400° to 700° F using a steam feed of 4-5 standard cubic feet per pound bituminous coal. The time of treatment was 60-75 minutes. Nathan[2/] patented a fluidized process for pretreating coal at a temperature of 316° to 441° C, requiring 10-60 minutes and using 0.02-0.08 pound of oxygen per pound coal feed. Char was recycled for temperature control. Karl[3/] preheated bituminous coal to less than 400° C with a gas containing oxygen. Sylvander[4/] also preheated coal, to a temperature below the plastic range, using oxygen. Welinsky[5/] operated a fluidized carbonizer, the first stage at temperatures within the plastic range of the coal (725° to 825° F).

Recycle char from the second stage is added to the feed in the first. Foch[6] carbonized coal in a three-stage system. He dried and preheated coal to 570° to 750° F in the first stage using gases resulting from partial combustion of pyrolysis gases from the second stage. The preheated coal in the second stage is carbonized using preheated air. The char is cooled in the third stage.

When a caking coal is heated it becomes viscous and plastic at a given temperature range that is characteristic of the coal. This property makes caking coals nonusable in fluidized-bed and fixed-bed gasifiers because the coal sticks to the walls and the particles agglomerate. The Bureau investigated a combined thermal and mild oxidation treatment to destroy in a fluidized bed the caking properties of typical coals found in the eastern United States. Although the method described in this paper was successful it is not known definitely why the pretreatment makes the coal nonagglomerating. It cannot be attributed entirely to oxidation of the surface of the particles, because the resultant char contains less oxygen than the original coal. (See table 1.) Rapid thermosetting of the liquid phase as it forms may be an explanation, but this needs to be confirmed by experimental studies that are beyond the objectives of the investigation.

A variable study was made to determine operable conditions for pretreating the coal to a nonagglomerating state in the minimum time with the least loss of valuable components.

APPARATUS AND EXPERIMENTATION

A flowsheet of the bench-scale unit is shown in figure 1 and a photograph of the unit is shown in figure 2. The reactor is a 1-inch diameter stainless steel tube with an effective length of 18 inches. It is surrounded by electric heaters capable of heating the reactor to 900° C. Thermocouples are inserted both from the bottom and the top of the reactor. The usual method of operation is to heat the reactor while setting the proper gas velocity to give fluidization. This velocity was determined by experimentation in a glass tube at atmospheric temperature and pressure and then was corrected for the operational conditions. After the desired temperature is reached, the coal is charged to the reactor. The gases are collected after leaving the reactor and passing through a condenser and flask to remove the tars. When inert gas is used for treating the coal, the exit gas is not collected because the gas originating from the coal is too highly diluted by the inert gas to give significant results.

Different conditions of operation were tried in the development of the process. The following fluidizing gases were used:

Steam
Steam plus air
Inert gas (N_2 + CO_2 + 0.1-1.0 percent O_2)
Nitrogen (contains 0.1-0.3 percent O_2)
Prepurified nitrogen (essentially O_2-free)
Helium (essentially O_2-free).

Heat was transferred to the coal through the reactor wall (gas entering cold) and from the preheated gas (reactor wall maintained at the same temperature as the bed).

Pittsburgh seam coal from the Bruceton mine was used principally, but Pocahontas, Illinois, Sewickley, and Taggart coals also were treated. The rank and analyses of the coals are shown in table 1. The free swelling indices of these coals range from 4.5 to 8.5. The free swelling index is indicative of the caking qualities of the coals. If the index is reduced below 2 by pretreatment, the residue is usually noncaking.

To supplement the indicated results from the free swelling index,[7/] another test was devised to verify that the char was nonagglomerating. A sample of the char was placed in a ceramic boat and the boat placed in a quartz tube in an electric furnace. The char was heated to 600° C while pure hydrogen was passed through the tube. The char was considered noncaking if after hydrogen treatment it flowed freely out of the boat. Later, to test it more severely, the char was exposed to hydrogen at 900° C. Usually if the free swelling index was less than 2, the hydrogen test indicated noncaking also.

Because this pretreatment process was developed primarily to make a nonagglomerating fuel for a gasification process, the hydrogen test is more pertinent than the free swelling index test. As the char is fed into the gasification unit, it will come in contact with hot hydrogen-containing product gases of the gasifier, a condition simulated by the hydrogen test at 600° or 900° C.

DISCUSSION OF RESULTS

Initially Pittsburgh seam coal, 10-14 mesh, was used with inert gas or nitrogen as the treating gas. The gas velocity for fluidizing at atmospheric pressure was about 2.5 feet per second, and the expansion of the bed was about 100 percent. Early tests showed that the individual coal particles expanded 100 percent or greater at temperatures of 400° to 450° C. Because of the expansion of the treated particles and the fluidized bed, the size of the charge was limited to 35 grams (60 cc). When the fluidized bed of coal was heated indirectly by transfer through the reactor wall, the coal particles agglomerated and adhered to the wall, making the unit inoperable. However, when the heat was supplied by direct transfer from the gas while the reactor wall was maintained at a temperature for adiabatic conditions, the coal's caking properties were destroyed by the treatment and the unit was operable. The coal particles swelled and became globular. Pretreatment was successful when inert gas, steam plus air, or nitrogen was used, whereas agglomeration occurred at the same operating conditions when helium, steam, or prepurified nitrogen was the treating gas. This difference in results was traced to the presence of a small quantity of oxygen (0.1-0.3 percent) in the inert gas and nitrogen, and the absence of a measurable quantity of oxygen in the other gases.

The effect of temperature on the caking properties of Pittsburgh seam coal is shown in figure 3. Four mesh sizes of coal were fluidized with an inert gas containing 0.8-1.0 percent oxygen. Plotted are the increase in volume, the weight loss of the coal, and the free swelling index of the resultant char with variation in treatment temperature. These results are more relative than absolute, but the trends of the different sizes are realistic. The larger particles were exposed to more oxygen than the smaller ones because the linear velocity was higher for the fluidization of the larger particles. The coal was maintained at the test temperature for 30 minutes in all tests. Poor fluidization occurred in all tests at 450° C, and with the 8-10 and 10-14 mesh sizes at 425° C. The 28-48 and 48-100 mesh were successfully pretreated at 425° C, as were all sizes at 400° C. While the fluidization of the coals was satisfactory in the reactor at 375° C, the chars caked when they were tested at 600° C with hydrogen, indicating insufficient treatment. The free swelling index test corroborates the hydrogen tests because the index was higher than 2 at 375° C and no higher than 2 for all tests at 400° C, and below 2 at 425° and 450° C. As the temperature of treatment increased, the weight loss increased as more of the volatiles were removed. There was a greater increase in bulk volume with increasing temperature. These tests showed that the caking quality of Pittsburgh seam coal of 28-48 and 48-100 mesh was destroyed at 400° to 425° C in 30 minutes.

The effect of pressure on the caking properties of Pittsburgh coal is shown in figure 4. During these tests a 48-100 mesh size coal was fluidized with an inert gas containing 0.8 to 1 percent oxygen for 30 minutes at 400° C. Chars made at all pressures were noncaking. The volumetric expansion became less as the pressure increased from 0 to 300 psig. The weight loss decreased as the pressure was increased from 0 to 75 psig, then did not change with further increase in pressure. A linear gas velocity of about 0.4 foot per second was necessary for fluidization of 48-100 mesh coal at all the pressures, so that at the higher pressures a larger quantity of gas flowed through the coal. Generally, there was no significant change due to pressure. The only novel effect occurred when the pressure was released when the char was removed from the reactor. Some of the particles seemed to explode, probably because trapped gas was released due to depressurization. This effect was observed at all pressures above atmospheric.

Varying the time of pretreatment of Pittsburgh seam coal of 18-100 mesh produced the results shown in figure 5. Nitrogen containing 0.2 percent oxygen was the treating gas, and operating temperatures were 400° and 425° C. As shown in this figure, the char made by treating at 425° C for five minutes could be subjected to a hydrogen atmosphere at 900° C without caking. The free swelling index of this char was 1.5. The weight loss of the coal was 10 percent. Pretreatment for only 1 minute at 425° C was enough to produce a char that did not agglomerate at 600° C with hydrogen. However, the free swelling index of the char was 6-1/2, still indicative of a caking coal. Apparently the test with hydrogen at 600° C is not severe enough to determine if the coal has been rendered noncaking throughout. Some difference between the free swelling index and hydrogen exposure tests can be expected because the char is ground for the free swelling index test but is used in its original state in the hydrogen tests. The weight loss in the 1-minute test was 8 percent. When the coal was treated at 400° C, the minimum pretreatment time was 20 minutes for the char to remain nonagglomerating in the hydrogen test at either 600° or 900° C. The free swelling index was 2, indicative of noncaking. The weight loss was 10 percent. Since the weight loss at both 400° and 425° C was about 10 percent, the higher temperature is more desirable because less time is required for treatment.

The effect of temperature on the volume and composition of the gas made during coal treatment with pure steam for 30 minutes at 375°, 400°, and 425° C is shown in figure 6. As the temperature increased, the hydrogen yield increased from about 5 to 9 cubic centimeters of gas per gram of coal charged. The methane yield increased from about 1 to 5 cubic centimeters per gram, and the C_2 yield increased also. The yields of carbon dioxide, nitrogen, carbon monoxide, and oxygen remained relatively constant. A gas of higher heating value was made at the higher temperature of operation.

The effect of varying the temperature of pretreatment of Pocahontas No. 4 (lvb), Taggart (hvab), Illinois No. 6 (hvbb), and Sewickley (hvab) coals is shown in figure 7. Nitrogen containing about 0.2 percent oxygen was used at a linear velocity of about 0.8 foot per second to fluidize the 28-48 mesh particles. Chars, made from Pocahontas or Illinois coal that had been treated at 375°, 400°, or 425° C, did not cake when subjected to a hydrogen test at 900° C. Taggart coal required treatment at 425° C to be satisfactory, while Sewickley could be treated at 400° only, as it agglomerated during pretreatment at 425° C and was ineffectively pretreated at 375° C. Taggart and Sewickley coals are similar in rank to Pittsburgh seam, all being hvab.

Pocahontas No. 4 and Illinois No. 6 require less drastic treatment than the hvab coals. This is not surprising for the lower rank Illinois coal, which has a free swelling index of 4.5 compared to 8-8.5 for the hvab coals. While the Pocahontas coal has the highest rank, it may respond to milder pretreatment because of its low volatile content. Taggart coal required treatment at 425° C. This coal also showed a drastic change in expansion as plotted in figure 7, having 0 percent volume increase at 375° C and 100 percent at 425° C.

These tests showed that the technique of pretreatment utilizing fluidization with gases containing small quantities of oxygen is applicable to several caking coals. However, conditions of pretreatment cannot be fixed exactly by the rank of coal; each coal must be tested to determine the most satisfactory temperature for pretreatment.

CONCLUSIONS

The caking properties of coals tested could be destroyed by fluidizing the coal with a gas such as nitrogen, nitrogen plus carbon dioxide, or steam, containing at least 0.2 percent oxygen at 400° or 425° C. In a batch system, a thoroughly nonagglomerating char could be produced at 425° C in a 5-minute treatment using 18-100 mesh size coal. The caking property cannot be destroyed by the treatment described if oxygen is absent. It is desirable and may be necessary to heat the coal internally by the treating gas to prevent the particles from adhering to the wall of the reactor.

To obtain data that will permit a more exact evaluation of the process and estimate of the cost of this method of pretreatment, a study of a continuous system is needed. We plan to modify the bench-scale equipment for continuous feed of coal and removal of char. This will allow a realistic determination of the optimum feed gas-to-coal ratio and minimum average residence time required for pretreatment. In a fluidized bed all the coal is not pretreated for a uniform length of time because of the rapid mixing of the raw coal and treated char. The discharged solids will contain particles treated to different degrees because the residence time of the individual particles varies. The results of the batch study will be used as a guide for the continuous studies, but the optimum solids residence time and conditions of operation may be different from those obtained in the present investigation.

References

1/ Chanabasappa, K. G., and H. R. Linden. Fluid-Bed Pretreatment of Bituminous Coals and Lignite. Ind. and Eng. Chem., 50, No. 4, 637-644 (April 1958).

2/ Nathan, M. F. U.S. patent 3,032,477, May 1, 1962.

3/ Karl, Alfred. German patent 1,041,192, Oct. 16, 1958.

4/ Sylvander, N. E. U. S. patent 3,070,515, filed May 6, 1957.

5/ Welinsky, Irving H. U. S. patent 2,955,077, Oct. 4, 1960.

6/ Foch, Pierre. U. S. patent 3,011,953, Dec. 5, 1961.

7/ The treated or processed coal is designated as char in this report.

TABLE 1.- Analyses of coals and chars from pretreatment tests

Classification 1/	Pocahontas #4 lvb		Taggart hvab		Illinois #6 hvbb		Sewickley hvab		Pittsburgh hvab	
	Raw	Char	Raw	Char	Raw	Char	Raw	Char	Raw	Char
Proximate analysis, percent 2/										
Moisture	2.7	0.4	1.1	0.1	6.1	0.5	1.3	0.4	1.7	0.8
Volatile matter	14.8	13.7	35.1	24.4	33.8	26.1	36.8	24.2	36.6	26.0
Fixed carbon	76.5	78.6	61.8	73.1	53.2	66.4	52.9	64.3	55.5	66.7
Ash	6.0	7.3	2.0	2.4	6.9	7.0	9.0	11.1	6.2	6.5
Ultimate analysis, percent 2/										
Hydrogen	4.4	4.0	5.4	4.7	5.2	4.4	5.2	4.4	5.3	4.6
Carbon	83.3	84.3	83.8	84.6	70.8	77.6	75.3	75.0	77.3	78.9
Nitrogen	1.3	1.3	1.5	1.6	1.7	1.9	1.6	1.7	1.6	1.7
Oxygen	4.5	2.6	6.6	6.0	14.3	8.1	6.5	5.2	8.4	7.2
Sulfur	0.5	0.5	0.7	0.7	1.1	1.0	2.4	2.6	1.2	1.1
Ash	6.0	7.3	2.0	2.4	6.9	7.0	9.0	11.1	6.2	6.5
Free swelling index	6.5	1.5	8	1.5	4.5	1.5	8.5	2	8.5	2
Heating value, Btu/lb	14,660	14,410	14,950	14,700	12,530	13,550	13,630	13,240	13,780	13,740

1/ American Society for Testing Materials, Standard Specifications for Classification of Coals by Rank. A.S.T.M. Designation D-388-38; A.S.A. M20.1-1938.

2/ As received basis.

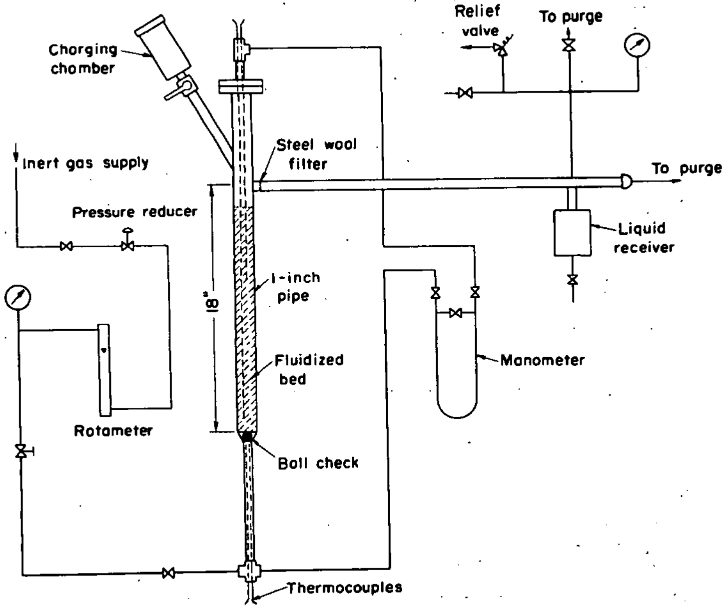
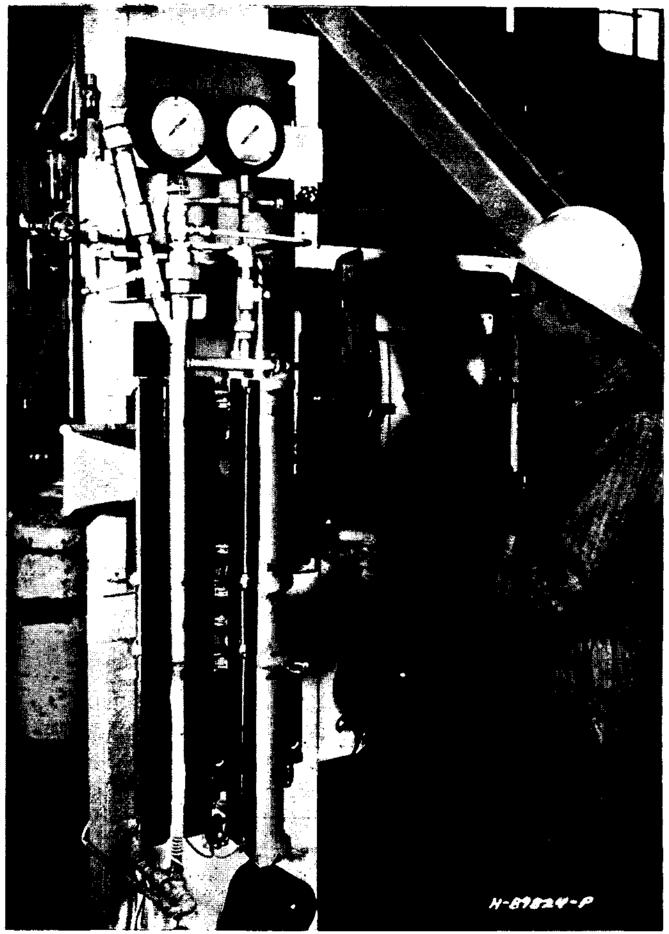


Figure 1.- 1-inch reactor for pretreating coal in a fluidized bed. L-79



The Bench-Scale Unit for the Destruction of Caking Properties of Coal.

Figure 2.

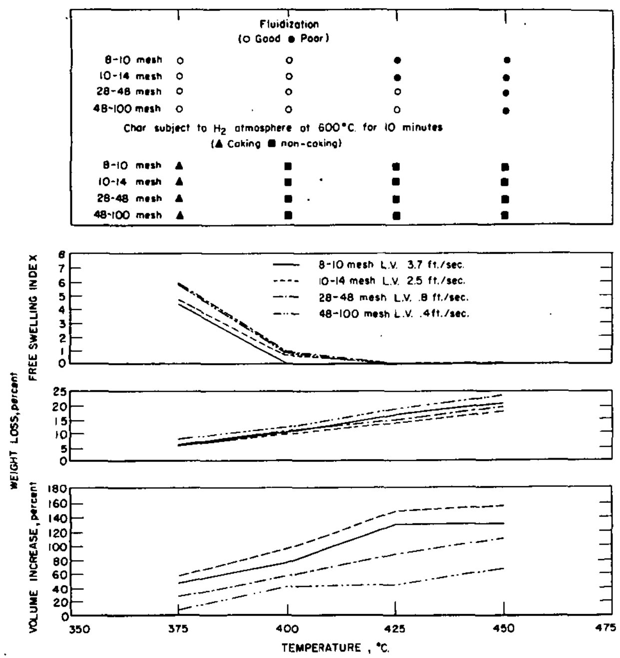


Figure 3 - Caking tests of Pittsburgh seam coal-temperature and size consist effect (coal held at indicated temperatures 30 minutes. Fluidization medium-inert gas containing 0.8-1.0% oxygen-atmospheric pressure).

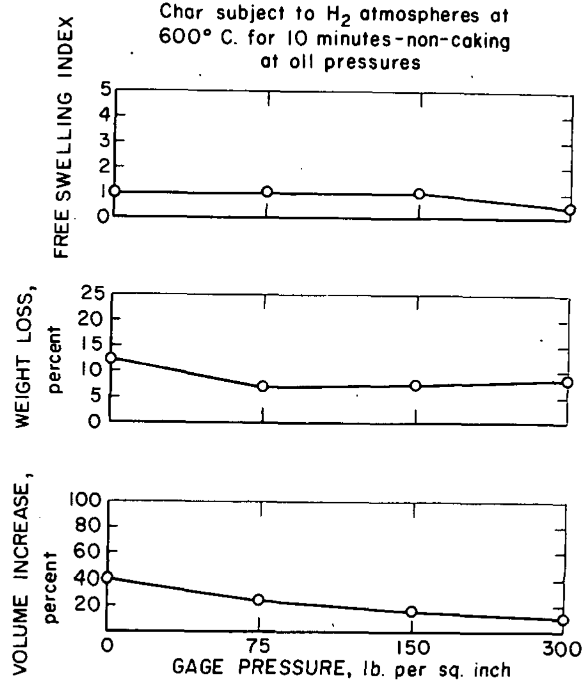


Figure 4. - The effect of pressure on the caking properties of Pittsburgh seam coal, and (48-100 mesh; coal held at 400° C. 30 minutes. Fluidization medium-inert gas containing 0.8-1.0% oxygen.)

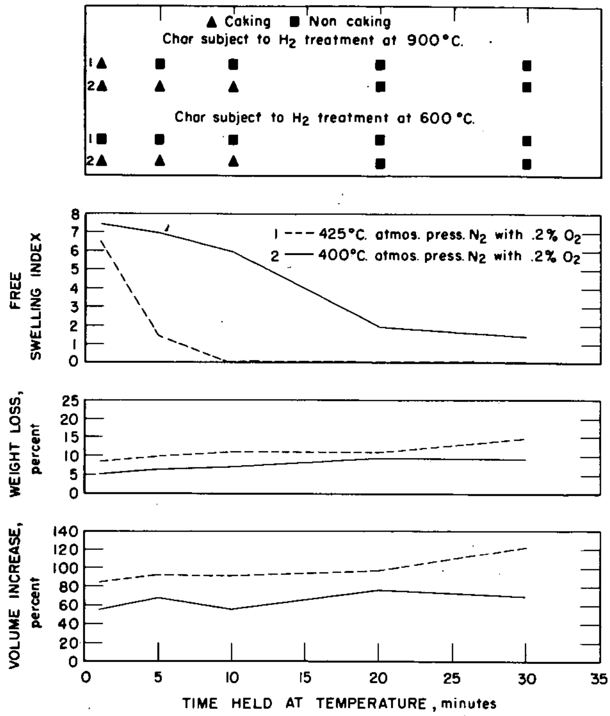


Figure 5.-The effect of time of pretreatment on the caking properties of Pittsburgh seam coal (18-100 mesh)

L-7891 1-17-63

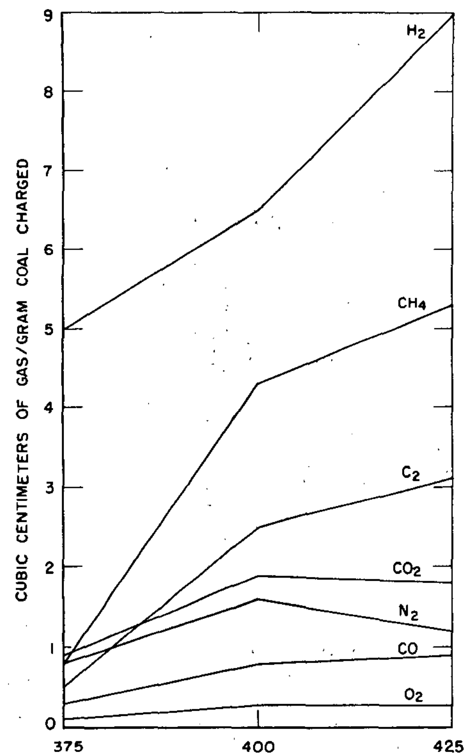


Figure 6.-The effect of temperature on the off gas made during steam pretreatment of Pittsburgh seam coal of 28-48 mesh. (Time of pretreatment 30 minutes).

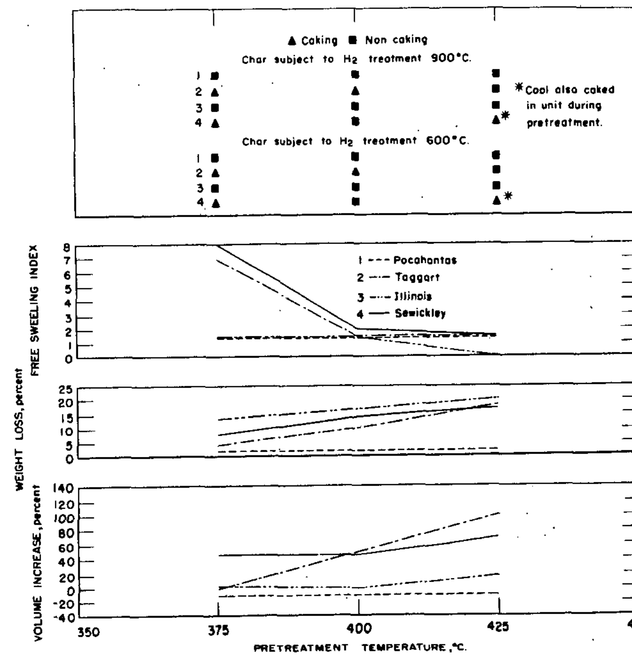


Figure 7.-The effect of temperature of pretreatment on caking properties of various coals 28-48 mesh. (Time of pretreatment 30 minutes.)