HIGH BTU GAS BY THE DIRECT CONVERSION OF COAL

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INTRODUCTION

Processes for the production of high-Btu gas from coal are being developed for future use when there is an economic need for manufactured gas. (2,5)[1] A number of processes based on both coal and petroleum are available, and various estimations of production costs or selling price have been published. (1,3,4,6) Those processes based on coal can be divided into two general categories: indirect and direct. Indirect processes are those requiring the coal carbon to be converted into synthesis gas (hydrogen and carbon monoxide) which, after adjustment of the gas composition and removal of impurities, is reacted catalytically at moderate pressure and temperature to produce methane. Direct processes are those in which the coal carbon is combined with hydrogen to produce methane in a noncatalytic operation taking place at high pressure and high temperature. Each approach to the production of high-Btu gas has advantages as well as disadvantages, and thus far, a clear-cut superiority has not been demonstrated for one or the other. This paper reports the progress made by the Pittsburgh Coal Research Center of the United States Bureau of Mines in developing a direct process for converting coal to high-Btu gas.

The Bureau's conception of hydrogenating coal to methane in dilute-phase concurrent flow originated from an earlier attempt to produce hydrocarbon gases by entraining feeds of strongly caking and noncaking coals in a stream of hydrogen which passed through a hot reactor in turbulent flow. Even though the gas velocity was high, carbonization of coal in the reactor always stopped the flow. These experiments indicated the possibility of devolatilizing the coal to dry char providing the coal particles were small and dispersed throughout a stream of hot gas. Under these conditions the coal particles would be heated very rapidly, and, if the diameter of the reactor was large relative to the entering feed stream, the coal would pass through its plastic range without agglomerating into a large mass or sticking to the wall of the reactor. This was successfully demonstrated experimentally several years ago using strongly caking coal, hvab Pittsburgh seam, and hydrogen at 1,000 psig. The reactor had a diameter of 3 inches, and was heated to a nominal temperature of 800° C while the entering stream of coal had a diameter of 5/16 inch. A dry, free-flowing, nonagglomerated char was produced during free-fall through a heated zone 4 feet in length.

Since that time, a dependable system for hydrogasifying coal in dilute-phase has been developed, and experimental data are being obtained. In addition, some data have been obtained for the hydrogenation of dilute-phase char. These experimental results are presented, and a conceptional process is discussed wherein these two operations are integrated for the production of high-Btu gas on a commercial scale.

DILUTE-PHASE HYDROGENATION

The reaction of coal with hydrogen in dilute-phase is intended to be a means whereby strongly caking coals can be reacted at high temperatures in the "as received" condition without incurring agglomeration. The primary products are hydrocarbon gases

1/ Underlined numbers in parentheses refer to items in the list of references at the end of this report.

and a solid residue of coal which is a dry, free-flowing, nonagglomerated char that can be processed further by hydrogenation, gasification, or burned as fuel; in addition, a minimal amount of hydrocarbon liquids might be produced. One anticipated application of dilute-phase hydrogasification is the direct conversion of coal to high-Btu gas.

Until recently, a major portion of the work was concerned with the development of means for feeding strongly caking coal into gas mixtures at high temperatures and high pressures. When this problem was solved, experiments were made with the objectives of determining the operability limits of the system with respect to coal throughput and to explore the effects of hydrogen-to-coal ratio on the quality of the product gas and char.

All experiments in dilute-phase hydrogasification used a feed of Pittsburgh seam coal having a free-swelling index of 8 and a volatile content of 41 percent, moisture-ash-free basis. Ultimate and proximate analyses are given in table 1. This choice

TABLE I

ANALYSES OF HIGH-VOLATILE A BITUMINOUS COAL

	As received, percent	Maf, percent
Ultimate		
Carbon	78.5	84.0
Hydrogen	5.4	5.7
Nitrogen	1.6	1.7
Sulfur	1.4	1.5
Oxygen[1/]	7.2	7.1
Ash	5.9	-
Moisture	0.7	-
Proximate		
Moisture	0.7	-
Volatile matter	38.2	40.9
Fixed carbon	55.2	59.1
Ash	5.9	-

1/ By difference.

of feed was based on the premise that procedures for overcoming agglomeration would apply to any other coal, whereas the reverse might not be true. The feed was sized 50 x 100 mesh sieve fraction, U.S. Standard.

The feed gas was a mixture of methane and hydrogen having a composition simulating that which could be obtained by the partial conversion of char with hydrogen to produce methane; various gas compositions were used. The feed rate closely approximated 175 scfh. The additional methane produced by hydrogenating coal in dilute-phase using a methane-rich mixture could conceivably raise the heating value of the gas leaving the reaction zone to better than 900 Btu per scf on a clean, dry basis. While the coal was being partially devolatilized, it was also being transformed into dry, free-flowing char which could be hydrogenated in a moving bed without agglomerating.

Equipment and Procedure

The basic elements of the dilute-phase system are shown schematically in figure 1. Feed gas of a given composition was made by blending metered quantities of methane and hydrogen in a gasholder which supplied the gas mixture to a compressor. The compressed gas was heated during flow through coiled tubing immersed in a lead bath to 700° C and entered the top of a reaction vessel heated by external furnaces where it contacted the incoming stream of coal. The coal entered the reactor through a nozzle having a diameter as large as one-half inch and in concurrent flow with the hot gas, passed through the reaction space which was 8 feet in length by 3 inches in diameter. The reactor was heated to a nominal temperature of 725° C which means that its temperature was brought to a maximum of 725° C and constant temperatures were attained over the system before starting the coal feed. Of course, some variations in temperatures occurred especially after coal feed was started. Pressure equalization throughout the coal feeding system was obtained by providing a parallel flow path between the feeder, the nozzle, and the reaction space. Product gas passed through a water-cooled vessel in which water and a small quantity of oil vapors were condensed and collected, and the gases were then reduced in pressure, metered, and collected in a gasholder. A small flow of gas was withdrawn and passed through an analyzer which continuously recorded the specific gravity of the gas, thereby showing when steady conditions had been attained; about 15 minutes were required to reach steady conditions. Samples of the product gas were withdrawn at intervals and analyz

Results and Discussion

In dilute-phase hydrogasification, the composition of the effluent gas is determined by the feed gas rate and composition and the gas yield. The feed gas rate and composition can be selected with some degree of freedom, but the gas yield is depende upon many variables some of which interact. Most prominent of the variables are: co rate, maximum temperature attained by the solids and the vapors, residence times of the solids and the vapors, total pressure, hydrogen partial pressure, particle size and density, gas viscosity, heat capacity of the feed gas, and thermal conductivity of the gases. Obviously, in an investigation which is primarily concerned with development of a process, a study of the variables is impractical. However, some experimental data have been obtained showing the gross effect of several important variables. The results are given in table 2 for experiments at 1,500 psig and in table 3 for 3,000 psig.

The effect of coal rate on the conversion of coal to gaseous and liquid products was investigated at both pressures using hot feed gas at a rate of 175 scfh and an approximate composition of 50 percent hydrogen, 48 percent methane, and 2 percent nitrogen. Over the relatively narrow range of 5 to 7 pounds per hour, the quantity of coal converted to gases plus a small amount of oil and water was approximately 35 percent to 33 percent based on maf coal. Coal conversion decreased with increasing coal rates, being approximately 27 percent at a rate of 9 pounds per hour because of the greater heat load imposed by the increased coal rate while the heat input was held constant. Carbon conversions were about 28 percent to 27 percent of maf coal at 6 to 7 pounds per hour and decreased to about 22 or 23 percent at 9 pounds per hou

The effect of coal rate on the yield of hydrocarbon gases (methane and ethane) is shown in figure 2. Approximately 24 percent of the maf coal was converted to methane plus a little ethane at 6 to 7 pounds per hour coal rate and 3,000 psig while the corresponding yield at 1,500 psig was approximately 20 percent. The greater yields were obtained at 3,000 psig because both the hydrogen partial pressure and the retention time of the coal volatiles were twice as great as that obtained at 1,500 psig, which accelerated the thermal decomposition and hydrogenation of the high-molecular weight vapors. Hydrocarbon gas yields showed the same decreasing trend with increased coal rate as was observed for conversion, resulting from the increased heat load causing coal temperatures to decrease.

TABLE 2

DILUTE-PHASE HYDROGASIFICATION AT 1,500 PSIG AND A NOMINAL 725° C REACTOR TEMPERATURE

Coal feed rate, lb/hr	5.9	6.0	6.3	6.4	6.5	6.7	7.5	7.6	9.1
Gas feed rate, scfh	173	173	175	179	177	175	174	176	177
Composition, percent methane 2/	42	3	44	47	61	43	43	44	42
Gross heating value, Btu/scf	617	346	627	648	747	621	623	632	617
Conversion, wt pct									
Coal, maf	35	37	1/	32	32	34	1/	32	28
Carbon	28	30	1/	26	26	27	1/	25	22
Product gas, nitrogen-oxygen free									
Hydrogen, vol pct	41.6	76.7	40.4	38.2	25.3	40.9	38.5	35.7	34.7
Methane, do.	56.4	20.3	57.2	58.5	73.2	56.7	58.5	61.2	62.2
Ethane, do.	1.4	2.1	1.7	2.5	1.5	1.7	2.0	2.4	2.1
Carbon monoxide, vol pct	0.6	0.9	0.7	0.8	0.5	0.7	1.0	0.7	1.0
Gross heating value, Btu/scf	734	495	744	764	853	741	757	780	784
Gain in heating value, Btu/scf	117	149	117	116	106	120	134	148	167
Percent based on feed gas	19	43	19	18	14	19	21	23	27
Yields, wt pct, maf coal									
Methane	18.4	22.0	15.9	14.6	13.3	16.4	15.3	17.2	17.1
Ethane	3.0	4.9	3.9	5.7	3.4	3.5	3.5	4.3	3.1
Carbon monoxide	1.4	2.0	1.5	1.8	0.9	1.4	1.8	1.3	1.5
Recoveries, wt pct									
Overall	97	96	92	97	95	96	92	96	101
Carbon	96	97	94	97	95	95	90	98	99
Hydrogen	100	102	99	100	97	99	97	100	102
Ash	115	101	103	98	102	105	100	88	110

1/ Conversion values not meaningful.
2/ Balance is hydrogen and 2 percent nitrogen.

TABLE 3

DILUTE PHASE HYDROGASIFICATION AT 3,000 PSIG AND A NOMINAL 725° C REACTOR TEMPERATURE

Coal feed rate, lb/hr	5.3	6.0	6.2	6.3	6.5	6.6	6.8	7.2	7.8	8.3
Gas feed rate, scfh	174	182	174	174	174	177	176	176	175	174
Composition, percent methane[1]	50	2	68	47	48	49	48	71	45	48
Gross heating value, Btu/scf	669	337	807	647	653	660	658	814	633	667
Conversion, wt pct										
Coal, maf	33	42	32	33	35	33	34	31	29	31
Carbon	26	35	24	26	28	26	27	23	23	23
Product gas, nitrogen-oxygen free										
Hydrogen, vol pct	34.0	70.1	17.1	34.9	31.3	32.9	30.9	16.9	31.8	28.6
Methane, do.	64.0	28.6	81.0	63.6	66.3	65.5	66.9	81.0	65.0	67.8
Ethane, do.	1.5	0.8	1.7	1.5	1.8	1.6	1.7	1.6	2.6	2.6
Carbon monoxide, vol pct	0.5	.6	0.1	0.0	0.5	0.0	0.4	0.3	0.6	1.0
Gross heating value, Btu/scf	792	533	910	786	808	798	811	905	810	829
Percent based on feed gas	18	58	13	21	24	21	23	11	28	20
Yields, wt pct, maf coal										
Methane	21.0	35.8	13.7	20.3	21.5	19.3	20.8	11.1	19.0	16.5
Ethane	3.9	1.9	3.5	3.5	3.7	3.6	3.7	3.3	4.5	4.2
Carbon monoxide	1.5	1.3	0.2	trace	1.0	0.0	0.8	0.6	1.0	1.6
Recoveries, wt pct										
Overall	98	97	95	97	96	102	96	91	98	97
Carbon	99	100	96	98	97	97	98	95	99	98
Hydrogen	101	97	98	100	100	101	100	98	102	99
Ash	100	102	101	98	100	103	101	105	90	100

1/ Balance is hydrogen and 2 percent nitrogen.

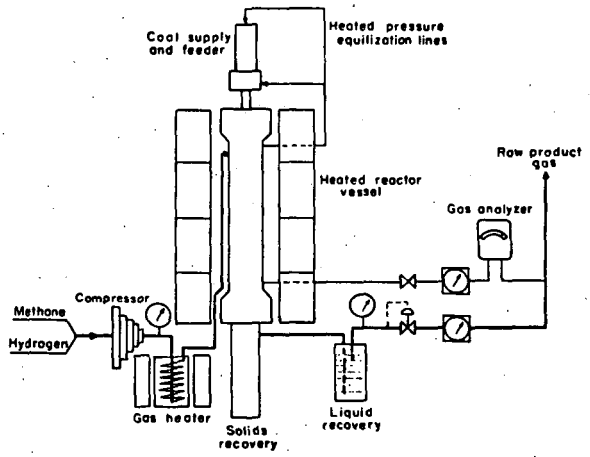

Figure 1. — Schematic diagram of dilute-phase hydrogasification apparatus.

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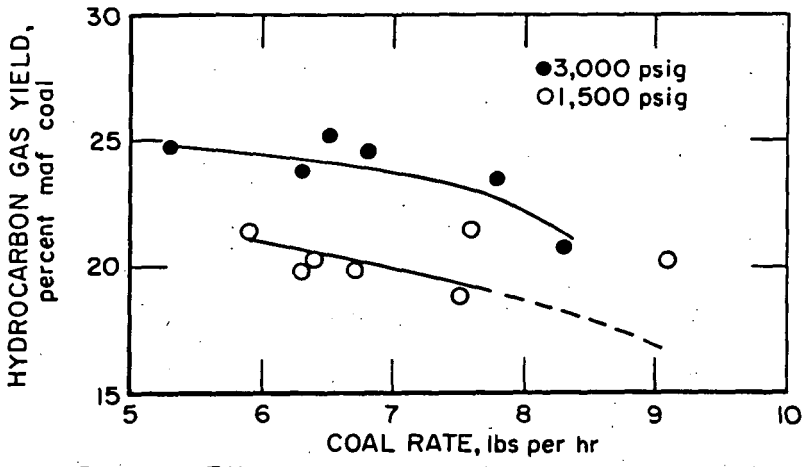

Figure 2.—Effect of coal rate on hydrocarbon gas yield at approximately constant gas feed rate and composition

The effect of pressure upon coal conversion appeared to be less than the accuracy of the conversion data--about 3 percent. Of course, when the total pressure was changed other dependent variables also changed and thereby effected conversion. A coal rate of 9 pounds per hour appeared to be close to the limit of operability because coal temperatures were low and the coal was not being devolatilized sufficiently to produce dry char.

In another series of experiments, the coal and gas rates were approximately constant at 6 to 7 pounds per hour and 175 scfh while the quantity of hydrogen supplied with the feed gas was varied over a fairly wide range between 50 and 175 scfh. Coal and carbon conversions and yields of hydrocarbon gases decreased with decreasing hydrogen concentration in the feed gas; however, some of this change can be attributed to lower reaction temperatures which resulted from the change in feed gas composition. The change in carbon conversion over the range of hydrogen-to-coal ratios between 10 and 30 is shown in figure 3. At 3,000 psig, reducing the hydrogen-to-coal ratio from 30 to 10 scf per pound of coal reduced the carbon conversion from 35 percent to 24 percent based on maf coal.

The hydrogen-to-coal ratio has an important bearing on the quality of the gas leaving the dilute-phase zone. If high-Btu gas is to be produced, the feed gas must have a composition that provides adequate hydrogen for conversion of the coal carbon to hydrocarbon gases in sufficient yield that the effluent gas exceeds 900 Btu per scf in gross heating value. This can be seen in figure 4 which shows how the heating value of the effluent gas changed with the hydrogen-to-coal ratio at total pressures of 1,500 and 3,000 psig. Conditions were the same as those relating to figure 3. The increase in heating value was least at the lowest hydrogen-to-coal ratio, an increase of about 100 Btu per scf with feed gas containing 75 scf per pound of coal at a total pressure of 3,000 psig; however, this was the feed ratio needed to produce an effluent gas having 910 Btu heating value. An increase of 200 Btu in the heating value was obtained at the opposite extreme where the hydrogen-to-coal ratio was 30 scf per pound. The reduction in the differential heating value reflects both decreasing hydrogen partial pressure and the resulting loss of heat of reaction. Of course, these data represent one of many possible feed gas-to-coal ratios, a number of which certainly would give a high-Btu effluent gas. Many experiments would be required before an optimum feed ratio could be selected.

HYDROGENATION OF CHAR

Char from the hydrogenation of coal in dilute-phase was hydrogenated continuously in a moving bed at 3,000 and 1,500 psig. The objective was to determine the hydrogen-to-feed ratio that would produce an effluent gas of a certain selected composition for a particular conversion.

Equipment and Procedure

A schematic diagram of the system is shown in figure 5. The reaction vessel filled completely with dilute-phase char consisted of a 5-foot length of 1-inch pipe connected to a 6-foot length of 1/2-inch pipe. The length of the heated zone was adjusted between limits of 6 and 24 inches according to the char conversion requirements of a particular experiment. A variable speed screw continuously discharged reacted char from the bottom of the vessel. A flow of compressed hydrogen was introduced into the screw housing, and heating occurred during upward flow in contact with the descending stream of hot char. The gases and vapors were withdrawn at the top of the heated zone and flowed through a cold vessel where the vapors condensed and were collected. The uncondensed gases were reduced in pressure, metered, and either collected in a holder from which samples were withdrawn or were discharged to the atmosphere. A small sidestream was passed continuously through a meter that measured its specific gravity. Gas composition could be controlled by varying the hydrogen-to-char ratio, and char conversion could be controlled by varying the retention time of the char in the reaction zone.

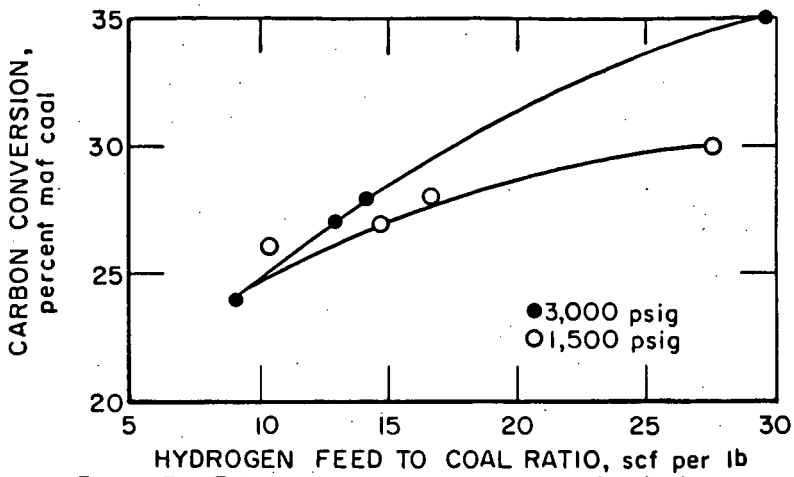

Figure 3.—Effect of hydrogen concentration in feed gas on carbon conversion at approximately constant gas and coal rates.

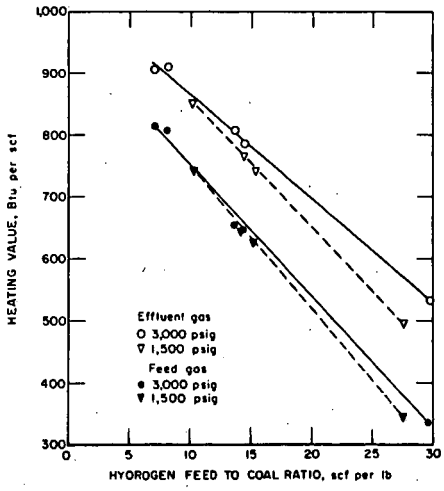

Figure 4.—Effect of hydrogen feed to coal ratio on increasing the heating value of gas by dilute-phase hydrogenation.

Results and Discussion

Table 4 shows the results obtained when dilute-phase char was hydrogenated. At

TABLE 4

HYDROGENATION OF DILUTE-PHASE CHAR

Pressure, psig	1,500	1,500	3,000
Temperature, ° C	900	900	700
Residence time, minutes	3.5	7.5	3.5
Hydrogen/char ratio, scf per pound	11	32	25
Conversion, wt pct of maf char	34	52	26
Effluent gas composition, percent			
Hydrogen	31	35	62
Methane	67	63	36
Ethane	1	1	1
Carbon monoxide	1	1	1
Volatile content of residue, wt pct maf basis 1/	2.6	2.4	2.6

1/ Volatile content of feed char-12.8 percent.

1,500 psig, 900° C, and a residence time of about 3-1/2 minutes the conversion of dilute-phase char was 34 percent, based on maf feed. At the hydrogen-to-char feed (maf) ratio of 11 scf per pound, the effluent gas contained 67 percent methane, 31 percent hydrogen, and 1 percent each of ethane and carbon monoxide. When the residence time was increased to 7-1/2 minutes, the conversion of char increased to 52 percent. The composition of the effluent gas was 63 percent methane, 35 percent hydrogen, and 1 percent each of ethane and carbon monoxide. The hydrogen-to-maf-char needed to produce gas of this composition was 32 scf per pound. An experiment at 700° C and 3,000 psig produced a char conversion of 26 percent with a residence time of 3-1/2 minutes. Because hydrogen-to-char ratio of 25 scf per pound was used in this experiment, the concentration of methane was only 36 percent; the other concentrations were 62 percent hydrogen with 1 percent each of ethane and carbon monoxide.

These data emphasize the considerable range of char conversion and effluent gas compositions that could be obtained simultaneously by varying hydrogen-to-char ratios and retention times. Only a few minutes retention time was required to convert one-quarter to one-third of the char to methane under the conditions used. For equal retention times, more char was converted at 1,500 psig and 900° C than was converted at 3,000 psig and 700° C; hence, temperature had a greater influence than pressure on char conversion.

CONCEPTIONAL PROCESS

Two reaction stages are required in this conceptional process for the direct conversion of coal to high-Btu gas: (1) a dilute-phase stage in which coal is partially devolatilized in a stream of hot gas containing a fairly high concentration of methane; decomposition and hydrogenation of the coal volatiles increases the methane concentration of the gas leaving this stage to the extent that removal of impurities will give a product exceeding 900 Btu per scf heating value, and (2) a dense-phase stage in which the char from the first

stage is hydrogenated in a moving bed thus producing the hot methane-hydrogen mixture that is fed into the first stage. Overall coal conversion can be varied over a wide range through choice of residence time, pressure, and temperature; however, residence time of char in the reaction zone has the greatest influence on overall conversion. Coal conversion is held at a level that will supply sufficient char for the production of the required amount of hydrogen. Conversion of coal would be approximately 54 percent, based on maf coal, and about 45 percent of the coal carbon would appear as hydrocarbon gases in the product.

Figure 6 is a simplified flow diagram of the conceptional process. Coal that has been crushed, dried, and sized to minus 100 mesh sieve size is fed through lock-hoppers into the top of a reaction vessel where it becomes dispersed into a dilute-phase during free-fall through hot gas entering in concurrent flow. The residence time of the coal in the dilute-phase stage is about 6 to 8 seconds and is assumed to result in the conversion of approximately 25 percent of the coal while the coal volatiles, having a residence time of about 30 seconds, are hydrocracked to gas. The partially devolatilized coal or char is held for 3 to 5 minutes in the bottom section of the reactor where the hydrogen feed enters. Approximately 35 percent (ash-free basis) of the char is converted to methane. The gas leaving the top of the char bed mixes with a portion of the gas from the dilute-phase stage and the combined stream is returned to the top of the dilute-phase stage. This very hot gas supplies the heat needed to bring the coal feed to reaction temperature. The hot, outgoing char residue exchanges heat with the cold incoming hydrogen feed before being discharged into lock-hoppers and conveyed to an entrained gasification plant where the hydrogen is produced. The raw product gas is withdrawn from the lower portion of the dilute-phase stage and contains mostly methane with some hydrogen and water vapor and small quantities of carbon oxides, ammonia, and hydrogen sulfide. This gas, being at 200 atm and about 800° C, has considerable potential for producing useful work. We propose to recover electrical power by first removing the entrained solids (dust) and then expanding the gas through a turbine to an exit pressure of 40 atm and temperature of 520° C (970° F). The gas, following cooling and cleaning at pressure to remove contaminants, could go directly into the transmission system, or it could be processed further to obtain some additional methane from the small quantity of residual carbon monoxide and hydrogen.

The hydrogenation reaction, being strongly exothermic, requires the removal of heat to control the temperature. This could be done by pumping water at 3,000 psig through thin-walled tubing distributed throughout the char hydrogenation stage. The superheated steam generated in the tubing is collected and expanded through a turbine to generate additional power, and the condensate is returned to the pump.

CONCLUSIONS

Exploratory experiments have shown that strongly caking coal can be partially devolatilized by dispersing it in a dilute-phase in a methane-hydrogen mixture which becomes enriched with hydrocarbon gases from the coal volatiles and thereby increased in gross heating value to 900 Btu per scf or more. The coal residue was a dry, free-flowing char which is very reactive and easily hydrogenated to produce a methane-rich gas. The composition of this gas was determined by the hydrocarbon gas yields and the hydrogen-to-char feed ratios, while the char conversion was fixed by the residence time and reaction temperature. The two operations were combined to form a conceptional process for producing high-Btu gas on a commercial scale.

Development of dilute-phase hydrogasification is continuing with the objective of determining the effect of higher coal temperatures on yields and gas composition. Coals other than Pittsburgh seam also will be tested.

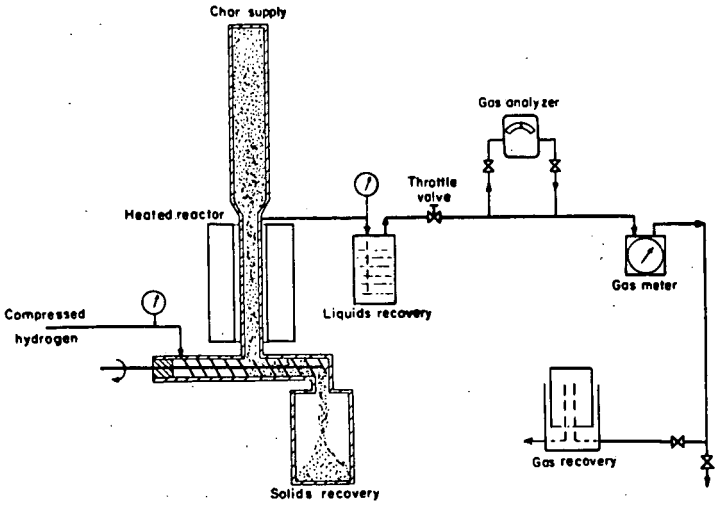

Figure 5.— Schematic diagram of char hydrogasification apparatus.

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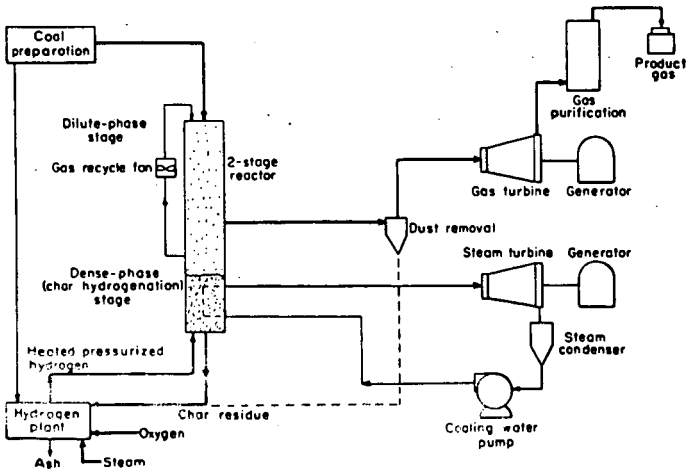

Figure 6.— Simplified flow diagram of the conceptional process.

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