

HYDROGASIFICATION OF PRETREATED COAL
FOR PIPELINE GAS PRODUCTIONB. S. LEE
E. J. PYRCIOCH
F. C. SCHORA, JR.Institute of Gas Technology
Chicago, Illinois

INTRODUCTION

There has been a long-standing need for an economic process to produce synthetic pipeline gas either as a supplement to or a substitute for natural gas. Development of a process for direct hydrogenation of coal to form an essentially methane gas has been in progress at IGT since 1955. Various facets of this hydrogasification process have been reported,^{3, 5, 6, 8, 9, 11, 12, 13} Process concepts were revised as experimental results became available.

In the current concept hydrogasification is carried out in two stages, with the gas flow countercurrent to the solids flow. The first stage, at temperatures of 1200°-1400°F, rapidly gasifies the most reactive fractions of the incoming coal, forming methane almost exclusively. The second stage, at 1700°-2000°F, gasifies the less reactive remainder from the first stage with hydrogen and steam to yield methane along with carbon oxides. The carbon residue from the second stage is used to generate the required hydrogen.

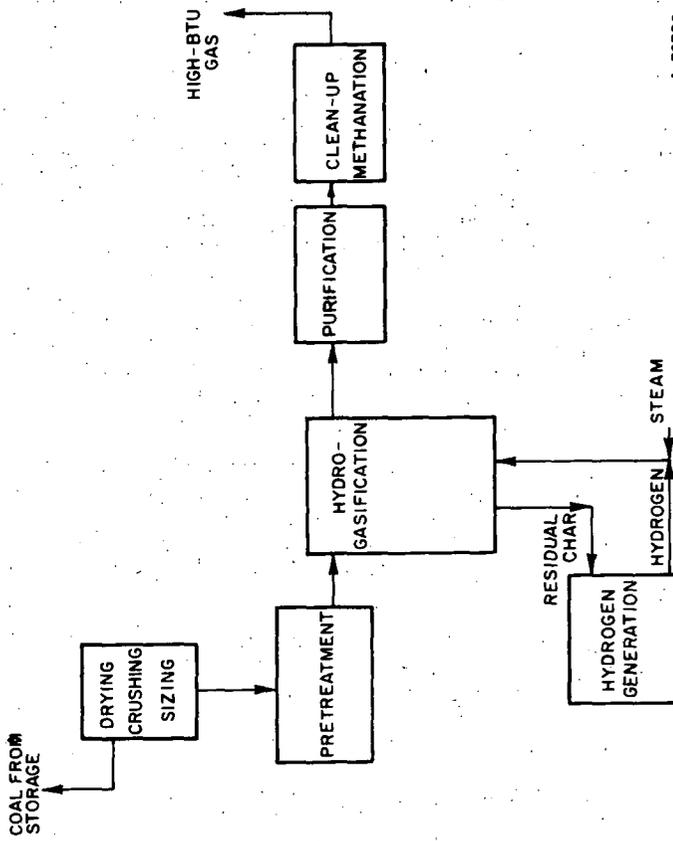
The low-temperature first stage permits high equilibrium methane concentration in the gas. The high-temperature second stage, on the other hand, favors the steam-carbon reaction for in situ hydrogen production.

The overall process is shown schematically in Figure 1. Raw coal is first rendered nonagglomerating in the pretreater, then is fed to the hydrogasifier. The residue is used to generate external hydrogen. The hydrogasifier effluent gas is first purified, then cleaned up in a methanator to reduce its carbon monoxide content and to upgrade the heating value. The entire system, except the pretreater, operates at 1000 psig or higher.

Although in our present program, coals ranging in rank from lignite to anthracite will be studied, we are focusing attention on high-volatile-content bituminous coals because the volatile matter in coal gasifies easily and produces a rich yield of methane. However, the high volatile content tends to make the coals strongly agglomerating when exposed to the hydrogasification conditions. As an operating necessity, the coals are pretreated by mild oxidation to destroy the agglomerating tendency. Such treatment is held to a minimum to preserve a maximum amount of the volatile matter for reaction.

The program objectives are:

1. To establish through operating experience the minimum pretreatment for coal.



A-76706

Figure 1. Block-Flow Diagram of IGT Coal Hydrogasification Process

2. To simulate in sequence the operation of the two-stage hydrogasification.
3. To study different modes of gas-solid contact, aiming at maximum throughput and controllable reaction rates.
4. To determine the extent of reaction equilibrium and kinetics limitations that relate to scale-up beyond this pilot unit.
5. To test and observe the mechanical operation of this high-pressure, high-temperature reactor system, in terms of materials of construction, instrumentation and control, special equipment, and safety.

EQUIPMENT AND PROCEDURE

The pilot reactor system has been described in detail.⁴ Briefly, referring to the schematic flowsheet in Figure 2, the balanced-pressure reactor is a 4-inch Schedule 40 pipe, made of Type 446 alloy steel, 21 feet in length of which 18 feet is electrically heated. The reactor is designed to withstand 2000 psig and 2200°F. Coal is stored in the hopper and fed to the reactor through a screw feeder. A screw at the bottom of the reactor discharges the residue to the receiver. Inlet gases are preheated in furnaces and enter the reactor at the bottom. Effluent gases leave at the top and are condensed, filtered, metered, sampled, then flared. Reactor operation is continuous within the limits of the 400-pound feed hopper capacity for pretreated coal. The entire system is tested at the pressure of the run before coal feed is charged to the hopper.

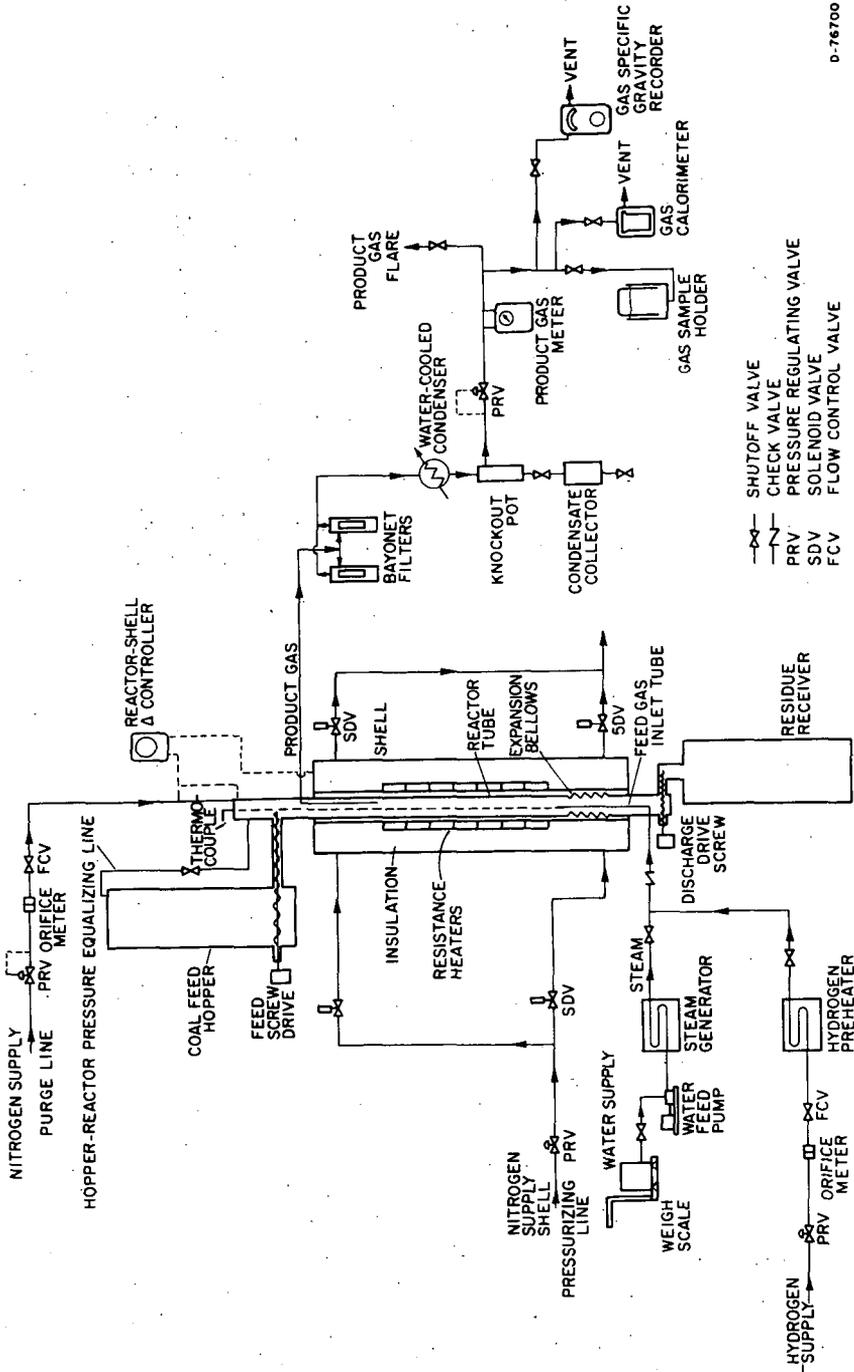
In simulating the two stages sequentially, pretreated coal is contacted in the low-temperature stage with a hydrogen-steam-natural gas mixture which approximates - except for the absence of carbon oxides - the gas leaving the high-temperature stage. The partially gasified coal is collected and fed against a hydrogen-steam mixture in the high-temperature stage.

By adjusting the feed and discharge rates of the coal, the reaction can be made to take place either in free fall, or in a combination of free-fall and moving-bed conditions. The moving bed was operated at a height of either 7 or 3.5 feet. Gas sample probes in the bed indicated reaction profile.

Coal feed rates ranged from 8 to 23 lb/hr. Gas rates corresponded to less than 0.1 ft/sec linear superficial velocity in order to stay below the threshold of fluidization and thus maintain true countercurrent gas-solid contact along the entire reactor length.

RESULTS AND DISCUSSIONS

Typical results of the hydrogasification tests are shown in Tables 1, 2, and 3. Reported coal residence times are based on measured bulk densities of the reactor residues and the coal bed volume. Time in free fall was negligible compared to that in the bed. Feed gas residence times are based on the flow rate at average bed conditions and coal bed volume. Time in the free-fall section is not included.



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Figure 2. SCHEMATIC FLOWSHEET FOR PILOT PLANT HYDROGASIFICATION SYSTEM

Table 1 (Cont.). HYDROGASIFICATION RUN DATA

Coal Feed Run	Partially Hydrogasified Pittsburgh Coal						Partially Hydrogasified Ohio Coal	
	HT-99	HT-80	HT-87	Hydrogen + Steam HT-86	HT-64	HT-72	HT-77	Hydrogen + Steam HT-81
OPERATING CONDITIONS								
Coal Bed Height, ft	3.5	3.5	3.5	3.5	7.0	7.0	7.0	7.0
Reactor Temperature, °F	1038	1041	1007	1023	1021	1023	1021	992
Maximum Average	1740	1740	1735	1740	1585	1835	2005	1720
Coal Rate, lb/hr	1310	1695	1735	1735	1950	1950	1950	1710
Feed Gas Rate, SCF/hr	506.77	13.20	17.10	18.44	8.02	16.74	17.22	13.63
Steam Concentration, mole %	29.71	31.9	31.9	31.9	29.10	29.10	29.10	29.10
Hydrogen/Coal Ratio, % of stoichiometric	52.3	32.7	30.3	32.5	41.6	36.6	33.6	33.2
Coal Space Velocity, lb/cu ft-hr	26.7	36.0	21.6	31.7	80.7	29.7	35.0	29.0
Coal Residence Time, min	141.87	36.20	55.98	40.00	12.95	27.95	27.84	44.04
Coal Residence Time, min	0.702	1.15	1.17	1.10	1.50	1.57	1.57	1.08
Coal Residence Time, min	8.14	24.1	21.8	21.5	83.3	38.2	39.5	27.8
OPERATING RESULTS								
Product Gas Rate, SCF/hr	971.5	348.7	346.6	370.7	411.8	585.2	551.2	413.2
Hydrocarbon Yield, SCF/lb	1.11	5.85	4.11	5.31	4.88	8.26	4.86	5.39
Yield, SCF/cu ft-hr	157.0	211.9	227.4	221.7	63.22	169.3	135.4	237.3
Carbon Oxide Yield, SCF/lb	0.266	3.58	2.85	3.31	1.80	5.32	4.09	2.99
Feed Hydrogen Reacted, SCF/lb	1.131	5.97	3.85	3.91	10.32	1.80	2.51	4.61
Coal Residue, lb/lb coal	0.940	0.678	0.769	0.754	0.866	0.460	0.671	0.594
Net MAF Coal Hydrogasified, wt %	0.747	0.134	0.164	0.176	1.136	0.113	0.0774	0.135
Carbon Gasified, wt %	5.73	37.5	26.4	36.0	21.5	52.0	43.6	33.1
Steam Decomposed, % of steam fed	6.52	36.1	24.7	34.9	27.8	48.8	36.9	32.7
Steam Decomposed, % of total	0.00	50.0	52.9	49.4	5.7	70.4	66.4	52.6
Overall Material Balance, %	0.00	53.4	56.0	51.0	6.9	71.9	69.3	54.2
Carbon Balance, %	95.8	93.1	100.9	101.9	102.3	86.0	100.1	99.8
Hydrogen Balance, %	102.3	102.5	103.9	97.2	112.4	102.7	102.7	99.8
Oxygen Balance, %	104.2	96.8	96.6	101.0	105.8	101.4	112.1	97.5
PRODUCT GAS PROPERTIES								
Gas Composition, mole %								
N ₂	36.6	35.0	34.9	32.5	37.4	33.2	31.9	43.5
CO	2.0	9.5	8.8	9.0	1.9	13.0	11.6	7.5
CO ₂	56.7	36.0	33.7	37.6	49.6	35.1	41.5	23.1
CH ₄	8.6	18.8	20.2	18.5	9.5	17.8	15.0	17.3
C ₂ H ₆	---	---	0.1	---	---	0.1	---	---
C ₂ H ₄	---	---	---	---	---	---	---	---
C ₂ H ₂	---	---	---	---	---	---	---	---
Benzene	---	---	---	---	---	---	---	---
High Boiling Value of Ne-Free Gas, Btu/SCF	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	401	505	520	495	414	521	464	515

TABLE 2. SOLID PRODUCTS FROM HYDROGASIFIER

Coal Feed Run	HT-60		HT-61c		HT-65		HT-66		HT-71		HT-76	
	Feed	Residue										
Proximate Analysis, wt %	0.5	2.1	0.6	0.5	0.6	0.5	0.6	2.1	1.1	1.3	0.9	0.9
Moisture	61.8	68.6	78.5	63.5	63.5	75.8	63.5	77.6	61.6	72.5	62.8	76.0
Fixed Carbon	33.7	35.0	17.6	10.0	17.2	18.7	17.2	18.0	13.7	18.0	11.4	15.8
Ash	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Ultimate Analysis (dry), wt %	70.5	68.5	78.2	71.7	78.2	71.7	76.9	68.5	73.0	71.8	70.5	70.5
Carbon	3.77	2.42	3.73	1.36	3.70	2.66	3.30	2.30	1.04	1.05	1.02	1.02
Hydrogen	0.36	0.27	0.24	0.24	0.27	0.24	0.27	0.24	0.24	0.24	0.24	0.24
Nitrogen	0.53	0.53	0.53	0.53	0.53	0.53	0.53	0.53	0.53	0.53	0.53	0.53
Sulfur	3.53	3.07	1.71	3.26	1.17	4.80	2.00	3.57	2.59	3.68	3.06	3.06
Oxygen	18.62	18.44	17.63	18.48	17.63	18.48	17.63	18.48	17.63	18.48	17.63	18.48
Ash	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Screen Analysis, USS, wt %	19.1	18.7	18.5	21.6	26.1	22.4	20.9	18.6	16.5	18.8	13.1	13.2
+20	38.8	24.0	16.9	21.4	21.1	22.4	20.9	18.6	16.5	18.8	13.1	13.2
+40	23.9	17.3	21.3	24.3	24.3	20.9	24.6	24.6	21.7	22.9	24.1	24.1
+60	1.6	1.9	4.5	1.2	3.4	1.9	2.3	2.3	2.1	2.9	2.1	2.1
+100	0.8	0.6	1.4	0.2	1.0	0.2	1.0	0.2	0.2	0.2	0.2	0.2
+200	0.2	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
+325	0.6	0.4	0.7	0.7	0.7	0.7	0.7	0.7	0.6	0.6	0.6	0.6
+355	0.6	0.4	0.7	0.7	0.7	0.7	0.7	0.7	0.6	0.6	0.6	0.6
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Coal Feed Run	HT-83		HT-84		HT-85		HT-89		HT-95		HT-99		HT-86		HT-87	
	Feed	Residue														
Proximate Analysis, wt %	1.9	1.0	3.9	0.5	1.5	0.7	2.7	0.7	0.7	0.7	0.5	0.5	2.6	1.4	1.9	0.0
Moisture	62.4	74.9	65.5	79.7	68.5	84.6	77.4	65.5	84.6	76.9	76.3	77.9	69.9	82.5	81.3	81.3
Fixed Carbon	32.4	18.8	18.8	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Ash	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Ultimate Analysis (dry), wt %	70.6	76.0	72.8	79.9	73.2	78.2	73.3	81.8	76.4	78.8	76.4	78.6	74.7	81.5	81.8	81.8
Carbon	3.68	1.37	3.68	1.37	2.29	1.37	3.86	0.87	1.21	1.21	0.87	1.55	0.53	1.02	0.53	0.53
Hydrogen	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76
Nitrogen	8.85	8.85	8.85	8.85	8.85	8.85	8.85	8.85	8.85	8.85	8.85	8.85	8.85	8.85	8.85	8.85
Oxygen	3.65	2.22	3.31	1.88	2.73	1.61	3.23	1.61	3.23	1.78	1.68	2.30	1.99	1.68	1.68	1.68
Sulfur	12.63	12.63	12.63	12.63	12.63	12.63	12.63	12.63	12.63	12.63	12.63	12.63	12.63	12.63	12.63	12.63
Ash	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Screen Analysis, USS, wt %	10.1	6.1	12.0	7.2	9.2	12.3	8.4	10.1	10.1	10.1	6.6	16.4	7.7	16.2	8.0	11.0
+20	26.1	26.7	22.2	20.3	24.5	24.5	24.5	24.5	24.5	24.5	24.5	24.5	24.5	24.5	24.5	24.5
+40	22.4	27.9	23.8	27.6	26.9	33.5	23.4	25.0	25.4	28.5	25.2	27.7	24.5	25.2	25.2	25.2
+60	10.6	10.3	9.8	7.4	11.1	16.5	4.1	3.9	3.9	4.5	4.5	4.7	4.7	4.7	4.7	4.7
+100	9.4	5.7	5.9	2.9	5.9	5.6	7.1	5.6	5.3	6.9	7.0	6.7	7.7	7.7	7.7	7.7
+200	3.4	0.6	1.0	0.3	1.2	0.8	1.1	0.8	0.8	1.1	1.0	1.0	1.0	1.0	1.0	1.0
+325	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
+355	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Coal Feed Run	HT-86		HT-64		HT-72		HT-73		HT-77		HT-81	
	Feed	Residue										
Proximate Analysis, wt %	1.1	0.7	0.9	1.1	1.2	2.0	0.6	0.6	0.6	0.6	1.0	1.9
Moisture	78.9	67.6	75.9	74.1	76.6	60.8	64.0	64.0	62.7	62.7	60.1	77.1
Fixed Carbon	16.3	20.4	21.5	16.9	16.9	18.7	32.4	7.9	11.2	13.4	19.1	19.1
Ash	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Ultimate Analysis (dry), wt %	80.2	68.1	76.1	76.9	76.9	62.3	65.6	73.7	83.2	81.2	78.5	78.5
Carbon	1.36	0.98	1.52	1.23	1.65	0.30	0.43	1.59	2.05	1.88	0.50	0.50
Hydrogen	0.76	0.69	0.67	0.57	0.76	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Nitrogen	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60
Sulfur	2.03	2.57	1.84	0.23	2.22	2.06	2.02	2.75	1.57	1.82	1.86	1.86
Oxygen	16.43	16.43	16.43	16.43	16.43	16.43	16.43	16.43	16.43	16.43	16.43	16.43
Ash	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Screen Analysis, USS, wt %	7.1	4.0	15.7	11.2	11.9	4.4	7.7	6.5	12.3	18.3	8.2	5.3
+20	13.4	12.6	10.0	14.6	10.9	15.0	17.7	15.0	17.7	20.3	17.9	13.3
+40	24.5	21.2	20.5	22.2	22.6	27.0	27.0	29.8	23.7	20.5	27.0	26.6
+60	11.5	11.1	4.4	6.1	10.3	12.7	12.9	11.6	10.7	9.0	10.7	12.3
+100	10.5	6.4	1.7	2.1	4.9	4.7	4.7	4.7	4.9	4.4	4.8	4.5
+200	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
+325	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
+355	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 3. LIQUID PRODUCTS FROM HYDROGASIFIER

Coal Feed	Pretreated Pittsburgh Coal											
	HT-50	HT-51e	HT-52	HT-53	HT-71	HT-72	HT-81	HT-84	HT-85	HT-86	HT-87	HT-88
Run	0.126	0.734	0.652	0.668	0.554	0.598	0.330	0.235	0.379	0.1127	0.379	0.1127
Weight, lb/lb coal	64.92	92.98	90.13	94.58	94.79	92.02	95.26	92.90	95.28	89.84	95.28	89.84
Composition, wt %	35.08	7.02	9.57	5.42	5.21	7.98	3.74	7.70	4.72	10.16	4.72	10.16
Oil												
Composition of Oil Fraction, wt %	87.4	92.0	88.2	87.8	85.5	85.2	84.8	87.4	82.1	86.4	82.1	86.4
Carbon	7.18	6.50	7.02	6.21	6.25	6.19	6.57	6.18	6.15	6.93	6.15	6.93
Hydrogen	94.58	96.50	95.25	94.11	91.75	91.69	91.27	93.58	88.25	93.35	88.25	93.35
Total												
Carbon in Oil Fraction, wt % of carbon in coal	6.05	6.56	7.68	4.67	2.56	5.12	1.48	2.17	2.00	1.36	2.00	1.36

Coal Feed	Partially Hydrogenated Pittsburgh Coal						Partially Hydrogenated Ohio Coal		
	HT-59	HT-60	HT-67	HT-66	HT-61	HT-72	HT-77	HT-81	HT-82
Run	0.747	0.194	0.1081	0.1764	1.198	0.119	0.0774	0.582	0.155
Weight, lb/lb coal	100.0	100.0	100.0	100.0	97.0	100.0	100.0	91.94	100.0
Composition, wt %					3.0			8.46	
Oil									
Composition of Oil Fraction, wt %									
Carbon					85.0			86.4	
Hydrogen					6.5			6.51	
Total					91.5			92.91	
Carbon in Oil Fraction, wt % of carbon in coal					4.01			5.77	

Minimum Coal Pretreatment

Two high-volatile-content bituminous coals were tested, one from the Pittsburgh No. 8 seam (Ireland mine) and the other from the Ohio No. 6 seam (Broken Arrow mine). Most of the work to date has been with the former. The proximate and ultimate analyses of these two coals are shown in Table 4. These coals were pretreated to various extents and then hydrogasified. Using volatile matter content as an index of severity of pretreatment, we found that pretreated coal with 24-26% volatile matter can be processed without agglomeration. Raw coal was tested but it swelled badly during the reaction and stuck to the reactor to cause bridging. It is entirely possible that in larger size reactors in which the coal feed would not contact reactor walls immediately, coals with less pretreatment - or even raw coal - could be fed successfully. However, we consider our ability to feed pretreated coal with as much as 24-26% volatile matter a significant achievement. Adjustment of feed tube size, length, and location; the amount of nitrogen purge gas through the tube; and the start-up sequence are factors that were learned through experience.

Two-Stage Simulation

The stage-by-stage simulation procedure used is realistic except for the fact that the partially gasified coal is fed to the second stage at ambient temperature instead of between 1200° and 1400°F. Since hydrogen represents the largest share of the total pipeline gas cost, practically all the runs were conducted at the minimum hydrogen/coal ratio that would produce a total carbon gasification of about 50%. At this degree of gasification, sufficient residual carbon would be available for generating the necessary hydrogen. These figures resulted from an overall system analysis based on existing data on equilibrium, kinetics, and heat and material balances.

Key results obtained in two-stage simulations are summarized in Figure 3a with pretreated Pittsburgh seam coal, and in Figure 3b with pretreated Ohio seam coal. Product gas analyses were adjusted to a nitrogen-free basis because of the high nitrogen purge rates actually used in the tests. The purge gas was needed to prevent hot reactor gases from entering the coal feed tube.

High concentrations of unreacted hydrogen in the product gas from the low-temperature stages limited the heating value to about 700 Btu/SCF. To obtain a high-Btu gas (900 Btu/SCF) requires catalytic methanation of the carbon oxides. Note the absence of carbon oxides in the feed gas to the first stage. Because of the low temperature in the first stage, no steam-carbon reaction is expected. Thus, CO is considered an inert insofar as methane formation is concerned. Therefore, to simplify preparation of the simulation gas mixture, CO was not included in this feed. This assumption appears valid, judging from the low carbon oxide concentration in the first-stage effluent. The amount measured came from the organic oxygen in the coal rather than from the steam-carbon reaction.

Steam, however, appears to play an active role in the low-temperature gasification. Two runs were made, one with a steam-natural gas-hydrogen mixture and the other with a nitrogen-natural gas-hydrogen mixture. Significantly greater amounts of carbon oxides were formed and significantly less water was released from the coal when steam was used. Steam, then, seems to suppress the release of organic

Table 4. ANALYSES OF HIGH-VOLATILE-CONTENT
BITUMINOUS COALS

Seam Mine	Pittsburgh No. 8 Ireland	Ohio No. 6 Broken Arrow
Proximate Analysis, wt %		
Moisture	1.0	1.0
Volatile Matter	35.9	39.6
Fixed Carbon	51.8	53.6
Ash	<u>11.3</u>	<u>5.8</u>
Total	100.0	100.0
Ultimate Analysis (dry), wt %		
Carbon	71.1	74.1
Hydrogen	4.95	5.41
Nitrogen	1.18	1.39
Oxygen	7.35	9.42
Sulfur	4.03	3.87
Ash	<u>11.39</u>	<u>5.81</u>
Total	100.00	100.00
Particle Size, USS		
(As prepared for pretreatment)	-16+80	-16+80

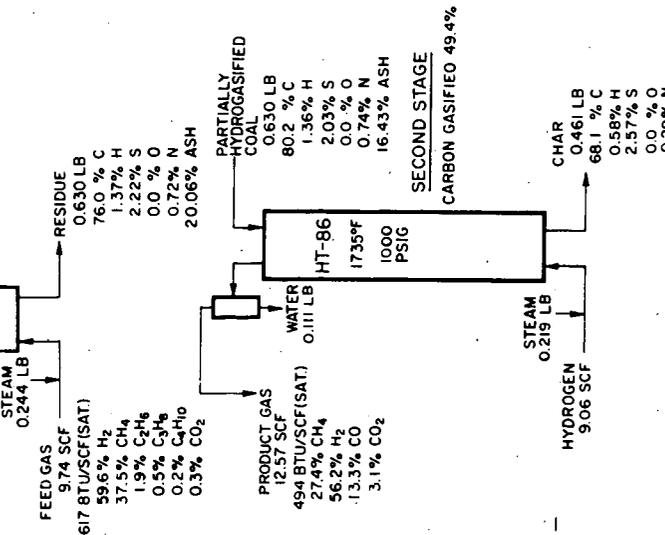
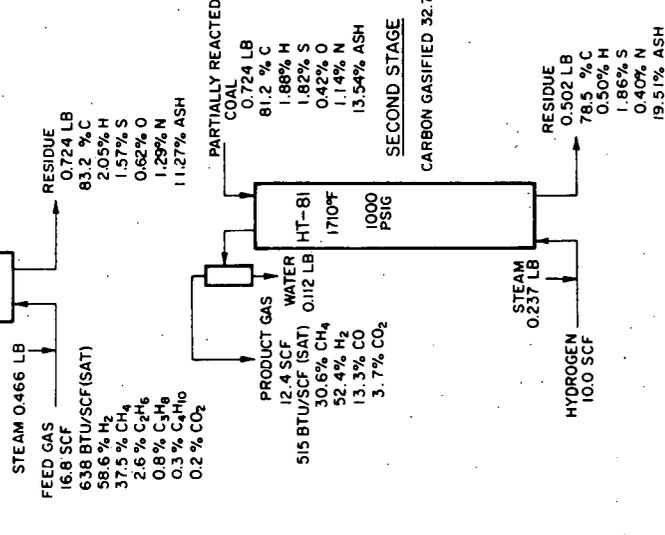
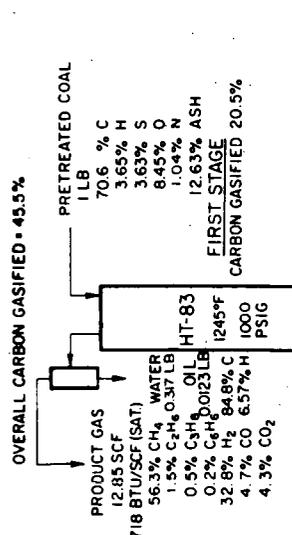
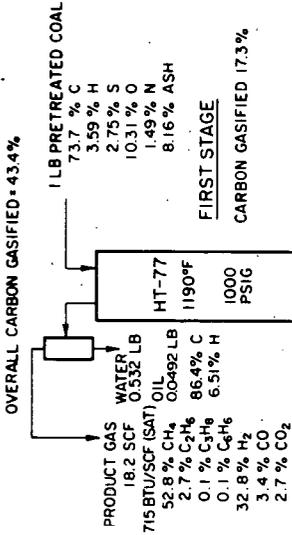


Figure 3b. STAGE-BY-STAGE SIMULATION IN

Figure 3a. STAGE-BY-STAGE SIMULATION IN

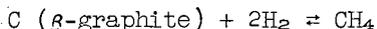
oxygen from coal as water, but forces the oxygen to leave as carbon oxides. This phenomenon seems plausible from the mass action standpoint. From a process standpoint, the release of organic oxygen in coal as carbon oxides is more desirable than as water. In the latter case, hydrogen (either from coal or from external sources) is lost by being combined with the oxygen to form water. In contrast, when the oxygen is released as carbon oxides, these can be converted to more hydrocarbon by subsequent catalytic methanation.

Methane Formation

Equilibrium

It has been well established that the hydrogenation of the volatile matter in coal proceeds very rapidly,¹² and yields methane concentrations higher than the equilibrium value in a β -graphite-hydrogen system. This excess is conveniently attributed to a greater-than-unity coal activity in reference to β -graphite activity. In fact, of course, the hydrogenation of the reactive carbon groups proceeds by splitting off the carbon chains and functional groups rather than by reacting with graphitic carbon. Such reactions lead to methane formation because methane is the predominant stable hydrocarbon at the temperature and pressure in question. The first-stage hydrogasification demonstrates this type of reaction as shown, for example, by the predominance of methane versus other hydrocarbons or carbon oxides in the effluent gas (Figure 3a).

Figure 4 presents the calculated "equilibrium ratio" obtained from the pilot plant tests as a function of the maximum bed temperatures. The curve represents true equilibrium ratio for the reaction:



We note the many runs yielding equilibrium ratios higher than the curve. The group of points below the curve between 1450° and 1550°F came from runs in which a high hydrogen/coal ratio was used, resulting in low methane concentration.

We found the initial gasification so rapid that 20% of the carbon was gasified in merely free-falling through a distance of 18 feet. There appears to be little equilibrium hindrance in view of the mechanism of methane formation discussed above. However, once the reactive carbon is gone, the remaining fixed carbon reacts much more slowly in the second stage. Here we check the approach to β -graphite equilibrium to see if the coal, after the first stage, still has sufficient reactive carbon left to show activity greater than unity. Since methane formation is exothermic, from the process standpoint, the more methane that is formed in the second stage, the more heat there would be available to furnish the endothermic heat for the steam-carbon reaction, which, in turn, would produce hydrogen *in situ* and reduce the external hydrogen requirement. With partially gasified Pittsburgh No. 8 seam coal, we have so far observed a carbon activity between 1 and 2 at 1700°-1950°F.

Reaction Rate

We compared the integral methane formation rates from our pilot plant tests with those reported by others.^{1, 2, 6, 14} To do so

on the same basis, we took the reaction rate to be pseudo-first order with respect to the hydrogen partial pressure. The calculated reaction rate constant for each run is plotted against carbon gasification in Figure 5. Several observations can be made:

1. The rate of methane formation for pretreated Pittsburgh coal is not slowed by the presence of methane in the feed gas. This is in agreement with Zielke and Gorin¹⁴ in their study of hydrogasification of Disco char.
2. The pretreated coal is quite reactive. For example, at 25-30% carbon gasification with steam-hydrogen mixtures, the rate constant is more than twice that reported by Feldkirchner and Linden⁶ in reacting low-temperature bituminous char with hydrogen. The greater reactivity is most likely attributable to the higher volatile content of our pretreated coal (24-26%) than that of their char (17%).
3. Partially hydrogasified coal, upon further reaction in the high-temperature second stage, gave rate constants quite similar to those obtained with Disco char¹⁴ and residual Australian brown coal,¹ both containing very little volatile matter.

Steam-Carbon Reaction

The reaction $C + H_2O = CO + H_2$ was significant only at temperatures above 1700°F, and was found to increase with temperature. For example, at 1695°F (Run HT-80), 50% of the feed steam decomposed, but at 1825°F (Run HT-72), 70% was decomposed. Carbon oxides formation was related directly to the steam fed and to the steam decomposition. As much as 5.5 SCF of carbon oxides per pound of coal were produced at the maximum 70% steam decomposition. With little or no feed steam decomposition, carbon oxides formation was about 1 SCF or less per pound of coal. In the low-temperature first stage, the presence of steam in the feed gas is responsible, through the laws of mass action, for converting a major fraction of the oxygen in coal to carbon oxides. This oxygen is converted to water when steam is omitted from the feed, e.g., when only hydrogen is fed.

The rate at which the steam-carbon reaction proceeds is highly temperature-dependent,⁹ requiring heat above 2000°F to approach equilibrium.¹¹ Since hydrogasification tests are conducted at less than 2000°F in order to preserve the methane formed, the carbon-steam reaction is expected to be substantially removed from equilibrium. This fact is shown by Figure 6 where calculated "equilibrium ratios" are plotted against maximum bed temperature. The curve represents true equilibrium for comparison.

The carbon-steam reaction is important from the process standpoint not only as a source of generating in situ hydrogen, but also as a temperature controller. When pure hydrogen is the gasifying medium, the strong heat release by the methane-forming reaction causes runaway temperatures. In a hydrogen-steam mixture, this released heat is absorbed by the carbon-steam reaction, thereby stabilizing temperature.

Reaction Profile

To gain some insight into the path of reaction in free-fall or moving-bed zones, gas sample probes were located at several levels

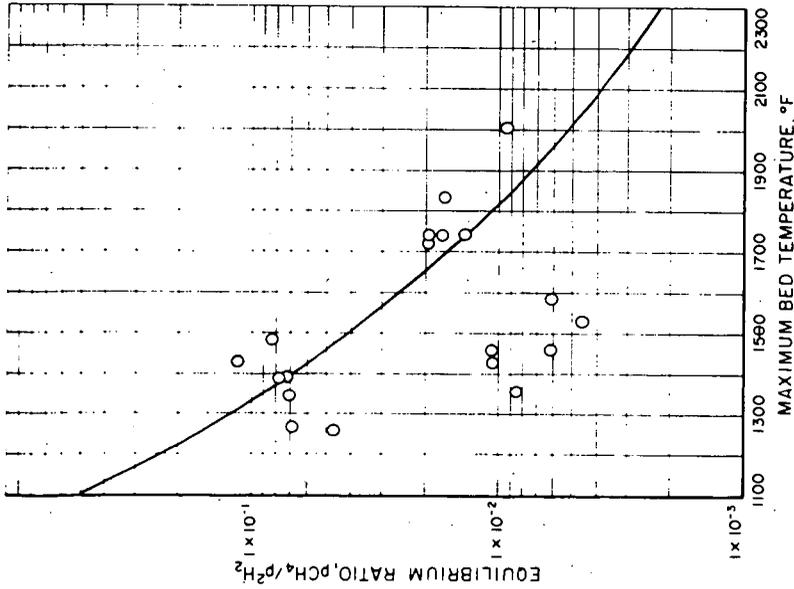


Figure 4. APPROACH TO CARBON-HYDROGEN REACTION EQUILIBRIUM FOR PRETREATED PITTSBURGH SEAM BITUMINOUS COAL

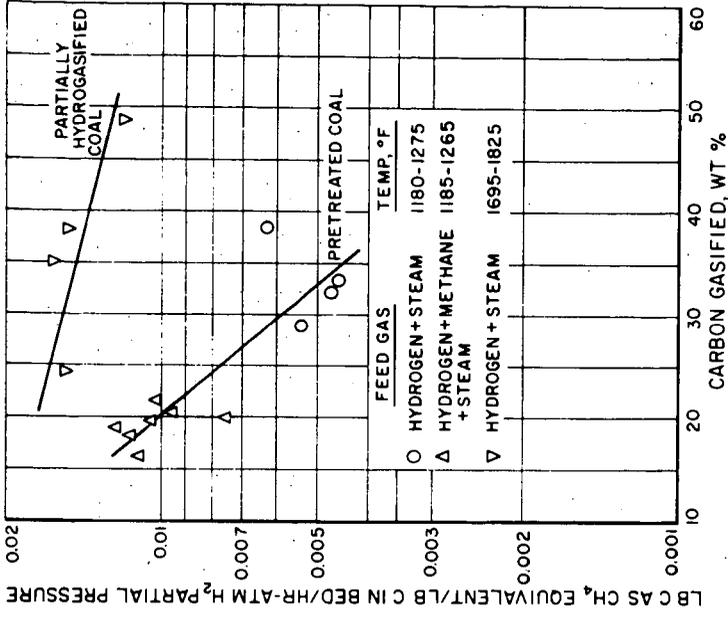


Figure 5. INTEGRAL METHANE FORMATION RATE FOR PRETREATED PITTSBURGH SEAM BITUMINOUS COAL

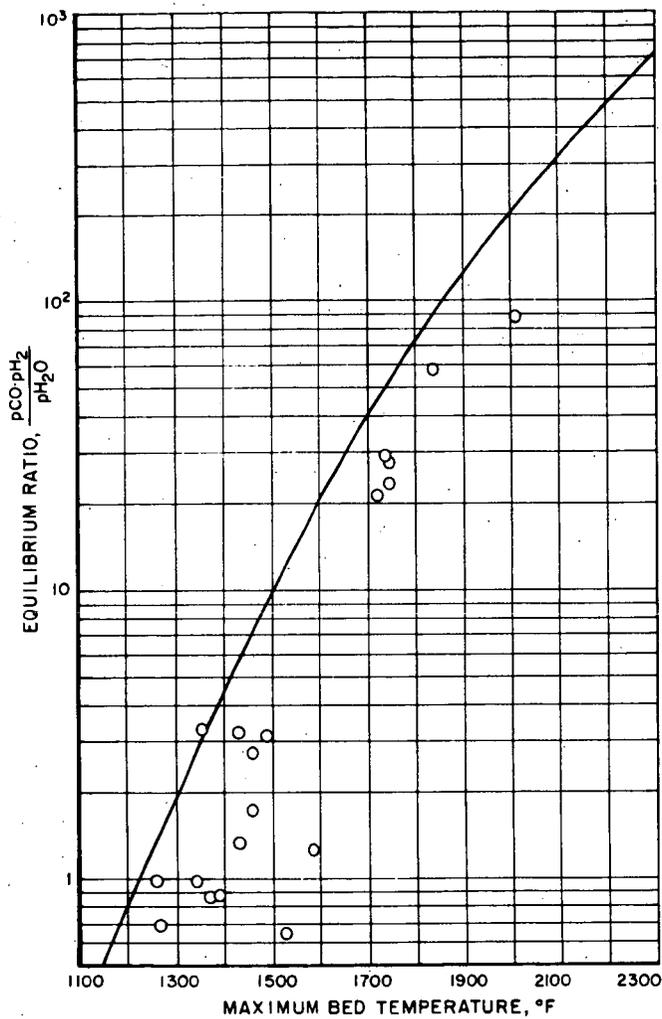


Figure 6. APPROACH TO STEAM-CARBON REACTION
EQUILIBRIUM FOR PRETREATED
PITTSBURGH SEAM BITUMINOUS COAL

in the bed. Compare (Table 5) the probe gas analyses from a low-temperature run, HT-67, and a high-temperature run, HT-72. Both runs were made with a 7-foot-deep moving bed. Note that in the high-temperature test, the reaction was practically complete in the lower half of the bed, with very little reaction in the upper half of the bed and in the free-fall zone above the bed. On the other hand, in the low-temperature test, the reverse was true: The bulk of the reaction took place in the free-fall zone and at the top of the bed, with very little reaction in the rest of the bed. It follows then that at both temperatures the bed height could be reduced to 3.5 feet without any loss of gasification. This is in fact the case as shown in Table 5 by the probe samples from HT-86, a high-temperature run using a 3.5-foot-deep bed.

The high-temperature reaction is apparently equilibrium-limited; it attains its limit in a relatively short contact time, in a short bed. The low-temperature reaction is extremely rapid, requiring only a matter of seconds to complete. The reactive portion of coal, discussed by Wen and Huebler,¹² is quickly gasified, after which the remainder of the carbon is not reactive at the low temperature. In view of these facts, a likely hydrogasifier configuration would incorporate a low-temperature free-fall zone followed by a shallow high-temperature stage.

ACKNOWLEDGMENT

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