Analyses of Gases in the Upper and Lower Annuli

A knowledge of the composition of the gases made in each reaction zone would be helpful in analyzing the performance of the gasification system. Attempts were made to gain some idea of the equilibrium attained in the upper and lower annuli by taking spot samples of gas at several positions near the outlet of each reaction zone. Table 17 shows the analysis of gases from the upper and lower zones during runs 10, 11, and 12 in the small pilot plant. Table 18 shows the properties of gases sampled in the two zones in the large pilot plant during runs 1, 2, 3, and 4.

In considering these analyses, attention is called to the fact that is is virtually impossible to obtain a representative sample of gas by extracting a spot sample from any place in either annulus. A spot sample cannot represent the average conditions because of the change in the rate of reaction and of the temperature, and consequently the equilibrium, as the point of sampling moves away from the single heated wall. Nevertheless, these spot samples are of value in obtaining a picture of what may be happening inside the reaction zones. A further deterrent in obtaining a representative sample of gas in either annulus by taking a spot sample at any given point is the fact that the temperature and movement of gas through a given vertical section of the reaction zone is not necessarily constant with respect to other sections. Therefore, the analyses reported in tables 17 and 18 are only indicative of the variability of the gas in either reaction zone.

ANALYSIS AND DISCUSSION OF TESTS AND EXPERIMENTAL DATA

Process of Distillation and Gasification

A conception of the process of distillation and gasification of low-rank fuels in externally heated retorts was known before either of the pilot plants was built. Reyerson and Gernes had conducted investigations in an electrically heated vertical retort,[14] and Davis and Parry had conducted studies on the carbonization and gasification properties of subbituminous coal.[15] In addition, a variety of small-scale studies had been made by the Bureau of Mines at Golden on the thermal decomposition of subbituminous coal and lignite. These investigations and the experience gained in the operation of the pilot plants revealed that the process of gasification in the present system proceeds about as follows:

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[14] Reyerson, L. H., and Gernes, D. C., A Method for Complete Gasification of Lignite: U. S. Patent No. 2,276,343, 1938.

[15] Davis, J. D., and Parry, V. F., Carbonizing Properties of a Subbituminous Coal from Puritan Mine, Dacono, Weld County, Colo.: Bureau of Mines Rept. of Investigations 3428, 1939, 32 pp.

TABLE 17. - Analyses of upper and lower annuli gases, runs 10, 11, and 12, Golden pilot plant, 1945.

Run and period	Date	Time1/	Analysis, percent							Specific gravity (air = 1.0) calculated	B.t.u. per cu. ft.	
			CO_2	Ill.2/	CO	H_2	CH_4	C_2H_6	N_2		Calc. gross	Calc. net
			Upper annulus samples 9 inches above offtake									
10-A	8-7	10:50A60	12.8	0.0	29.7	51.4	3.5	0.0	2.6	0.563	293	264
10-B	8-8	7:50A65	10.6	.0	29.9	56.9	2.3	.0	.3	.507	300	269
11-A	9-19	9:04A7	10.2	.1	30.2	57.0	1.9	.0	.6	.506	298	268
			Upper annulus samples 1 inch above louvres									
12-A	11-7	8:45A70	14.0	0.4	23.2	57.5	4.2	0.0	0.7	0.513	307	273
12-B	11-8	9:10A80	14.2	.2	22.3	59.7	3.1	.0	.5	.499	296	263
12-C	11-9	10:25A	21.5	.6	14.4	59.3	3.8	.2	.2	.542	288	254
			Lower annulus samples 12 inches below offtake									
10-A	8-7	10:50A60	15.4	0.0	19.7	63.9	0.5	0.0	0.5	0.478	271	239
10-B	8-8	7:50A55	15.8	.0	20.2	63.6	.4	.0	.0	.463	271	239
11-A	9-19	8:55A16	14.6	.1	23.1	60.7	.8	.0	.7	.500	276	246
			Lower annulus samples 1 inch below louvres									
12-A	11-7	8:45A70	7.1	0.2	39.8	52.3	0.6	0.0	0.0	0.536	303	276
12-B	11-8	9:10A80	13.7	.2	19.1	64.0	2.5	.0	.5	.460	294	259
12-C	11-9	10:25A	6.9	.1	36.4	53.9	.5	.0	.2	.520	300	273

1/ Samples for analyses were taken in a container over a confining solution of saturated brine at a constant rate beginning at the time indicated and continuing for the given number of minutes. For example, during period 10-A designated 10:50A60, the sampling was started at 10:50 A.M. and continued for 60 minutes.

2/ Illuminants are assumed to have the average composition of $C_{2.8}H_{5.6}$. The composition was estimated from heat and material balances of several tests on the small and large pilot plants.

TABLE 18. – Analyses of upper and lower annuli gases, run 1, Grand Forks pilot plant, June 1945.

Run and period	Date	Time[1/]	Analysis, percent							Specific gravity (air = 1.0) calculated	B.t.u. per cu. ft.		Remarks[3/]
			CO2	Ill.[2/]	CO	H2	CH4	C2H6	N2		Calc. gross	Calc. net	
Upper annulus samples approximately 9 inches above offtake													
1-A	18	1:15P90	23.9	0.7	13.6	53.1	6.4	0.7	1.6	0.600	303	268	P
			24.0	.7	13.8	53.8	6.5	.7	.5	.594	307	271	G
1-B	19	8:15P30	25.1	.7	14.2	54.9	4.7	.0	.4	.598	281	248	P
			25.1	.7	14.2	54.9	4.7	.0	.4	.598	281	248	G
1-B	20	9:30A40	24.4	.5	13.2	55.3	3.7	.0	2.9	.595	265	233	P
			24.6	.5	13.6	57.0	3.8	.0	.5	.581	273	240	G
1-BC ...	22	9:30A45	23.8	.8	15.6	52.6	6.2	.0	1.0	.607	295	262	P
			23.8	.8	15.7	53.0	6.2	.0	.5	.603	297	263	G
1-C	22	7:35P55	22.9	.7	13.8	53.2	6.3	.0	2.7	.590	290	257	P
			23.5	.7	14.2	54.6	6.5	.0	.5	.584	298	264	G
1-C	23	4:20P35	23.3	.9	15.5	52.7	6.3	.8	.5	.603	312	277	P
			23.3	.9	15.5	52.7	6.3	.8	.5	.603	312	277	G
Lower annulus samples approximately 9 inches below offtake													
1-A	18	9:45P	23.7	0.0	4.2	70.3	1.5	0.0	0.3	0.463	253	216	P
			23.7	.0	4.2	70.3	1.5	.0	.3	.463	253	216	G
1-B	19	8:15P30	23.5	.0	3.6	70.0	.6	.0	2.3	.468	241	205	P
			23.6	.0	3.7	71.6	.6	.0	.5	.455	246	210	G
1-B	20	9:30A40	24.2	.0	4.9	68.9	1.5	.0	.5	.478	250	215	P
			24.2	.0	4.9	68.9	1.5	.0	.5	.478	250	215	G
1-BC ...	22	9:30A45	23.6	.0	3.0	72.6	.4	.0	.4	.446	245	209	P
			23.6	.0	3.0	72.6	.4	.0	.4	.446	245	209	G
1-C	23	4:20P35	25.9	.1	3.4	68.9	1.4	.0	.3	.489	247	211	P
			25.9	.1	3.4	68.9	1.4	.0	.3	.489	247	211	G

See footnotes on page 55.

TABLE 18. - Analyses of upper and lower annuli gases, run 2, Grand Forks pilot plant, December 1945. (cont'd.)

Run and period	Date	Time1/	Analysis, percent							Specific gravity (air = 1.0) calculated	B.t.u. per cu. ft.	
			CO2	Ill.2/	CO	H2	CH4	C2H6	N2		Calc. gross	Calc. net
			Upper annulus samples 6 inches above offtake									
2-A	9	12:30P70	17.6	0.6	18.9	58.2	4.6	0.1	0.0	0.527	305	271
2-B	11	3:10P70	16.3	.4	21.7	56.8	4.5	.0	.3	.531	303	270
2-C	12	10:05P65	17.1	.4	20.9	57.3	4.2	.0	.1	.532	299	266
2-D	13	1:00P75	20.0	.6	17.2	54.9	5.7	.0	1.6	.565	298	265
2-E	15	3:30P60	19.2	.8	17.2	56.5	6.3	.0	.0	.545	313	278
			Lower annulus samples 10 inches below offtake									
2-A	9	12:35P65	27.4	0.2	5.1	65.5	0.8	0.0	1.0	0.531	237	203
2-B	11	3:05P80	27.4	.2	7.3	63.6	.7	.0	.8	.549	237	205
2-C	12	10:10P60	24.5	.2	9.7	64.6	.4	.0	.6	.525	245	212
2-D	13	1:00P75	19.6	.1	18.2	60.8	.6	.1	.6	.529	261	230
2-E	15	3:30P60	19.8	.2	17.5	61.9	.5	.1	.0	.522	271	239

See footnotes on page 55.

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TABLE 18. - *Analyses of upper and lower annuli gases, run 3, Grand Forks pilot plant,*
March 1946. (cont'd.)

Run and period	Date	Time[1]	Analysis, percent							Specific gravity (air = 1.0) calculated	B.t.u. per cu. ft.	
			CO_2	Ill.[2]	CO	H_2	CH_4	C_2H_6	N_2		Calc. gross	Calc. net
			Upper annulus samples between offtakes									
3-A	10	9:30A45	25.7	0.2	10.3	61.0	2.7	0.1	0.0	0.554	260	226
3-C	16	11:40A20	15.3	.3	15.6	65.3	3.2	.2	.1	.455	299	263
3-D	17	3:25P35	15.6	.4	17.9	61.8	3.6	.7	.0	.487	310	274
3-F	19	1:45P85	15.6	0.2	23.3	55.5	3.8	0.0	1.6	.542	293	261
3-G	21	10:45A60	12.5	.3	28.2	54.3	3.4	.0	1.3	.538	302	272
3-H	23	2:10P25	13.3	.2	25.8	55.2	2.6	1.3	1.6	.537	310	278
			Lower annulus samples 9 inches below gas offtakes									
3-A	10	9:30A45	25.2	0.3	7.9	63.5	0.0	1.0	2.1	0.539	251	218
3-C	16	1:45P15	26.9	.0	8.2	63.5	.2	.1	1.1	.547	232	200
3-D	17	3:25P50	25.2	.1	8.9	64.2	.7	.1	.8	.530	244	211
3-E	18	4:00P25	23.0	.1	13.8	62.2	.7	.0	.2	.535	251	219
3-F	19	1:45P85	23.2	0.2	13.2	61.2	0.6	0.0	1.6	.547	247	216
3-G	21	10:45A60	22.6	.2	13.1	59.9	.0	.9	3.3	.559	252	221
3-H	23	2:10P55	23.0	.2	12.0	62.4	.6	.0	1.8	.534	247	215
3-J	24	10:15A45	18.5	.2	20.2	58.8	.6	.0	1.7	.541	262	231

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TABLE 18. - Analyses of upper and lower annuli gases, run 4, Grand Forks pilot plant, April-May 1946. (cont'd.)

| Run and period | Date | Time[1] | Analysis, percent | | | | | | | Specific gravity (air = 1.0) calculated | B.t.u. per cu. ft. | |
			CO2	Ill.[2]	CO	H2	CH4	C2H6	N2		Calc. gross	Calc. net
					Upper annulus samples between offtakes							
4-B	19	9:00A50	17.8	0.4	21.6	56.2	1.0	0.6	2.4	0.560	277	247
4-D	23	10:35P35	15.2	.5	22.3	58.6	1.7	.4	1.3	.522	292	260
4-G	30	4:45P35	16.4	.2	30.0	50.4	2.1	.6	.3	.600	291	263
4-H	2	4:25P50	19.7	.3	17.8	59.8	1.7	.4	.3	.535	278	245
4-I	4	5:20P25	17.0	.7	19.2	57.1	4.3	1.2	.5	.535	322	286
4-J	6	4:00P50	15.7	.2	24.0	57.6	1.7	.2	.6	.532	285	254
4-K	8	5:15P40	14.5	.6	25.1	57.7	2.4	.2	.5	.533	304	271
4-L	10	4:45P50	21.1	.4	16.7	57.9	3.0	.5	.4	.556	285	252
4-M	12	11:20A40	20.5	.4	18.8	56.0	3.4	.4	.5	.567	288	255
4-0	15	11:35A60	3.6	.1	43.6	51.8	.5	.0	.4	.521	310	284

See footnotes on page 55.

TABLE 18. - *Analyses of upper and lower annuli gases, run 4, Grand Forks pilot plant, April-May 1946.* (cont'd.)

Run and period	Date	Time[1]	Analysis, percent							Specific gravity (air = 1.0) calculated	B.t.u. per cu. ft.	
			CO_2	Ill.[2]	CO	H_2	CH_4	C_2H_6	N_2		Calc. gross	Calc. net
			Lower annulus samples 9 inches below offtake									
4-B	19	9:00A30	21.6	0.4	13.1	63.1	0.4	0.0	1.4	0.508	256	223
4-C	21	11:50A55	24.1	.0	7.7	66.1	1.2	.0	.9	.505	247	213
4-D	23	8:30P40	26.0	.0	4.7	67.8	.9	.4	.2	.501	247	212
4-E	25	7:45P60	24.4	.5	6.2	66.8	1.0	.4	.7	.503	260	225
4-F	28	10:30A70	26.4	.4	7.0	64.6	.8	.2	.6	.534	249	215
4-G	30	3:10P35	27.6	.2	4.6	66.2	.9	.1	.4	.525	241	206
4-H	2	2:50P75	21.0	.4	15.6	60.3	2.0	.3	.4	.537	276	243
4-I	4	3:10P80	22.4	0.3	14.7	60.6	1.1	0.4	0.5	.546	265	232
4-J	6	2:45P30	23.1	.2	11.2	63.7	1.1	.2	.5	.521	258	225
4-K	8	3:45P65	24.2	.3	9.3	63.9	1.7	.2	.4	.523	260	226
4-L	10	3:25P65	19.9	.2	16.2	62.4	.9	.0	.4	.516	264	232
4-M	12	9:20A70	24.6	.1	8.2	65.2	1.4	.1	.4	.514	252	218
4-N	13	4:50P40	23.6	.0	11.1	63.7	1.1	.1	.4	.523	252	219
4-O	15	9:40A55	21.0	.0	9.5	68.3	1.0	.0	.2	.468	258	223

1/ Samples were taken at a constant rate beginning at the time indicated and continuing for the given number of minutes, e.g., Period 1-A designated 1:15P90, the sampling was started at 1:15 P.M. and continued for 90 minutes.

2/ The composition of illuminants is $C_2.8H5.6$ estimated from heat and material balances from several tests on both pilot plants.

3/ During run 1, purge gas of 17 percent CO_2 and 83 percent N_2 was introduced in the top and bottom of the generator to reduce condensation and $_2$ to avoid explosive mixtures. Corrections were calculated for this dilution, assuming the generator gas to contain only 5 percent nitrogen. P designates the plant gas containing purge gas; G, the calculated generator gas.

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Natural lignite containing about 37 percent bed moisture is introduced in the externally heated retort. As heat is received by the lignite, the bed moisture is evaporated and moved with the solid residue into hotter sections of the retort. When the solid dried lignite is heated through the temperature range of $400^{\circ}F.$ to $750^{\circ}F.$, thermal decomposition occurs, first with the evolution of CO_2 and the formation of water vapor from oxygen in the coal substance, followed closely by the decomposition of volatile matter to form tars and hydrocarbon gases. At this point, the heated solid residue retains carbon, hydrogen which is driven off as the temperature increases, some oxygen, and small amounts of sulfur and nitrogen. This complex mixture, consisting of water vapor, tar vapors, free hydrogen, carbon dioxide, hydrocarbon gases, and a solid containing active carbon and some available hydrogen, descends into the hotter regions of the retort, where further decomposition occurs and water gases are formed by reaction of the various constituents. The apparent equilibrium of the water-gas mixture is influenced by the concentration of the steam and by the temperature. Thus, by regulating the quantity of steam entering the reaction zone, or by the adjustment of temperature, as independent variables, the composition of the gases leaving the highest temperature zone can be controlled over a wide range.

As the devolatilized and partly gasified carbonaceous residue passes into the lower zone, it contacts water vapor traveling countercurrently. The steam is introduced into the lower annulus to cool the residue and to make water gas in the hottest section. The apparent equilibrium of the water gases in this section is controlled by the concentration of steam and by the temperature. The rate of removal of residue from the bottom annulus controls the degree of gasification of the carbonaceous fuel. If the original carbon in the coal converted to gas is on the order of 50 percent, the gases made are derived principally from products of distillation; but if 90 percent of complete gasification is attained, the gases formed are derived principally from reactions between carbon and water vapor. The percentage of carbon converted to gas is simply controlled by regulating the rate of removal of residue. Thus, the three primary variables in gasification of lignite in an externally heated retort are:

1. Concentration of steam.
2. Temperature.
3. Percentage of gasification.

When lignite is distilled, the principal products of distillation are water, carbon dioxide, tar vapors, light oil vapors, hydrocarbon gases, and hydrogen. The combined hydrogen in the form of tar, light-oil, and hydrocarbon gases passes through hotter sections of the retort in company with water vapor and is decomposed to fixed hydrocarbon gases. It is interesting to note that the amount of combined hydrogen in the make gases in the form of CH_4 and illuminants is equal to or greater than that in the products of distillation. Therefore, it is probable that under the conditions of gasifications encountered in the pilot plants, some CH_4 probably forms by interaction of H_2 and CO, or by the direct hydrogenation of the carbon, if this type of reaction is possible.
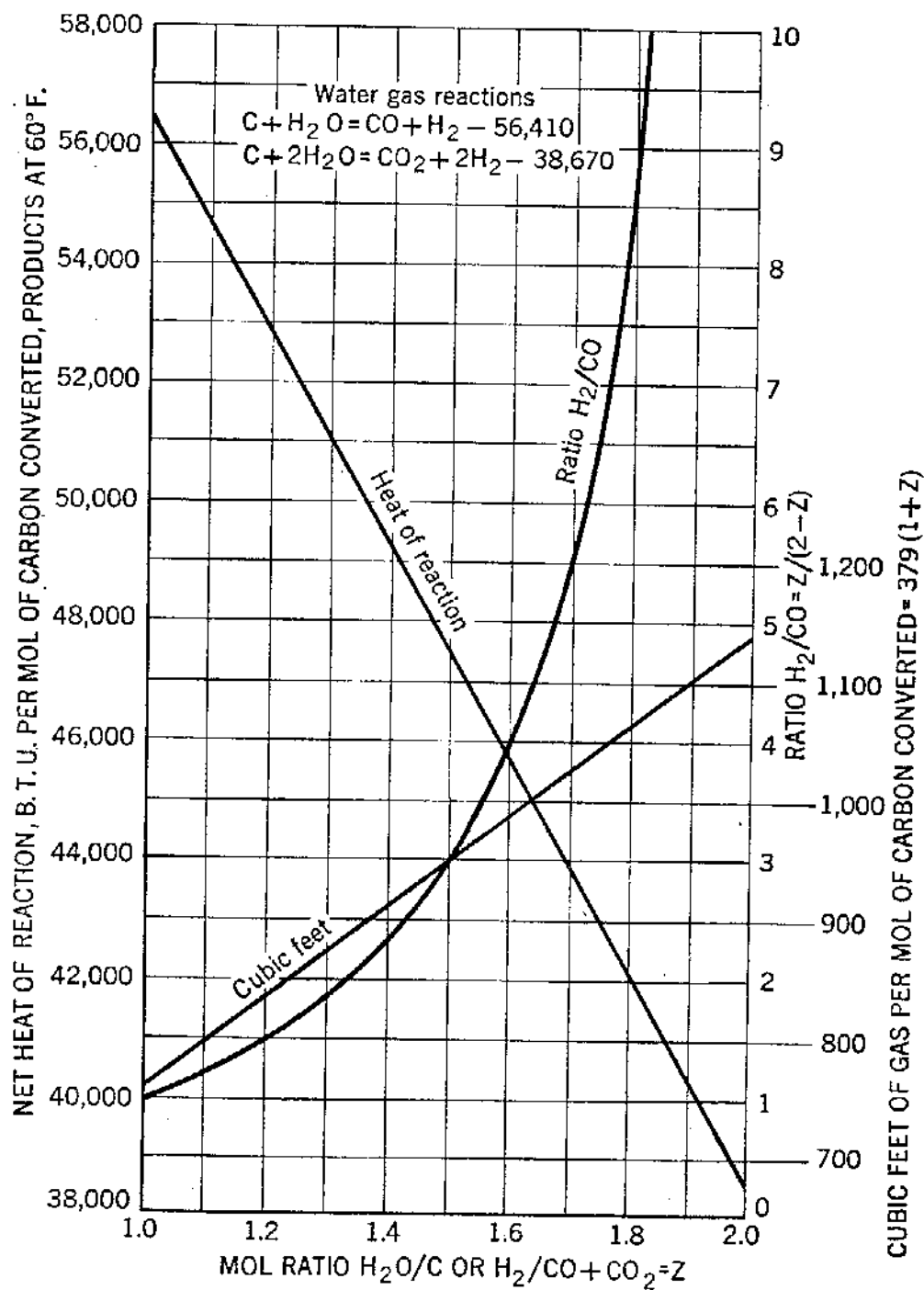
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Figure 26. - Water-gas reactions.

An estimate of the products of distillation that will form when coal is distilled at various temperatures can be made from the ultimate analysis of the coal.[16] The weight of water, carbon dioxide, combined and free hydrogen, and carbon entering the reaction to form gaseous products can be estimated if certain assumptions are made as to the amount and analysis of char residues. From the gas analysis, the materials involved in the water-gas reactions and the heat of reaction can then be calculated. The method of making these calculations will be discussed in a forthcoming report, which will analyze the process from a theoretical point of view. Most of the heat passing through the externally heated retort is used in completing the water gas reactions. Figure 26 shows the range of these reactions with respect to H_2/CO ratio, heat of reaction, and volume of gas. The different grades of water gas are stated in terms of the H_2/CO ratio, which can vary from 1 to infinity, or "Z," which can vary from 1.0 to 2.0 under ideal conditions. In the process under investigation, the $H_2/(CO + CO_2)$ ratio in the water gas, designated by "Z," can be varied from 1.35 to 1.80 by adjustments in steam concentration and temperature. An important object of the pilot-plant tests has been to work out the operating problems in making these different grades of water gas.

If the water gas is to be used for manufacture of industrial hydrogen, the value of "Z" should be 1.7 to 1.8, which requires a higher concentration of steam and relatively lower temperatures in making the gas. Because of the additional steam required and the resulting operating problems, industrial hydrogen might be produced more cheaply by this process by making the easier obtainable water gases having values of "Z" of 1.4 to 1.6. The CO thus produced would be shifted to H_2 in a later operation. If the gas is to be used for making synthetic gasoline which needs a gas having a H_2/CO ratio of about 2.0, the apparent equilibrium or "Z," will be 1.3 to 1.5. Low concentration of steam and relatively high temperatures are necessary for these conditions. The intermediate water gases, which have an apparent equilibrium, denoted by "Z," of 1.5 to 1.7 are the easiest type of gases to make in the externally heated retort, because the natural balance of hydrogen and carbon in the low-rank fuels favors this equilibrium at moderate temperatures. These intermediate gases probably will be useful for industrial heating.

Comparison of Performance of the Pilot Plants

The operating characteristics of both pilot plants are about the same, but the large plant is inherently more efficient. Tables 19 and 20 compare the performance of the plants upon a unit basis that converts most of the measurements to the common unit of a square foot of heated surface. In the small plant, several different coals have been gasified, but in the large plant only natural lignite has been treated. Experience has shown that there is little difference between the gasification properties of any of the low-rank fuels if corrections are made for moisture content of the ingoing coal.

16/ Parry, V. F., Correlation of Analysis of Coal with the Products of Carbonization in Externally Heated Retorts: Bureau of Mines Rept. of Investigations 3482, 1939, 37 pp.

TABLE 19. - Gasification of coal in small pilot plant, Golden, Colo.

Test number	5B	5C	8B	9D	10B	12C
Kind of coal	Subb.	Steam-dried lignite	Natural lignite	Wyoming subb.	Subb.	Natural lignite
Coal charging rate, pounds per hour per square foot of retort surface	1.44	1.24	1.45	1.68	2.95	3.25
Percentage gasified[1]	76.6	94.4	89.8	74.7	73.4	64.2
Steam:						
Pounds per hour per square foot of retort surface:						
Upper annulus	4.0	3.8	1.9	2.6	3.1	3.6
Lower annulus	8.0	8.2	2.2	4.4	5.4	4.9
Used per mol of carbon gasified	7.0	6.25	2.93	3.65	2.02	2.81
Converted = Z[2]	1.75	1.65	1.49	1.47	1.37	1.36
Net heat used:						
B.t.u. per cubic foot of gas made	190	180	202	180	138	166
M B.t.u. per hour per square foot of retort surface	9.19	9.40	8.03	9.29	11.29	10.52
Average furnace temperature, °F.	1,540	1,605	1,690	1,730	1,800	1,750
Gas made:						
Cubic feet per hour per square foot, SGC[3]	46.6	50.5	38.7	50.3	81.5	63.3
Cubic feet of dry gas per pound of coal	32.9	41.4	27.0	30.4	27.1	19.1
H_2/CO ratio = R	7.18	4.73	2.72	3.04	2.0	2.11
Retort arrangement:						
Width of annulus, inches	3	3	3	3	2	2
Ratio of length of top to bottom annuli	2.45	2.45	2.45	2.45	2.79	2.11

[1] Percentage of carbon in coal converted to gas.
[2] Per mol of carbon gasified. $Z = H_2/(CO + CO_2)$ in the water gas formed.
[3] Saturated at 60°F. and 30 in. Hg.

TABLE 20. - Gasification of coal in large pilot plant, Grand Forks, N. Dak.

Test number	Prelim- inary A	1B	2B	2E	3A	3B	3G	x[1]
Kind of coal	Lig.	Lig.	Lig.	Lig.	Lig.	Lig.	Lig.	Lig.
Coal charging rate, pounds per hour per square foot of retort surface.	3.00	3.46	2.43	3.64	2.00	3.30	2.69	3.71
Percentage gasified[2]	48.7	47.0	85.7	74.9	58.8	77.4	74.6	80.0
Steam:								
Pounds per hour per square foot of retort surface:								
Upper annulus ...	3.5	3.0	2.0	2.4	4.9	2.5	1.8	2.0
Lower annulus ...	2.9	9.7	3.2	4.0	4.6	4.6	2.3	4.0
Used per mol of carbon gasified	4.86	5.76	2.30	2.20	8.74	2.61	1.94	1.90
Converted = Z[3]	1.56	1.65	1.41	1.42	1.70	1.48	1.37	1.33
Net heat used:								
B.t.u. per cubic foot of gas made	144	130	126	127	201	123	121	110
M B.t.u. per hour per square foot of retort surface	6.47	6.54	7.80	9.84	7.66	9.23	7.22	9.35
Average furnace temperature, °F.	1,825	1,670	1,770	1,790	1,345	1,785	1,810	1,825
Gas made:								
Cubic feet per hour per square foot, SGC[4] .	46.1	50.3	61.7	77.6	38.2	74.9	59.9	85
Cubic feet of dry gas per pound of coal ..	15.1	14.3	25.0	20.9	18.8	22.3	21.8	22.5
H_2/CO ratio = R	2.37	2.58	2.44	2.48	5.43	2.71	2.18	2.0
Retort arrangement:								
Width of annulus, inches	4	4	3	3	3	3	3	2.5
Ratio of length of top to bottom annuli ...	2.02	4.03	2.26	2.26	2.11	2.11	2.11	2.0

[1] Desired conditions for 2,000-hour test.
[2] Percentage of carbon in coal converted to gas.
[3] Per mol of carbon gasified. $Z = H_2/(CO + CO_2)$ in the water gas formed.
[4] Saturated at 60°F. and 30 in. Hg.