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PROCESS ANALYSIS OF COAL HYDROGASIFICATION WITH STEAM AND RECYCLED HYDROGEN

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Processes currently under investigation for the production of pipeline gas when needed comprise 1) direct pressure hydrogenation or hydrogasification of hydrocarbonaceous materials as coal and oil shale and 2) catalytic conversion to methane of synthesis gas from coal gasification. Although the latter is the technically more advanced method for synthesis of high heating value gases, coal hydrogasification is considered the more acceptable process for adoption for three principal reasons 1) achievable large reduction to potential elimination of oxygen requirements 2) elimination of sulfur purification necessity except in product gas, and 3) improvement in thermal efficiency through reduction of exothermic heats of reaction.

The hydrogasification process requires external hydrogen, which, as with the synthesis gas methanation process, is obtained, of course, through steam decomposition. The requisite steam decomposition proceeds either by 1) catalytic or partial-combustion reforming of a portion of the product gas or of the primary natural gas supply preferably in those instances where nearly complete conversion of solid fuels to high Btu gas may be realized, i.e. hydrogasification of lignite, reactive non-caking subbituminous coals and chars, oil shale and tar sands or 2) oxygen-steam gasification of solid fuel residues from incomplete hydrogasification of less reactive coals and coal chars. Generally, pressure hydrogasification will not readily convert much over 50% of the carbonaceous matter of most bituminous coals, and due to thermodynamic and kinetic limitations, product gases contain moderate quantities of unreacted hydrogen.

Since costs chargeable to hydrogen production represent a major portion of the total cost of pipeline gas, a potentially advantageous modification of the coal hydrogasification process comprises 1) methane separation by liquefaction or other suitable means to insure maximum heating value of the product gas 2) recycling of the recovered hydrogen to insure full utilization of the gasifying medium and 3) admission of steam in the reactor hydrogasification zone to promote additional hydrogen formation via steam decomposition from the exothermic heat of the coal hydrogenation reactions, thereby improving the heat balance and further decreasing fuel requirements. To be economically attractive the advantages gained must, of course, outweigh the cost increment of product gas separation.

The key concept of the hydrogen recycle process is gasification of coal by simultaneous reaction with steam and recycled hydrogen at elevated pressure and temperature to achieve as near as possible a thermal balance between exothermic and endothermic reactions and to substantially eliminate external hydrogen requirements. The hydrogen produced internally by this scheme would be supplemented by water-gas shift of the hot product gas with additional steam to convert available carbon monoxide. An evaluation of process feasibility requires a thermodynamic

analysis of the $C-H_2-H_2O$ and $C-H_2-H_2O-O_2$ systems supplemented with interpretation of available kinetic data.

THERMODYNAMIC ANALYSIS OF COAL GASIFICATION WITH STEAM AND HYDROGEN

I. Definition of the Process

Fig. 1 shows a schematic diagram of the proposed coal gasification process. Recycled hydrogen is assumed at 800°F. through heat exchange with the product gas. Process steam is assumed superheated to 1000°F. from an external source. For fixed-bed operation the solid fuel may be fed at the top of the reactor, and for fluid-bed operation the coal charge may be injected with the hydrogen feed stream. After preliminary cleaning of dust, the raw gas, comprising essentially CH_4, H_2, CO, CO_2 and unreacted steam is passed to catalytic water-gas-shift. The gas, then at approximately 1000°F., is cooled in the hydrogen recycle heat exchanger, scrubbed with water to condense unreacted steam, and purified of CO_2, H_2S and other sulfur bearing gases prior to methane separation by liquefaction. Some arrangement of heat exchangers as shown would be necessary to preserve refrigeration economy in liquefaction. The liquid methane could be vaporized and the cold H_2 reheated by the incoming warm gases. The warm H_2 is recompressed by a booster to complete the recycle circuit.

This process may not necessarily require a water-gas shift step, in which event the recycled gas comprises a mixture of hydrogen with moderate amounts of carbon monoxide. Some CO shift would presumably occur in the gasification reactor itself, since moderate excess steam would always be present at the recycle gas introduction point. However, the presence of CO may interfere with the efficient separation of CH_4 by liquefaction. If a water-gas shift reactor is used, then the methane could be separated from the CH_4-H_2 mixture by molecular effusion in "diffusion" cascades, as an alternative to liquefaction.

In the process analysis, which will be directed to operating conditions of the reactor it is assumed that recycled gas consists of hydrogen only. The important variables to be established are temperatures and pressures to make the process thermodynamically feasible. The criteria of feasibility are 1) heat requirements of the reactor per MCF of methane produced, and 2) ratio of hydrogen produced to hydrogen consumed in the process. An analysis of the equilibria and heat effects of the $C-H_2-H_2O$ system is first necessary to establish whether the process can be operated without oxygen as a source of heat through partial combustion.

II. Thermodynamic Analysis of $C-H_2-H_2O$ System

A. Defining Equations

The system is completely defined by the reactions:

$$C + 2H_2 \longrightarrow CH_4 \qquad \text{Reaction 1}$$

$$C + H_2O \longrightarrow CO + H_2 \qquad \text{Reaction 2}$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad \text{Reaction 3}$$

The concentrations of the five gaseous components are solved by a procedure of Parent and Katz.[8] The material balance (Table 1) and relationships are:

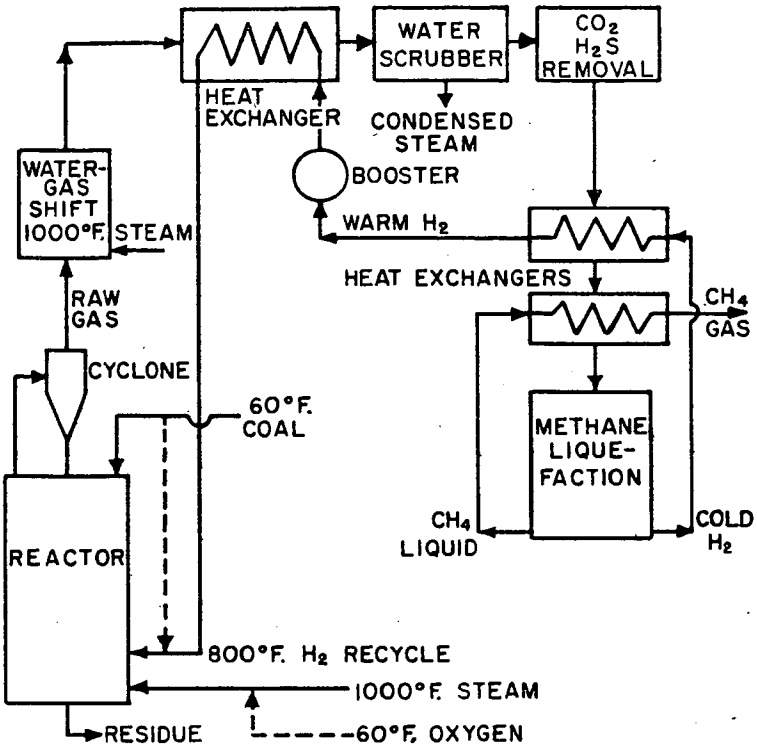

Fig. 1.-SCHEMATIC FLOW DIAGRAM OF HYDROGEN RECYCLE GASIFICATION PROCESS

Table 1.-MATERIAL BALANCE OF THE C-H_2-H_2O SYSTEM

Component	Initial Amount Moles/Mole Inlet Steam	Equilibrium Partial Pressure, Atm.	Equilibrium Molar Quantities, Moles/ Mole Inlet Steam
C	excess	--	--
H_2	a	X	x
H_2O	1.0	Y	y
CO	0	Z	z
CO_2	0	M	m
CH_4	0	W	w
Total		P	N

a) Reaction 1. Equilibrium, for ideal gases

$$K_1 = W/\gamma_c X^2 \tag{1}$$

where γ_c = activity of carbon to hydrogenation

b) Reaction 2. Equilibrium, for ideal gases

$$K_2 = ZX/\gamma_c' Y \tag{2}$$

where γ_c' = activity of carbon to steam

c) Reaction 3. Equilibrium, for ideal gases

$$K_3 = XM/ZY \tag{3}$$

d) Hydrogen balance

$$a = x + y + 2w - 1 \tag{4}$$

e) Oxygen balance

$$y + z + 2m = 1 \tag{5}$$

f) Carbon balance

$$c_g = z + m + w = \text{moles carbon gasified per mole inlet steam} \tag{6}$$

g) Total pressure

$$P = X + Y + Z + M + W \tag{7}$$

h) Total moles at equilibrium

$$N = x + y + z + m + w \tag{8}$$

The following solution from Equations 1, 2, 3 and 7 obtains:

a) CH_4 partial pressure, Atm

$$W = K_1 \gamma_c X^2 \tag{9}$$

b) H_2O partial pressure, Atm

$$Y = \frac{X(X+K_2 \gamma_c')}{2K_2K_3 \gamma_c'} \left[-1 + \sqrt{1 + \frac{4K_2K_3 \gamma_c' (P-X-W)}{(X + K_2 \gamma_c')^2}} \right] \tag{10}$$

c) CO partial pressure, Atm

$$Z = K_2Y \gamma_c'/X \tag{11}$$

d) CO_2 partial pressure, Atm

$$M = P - X - Y - Z - W = K_3YZ/X \qquad (12)$$

For selected temperature, total pressure and assumed carbon activity, equilibrium partial pressures are computed successively by assigning arbitrary X values, or hydrogen partial pressure. Molar quantities are found from:

a) multiplication of the oxygen balance (Equation 5) by P/N, yielding:

$$N = P/\left[Y + Z + 2M\right] \qquad (13)$$

b) law of additive pressures:

$$x = NX/P,\ y = NY/P,\ z = NZ/P,\ m = NM/P,\ w = NW/P \qquad (14)$$

The required H_2/H_2O inlet molar ratio for the system, from Equation 4, must be zero or positive for a valid solution. Equation 6 yields the quantity of carbon gasified, and the gas composition is defined by the molar quantities. The fraction of steam decomposed, SD, is given by:

$$SD = 1-y \qquad (15)$$

One criterion of process feasibility is the ratio, R, of hydrogen produced to hydrogen consumed, taking into account the CO as equivalent to hydrogen,

$$R = \frac{1-y+z}{2w}, \quad \frac{\text{moles } H_2 \text{ available}}{\text{moles } H_2 \text{ consumed}} \qquad (16)$$

As a basis for correction of R for actual fuels, experimental data of Channabassappa and Linden on bituminous coal containing about 75 weight % carbon, and 5 weight % hydrogen, (dry basis) indicate that approximately 80% of the coal feed hydrogen content appears as CH_4 and higher hydrocarbons in the product gas.[2] An approximation of the quantity of hydrogen available from coal for hydrogasification, expressed as moles/mole inlet steam, is therefore taken to be $0.8\ r_H\ C_g/f$, where R_H = hydrogen/carbon molar ratio in coal, and f = fraction carbon gasified. With a coal feed containing 75 weight % C and 5 weight % H, and 95% carbon gasification, this becomes $(0.8)(0.4)c_g/0.95 = 0.336\ c_g$. The corrected ratio, R', hydrogen available to hydrogen consumed, may be written for this case:

$$R' = \frac{1-y+z+0.336c_g}{2w} \quad \text{(corrected for coal)} \qquad (17)$$

The recycle gasification process will be independent of an external source of hydrogen if $R' \geqq 1.0$.

The second test of process feasibility is the net heat effect of the system, ΔH_R, in Btu/lb. mole CH_4 produced. This is given by:

$$\Delta H_R = \Delta H_1 + \frac{1}{w}\left[(1-m-y)\,\Delta H_2 + m\,\Delta H_3 + C_g\,\Delta H_c + a\,\Delta H_{H_2} + \Delta H_{H_2O}\right] \qquad (18)$$

where ΔH_1, ΔH_2, ΔH_3 = heat of reaction, in Btu/lb. mole, of Reactions 1, 2 and 3, respectively, with reactants and products at the temperature of the system, and ΔH = enthalpy of reactant, Btu/lb. mole, between inlet and system outlet temperature.

Thermodynamic equilibrium constants and enthalpy data of the Bureau of Standards[12] were used in all calculations.

B. Equilibrium Computations

The range of variables considered for the $C-H_2-H_2O$ system are 50,100 and 200 atmospheres, and 1000, 1100, 1200 and 1300°K. with 60°F. inlet carbon, 1000°F. inlet steam, and 800°F. recycled hydrogen. The activity of carbon, γ_c', with respect to the carbon-steam Reaction 2 is taken at unity in all cases. Since experimental results on coal hydrogenation have demonstrated that methane concentrations based on β-graphite-hydrogen equilibrium can be exceeded by as much as 10-20%,[2] it is necessary to consider at least two activities of the carbon, i.e., γ_c = 1.0 and 1.5, with respect to the carbon-hydrogen Reaction 1. The choice of γ_c = 1.5 results in CH_4 concentrations approximately 20% in excess of β-graphite-hydrogen equilibrium.

Results of the computations, the majority of which were performed on an ALWAC III digital computer, are listed in Table 2; although many more results were obtained than are tabulated there, those presented are selected as representative of conditions for which the ratios: H_2 available/H_2 consumed, are within the range 0.5-1.4. These data can be plotted against H_2/H_2O inlet molar ratio to determine conditions for which R is exactly 1.0, the point at which the process, at equilibrium, would be independent of external hydrogen.

Typical plots over a wide range of H_2/H_2O inlet molar ratios are given in Fig. 2 for 200 atmospheres, γ_c = 1.0, 1200°K. (1700°F.) and 1300°K. (1880°F.). In these plots the equilibrium gas compositions and heat effects are shown, and two curves for H_2 available/H_2 consumed are included: one for pure carbon and one for coal containing 75 weight % C and 5 weight % H. It can be seen for the conditions 200 atmospheres, = 1200°K. (1700°F.), and γ_c = 1.0 (Fig. 2A), that at a 1.0 ratio of H_2 available/H_2 consumed, with coal as fuel, the process is endothermic by 35,000 Btu/lb. mole CH_4, and that the equilibrium CH_4 content is nearly 30% (wet basis). The endothermicity decreases with increasing H_2/H_2O inlet molar ratio; however, the ratio of H_2 available/H_2 produced also decreases. Thus at extremely high H_2/H_2O inlet molar ratios the process approaches thermal balance, but requires external hydrogen. At low H_2/H_2O inlet molar ratios the process has sufficient hydrogen, but lacks heat. This is as anticipated, since at low H_2/H_2O inlet molar ratios the endothermic steam decomposition reactions predominate because steam is present in large excess, whereas at high H_2/H_2O inlet molar ratios, the exothermic hydrogenation reactions predominate, since hydrogen is present in large excess.

Therefore, the process cannot attain a self-balanced condition from the standpoint of both hydrogen and heat requirements at 200 atmospheres, 1200°K. (1700°F.), with 1000°F. preheated steam and 800°F. preheated hydrogen. The same results are observed at 200 atmospheres, 1300°K. (1800°F.), and γ_c = 1.0 (Fig. 2B), where, with a 1.0 ratio of H_2 available/H_2 consumed for coal as fuel, the heat requirement is nearly 50,000 Btu/lb. mole CH_4. An examination of all other conditions given in Table 2 shows that process heat requirements are in the range 25,000-100,000 Btu/lb. mole CH_4 at the operating point determined by a 1.0 ratio of H_2 available/H_2 produced. This heat deficiency will always prevail at all possible gasification temperatures.

Alternate methods for supplying the heat requirements are 1) high preheat of reactants, 2) indirect internal heat exchange with a high-temperature heat transfer fluid, or 3) partial combustion of coal with oxygen within the reactor. In view of the large heat deficiency and the need for rapid heat transfer, the third alternative appears most attractive. This automatically provides a high-temperature zone where a portion of the inlet steam is rapidly decomposed, desirable because

Table 2, Part 1.-EQUILIBRIUM CONCENTRATIONS AND HEAT EFFECTS OF THE C-H_2-H_2O SYSTEM

C as β-Graphite, 60°F.; Inlet H_2 at 800°F.; Inlet Steam at 1000°F.; $\gamma_c' = 1.0$

Pressure, Atm. Abs.	50	50	50	50	50	50	50	50	50	50	50	50
Temp., °K.	1000	1000	1000	1100	1100	1100	1200	1200	1200	1300	1300	1300
Inlet H_2/H_2O Molar Ratio	0.157	0.465	0.877	0.537	0.831	1.21	1.63	2.11	2.73	2.52	3.14	3.98
Carbon Activity, γ_c	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Mole %												
H_2	20.00	22.00	24.00	32.00	34.00	36.00	48.00	50.00	52.00	60.00	62.00	64.00
H_2O	32.68	31.75	29.99	22.35	21.45	20.24	11.41	10.58	9.62	5.18	4.72	4.22
CO	8.52	7.53	6.51	16.16	14.60	13.02	18.93	16.83	14.73	19.62	17.31	14.97
CO_2	19.14	14.93	11.19	10.66	8.70	6.91	3.13	2.48	1.90	0.92	0.72	0.53
CH_4	19.66	23.79	28.31	18.83	21.25	23.83	18.53	20.11	21.75	14.28	15.25	16.28
Wet Products/Inlet H_2O, Molar Ratio	1.258	1.446	1.698	1.671	1.870	2.123	2.731	3.087	3.550	3.752	4.258	4.940
C Gasified/Inlet H_2O, Molar Ratio	0.595	0.669	0.781	0.763	0.833	0.929	1.11	1.22	1.36	1.31	1.42	1.57
Steam Decomp., %	58.9	54.1	49.1	62.7	59.9	57.0	68.8	67.3	65.8	80.5	79.9	79.1
H_2 Available/H_2 Consumed, for pure C	1.41	0.945	0.626	1.43	1.10	0.837	1.19	0.961	0.765	1.44	1.18	0.953
ΔH_R, MBtu/lb. Mole CH_4	57.1	31.8	14.2	75.6	55.4	39.1	77.9	62.1	48.4	116.3	97.7	80.7

Pressure, Atm. Abs.	50	50	50	50	50	50	50	50	50	50	50	50
Temp., °K.	1000	1000	1000	1100	1100	1100	1200	1200	1200	1300	1300	1300
Inlet H_2/H_2O Molar Ratio	0.228	0.650	1.28	0.472	0.814	1.27	1.35	1.83	2.45	1.69	2.15	2.74
Carbon Activity, γ_c	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Mole %												
H_2	18.00	20.00	22.00	28.00	30.00	32.00	42.00	44.00	46.00	52.00	54.00	56.00
H_2O	29.81	28.51	26.07	20.90	20.01	18.72	11.30	10.50	9.56	5.67	5.27	4.83
CO	8.64	7.43	6.18	17.28	15.44	13.55	21.41	18.99	16.53	24.77	22.19	19.59
CO_2	19.66	14.57	10.07	12.19	9.73	7.49	4.01	3.16	2.39	1.47	1.19	0.92
CH_4	23.89	29.49	35.68	21.63	24.82	28.24	21.28	23.35	25.52	16.09	17.35	18.66
Wet Products/Inlet H_2O, Molar Ratio	1.285	1.536	1.908	1.598	1.821	2.116	2.454	2.792	3.238	2.995	3.350	3.806
C Gasified/Inlet H_2O, Molar Ratio	0.671	0.791	0.991	0.817	0.910	1.04	1.15	1.27	1.44	1.27	1.36	1.49
Steam Decomp., %	61.7	56.2	50.3	66.6	63.6	60.4	72.3	70.7	69.1	83.0	82.3	81.6
H_2 Available/H_2 Consumed, for pure C	1.19	0.747	0.456	1.36	1.01	0.745	1.19	0.949	0.742	1.63	1.35	1.10
ΔH_R, MBtu/lb. Mole CH_4	43.1	19.3	3.3	68.5	47.3	30.7	73.4	56.7	42.6	121.3	101.1	83.3

Table 2, Part 2.-EQUILIBRIUM CONCENTRATIONS AND HEAT EFFECTS OF THE C-H_2-H_2O SYSTEM

C as β-Graphite, 60°F.; Inlet H_2 at 800°F.; Inlet Steam at 1000°F.; $\gamma_C' = 1.0$

Pressure, Atm. Abs.	100	100	100	100	100	100	100	100	100	100	100	100
Temp., °K.	1000	1000	1000	1100	1100	1100	1200	1200	1200	1300	1300	1300
Inlet H_2/H_2O Molar Ratio	0.139	0.331	0.560	0.512	0.689	0.896	1.092	1.29	1.52	2.07	2.35	2.67
Carbon Activity, γ_C	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Mole %												
H_2	15.00	16.00	17.00	25.00	26.00	27.00	37.00	38.00	39.00	50.00	51.00	52.00
H_2O	35.99	35.46	34.52	26.90	26.28	25.51	16.95	16.42	15.83	8.66	8.28	7.89
CO	6.25	5.78	5.29	12.45	11.70	10.93	18.22	17.19	16.15	19.65	18.45	17.24
CO_2	20.64	17.60	14.78	12.66	11.17	9.75	5.81	5.17	4.56	1.85	1.63	1.42
CH_4	22.12	25.16	28.41	22.99	24.85	26.81	22.02	23.22	24.46	19.84	20.64	21.45
Wet Products/Inlet H_2O, Molar Ratio	1.197	1.308	1.441	1.546	1.657	1.787	2.136	2.275	2.432	3.122	3.333	3.574
C Gasified/Inlet H_2O, Molar Ratio	0.587	0.635	0.699	0.744	0.791	0.849	0.934	1.04	1.10	1.29	1.36	1.43
Steam Decomp., %	56.9	53.6	50.3	58.4	56.5	54.4	63.8	62.6	61.5	72.9	72.4	71.8
H_2 Available/H_2 Consumed, for pure C	1.22	0.930	0.707	1.09	0.921	0.772	1.09	0.963	0.847	1.08	0.973	0.870
ΔH_R, MBtu/lb. Mole CH_4	44.3	28.9	16.9	51.2	40.8	31.8	65.3	56.6	48.8	79.6	71.6	64.1

Pressure, Atm. Abs.	100	100	100	100	100	100	100	100	100	100	100	100
Temp., °K.	1000	1000	1000	1100	1100	1100	1200	1200	1200	1300	1300	1300
Inlet H_2/H_2O Molar Ratio	0.125	0.367	0.672	0.346	0.538	0.763	0.936	1.15	1.41	1.79	2.08	2.40
Carbon Activity, γ_C	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Mole %												
H_2	13.00	14.00	15.00	21.00	22.00	23.00	32.00	33.00	34.00	44.00	45.00	46.00
H_2O	32.76	32.18	31.05	25.14	24.63	23.94	16.15	15.64	15.06	8.55	8.19	7.80
CO	6.57	5.99	5.40	13.86	12.96	12.04	20.09	18.86	17.62	22.08	20.66	19.25
CO_2	22.75	18.93	15.37	15.67	13.71	11.84	7.06	6.23	5.43	2.33	2.05	1.77
CH_4	24.92	28.90	33.18	24.33	26.70	29.18	24.70	26.27	27.89	23.04	24.10	25.18
Wet Products/Inlet H_2O, Molar Ratio	1.178	1.315	1.488	1.421	1.538	1.675	1.985	2.129	2.295	2.832	3.034	3.268
C Gasified/Inlet H_2O, Molar Ratio	0.639	0.708	0.803	0.765	0.821	0.888	1.03	1.09	1.17	1.34	1.42	1.51
Steam Decomp., %	61.4	57.7	53.8	64.3	62.1	59.9	67.9	66.7	65.4	75.8	75.1	74.5
H_2 Available/H_2 Consumed, for pure C	1.18	0.863	0.626	1.21	0.999	0.819	1.10	0.955	0.827	1.06	0.943	0.835
ΔH_R, MBtu/lb. Mole CH_4	40.6	23.9	11.2	55.9	43.1	32.4	62.2	52.7	44.2	72.5	64.2	56.5

Table 2, Part 3.-EQUILIBRIUM CONCENTRATIONS AND HEAT EFFECTS OF THE C-H_2-H_2O SYSTEM

C as β-Graphite, 60°F.; Inlet H_2 at 800°F.; Inlet Steam at 1000°F.; $\gamma_C' = 1.0$

Pressure, Atm. Abs.	200	200	200	200	200	200	200	200	200	200	200	200
Temp., °K.	1000	1000	1000	1100	1100	1100	1200	1200	1200	1300	1300	1300
Inlet H_2/H_2O Molar Ratio	0.112	0.234	0.372	0.214	0.725	3.12	0.025	1.281	2.367	1.158	1.739	2.578
Carbon Activity, γ_C	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Mole %												
H_2	11.00	11.50	12.00	17.50	20.00	25.00	22.50	30.00	33.00	37.50	40.00	42.50
H_2O	38.59	38.29	37.80	31.75	29.73	20.64	23.98	20.73	17.60	14.23	12.97	11.40
CO	4.57	4.34	4.10	10.50	8.61	4.77	21.18	13.69	10.60	21.53	18.40	15.22
CO_2	22.05	19.87	17.79	17.75	12.27	3.73	16.04	6.64	3.80	4.43	3.24	2.22
CH_4	23.79	26.00	28.31	22.50	29.39	45.86	16.30	28.94	35.00	22.31	25.39	28.66
Wet Products/Inlet H_2O, Molar Ratio	1.145	1.213	1.290	1.287	1.590	3.00	1.296	2.100	2.792	2.240	2.641	3.218
C Gasified/Inlet H_2O, Molar Ratio	0.577	0.609	0.648	0.654	0.799	1.63	0.694	1.035	1.379	1.08	1.24	1.48
Steam Decomp., %	55.8	53.6	51.2	59.1	52.7	38.2	69.9	56.5	50.9	68.1	65.7	63.3
H_2 Available/H_2 Consumed, for pure C	1.12	0.933	0.774	1.25	0.711	0.191	2.30	0.701	0.411	1.16	0.853	0.609
ΔH_R, MBtu/lb. Mole CH_4	37.5	27.6	19.2	57.5	25.5	-13.5	136.8	34.4	16.0	78.9	56.8	39.4

Pressure, Atm. Abs.	200	200	200	200	200	200	200	200	200	200	200	200
Temp., °K.	1000	1000	1000	1100	1100	1100	1200	1200	1200	1300	1300	1300
Inlet H_2/H_2O Molar Ratio	1.108	0.263	0.444	0.266	0.382	0.510	0.604	0.712	0.830	1.128	1.375	1.662
Carbon Activity, γ_C	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Mole %												
H_2	9.50	10.00	10.50	15.50	16.00	16.50	23.50	24.00	24.50	33.00	34.00	35.00
H_2O	34.91	34.58	33.99	28.64	28.35	27.95	21.01	20.73	20.40	13.27	12.78	12.23
CO	4.79	4.51	4.22	10.69	10.25	9.81	17.77	17.16	16.55	22.82	21.35	19.84
CO_2	24.19	21.42	18.78	18.66	17.16	15.70	11.07	10.32	9.59	4.99	4.36	3.77
CH_4	26.61	29.49	32.51	26.51	28.24	30.04	26.65	27.79	28.96	25.92	27.51	29.16
Wet Products/Inlet H_2O, Molar Ratio	1.135	1.220	1.319	1.304	1.371	1.445	1.641	1.708	1.781	2.170	2.333	2.523
C Gasified/Inlet H_2O, Molar Ratio	0.631	0.676	0.732	0.728	0.763	0.803	0.911	0.944	0.981	1.17	1.24	1.33
Steam Decomp., %	60.4	57.8	55.2	62.6	61.1	59.6	65.5	64.6	63.7	71.2	70.2	69.1
H_2 Available/H_2 Consumed, for pure C	1.09	0.880	0.708	1.11	0.971	0.850	1.08	0.990	0.903	1.07	0.935	0.810
ΔH_R, MBtu/lb. Mole CH_4	34.4	23.5	14.5	46.9	39.0	32.0	57.6	51.6	46.1	68.5	58.9	50.2

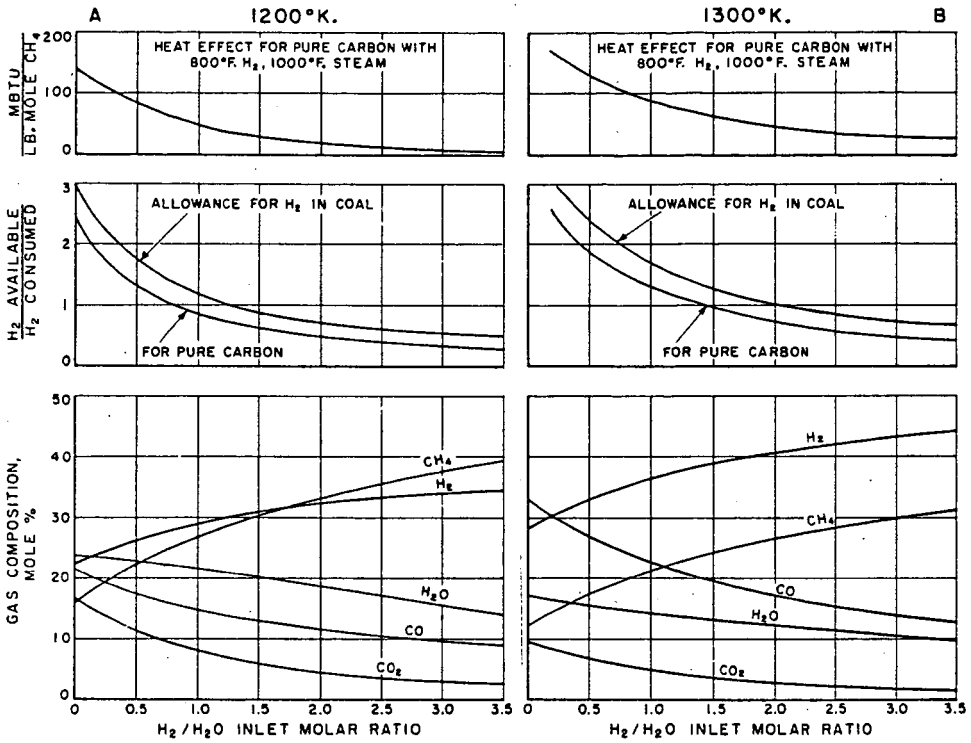

Fig. 2.-EFFECT OF H_2/H_2O RATIO ON EQUILIBRIUM GAS COMPOSITION, H_2 PRODUCTION/CONSUMPTION RATIO, AND NET HEAT EFFECT, FOR THE $C-H_2-H_2O$ SYSTEM AT 200 ATMOSPHERES AND 1200° AND 1300°K.

steam decomposition rates are relatively slow at the temperatures most favorable to high methane production rates. Since equilibrium steam decompositions cannot be achieved in practice, the $C-H_2-H_2O$ system with oxygen admission is analyzed below on the more realistic basis of equilibrium attained only in the carbon-hydrogen and water-gas-shift reactions, with arbitrary assignment of steam decomposition values.

III. Thermodynamic Analysis of $C-H_2-H_2O-O_2$ System with Arbitrary Inlet Steam Decomposition

A. Defining Equations

The system is completely defined by Reactions 1 and 3 in equilibrium, Reaction 2 nonequilibrium, and Reaction 4 to completion:

$$C + O_2 \longrightarrow CO_2 \qquad \text{Reaction 4}$$

The method of solution is similar to that given for the $C-H_2-H_2O$ system. The material balance is given in Table 3.

Table 3.-MATERIAL BALANCE OF THE $C-H_2-H_2O$ SYSTEM WITH OXYGEN

Component	Initial Amount Moles/Mole Inlet Steam	Equilibrium Partial Pressure, Atm.	Equilibrium Molar Quantities, Moles/Mole Inlet Steam
C	excess	--	--
O_2	b	0	0
H_2	a	X	x
H_2O	1.0	Y	y
CO	0	Z	z
CO_2	0	M	m
CH_4	0	W	w
Total		P	N

All previous material balance and equilibrium relationships apply except that Equation 2 is not used, and the new oxygen balance becomes:

$$y + z + 2m = 1 + 2b \tag{19}$$

By manipulation of Equations 1, 3, 7, 15 and 19, the solution for partial pressures and total moles at equilibrium may be written in iterative form:

a) CH_4 partial pressure, Atm.

$$W = K_1 \gamma_c X^2 \tag{9}$$

b) CO partial pressure, Atm.

$$Z = \frac{1}{2}\left[\frac{X(1+d)}{K_3} + 2e\right]\left[1 - \sqrt{1 - \frac{4Xde}{K_3\,[X(1+d)/K_3+2e]^2}}\right] \tag{20}$$

where $d = \dfrac{SD + 2b}{1-SD}$

$$e = P - X - W$$

SD = fraction steam decomposed

c) CO_2 partial pressure, Atm.

$$M = Z\Big/\left[\frac{Xd}{K_3 Z} - 2\right] \tag{21}$$

d) H_2O partial pressure, Atm.

$$Y = P-X-M-Z-W = XM/K_3Z \tag{22}$$

e) Total moles at equilibrium/mole inlet steam

$$N = P(1+2b)/(Y + Z + 2M) \quad (23)$$

By assigning arbitrary X (H_2 partial pressure) values, equilibrium concentrations of all other components are computed for a given temperature, pressure, oxygen/steam inlet molar ratio, assumed steam decomposition and assumed activity of the carbon. Gas compositions are computed from Equation 14, and the amount of carbon gasified from Equation 6. The inlet H_2/H_2O molar ratio is determined by Equation 4, for the case of pure carbon as gasification fuel. The ratio may be corrected for hydrogen available from coal as gasification fuel. Under the conditions assumed in the derivation of the previous correction term, the actual H_2/H_2O inlet molar ratio, a', to the reactor, with coal as fuel, would be:

$$a' = x + y + 2w - 1 - 0.336\ c_g \quad (24)$$

One feasibility criterion of the recycle gasification process with oxygen admission is again the ratio H_2 available/H_2 consumed, Equations 16 and 17. If this ratio is equal to or greater than unity, the process will be independent of an external hydrogen source. By selection of the proper O_2/H_2O inlet molar ratio, the process may be made thermally balanced or slightly exothermic to compensate for heat losses. The net heat effect, Btu/lb mole CH_4 produced, is written in the form:

$$\Delta H_R = \Delta H_1 + \frac{1}{w}\left[(1 - m - y)\ \Delta H_2 + m\Delta H_3 + b\Delta H_4 + c_g\Delta H_c + a\Delta H_{H_2} + b\Delta H_{O_2} + \Delta H_{H_2O}\right] \quad (25)$$

where ΔH_1, ΔH_2, ΔH_3 and ΔH_4 = heat of the respective reactions, in Btu/lb. mole, with reactants and products at the temperature of the system, and ΔH = enthalpy of reactant, Btu/lb. mole, between inlet and system outlet temperatures.

An additional calculation for judging the potential efficiency of the gasification process comprises estimation of reactant requirements per MCF CH_4 produced:

a) Lb. steam (reactor only) = 47.5/w (26)

b) Lb. carbon = 31.7 c_g/w (27)

c) Lb. coal (75% C, 5% H, at 95% carbon gasification) = 44.5 c_g/w (28)

d) SCF Oxygen = 1000 b/w (29)

e) Fraction carbon gasified to CH_4 = w/c_g (30)

B. Equilibrium Computations

A limited number of calculations were made at conditions believed favorable for the practical operation of the proposed process. The choice of conditions is based on:

a) Inlet steam decompositions in the range 30-50%, comparable to those achieved in oxygen-steam gasification of pulverized coal,[9,11] or in oxygen-steam fired fixed-bed gasification processes.[1,13]

b) Experimental data on the hydrogenation of coal char in the presence of steam indicate that methane formation rates are too slow to be of commercial interest at pressures below 30 atmospheres and temperatures much below 1200°K. (1700°F.).[15] Hydrogenation rates increase moderately with pressure and rapidly with temperature. However, temperatures above 1200°K. are thermodynamically unfavorable for high methane content of the product gases, despite the increased

hydrogenation rates. Favorable operating conditions appear to be 1200°K. (1700°F.) and 30-50 atmospheres. An increase to 200 atmospheres would permit lower operating temperatures of the hydrogenation zone, perhaps 1000-1100°K. (1340-1520°F.), to take advantage of the more favorable thermodynamic conditions without significantly affecting the hydrogenation reaction rates.

Results of the equilibrium computations and heat effects at 50 and 200 atmospheres, 1200°K. (1700°F.) and 1.0 activity of carbon, are given in Figs. 3 and 4 for 30-40% steam decomposition and 0.1-0.15 O_2/H_2O inlet molar ratio. All data are plotted against H_2/H_2O inlet molar ratio based on pure carbon as fuel. If desired, a correction may be applied for H_2/H_2O inlet molar ratios based on coal as fuel (Equation 24). The plots show general trends:

a) The ratio H_2 available/H_2 consumed decreases from values greater than 1.0 at low H_2/H_2O inlet molar ratios to values less than 1.0 at high H_2/H_2O inlet molar ratio.

b) Equilibrium CH_4 contents increase with H_2/H_2O inlet molar ratios.

c) At the chosen O_2/H_2O inlet molar ratios, the net heat effect, ΔH_R Btu per lb. mole CH_4, is highly negative (exothermic) at low H_2/H_2O inlet molar ratios, and becomes less negative at high H_2/H_2O inlet molar ratios.

The explanation of the trend of the ΔH_R curve lies in the fact that both the O_2/H_2O inlet molar ratio and total inlet steam decomposition were fixed at arbitrary values in these calculations. Under the conditions assumed, the heat available from oxidation is always somewhat greater than that required to decompose the given amount of steam. At a low H_2/H_2O inlet molar ratio to the gasifier, the quantity of methane formed is small. As a consequence the net heat effect per mole CH_4 produced is highly negative (exothermic). At higher H_2/H_2O inlet molar ratios, the quantity of methane increases and more sensible heat is required to bring the reactants to the operating temperature, resulting in a less exothermic heat effect per mole CH_4 produced.

In Fig. 3A for 30% steam decomposition, 0.1 O_2/H_2O inlet molar ratio, 50 atmospheres and 1200°K. (1700°F.), the gasification process becomes independent of external hydrogen if the H_2/H_2O inlet molar ratio is no greater than 1.8, the point at which the ratio H_2 available/H_2 consumed (corrected for coal) approaches unity. At this point, 1) the net heat effect is practically zero with 800°F. preheated recycled hydrogen, 1000°F. steam and 60°F. coal and oxygen, and 2) equilibrium methane content of the wet gas is approximately 15% (21% dry basis). The process would require H_2 recycle in the ratio 3.5 moles/mole CH_4.

In Fig. 3B, for 40% steam decomposition, 0.15 O_2/H_2O inlet molar ratio, 50 atmospheres and 1200°K. (1700°F.), the process would be independent of external hydrogen if the H_2/H_2O inlet molar ratio were no greater than 2.5, the point at which the corrected ratio, for coal, of H_2 available/H_2 consumed approaches unity. In this case the net heat effect is again practically zero for the same reactant preheats, and the equilibrium methane content of the wet gas is approximately 18% (22% dry basis). Under these conditions, the required H_2 recycle is 3.4 moles/mole CH_4 produced.

In Fig. 4A, 30% steam decomposition, 0.1 O_2/H_2O inlet molar ratio, 200 atmospheres and 1200°K. (1700°F.), the process would be hydrogen self-sufficient at H_2/H_2O inlet molar ratios no greater than 0.75, the point at which the corrected ratio, for coal, of H_2 available/H_2 consumed approaches unity. Here the net heat effect is approximately 20,000 Btu/lb. mole CH_4 exothermic, which would be sufficient to compensate for radiation and convection heat losses. The equilibrium

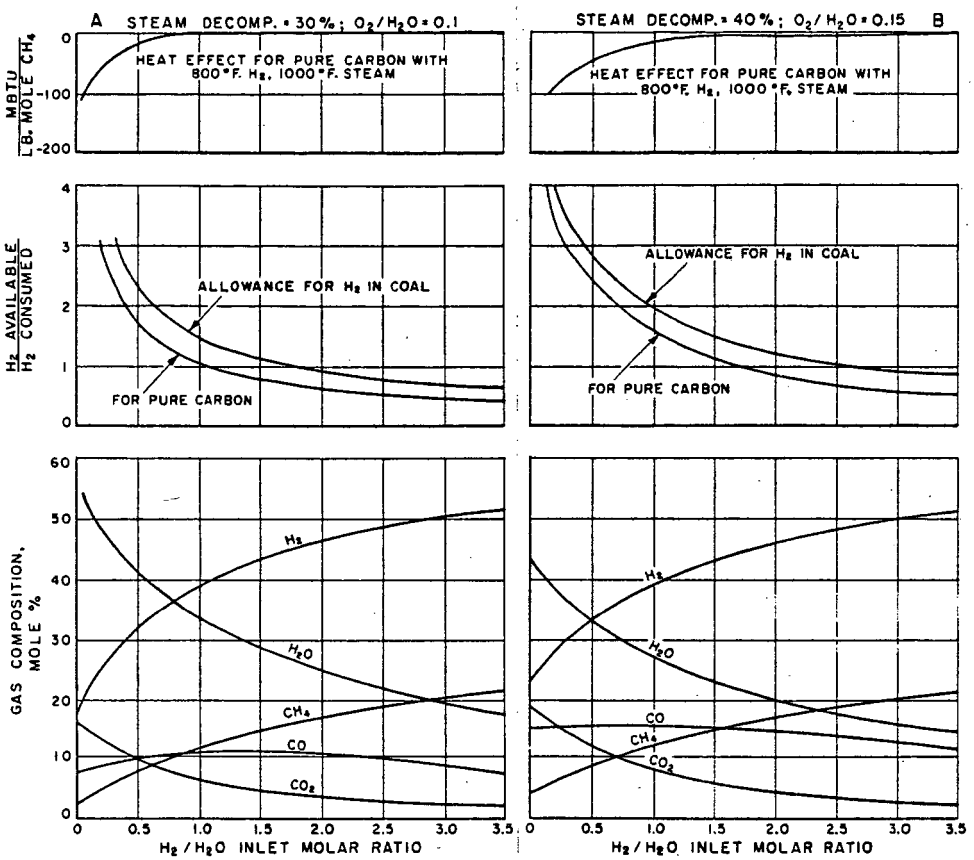

Fig. 3.-EFFECT OF H_2/H_2O RATIO ON EQUILIBRIUM GAS COMPOSITION, H_2 PRODUCTION/CONSUMPTION RATIO, AND NET HEAT EFFECT, FOR THE $C-H_2-H_2O$ SYSTEM AT 1200°K. AND 50 ATMOSPHERES, WITH 30 AND 40% STEAM DECOMPOSITION, AND 0.1 AND 0.15 O_2/H_2O INLET MOLAR RATIO, RESPECTIVELY

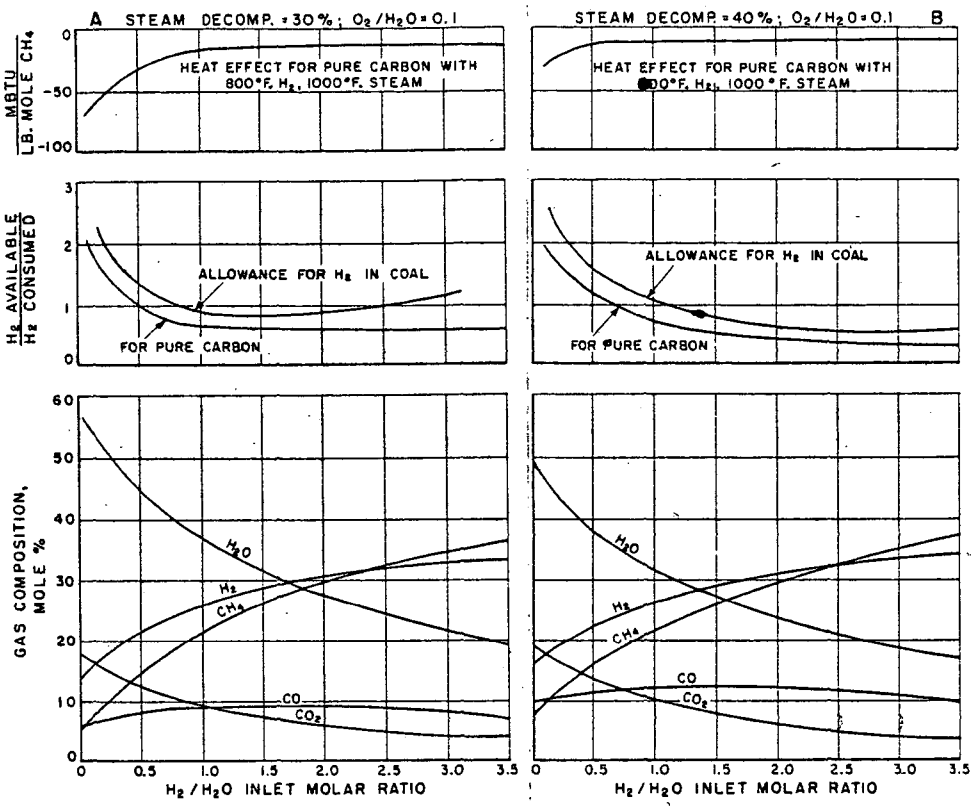

Fig. 4.-EFFECT OF H_2/H_2O RATIO ON EQUILIBRIUM GAS COMPOSITION, H_2 PRODUCTION/CONSUMPTION RATIO, AND NET HEAT EFFECT, FOR THE $C-H_2-H_2O$ SYSTEM AT 1200°K. AND 200 ATMOSPHERES, WITH 0.1 O_2/H_2O INLET MOLAR RATIO 30 AND 40% STEAM DECOMPOSITION

methane content is approximately 18% on the wet basis, (30% dry basis), and the process would require H_2 recycle of 1.8 moles/mole CH_4 produced.

In Fig. 4B, 40% steam decomposition, 0.1 O_2/H_2 inlet molar ratio, 200 atmospheres and 1200°K. (1700°F.), the process would again be self-sufficient with respect to hydrogen if the H_2/H_2O inlet molar ratio were no greater than 1.0. The net heat effect is less exothermic than in the previous case, approximately 10,000 Btu/lb. mole CH_4 at the same reactant preheats. The equilibrium methane content is approximately 21% on the wet basis, or 31% dry basis, with a required H_2 recycle of 1.7 moles/mole CH_4 produced.

These results demonstrate that operating conditions can be found where the proposed process, with O_2 admission and H_2 recycle, appears thermodynamically feasible. It should be noted, since oxygen is required, that the process reduces to an adaptation of the Lurgi pressure gasifier with provision for H_2 recycle in the upper portions of the fixed fuel bed, or to an adaptation of present fluid-bed coal hydrogenation reactors with provision for addition of steam and oxygen either in the same reactor or in a separate vessel to gasify the coal residue. Since this method of methane production by H_2 recycle takes advantage of the exothermic heat of coal hydrogenation to compensate in part for the endothermic heats of the steam decomposition reactions which continue to occur to a small extent at hydrogenation temperatures, it appears that by virtue of the potentially greater thermal efficiency, both oxygen and coal requirements per MCF CH_4 can be reduced from those of other gasification processes. The potential magnitude of this reduction can be seen from a comparison of the theoretical material requirements in Table 4, based on Figs. 3 and 4, with actual requirements for several gasification processes operated on pilot plant and large scale (Table 5). In Table 4, the oxygen and coal requirements based on Figs. 3A and 3B were increased by 20% to compensate for radiation and convection heat losses, since the theoretical heat effects were not sufficiently exothermic for these two cases.

Table 4.-THEORETICAL MATERIAL REQUIREMENTS (REACTOR ONLY) FOR METHANE PRODUCTION BY HYDROGEN RECYCLE AND OXYGEN-STEAM ADMISSION

Reference Figure	Fig. 3A	Fig. 3B	Fig. 4A	Fig. 4B
Conditions:				
Pressure, Atm.	50	50	200	200
Outlet Temp., °F.	1700	1700	1700	1700
O_2/H_2O Inlet Molar Ratio	0.1	0.15	0.1	0.1
H_2/H_2O Inlet Molar Ratio	1.8	2.4	0.75	1.0
Inlet Steam, °F.	1000	1000	1000	1000
Recycled Hydrogen, °F.	800	800	800	800
Inlet Oxygen, °F.	60	60	60	60
Inlet Steam Decomp., %	30	40	30	40
Requirements/MCF CH_4:				
Pure Carbon, lb.	73.5*	74.5*	64.5	63
Coal, at 95% Gasification, lb.	103*	104*	90.5	88
Steam, lb.	111	79	151	110
Oxygen, 100%, SCF	280*	298*	318	230
Oxygen, 95%, SCF	295*	314*	335	242
Theoretical Percent Carbon Appearing as CH_4	43	43	49	51

* Increased by 20% over theoretical values.

Table 5.-TYPICAL MATERIAL REQUIREMENTS FOR METHANE PRODUCTION FROM SYNTHESIS GAS (COAL GASIFIER ONLY)

Process*	USBM[9]	PAN[4]	K-T[10]	IGT[11]	L[3]	WGS[1]	PROD.[13]
Nominal Conditions:							
Coal Type	Bit.	Bit.	Bit.	Bit.	Char	Coke	Barley Anth.
Pressure, Atm.	21	1	1	7.5	21	1	1
Outlet Temp., °F.	2500	2350	2300	2500	1100	1200	880
O_2/H_2O Inlet Molar Ratio	1.5	0.65	0.81	0.45	0.77	0.38	0.29
Inlet Steam, °F.	625	930	250	1500	500	210	285
Inlet Oxygen, °F.	625	930	100	100	500	210	285
Inlet Steam Decomp., %	25	25	25	31	34	54	52
Carbon Gasified, %	90	84	85	92	97	99.5	99.4
Requirements/MCF CH_4:							
Carbon, lb.	96.5	119	112	93.5	84	100	87
Coal (or coke), lb.	137	185	168	125	112	111	110
Steam, lb.	42	77	85	131	360	152	154
Oxygen, 100%, SCF	1332	1060	1444	1248	584	1144	951
Oxygen, 95%, SCF	1408	1118	1520	1312	615	1204	1000
Percent Carbon Appearing as CH_4 by Methanation	33	26.7	28	34	38	32	36.6

*PAN = Panindco Process; K-T = Koppers-Totzek Gasifier; L = Lurgi Unit; WGS = Water Gas Set; PROD. = Producer

The data in Table 5 were computed on the basis of 4 SCF CO-plus-H_2 in synthesis gas from coal to yield 1 SCF CH_4 by catalytic methanation. The material requirements pertain only to the coal gasification reactor. Data for Lurgi pressure gasification were adjusted to take into account the methane content of the raw gas.

ESTIMATION OF REACTOR SIZE FROM AVAILABLE DATA ON REACTION RATES

I. Reaction Rate Data

Comprehensive experimental data on reaction rates of hydrogen-steam mixtures with carbon in the form of low temperature (Disco) char have been reported by Gorin, Goring, Zielke and coworkers.[3,6,14,15] The data were obtained from a 1.5-inch I.D. fluidized bed of 65/100 mesh fuel particles, operated at 1-30 atmospheres and 1500-1700°F. Methane production rates and total carbon gasification rates, expressed as moles C gasified/mole C-min., were determined for pure H_2 and for H_2/H_2O inlet molar ratios in the range 0.1-2.0 at carbon burnoffs or percent gasifications of 0-100%. The total carbon gasification rate is the sum of the rate of CH_4 production and the rate of the steam reactions with carbon. Under the conditions of the investigations, the percent utilization of H_2 and decomposition of steam were small, so the exit gases contained only a few percent CH_4, CO and CO_2. As a consequence, the data do not take into account the retarding effects on the rates as appreciable concentrations of methane and other components appear in the gas in a practical gasification system.

The data reported by Zielke and Gorin[15] indicate that steam has a marked effect in increasing the methane-formation rate; the increase, which is pressure dependent, ranges from 2 to 100 times the rate in a pure H_2 atmosphere, at 1700°F. and 1-30 atmospheres total pressure. The CH_4 rate increases with total pressure raised to a power between 0.1 and 1.5, depending upon H_2/H_2O inlet molar ratio and percent carbon burnoff, and decreases rapidly with decreasing temperature. The total carbon gasification rate follows approximately the same trends, except that at high H_2/H_2O inlet molar ratios this rate becomes equal to the CH_4 rate by virtue of less steam being available for carbon gasification under these conditions. The CH_4 formation rates for Disco char do not appear to be sufficiently high at pressures below 30 atmospheres and temperatures less than 1700°F. to be of particular interest commercially.

To facilitate reactor calculations, plots of data are required showing CH_4 formation and total carbon gasification rates at 50 atmospheres as affected by H_2/H_2O inlet molar ratio and percent carbon burnoff. These graphs were obtained by first plotting the reported rates against pressure (1-30 atmospheres) on logarithmic scales, for each H_2/H_2O inlet molar ratio investigated (0.32, 1.0 and 2.0) at 0-100% carbon burnoff. The resulting nearly straight lines were extrapolated to 50 atmospheres. The extrapolated points were then replotted in the desired form, Fig. 5. The linear CH_4 rate plot, Fig. 5A, was extended (dotted lines) beyond the range of H_2/H_2O inlet molar ratios investigated. The total carbon gasification rate plot, Fig. 5B, was also extended by continuing the trend of the curves (dotted lines) to a 4.0 H_2/H_2O inlet molar ratio. In effect, Figs. 5A and 5B are based entirely upon moderate extrapolations; however, they are believed to be justified.

II. Reactor Design Estimate

A. Procedure

Evaluation, from the standpoint of kinetics, of the hydrogen recycle gasification process with oxygen-steam admission, requires an estimate of the hydrogenation zone fuel bed depth. To avoid unnecessary complications it is assumed that 1) the temperature gradient in the hydrogenation zone of an actual reactor may be approximated with an effective average temperature (1700°F.), and 2) the velocity distribution of gases at a given cross-section of the reactor may be approximated by piston-type flow at an average velocity (constant velocity distribution).

The basic design relationship is given by a material balance[7] over a differential bed height, dh, in which an incremental quantity of CH_4, dn_m, is formed:

$$dn_m = r_m \, dh = -q \, F_o \, dB \qquad (31)$$

where dB = incremental fractional burnup of carbon in the element of fuel bed

dn_m = incremental CH_4 formed, lb. mole hr.-sq. ft. reactor cross section

r_m = CH_4 formation rate, lb. mole/hr.-cu. ft. reactor

$q = r_m/r_t$ = ratio, CH_4 formation rate/total gasification rate

F_o = carbon input rate to reactor, lb. mole/hr.-sq. ft.

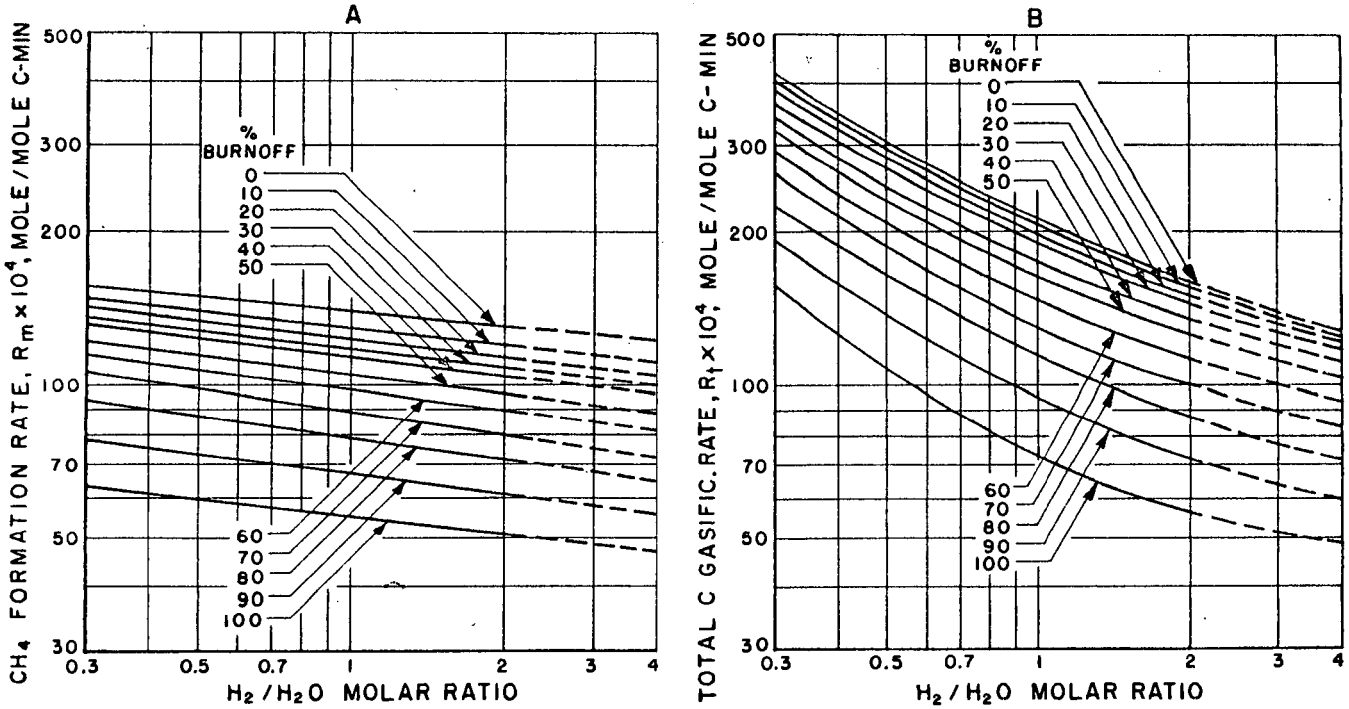

Fig. 5.-METHANE FORMATION AND TOTAL CARBON GASIFICATION RATES FOR DISCO CHAR IN H_2-H_2O ATMOSPHERE AT 1700°F., 50 ATMOSPHERES, AND VARIOUS BURNOFFS OF CARBON

For a fixed fuel bed, with countercurrent flow of gases with respect to the coal feed, this relationship may be integrated graphically over the limits from the start of the hydrogenation zone, $h = 0$, where the burnup is B_o, to the top of the bed, $h = H$, where the burnup $B = 0$ (fresh coal feed):

$$\int_0^H \frac{dh}{F_o} = \frac{H}{F_o} = -\int_{B_o}^0 \frac{q\,dB}{r_m} = -\int_{B_o}^0 \frac{dB}{r_t} \qquad (32)$$

At a fixed temperature and pressure the quantities r_m, r_t and q are dependent upon carbon burnoff and the composition of the reacting gases. An acceptable relationship to take into account the effect of gas composition in retarding the reaction rates is given by the ratio of the actual partial-pressure product of the reacting components to the equilibrium constant of the particular reaction. By use of this concept, the recommended forms of the rate equations are:

$$R_t' = R_m \left[1 - \frac{p_{CH_4}}{K_1 p_{H_2}{}^2 \gamma_c}\right] + \left[R_t - R_m\right] \left[1 - \frac{p_{CO}\, p_{H_2}}{K_2 p_{H_2O}\, \gamma_c'}\right] \qquad (33)$$

$$R_m' = R_m \left[1 - \frac{p_{CH_4}}{K_1 p_{H_2}{}^2 \gamma_c}\right] \qquad (34)$$

where R_m = CH_4 formation rate given in Fig. 5A, uncorrected for retarding effects, lb. mole/lb. mole C-min.

R_t = total carbon gasification rate given in Fig. 5B, uncorrected for retarding effects, lb. mole/lb. mole C-min.

R_m' = CH_4 formation rate, corrected for retarding effects, lb. mole/lb. mole C-min.

R_t' = total carbon gasification rate, corrected for retarding effects, lb. mole/lb. mole C-min.

p = actual partial pressure of gaseous components at point of reaction, atm.

γ_c = activity of carbon with respect to hydrogenation reaction

γ_c' = activity of carbon with respect to carbon - steam reaction

These rate equations are considered to give conservative results.[15]

The conversion factors between Equations 32-34 are:

$$r_m = 60\, \rho_c y_c\, R_m'/12 \qquad (35)$$

$$r_t = 60\, \rho_c y_c\, R_t'/12 \qquad (36)$$

where ρ_c = bulk density of fuel, lb./cu. ft.

y_c = weight fraction carbon in fuel

For practical purposes the product $\rho_c y_c$ can be considered constant throughout the hydrogenation zone, for fuels of normal ash content. By use of Equation 36, the design Equation 32 may be put in the form:

$$(5\rho_c y_c)\left[\frac{H}{F_o}\right] = \int_0^{B_o} \frac{dB}{R_t'} \qquad (37)$$

B. Fixed-Bed Reactor

1. Design Conditions. The integral in Equation 37 is the area under a curve of reciprocal total carbon gasification rate, $1/R_t'$, plotted against fractional burnoff, B, in the hydrogenation zone. Since R_t' (Equation 33) depends upon the partial pressures of gaseous constituents and upon the burnoff at a given position in the fuel bed, a material balance is required to relate the variation of gas composition with burnoff throughout the fuel bed. The outlet gas composition of the reactor is based on the equilibrium values given in Fig. 3B at the point where the ratio H_2 available/H_2 consumed (for coal) is unity, for 1200°K. (1700°F.), 50 atmospheres, 40% steam decomposition, 0.15 O_2/H_2O inlet molar ratio, and 2.4 H_2/H_2O inlet molar ratio. This outlet composition is 47.2% H_2, 17.9% H_2O, 13.5% CO, 3.5% CO_2 and 17.9% CH_4.

The calculation of gas composition variation with burnoff through the fuel bed is based on, 1) hydrogen, oxygen and carbon balances, 2) 80% of the hydrogen content of the coal released to appear in CH_4 in the hydrogenation zone, weighted linearly according to percent carbon burnoff, and 3) maintenance of water-gas-shift equilibrium. The third assumption is not strictly correct, since experimental evidence indicates that the water-gas shift reaction may be far removed from equilibrium under the operating conditions in coal gasification with H_2-H_2O mixtures.[6] However, since the principal discrepancy would lie in the actual CO_2/CO ratio over that theoretically calculated, the assumption of water-gas shift equilibrium will be sufficiently accurate. Final results of the material balances are given in the following.

2. Material Balance for Oxidation Zone. Expressions for the molar quantities of hydrogen (x'), steam (y'), carbon monoxide (z'), carbon dioxide (m'), methane (w'), total moles (N'), and carbon gasified (c_g'), as moles/mole inlet steam are:

$$w' = 0 \text{ (no } CH_4) \qquad (38)$$

$$m' = \frac{K_3\,(1-SD')\,(SD' + 2b)}{2K_3\,(1-SD') + a' + SD' - 2w'} \qquad (39)$$

$$z' = SD' + 2b - 2m' \qquad (40)$$

$$y' = 1 - SD' \qquad (41)$$

$$x' = K_3 y' z'/m' \qquad (42)$$

$$N' = x' + y' + z' + m' + w' \qquad (43)$$

$$c_g' = z' + m' + w' \qquad (44)$$

Fractional burnoff in oxidation zone:

$$B' = c_g'/c_g \qquad (45)$$

where SD' = steam decomposition in oxidation zone:

a' = H_2/H_2O inlet molar ratio corrected for coal. Note a' = 0 prior to H_2 recycle point

b = O_2/H_2O inlet molar ratio

c_g = carbon gasified at equilibrium outlet conditions of the hydrogenation zone.

These relationships are readily solved for a given temperature (which determines K_3), known values of a' and b, assumed value of steam decomposition, SD', and known value of equilibrium carbon gasification, c_g.

3. Material Balance for Hydrogenation Zone. Expressions for the molar quantities of hydrogen (x"), steam (y"), carbon monoxide (z"), carbon dioxide (m"), methane (w"), total moles (N") and carbon gasified (c_g"), as moles/mole inlet steam are:

$$w'' = \left[\frac{B''-B'}{B-B'}\right] w \tag{46}$$

$$m'' = \frac{\mu}{2\delta}\left[1 - \sqrt{1 - \frac{4\delta\eta}{\mu^2}}\right] \tag{47}$$

$$z'' = SD'' + 2b - 2m'' \tag{48}$$

$$y'' = 1-SD'' \tag{49}$$

$$x'' = K_3\, y''\, z''/m'' \tag{50}$$

$$N'' = x'' + y'' + z'' + m'' + w'' \tag{51}$$

$$c_g'' = z'' + m'' + w'' \tag{52}$$

Incremental steam decomposition occurring in hydrogenation zone:

$$\Delta SD'' = \left[\frac{B''-B'}{B-B'}\right] (SD - SD') \tag{53}$$

Total steam decomposition:

$$SD'' = SD' + \Delta SD'' \tag{54}$$

where $\mu = (2K_3-1)\,(1-SD'') + \delta(SD'' + 2b) + \alpha$

$$\eta = K_3\,(SD'' + 2b)\,(1-SD'')$$

$$\alpha = a' - \left[\frac{c_g' - w''}{c_g - c_g'}\right](0.336\, c_g) - 2w'' + 1$$

$$\delta = \frac{0.336\, c_g}{c_g - c_g'}$$

B = theoretical total burnoff of fuel residue = 100%

B" = fractional burnoff in hydrogenation zone

SD" = total steam decomposition in hydrogenation zone

These relationships are solved for a given temperature, assumed reactor inlet and outlet conditions (which determine the values of K_3, a', w, c_g, B, SD), and known values of B', SD' and c_g' (from oxidation zone), by the assigning of arbitrary values to the hydrogenation zone burnoff B".

Solution of the material balance equations for the oxidation, steam decomposition, and hydrogenation zones under the condition of exit gas equilibrium resulted in the values given in Table 6. Here the exothermic heat of the oxidation zone is balanced approximately by the endothermic effect of the steam decomposition zone. Beyond the H_2 recycle point, the exothermic heat of coal hydrogenation is

balanced approximately by, 1) the heat requirement of steam decomposition which continues to occur to a small extent in the hydrogenation zone, and 2) the sensible heat required for preheating the coal feed and recycled hydrogen to the operating temperature.

4. Fuel Depth and Flow Rates. The assumption that 10% steam decomposition occurs in the hydrogenation zone (Table 6) can be checked for accuracy after completion of the rate calculations. The results in Table 6 are shown graphically in Fig. 6. The reaction rates of Equations 33 and 34 can now be evaluated at any fractional burnoff and assumed activity of carbon in the hydrogenation zone by reading partial pressure values from this plot and by obtaining the rates R_m and R_t from Figs. 5A and 5B. The results of these calculations, which are required for graphical integration of Equation 37, and later for Equation 31, are summarized in Table 7. The assumption of 1.1 activity of carbon with respect to the hydrogenation reactions is justified on the basis that, given sufficient residence time, the equilibrium CH_4 content based on carbon as β-graphite may be exceeded with carbon as coal.

Table 6.-COMPUTED GAS COMPOSITIONS AT VARIOUS POINTS IN FIXED BED REACTOR

Basis: O_2/H_2O inlet molar ratio = 0.15; H_2/H_2O inlet molar ratio for pure carbon = 2.41, for coal = 2.01; coal contains 75 wt. % C, 5 wt. % H.

Position	Assumed Inlet Steam Decomp., %	Theoretical Carbon Burnoff, %	Gas Comp., Mole %					
			O_2	H_2	H_2O	CO	CO_2	CH_4
O_2-H_2O Inlet to Reactor	0	100	13	--	87	--	--	--
End of Oxidation Zone	0	87.3	--	--	87	--	13	--
End of Steam Decomposition Zone	30	58.3	--	21.3	49.8	15.1	13.8	--
Point of H_2 Recycle	30	56.8	--	65.7	19.8	12.0	2.5	--
50% through Hydrogenation Zone	35	28.2	--	56.6	18.8	12.8	3.0	8.8
Outlet of Reactor	40	0	--	47.2	17.9	13.5	3.5	17.9

Position	Molar Quantities, mole/mole inlet steam							
	O_2	H_2	H_2O	CO	CO_2	CH_4	Total	Carbon Gasified
O_2-H_2O Inlet to Reactor	0.15	--	1.0	--	--	--	1.15	--
End of Oxidation Zone	--	--	1.0	--	0.15	--	1.15	0.150
End of Steam Decomposition Zone	--	0.30	0.70	0.21	0.19	--	1.40	0.493
Point of H_2 Recycle	--	2.32	0.70	0.42	0.09	--	3.53	0.511
50% through Hydrogenation Zone	--	1.96	0.65	0.44	0.10	0.303	3.45	0.850
Outlet Reactor	--	1.60	0.60	0.46	0.12	0.605	3.39	1.182

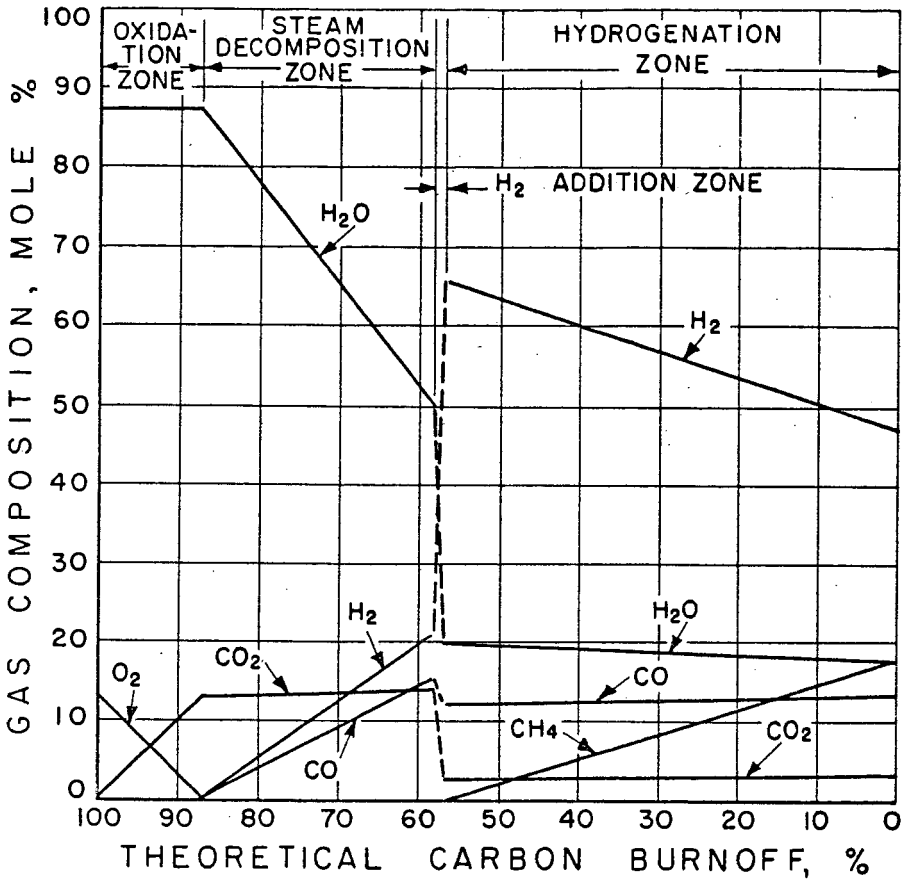

Fig. 6.-COMPUTED VARIATION OF GAS COMPOSITION WITH CARBON BURNOFF IN FIXED-BED REACTOR AT 1700°F. AND 50 ATMOSPHERES

Table 7.-REACTION RATES FOR VARIOUS PERCENT BURNOFF IN FIXED-BED REACTOR HYDROGENATION ZONE OPERATING AT 1700°F. AND 50 ATM.

(Activity of Carbon, $\gamma_c = 1.1$, $\gamma_c' = 1.0$)

Burnoff %	Ratio H_2/H_2O	Inhibiting Terms $\frac{p_{CH_4}}{K_1 p_{H_2}^2 \gamma_c}$	Inhibiting Terms $\frac{p_{CO} p_{H_2}}{K_2 p_{H_2O} \gamma_c'}$	Rates, moles/mole C-min. $R_m' \times 10^4$	Rates, moles/mole C-min. $R_t' \times 10^4$	Ratio $q = R_m'/R_t'$
56.8	3.32	0	0.499	87.0	94.5	0.921
50	3.25	0.06	0.498	85.5	95.1	0.900
40	3.15	0.16	0.492	84.0	93.1	0.902
30	3.04	0.28	0.489	74.1	86.1	0.861
20	2.90	0.45	0.478	60.0	72.0	0.834
10	2.78	0.66	0.462	40.4	52.2	0.774
5	2.71	0.77	0.462	28.1	38.3	0.734
0	2.65	0.91	0.450	11.6	21.0	0.555

From the data in Table 7, graphical integration of Equation 37 yielded a value of 86.25 min.-mole C/mole (inverse space velocity). The probable height of the hydrogenation zone is therefore:

$$H = 86.25\ F_o/5\rho_c\ y_c \tag{55}$$

Practical values of the inlet feed rate F_o, moles C/hr. sq. ft., can be selected on the basis of a conservative Lurgi rate, 140 lb. coal/hr. sq. ft., and the fact that the incremental burnoff prior to the hydrogenation zone was estimated as 100-56.8, or 43.2% (Table 6):

$$F_o = (140)(0.75)/(12)(0.432) = 20.2 \text{ moles C/hr.-sq. ft. for a coal containing 75 wt. \% carbon.}$$

Assuming a 40 lb./cu. ft. fuel bed bulk density, the estimated height of the hydrogenation zone is:

$$H = (86.25)(20.2)/(5)(40)(0.75) = 11.6 \text{ ft.}$$

which is applicable only for 65/100 mesh fuel particles. A fixed bed would operate with perhaps 1/4-inch average size fuel. Some correction is therefore required, but necessary data are lacking, for the effect of fuel size, since reaction rates per unit mass of fuel vary with effective surface area and method of contacting.

A verification of the amount of steam decomposition occurring simultaneously with the hydrogenation reactions can now be made, based on the fluid-bed rate data (Figs. 5A, 5B and Table 7), through integration of Equation 31:

$$n_m = -F_o \int_{B_o}^{0} q\ dB \tag{56}$$

and the additional relationship,

$$n_t = -F_o \int_{B_o}^{0} dB = F_o B_o \tag{57}$$

where n_m = methane produced in hydrogenation zone, lb. mole/hr.-sq. ft.

n_t = total carbon gasified by hydrogenation and by steam decomposition, lb. mole/hr.-sq. ft.

The incremental steam decomposition occurring in the hydrogenation zone, $\Delta SD''$, is then given by:

$$\Delta SD'' = w\ (n_t/n_m - 1) \qquad (58)$$

where w = methane produced (equilibrium value at outlet of reactor), mole/mole inlet steam. For this case w = 0.605 (Table 7), and the ratio n_t/n_m = 1.19 (graphical integration), so:

$$\Delta SD'' = 0.605\ (1.19-1) \text{ or } 11.5\%$$

which is in close agreement with the 10% steam decomposition previously assumed.

Based on these results, the estimated flow rates, space velocities and residence times for the proposed gasification process are:

a) Steam feed rate, lb./hr. sq. ft., = 18 F_o/c_g = (18)(20.2)/1.182 = 308

b) Oxygen feed rate, SCF/hr. sq. ft., = 379 bF_o/c_g = (379)(0.15)(20.2)/1.182 = 970

c) Hydrogen recycle space velocity, SCF/hr. cu. ft. hydrogenation zone = 379 $a'F_o/Hc_g$ = (379)(2.014)(20.2)/(11.6)(1.182) = 1125

d) Methane space velocity, SCF/hr. cu. ft. hydrogenation zone = (379) wF_o/Hc_g = (379)(0.605)(20.2)/(11.6)(1.182) = 336

e) Approximate coal residence time in hydrogenation zone, hr., based on inlet volume of coal

$$= \frac{H\rho_c\ y_c}{12\ F_o} = \frac{(11.6)(40)(0.75)}{(12)(20.2)} = 1.44$$

f) Approximate gas residence time in hydrogenation zone, sec., based on average gas volume and 40% void space (ϵ) of the fuel bed

$$= \frac{4940PH\ c_g\epsilon}{N_{avg}\ F_oT} = \frac{(4940)(50)(11.6)(1.182)(0.40)}{(3.46)(20.2)(2160)} = 9$$

C. Fluid-Bed Reactor

1. Design Conditions. In the analysis of the fluid-bed reactor it is assumed:

a) The reactor is completely stirred with respect to coal, i.e., the percent carbon burnoff is uniform throughout the hydrogenation zone.

b) Gases move through the reactor in piston-type flow, i.e., back-mixing is neglected.

c) The hydrogenation zone is at constant temperature (1700°F.) and constant pressure (50 atm.).

d) The same equilibrium outlet gas composition will be attained as was assumed for the fixed-bed case calculations.

e) 30% steam decomposition will be attained prior to the hydrogenation zone. In the hydrogenation zone, an additional 10% steam decomposition will occur.

f) The water-gas shift reaction is in continual equilibrium in the hydrogenation zone.

g) With the conditions of Items b, e and f above, the gas composition will vary with burnoff as in Fig. 6.

2. Fuel Depth and Flow Rates. By use of the procedure already described, graphical integration of Equation 37 gave 102.9 min.-mole C/mole for the reciprocal total carbon gasification rate (corrected for retarding effects) under the conditions listed above. Details are summarized in Table 8. The probable height of the hydrogenation zone is therefore $H = 102.9\ F_o/5\ \rho_c y_c$.

Table 8.-REACTION RATES FOR VARIOUS PERCENT BURNOFF IN FLUID-BED REACTOR HYDROGENATION ZONE OPERATING AT 1700°F. AND 50 ATM.

(Average Burnoff of Fluid Bed = 56.8%; Activity of Carbon $\gamma_c = 1.1$, $\gamma_c' = 1.0$)

Burnoff, %	Ratio H_2/H_2O	Inhibiting Terms $\frac{p_{CH_4}}{K_1 p_{H_2}^2 \gamma_c}$	Inhibiting Terms $\frac{p_{CO}\ p_{H_2}}{K_2 p_{H_2O} \gamma_c'}$	Reaction Rates, mole/mole C-min. $R_m' \times 10^4$	Reaction Rates, mole/mole C-min. $R_t' \times 10^4$	Ratio $q = R_m'/R_t'$
56.8	3.32	0	0.499	87.0	94.5	0.921
50	3.25	0.06	0.498	80.8	88.8	0.910
40	3.15	0.16	0.492	73.1	81.2	0.901
30	3.04	0.28	0.489	63.0	71.5	0.883
20	2.90	0.45	0.478	48.4	57.8	0.837
10	2.78	0.66	0.462	30.7	40.9	0.752
5	2.71	0.77	0.458	20.5	30.7	0.668
0	2.65	0.91	0.450	8.1	19.1	0.423

The carbon gasification capacity, F_o, is estimated by assigning a superficial velocity (v_f) of, say, 0.3 ft./sec. at the point of maximum gas flow. The total moles of gases permissible at a chosen pressure, temperature and fluidizing velocity is then $M_t = 4940\ Pv_f/T$ which with P = 50, T = 2160°R. becomes $M_t = 34.4$ moles gases/hr.-sq. ft. The total gases are at a maximum at the point of hydrogen recycle. From previous computations (Equations 38 to 45 and Table 6) the ratio of gases at this point is 3.531 moles/mole inlet steam. The total amount of carbon gasified was 1.182 moles/mole inlet steam. Therefore, the carbon input rate is:

$$F_o = \frac{(1.182)(34.4)}{3.531} = 11.5 \text{ moles C/hr.-sq. ft.}$$

For a fluid bed density of 35 lb. cu. ft. and fuel containing 75 wt. % carbon, the estimated height of the hydrogenation zone is:

$$H = (102.9)(11.5)/(5)(35)(0.75) = 9 \text{ ft.}$$

which again would be applicable only for 65/100 mesh fuel particles.

By use of the procedure of Equations 56-58, the estimated steam decomposition occurring simultaneously with the hydrogenation reactions in the fluid bed is found to be:

$$\Delta SD'' = 0.605\ (1.20 - 1) \text{ or } 12.1\%$$

which is in acceptable agreement with the 10% assumption on which the reaction rate calculations were based.

From these results the estimated flow rates, space velocities and residence times for the proposed gasification process are:

a) Steam feed rate, lb./hr.-sq. ft. = (18)(11.5)/1.182 = 175

b) Oxygen feed rate, SCF/hr.-sq. ft. = (379)(0.15)(11.5)/1.182 = 555

c) Hydrogen recycle space velocity, SCF/hr. cu. ft. hydrogenation zone = (379)(2.014)(11.5)/(9)(1.182) = 825

d) Methane space velocity, SCF/hr. cu. ft. hydrogenation zone = (379)(0.605)(11.5)/(9)(1.182) = 250

e) Approximate coal residence time in hydrogenation zone, hr., based on constant density of fluid bed = (9)(35)(0.75)/(12)(11.5) = 1.7

f) Approximate gas residence time in hydrogenation zone, sec., based on arithmetic average superficial velocity ($\bar{v}_f$) of the fluidizing gases and 60% void space (ϵ) of the fluid-bed = $H\epsilon/\bar{v}_f$ = (9)(0.60)/0.294 = 18.4

These approximate reactor calculations indicate that the hydrogenation zone fuel bed depths for either fixed-bed or a fluid-bed operation are within reasonable values for a practical system. It must be stressed, however, that no interpretation of these results should be made under conditions and assumptions other than those set forth. In particular, the results apply strictly to 65/100 mesh low-temperature coal char made by the Disco process. For lack of experimental reaction rate data at higher pressures, the reported rate data for 1700°F. were extrapolated to 50 atmospheres and were also extended beyond the range of H_2/H_2O inlet molar ratios investigated. The data also apply strictly to a fluid-bed operation, since they were obtained in this type of equipment.

The results derived by application of these rate data to the fixed-bed reactor, although indicative, must be viewed with reservation, since sufficient information is not presently available to correct for possible effects of particle size and of different flow characteristics and gas-contacting efficiencies between fluid-bed vs. fixed-bed operation. For simplicity in the calculations, a constant operating temperature, 1700°F., was assumed throughout the hydrogenation zone. It is possible to improve the results given here by taking into account the expected temperature distribution in the hydrogenation zone through a simultaneous heat balance with the reaction rate calculations.

Further information which is lacking for a more complete evaluation is:

a) Effect of moderate concentrations of CO and CO_2 in inhibiting the rates of the hydrogenation reactions.

b) Effect of gasification properties of various fuels, and

c) Exact costs of methane separation by liquefaction.

SUMMARY AND CONCLUSIONS

Thermodynamic analyses indicate that the proposed process for methane production via coal gasification with recycled hydrogen cannot be independent simultaneously of both external hydrogen and external heat. Operating conditions can be found where, theoretically, either 1) the process is thermally self-sufficient but lacks hydrogen, or 2) the process is self-sufficient with respect to hydrogen, but lacks heat. It is believed that it would be of greater advantage to operate the process according to Item 2 above, since the thermal requirements could be readily met by internal combustion of residual carbon with oxygen. The theoretical heat requirements based on carbon

as β-graphite were found to be in the range 25,000-100,000 Btu/lb. mole CH_4 produced. The heat requirements with coal as the gasification fuel would be still larger, since the exothermic heat of coal hydrogenation is not as large as that for hydrogenation of pure carbon. The use of oxygen for partial combustion would provide, simultaneously, a high-temperature zone for rapid steam decomposition. Decompositions of at least 30% are required for economical utilization of steam, since this is the primary hydrogen source.

Thermodynamic calculations of the revised process, with oxygen admission below the point of hydrogen recycle, show that both thermal and hydrogen self-sufficiency can theoretically be attained at 1700°F. and 50-200 atmospheres. The process is potentially more efficient in respect to the proportion of carbon in the fuel appearing as methane, and represents a method of achieving, theoretically, oxygen requirements less than those of the conventional Lurgi pressure gasifier.

Based on available data on reaction rates of 65/100 mesh low-temperature coal char (Disco) with hydrogen-steam mixtures, fuel bed heights for the hydrogenation zone were estimated at 9 feet for a fluidized-bed reactor, and approximately 11-12 feet for a fixed-bed reactor, at 1700°F., 50 atmospheres, with equilibrium exit gas compositions. These bed heights appear to be within achievable values for a practical gasifier design.

Since the use of oxygen is the preferred method of supplying the heat deficiency, then the proposed process, if operated as a fixed fuel bed, reduces to an adaptation of the Lurgi pressure gasifier modified for hydrogen recycle in the upper portions of the fuel bed. If operated as a fluidized bed, the proposed process with oxygen admission does not differ in principle from fluidized-hydrogenation-residual-fuel-gasification schemes already proposed or already under investigation.

As a single-vessel reactor, the method of methane production by hydrogen recycle would appear to be more effective in a fixed bed by virtue of the countercurrent movement of fuel with respect to the reacting gases. The use of a single-vessel fluid-bed reactor, where both oxygen and hydrogen are introduced, is seen to be of disadvantage by virtue of rapid mixing of fuel, resulting in some volatile matter being burned by oxygen. Since the volatile matter portion of the fuel is the most readily hydrogenated component, it appears that an effective fluid-bed system would require a separate reactor to conduct to completion the volatile-matter hydrogenating reactions, and a second vessel, immediately below the first, to gasify residual carbon with oxygen and steam. The hot gases from the second vessel would be passed directly into the hydrogenation reactor.

From the results of this feasibility study it can be concluded:

1) Hydrogen separation by methane liquefaction, coupled with hydrogen recycle, appears to be an attractive approach for pipeline gas production and therefore should be further explored for potential application to present coal hydrogenation methods under laboratory investigation.

2) The use of hydrogen recycle to the Lurgi pressure gasifier offers potential improvements in gasification efficiency and oxygen requirement per unit volume of pipeline gas produced.

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