In our analysis, experimental values of k_T were obtained using two procedures. In cases where the total weight loss fraction after a test was less than 0.6, k_T was computed from the expression –

$$k_T = \frac{\displaystyle\int_{0.43}^{X_f} \frac{e^{\beta X^2} \, dX}{(1 - X)^{2/3}}}{t_f} \qquad (2)$$

where

X_f = base carbon conversion fraction at end of test
t_f = test period, min

When values of the total weight loss fraction at the end of a test were greater than 0.6, Equation 2 could not be used to provide an accurate value of k_T. A graphical procedure was used, based on the expression –

$$M(X) = \int_{0.43}^{X} \frac{e^{\beta X^2} \, dX}{(1 - X)^{2/3}} = k_T t \qquad (3)$$

where

X = base carbon conversion fraction at any time, t, during a test.

According to the reaction model assumed, a plot of M(X), determined from the experimental data, versus time t should yield a straight line with a slope equal to k_T. X was computed from the weight loss fraction, W, using the following equation:

$$X = \left(\frac{W - V}{W - V - A}\right) (1 - X_o) + X_o \qquad (4)$$

where

V = moisture plus volatile matter in char, g/g feed char
A = nongasifiable fraction of feed char, g/g feed char

The value of V, based on the feed char analysis, was estimated at 0.04. A was estimated at 0.248, based on the residue analyses obtained in this study. Thus, Equation can be quantitatively represented as follows:

$$X = 0.801 \ W + 0.398 \qquad (5)$$

Figure 4b-3 illustrates the typical weight loss versus time characteristics obtained in this study. Corresponding plots of X versus time and M(X) versus time for Runs HT-39 and HT-44 are shown in Figures 4b-4 and 4b-5. Table 4b-2 summarizes the conditions and results of the experimental tests considered in this initial analysis. The comparison of the calculated and experimental values of k_T, included in Table 4b-2, is graphically illustrated in Figures 4b-6, 7 and 8. Their generally good agreement indicates that no adjustment of the parameters used in the mathematical model is necessary for the conditions studied thus far.

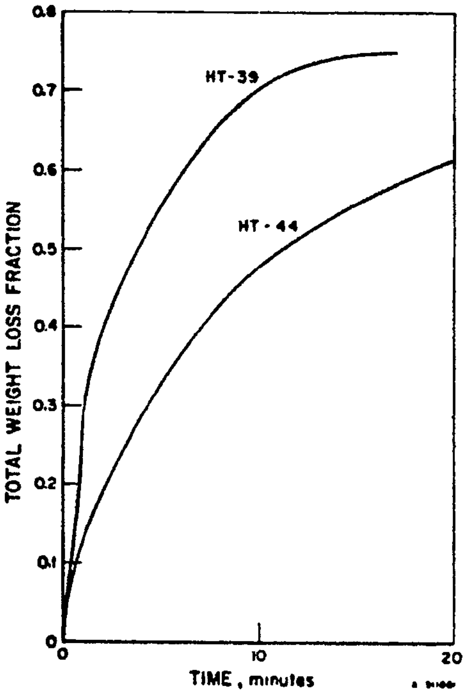

Figure 4b-3. TYPICAL WEIGHT LOSS VERSUS TIME CHARACTERISTICS

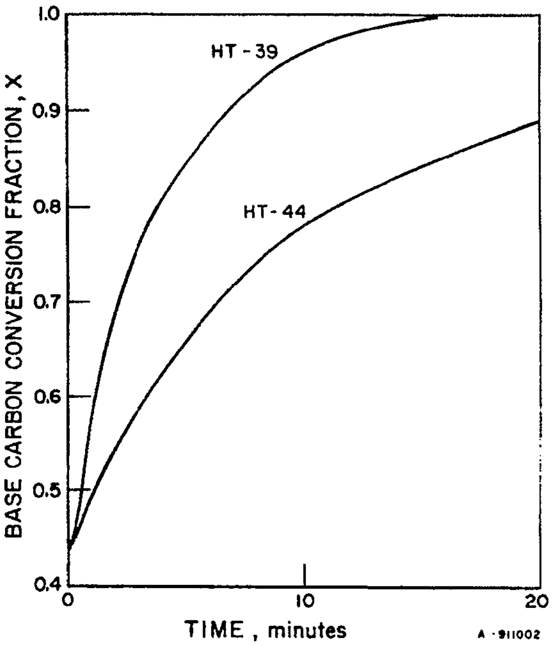

Figure 4b-4. TYPICAL CONVERSION FRACTION VERSUS TIME CHARACTERISTICS

Table 4b-2. CONDITIONS AND RESULTS OF TESTS CONDUCTED ON THE HIGH-PRESSURE THERMOBALANCE

Run No.	Gas Composition, atm					Time, min	Weight Loss Fraction	Solids Residue Composition, wt%		Rate Constant min^{-1}	
	CO	CO_2	H_2	H_2O	CH_4			C	H_2	Calcd.	Exptl.
						1700 °F					
16	--	--	35.0	--	--	59.0	0.492	48.9	0.50	0.0175*	0.0179
37	--	--	28.3	32.5	--	39.6	0.540	44.4	0.49	0.0564*	0.0474
40	--	--	46.5	16.2	--	30.6	0.477	55.1	.50	0.0385*	0.0449
42	--	--	13.7	48.5	--	35.5	0.635	55.6	0.93	0.111*	0.0820
45	5.0	9.4	19.8	25.8	2.1	35.0	0.330	67.9	0.75	0.0169*	0.0200
52	1.8	3.1	6.3	19.2	0.4	35.6	0.325	61.7	0.62	0.0274*	0.0188
59	5.9	10.8	13.2	28.0	0.9	50.0	0.327	53.7	0.60	0.0172*	0.0136
66	4.3	5.1	6.7	16.8	0.5	29.3	0.196	67.6	0.73	0.0117*	0.0110
						1760 °F					
44	--	--	32.5	34.1	--	33.3	0.750	30.8	0.60	0.124	0.134
						1800 °F					
17	--	--	35.0	--	--	57.6	0.661	22.2	0.25	0.0418*	0.0380
33	--	--	32.4	27.6	--	39.3	0.726	14.7	0.26	0.171	0.160
34	--	--	48.4	16.6	--	34.6	0.696	20.8	0.32	0.113*	0.123
46	6.2	7.4	18.1	31.6	0.3	40.7	0.667	19.5	0.39	0.0880*	0.0880
48	1.8	4.9	11.6	17.7	0.2	21.7	0.724	17.6	0.56	0.248	0.236
50	10.7	6.7	17.7	19.1	1.5	31.0	0.471	58.4	0.58	0.0300*	0.0430
53	4.5	2.6	7.4	13.3	0.3	35.2	0.481	58.3	0.46	0.0448*	0.0395
55	6.9	3.4	10.7	8.4	0.4	33.3	0.348	55.4	0.57	0.0193*	0.0229
60	6.0	9.7	13.4	30.5	0.4	34.0	0.598	47.5	0.52	0.0849*	0.0736
64	2.9	11.1	14.1	36.5	0.4	27.0	0.624	26.8	0.43	0.146	0.105
67	5.9	4.9	7.6	14.1	0.2	30.0	0.465	63.4	0.54	0.0389*	0.0431
69	1.1	3.3	4.3	24.7	0.2	25.1	0.699	--	--	0.199	0.182
						1850 °F					
43	--	--	31.7	35.2	--	20.7	0.862	6.5	0.44	0.377	0.432
						1900 °F					
18	--	--	35.3	--	--	48.4	0.752	6.9	0.11	0.0922	0.102
38	--	--	33.2	33.2	--	20.7	0.768	0.7	0.19	0.607	0.649
39	--	--	47.0	20.0	--	17.1	0.749	0.7	0.17	0.390	0.421
41	--	--	17.2	42.7	--	15.0	0.796	0.3	0.21	0.875	0.727
47	4.0	7.4	18.0	35.7	0.2	35.4	0.830	1.5	0.26	0.395	0.391
49	3.2	5.3	11.8	42.9	0.1	14.7	0.763	2.0	1.90	0.513	0.579
51	12.3	7.8	23.7	16.0	1.3	25.4	0.557	58.4	0.52	0.0964*	0.0820
54	3.9	2.9	8.8	11.9	0.1	31.1	0.695	12.7	0.24	0.169	0.141
56	7.1	3.3	11.4	7.9	0.2	30.3	0.550	24.6	0.43	0.0713*	0.0638
58	1.5	3.1	6.6	20.7	0.2	18.5	0.726	1.7	0.18	0.415	0.364
61	8.9	10.5	15.2	28.2	0.5	30.5	0.825	7.6	0.28	0.200	0.227
63	19.2	11.6	16.6	15.5	0.7	25.0	0.530	45.8	0.43	0.0609*	0.0721
65	3.8	7.8	11.0	41.0	0.3	19.3	0.761	3.5	0.18	0.442	0.438
68	6.1	5.3	8.3	13.5	0.1	22.0	0.731	--	--	0.142	0.191

*Experimental rate constants for these runs were based on the final fixed carbon conversion fraction. The rate constants for all of the other runs were obtained graphically, using weight loss versus time data.

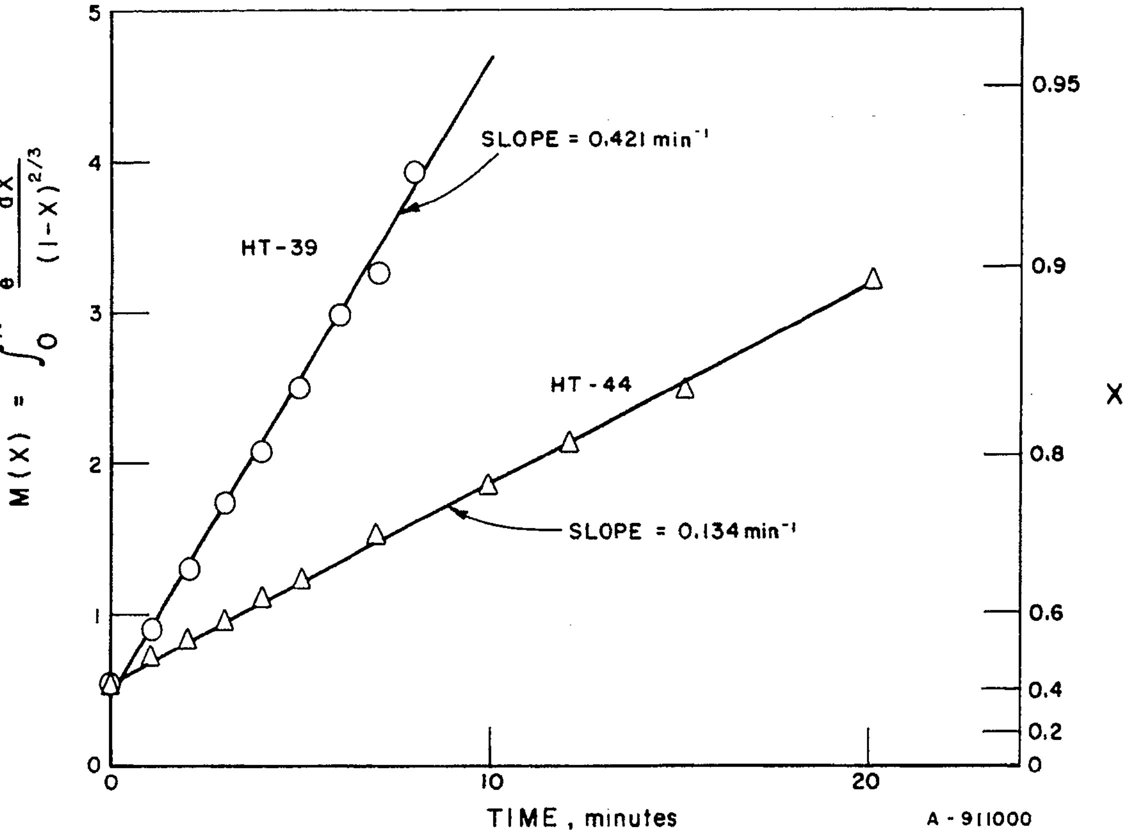

Figure 4b-5. EXAMPLES OF DATA CONVERSION

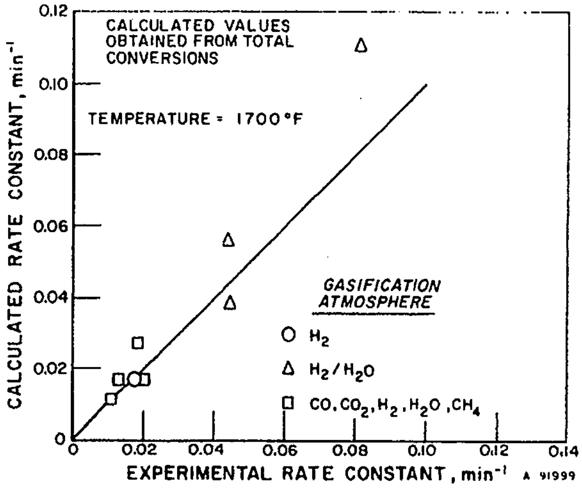

Figure 4b-6. COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF k_T AT 1700°F

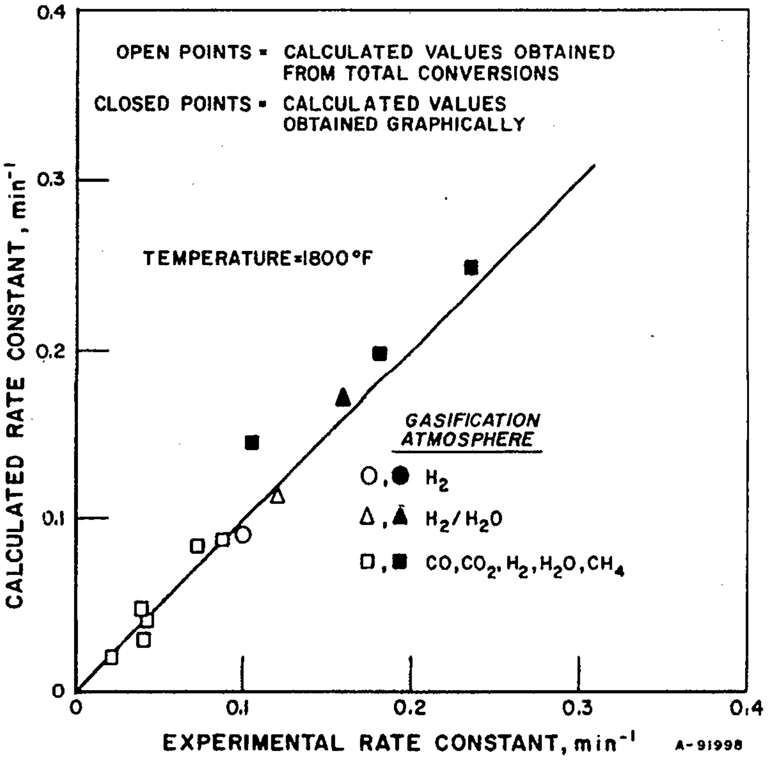

Figure 4b-7. COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF k_T AT 1800°F

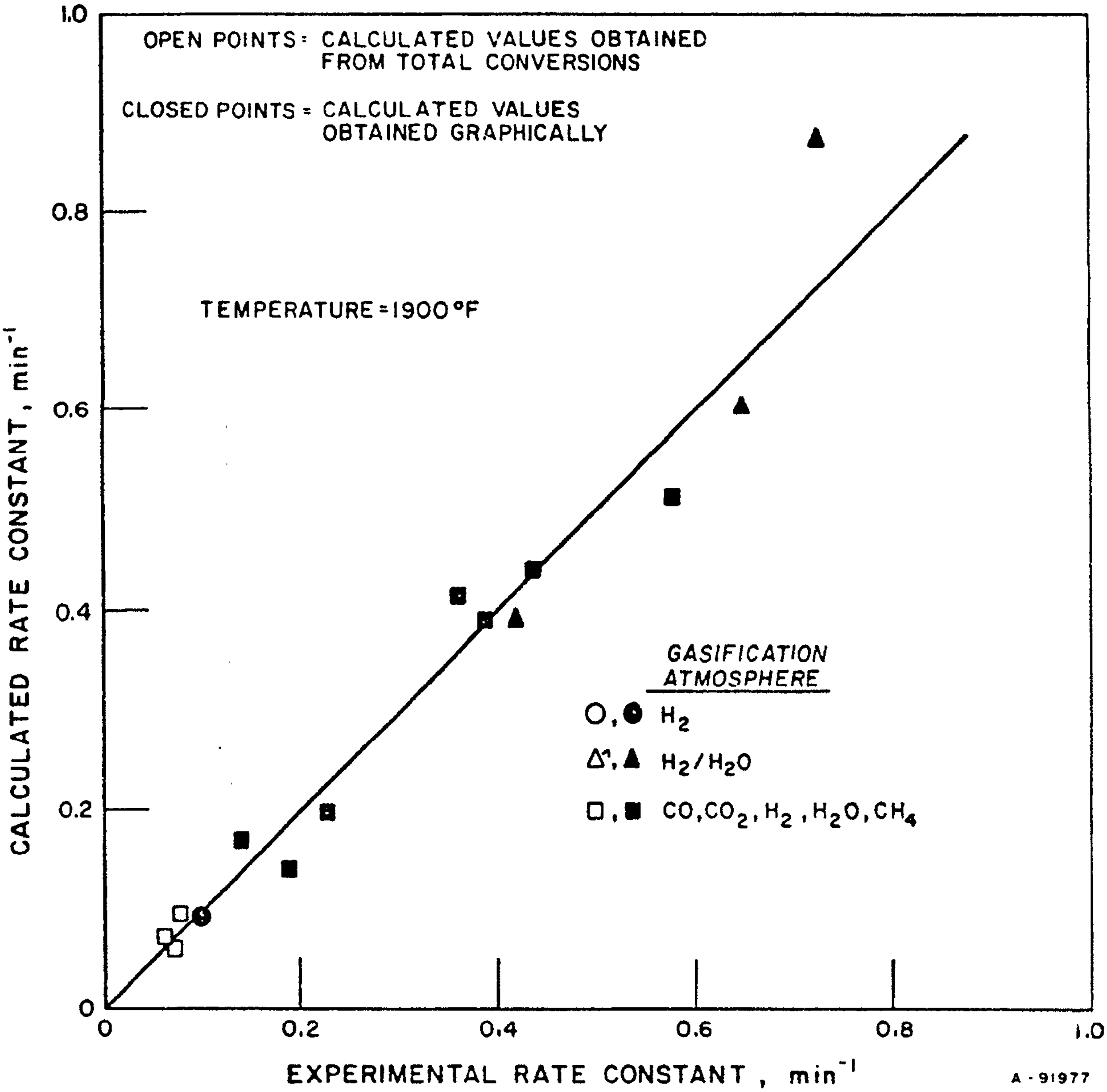

Figure 4b-8. COMPARISON OF CALCULATED AND EXPERIMENTAL VALUES OF k_T AT 1900°F

4b.3. Steam-Oxygen Gasifier Development

4b.3.1 Experimental Equipment

4b.3.1.1 Fluidized-Bed Studies

The fluidized-bed studies, as well as the initial synthesis gas test program were conducted in the balanced-pressure, high-temperature hydrogasification unit. This unit, with a 4-inch-diameter reactor tube, has been described in Part II of this report, which covers the hydrogasification development test program. Only minor modifications were made in order to adapt the unit for synthesis-gas generation studies. A gaseous oxygen supply, feed, and metering system was added to the unit. Purchased, technical-grade gaseous oxygen was stored in a manifolded bank of high-pressure storage cylinders. The oxygen was transferred to the bottom of the reactor through a feed line with an orifice disk for metering the oxygen flow. Oxygen flow was regulated by a needle valve downstream of the orifice flanges. There was no provision for preheating the oxygen.

In the first three synthesis gas tests that were performed, char was fed to the reactor through an 80-inch-long char-feed tube equipped with a rotating coiled stirrer through the length of the tube to promote char flow. Although successful in hydrogasification tests, the coiled stirrer was not effective in keeping the feed tube from plugging. The coiled stirrer was therefore replaced with a short vertical feed screw for Run SO-4. The feed screw, with its positive displacement, would keep the throat of the insert and the top of the char-feed tube clear of obstructions. Dimensions of the vertical feed screw were: 7/8-inch OD x 3/8-inch shaft diameter, 5/8-inch pitch. The feed screw extended to 1 inch below the throat of the insert and into the top of the 80-inch-long char-feed tube. It was coupled by a 3/8-inch-diameter flexible cable to the drive shaft of a Magna Drive, and rotated at a speed of 40 rpm, the same as that of the coiled stirrer.

In Run SO-4, we found that the vertical screw kept the char-feed tube clear, but the hopper feed screw jammed when char packed in the throat of the insert at the top of the vertical feed tube. Because the char packed in a zone the vertical screw could not keep clear, the vertical screw was removed after Run SO-4 in order to have an unobstructed cross-section in the throat of the insert. The char-feed tube was also shortened to a length of 50 inches to allow a longer free-fall distance for the char. Later, for Run SO-7, to further promote char feeding, a purge-nitrogen injection tube was installed; this injected nitrogen at high velocity just above the throat of the reactor insert. This purge nitrogen proved effective in keeping the throat area clear.

Steam and oxygen were fed to the bottom of the fluidized char bed through a multiple-port feed-gas distributor, as shown in Figure 4b-9. This feed-gas distributor was used successfully in hydrogasification tests. In the synthesis-gas generation tests, however, we found that when ash slagging occurred, it was near the gas inlet ports. Slag formation could be attributed to one or more of the following reasons:

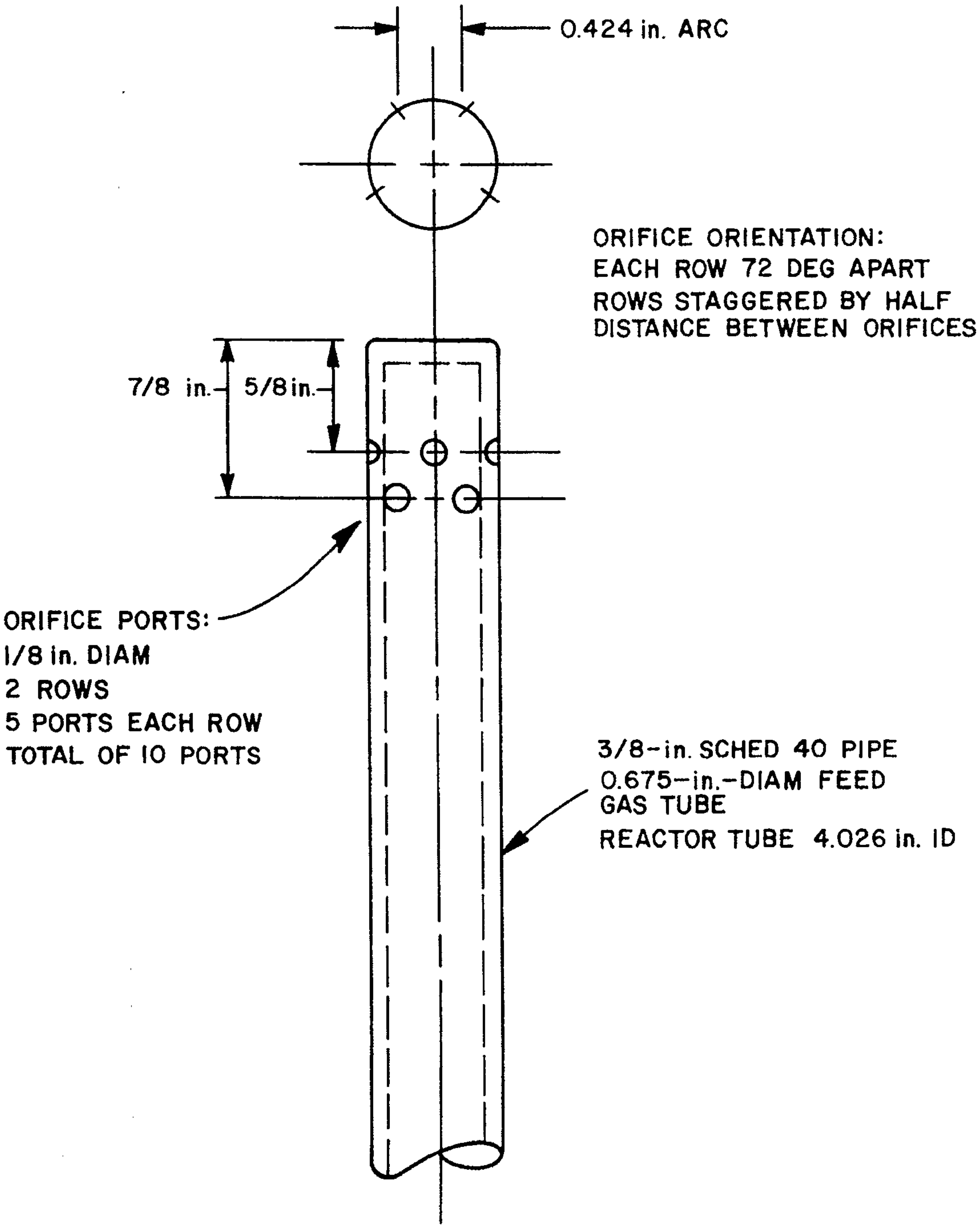

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Figure 4b-9. MULTIPLE-PORT FEED-GAS DISTRIBUTOR

a. Insufficient gas velocity in the bed.

b. Too many small bubbles at the gas inlet, providing a large mass-transfer area and resulting in a poor distribution of oxygen along the length of the char bed with most of the oxygen reacting near the inlet.

c. Direct contact of oxygen with the stagnant solids just below the inlet ports.

For Run SO-11, a new feed-gas distributor was installed. This single-port, coned distributor, shown in Figure 4b-10, was designed to correct the deficiencies in the multiple-port side-feed distributor. The feed gas distributor consists of an inverted cone with a slope of 70° placed over an orifice inlet through which the steam-oxygen is injected into the reactor. A basis of the design was to avoid direct contact between the oxygen and the stagnant solids and, also, to generate large bubbles. Large bubbles have an advantage: They rise faster and have less surface area per unit volume; therefore, they should distribute the feed gas better along the length of the char bed, thereby avoiding slagging temperatures.

The feed gas inlet port size in the cone-shaped feed-gas distributor was initially 9/32-inch diameter. It was sized to handle feed gas flow rates that would result in a fluidization velocity of 0.30 ft/s at a reactor pressure of 500 psig. To obtain the same fluidization velocity at 1000 psig, the feed gas flow rates had to be twice as large as at 500 psig. For these higher flow rates, the port size was increased to 3/8-inch diameter for Run SO-14.

4b.3.1.2 Steam-Oxygen-Char Gasification

One of the requirements for the test operation of an integrated steam-oxygen gasifier was that it be of sufficient size to operate at essentially adiabatic conditions. The volume of the char bed and the heat release from the reaction of the char with the oxygen must be large enough so that heat losses from the reactor are negligible. Calculations indicated that a reaction bed 6 to 8 inches in diameter, by 4 to 8 feet in depth would provide sufficient volume for adiabatic operation at temperatures in the range of 1800° to 1900°F, over a range of char feed rates of from 40 to 120 lb/hr, at gas velocities of 0.1 to 0.3 ft/s and solids residence times of 20 to 60 minutes. This reaction bed would be contained in an internally insulated pressure shell. To cover the above range of operating variables, the reaction bed should be contained within a thin-walled liner that can be readily changed without affecting the configuration of the cold pressure shell. About 6 inches of internal insulation between the liner and shell would be sufficient to iminmize heat loss from the system. Thus, a reactor shell of 20 inches would allow for operation of an 8-inch-diameter liner with 6 inches of internal insulation.

The above design requirements were very nearly met by a 6-inch-diameter internally insulated reactor, with a 24 inch outside shell, used for electrothermal char gasification studies for hydrogen production. The electrothermal gasification unit was modified, therefore, to satisfy the design requirements of the steam-oxygen-char gasifier. The principal modification concerned the reactor liner and the exit gas-cooling system.

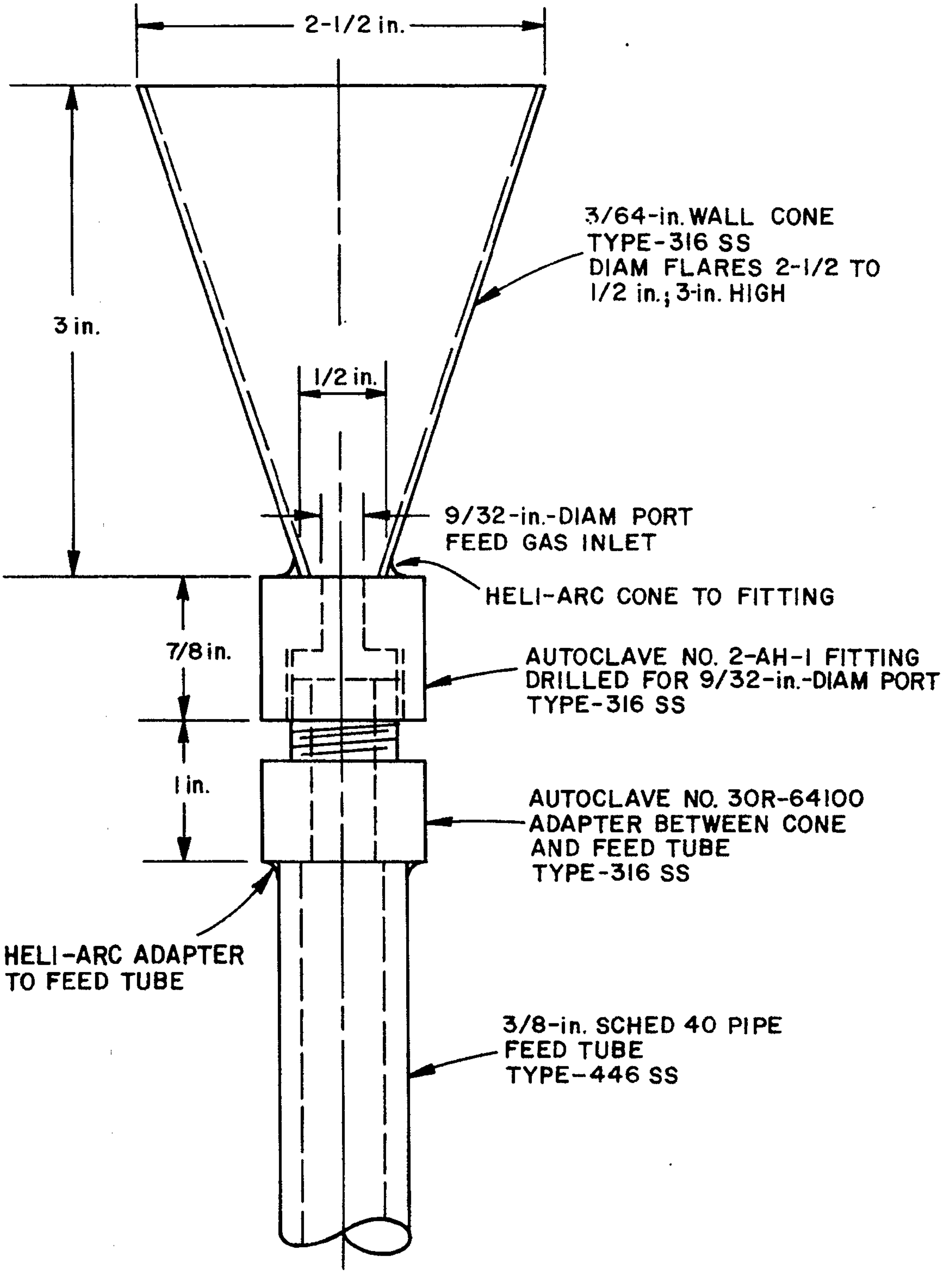

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Figure 4b-10. CONE-SHAPED FEED-GAS DISTRIBUTOR FOR STEAM-OXYGEN GASIFICATION TESTS

The liner was designed with an upper expanded section to minimize solids carry-over from the bed. Solids are fed directly to the bed and exit gas is removed well above the solids feed point (in a low gas velocity zone) to eliminate carry-over of fines. Provision was also made for special steam-oxygen inlet ports to ensure good solids mixing at the gas-injection point. These ports are coned so that solids cannot stagnate and initiate slagging. Some of the feed steam is fed below these coned ports to fluidize the bed adjacent to the coned ports.

A novel steam-oxygen injection feed system was designed for the 6-inch-diameter reactor based on IGT experiences with the coned-shaped feed port in the 4-inch-diameter reactor. Details of this triple-coned feed gas system design are given in Figure 4b-11. These cones are manifolded and sized to split the main steam-oxygen feed stream at three symmetrically located feed points across the area of the reactor. Not illustrated is a provision for diverting a part of the feed steam (about 25% of the total flow) to a nozzle located below the cone feed ports to fluidize the solids around the feed cones and keep them from stagnating. Flows of steam to this nozzle came from the steam generator and into the lower coil of the steam superheater through an orifice meter.

The exit-gas system was designed so that hot gases from the gasifier quickly cooled (in 1 to 2 seconds) from 1900° to 1000°F. Rapid cooling to below 1200°F is important to prevent the water-gas shift reaction from occurring and altering the true hot-gas composition. A water-jacketed cooler was designed for indirect cooling of the gases. The gas cooler consists of a 10-foot-long, 1-1/2 inch diameter, Schedule 160, Type 316 stainless steel pipe. It is jacketed with a 3-inch-diameter Schedule 40 carbon steel pipe and is erected so that hot-reactor product gas directly enters the cooler. Gas from the cooler is filtered in a 6-inch-diameter 6-foot-long filter vessel in which char fines are removed as the gas passes through a sintered-metal bayonet-shaped filter. This vessel is operated at 1000°F to avoid condensation until the gas enters the condenser, where it is further cooled at 150°F. Condensate is removed by a float-actuated valve located at the bottom of the condenser. This valve discharges all the condensed water (up to 8 gal/hr) from 1000-psig operating pressure to atmospheric pressure, where it is continually weighed during the course of the run. Gas from the condenser passes through a mist filter before entering the exit-gas metering system.

In summary, modification of the electrothermal gasifier development unit to adapt it for steam-oxygen gasification include:

- The installation of a new 6-inch-diameter reactor tube with thermocouples peened to the outside wall of the tube.
- an exit-gas precooler,
- a filter body with a porous metal filter element,
- a water-jacketed condenser with an automatic float-actuated drain system, and
- a modified reactor head for product gas offtake and char feeding.

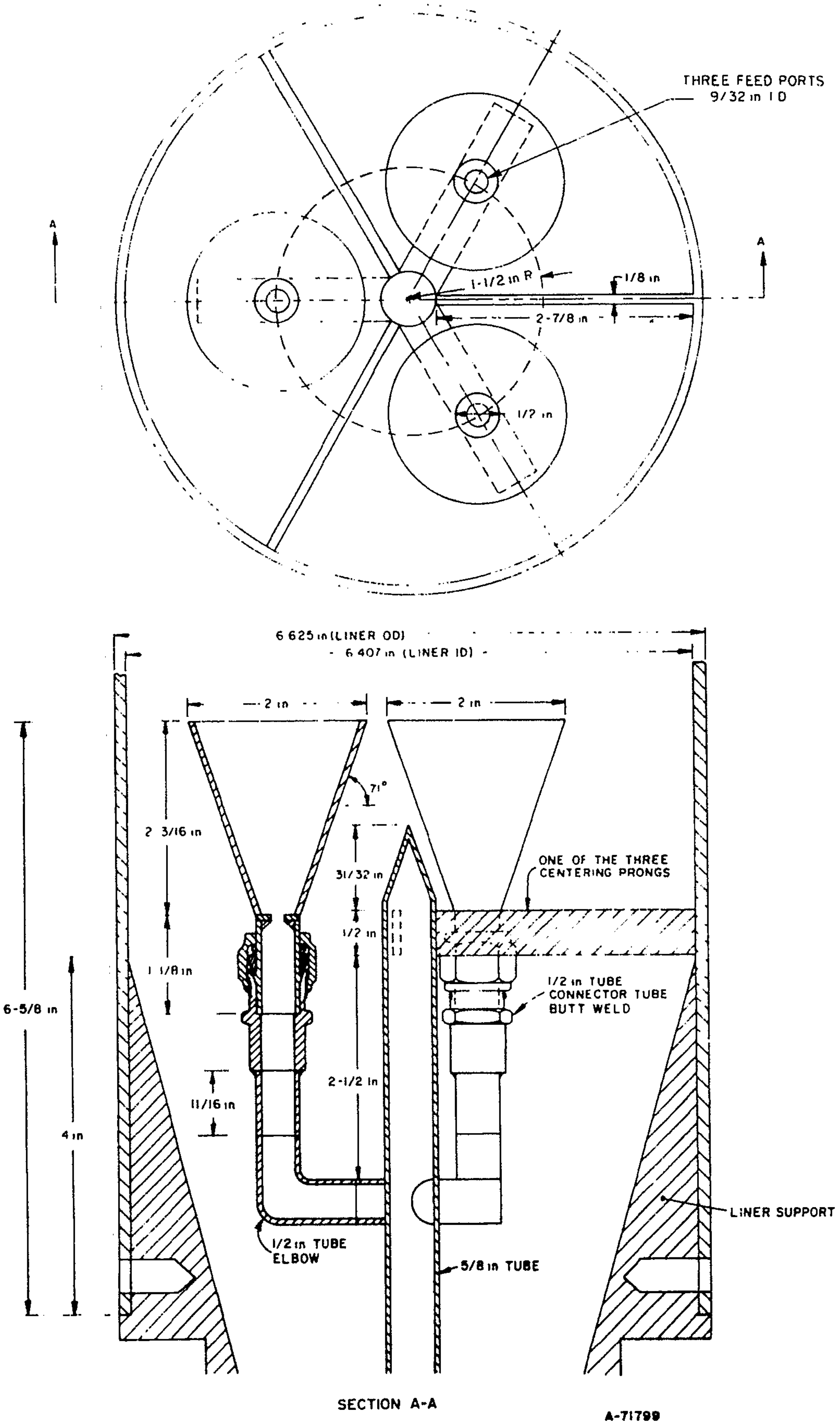

Figure 4b-11. THREE-CONE FEED GAS DISTRIBUTOR

A simplified flow diagram of the modified electrothermal gasification unit is shown in Figure 4b-12. In Figure 4b-13, the gasifier shell is shown in section, with details of the 6-inch-diameter reactor tube, electrode, and the reactor head with its passage for solids feed and make gas outlet. The positions of 22 tube-wall thermocouples are indicated. These thermocouples are oriented 120° apart, staggered with position, around the outside wall of the reactor tube.

After Run EGO-15, the original 6-inch-diameter reactor tube was replaced; the tube had been damaged during Run EGO-9. The dimensions and composition of the replacement tube were similar to the damaged tube (6-inch-diameter, Type 316 stainless steel, 83-inch-long Schedule 5 pipe). Sixteen new Chromel/Alumel sheathed, 1/16-inch-diameter thermocouples were also installed for sensing the outside tube wall temperatures. They are housed in the three longitudinal thermowells tackwelded to the outside of the reactor tube. The thermowells have a 5/16-inch outer diameter, a 20 gauge wall, and are made of Type 304 stainless steel tubing, capped at the top. For tests in which no electrode would be used, we also installed four thermocouples through the top reactor closure to sense char-bed temperatures at levels of 30, 45, 60, and 87 inches above the bottom of the reactor tube. The positions of the tube wall thermocouples along the tube wall and the orientation of the three thermowells around the outside of the tube are shown in Figure 4b-14.

For Run EGO-33 we installed a new six-port feed gas distributing system at the bottom of the reactor to replace the original three-port distributor. As in the original distributor, cones were used at each port to keep the ports clear of stagnant solids. A distributor with a larger number of ports was chosen to improve feed gas distribution and gas-solids contacting at the bottom of the char bed. The improved feed gas distribution was intended to increase carbon and steam conversions, and result in smoother fluidization of the char. The feed ports of the six-cone distributor have a 23/64-inch diameter, in contrast to the 9/32-inch-diameter ports of the original three-cone distributor. Because of the larger cross-sectional port area of the six-cone distributor, the feed gas bubbles should be smaller than those formed in the three-cone distributor. The smaller feed gas bubbles should result in longer gas residence time and better oxygen utilization. In addition, char-bed slagging should be minimized and a smoother fluidization should be obtained. The six-port feed gas distributor was used in all tests following Run EGO-33. A dimensional drawing of the feed gas distributor is shown in Figure 4b-15.

4b.3.2 Char Feeds

For the fluidized-bed study phase of the gasifier development program performed in the 4-inch-diameter balanced-pressure reactor, the char feed was a hydrogasified Ireland mine bituminous coal. This Pittsburgh No. 8 seam coal was first pretreated with air and then hydrogasified with hydrogen and steam. Typically, the hydrogasified Ireland mine bituminous coal was composed of 24% ash and 72% carbon.

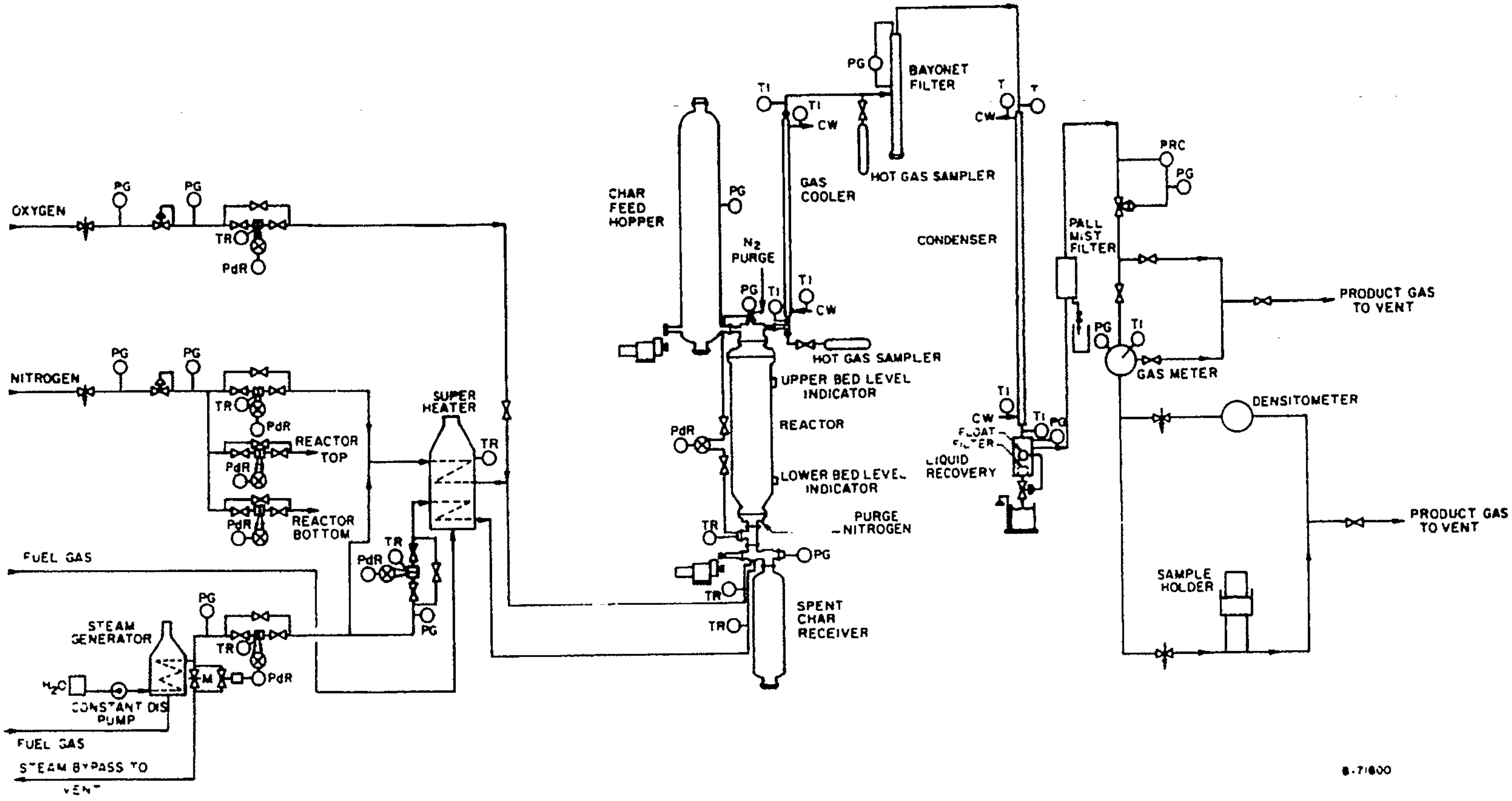

Figure 4b-12. ELECTROTHERMAL GASIFICATION UNIT MODIFIED FOR STEAM-OXYGEN TEST

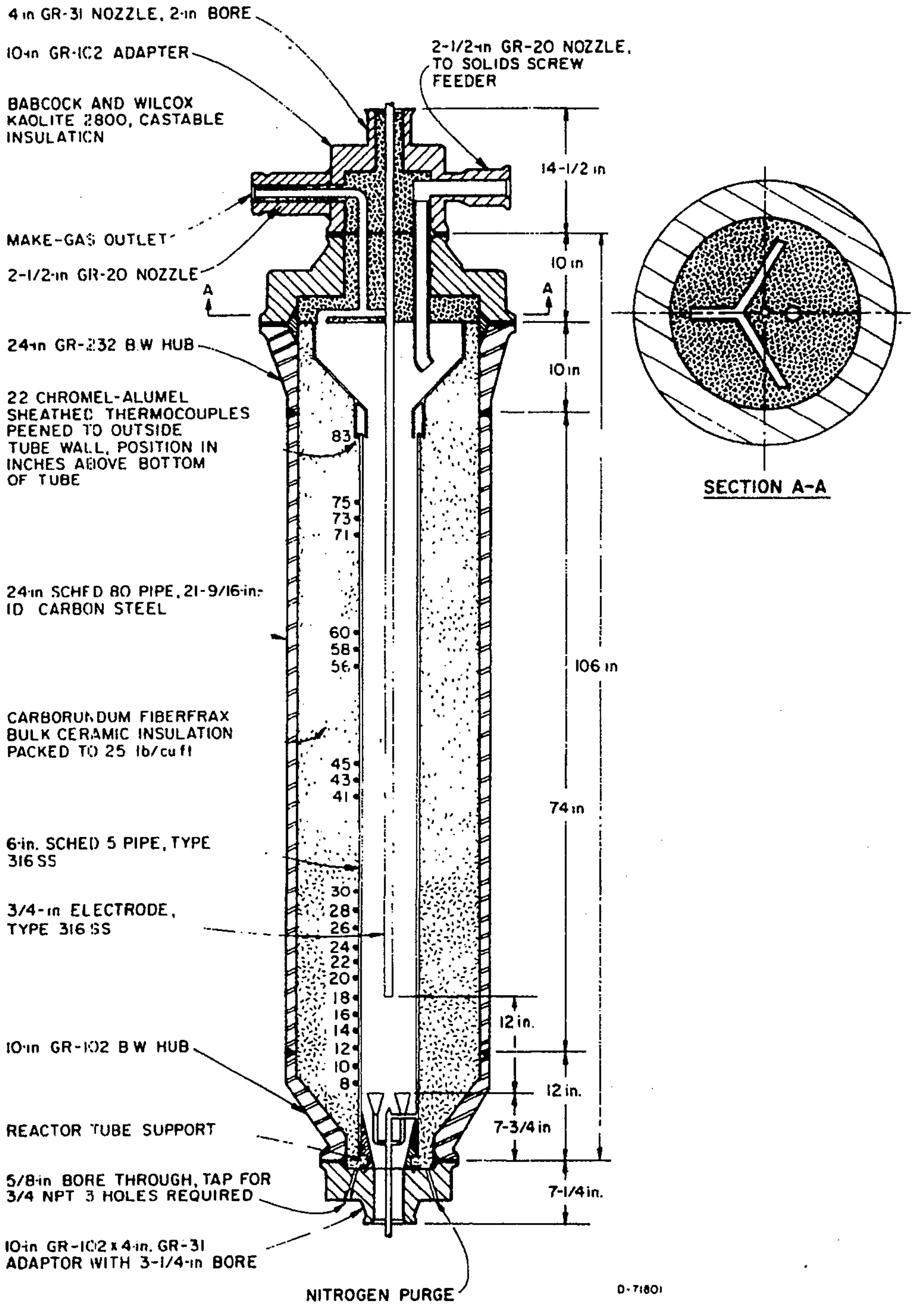

Figure 4b-13. STEAM-OXYGEN-CHAR GASIFIER

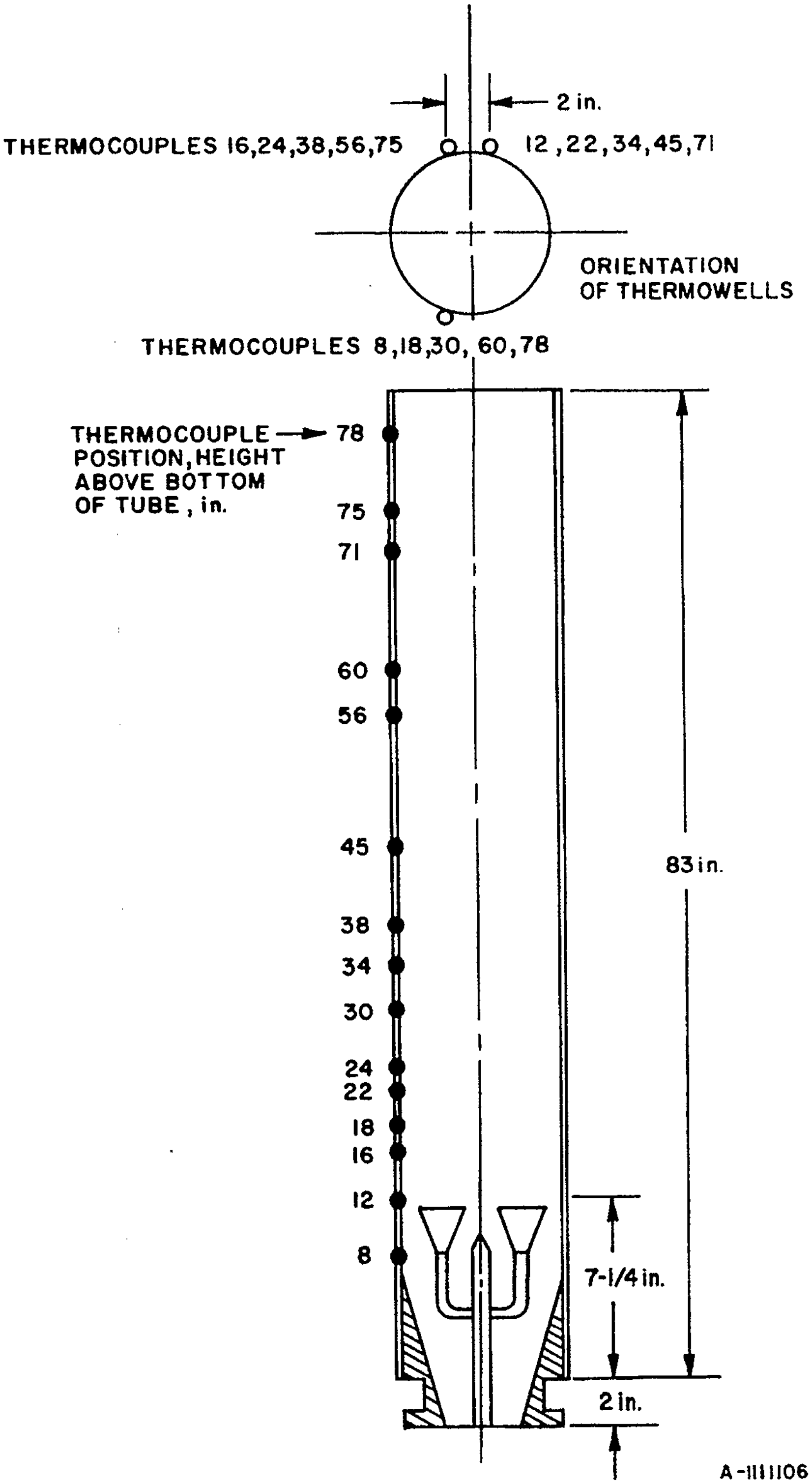

Figure 4b-14. REACTOR TUBE WALL TEMPERATURES

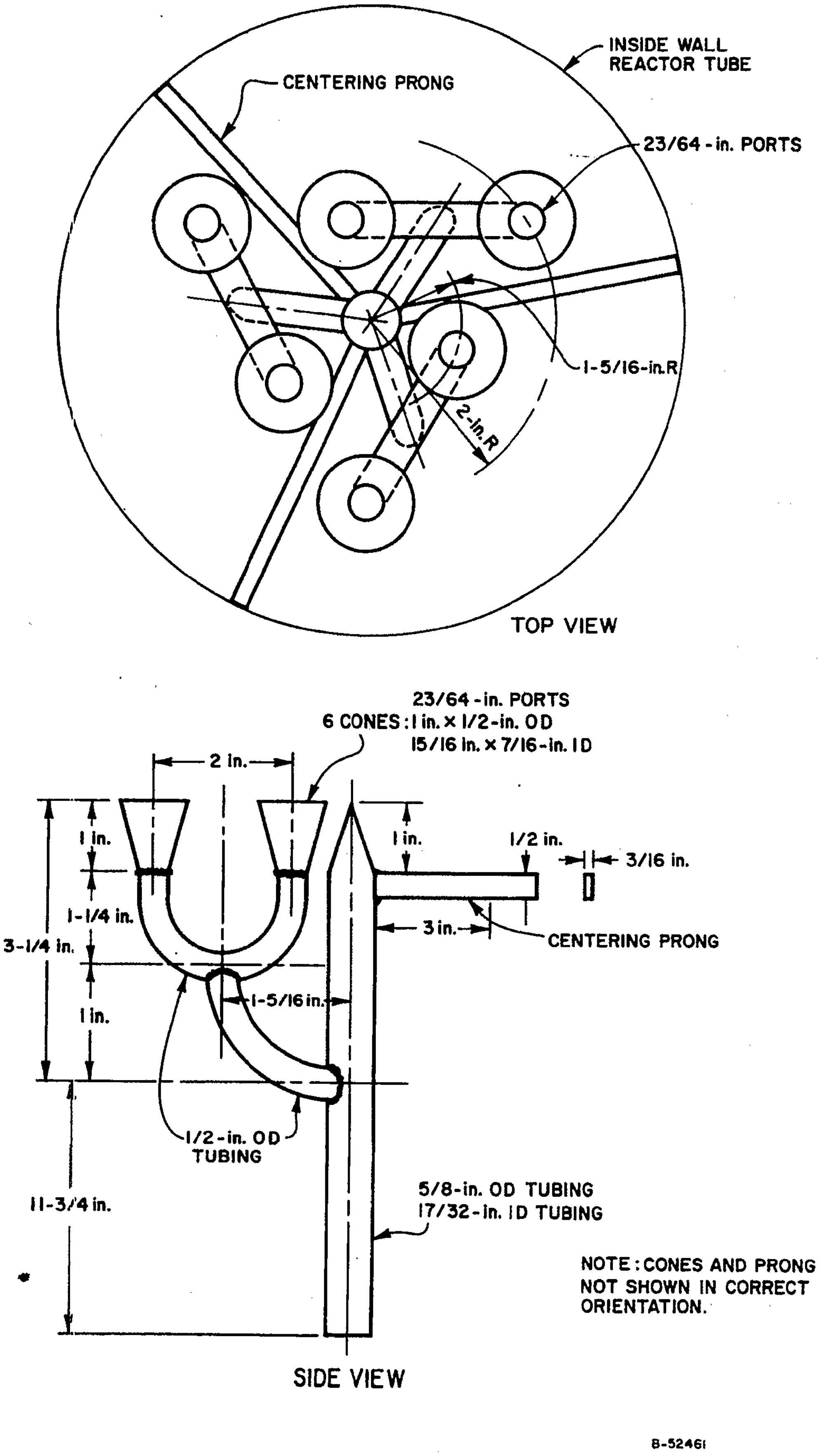

Figure 4b-15. DIMENSIONED DIAGRAM OF SIX-CONE FEED GAS DISTRIBUTOR

The hydrogasified Ireland mine bituminous coal was used in only a small number of tests in the steam-oxygen gasifier development phase conducted in the 6-inch-diameter reactor. Feed for all of the other tests was char obtained from the FMC Corporation, Project COED (Char Oil Energy Development). This char was produced from an Illinois No. 6 seam, Crown mine, high-volatile C bituminous coal. Typically, ash content of the FMC char was 12% and the carbon content was 82%.

Critical temperature points of the ashes of both feeds were determined in the laboratory. These are listed below:

	FMC Char, °F	Ireland Mine Char, °F
Initial Deformation Temperature	2405	1950
Softening Temperature	2520	2025
Hemispherical Temperature	2580	2060
Fluid Temperature	2600	2440

All feeds were ground and screened to a – 10 + 80 U. S. Standard sieve size. The ground feed was air dried to a moisture level of 3%, or less.

4b. 3. 3 Fluidized-Bed Tests in 4-Inch-Diameter Reactor

Two steam gasification tests were performed to determine the operability of the 4-inch reactor under highly endothermic operating conditions. No oxygen was fed to the char bed. Sweep nitrogen was fed with the steam to attain the desired fluidization velocities. The char feed in the two tests – Runs S-1 and S-3 – was hydrogasified Ireland mine bituminous coal. Both tests were performed at a nominal pressure of 1000 psig. Good fluidization was established in Run S-1 with the char bed temperature at 1505°F and a fluidization velocity of 0.12 ft/s. In Run S-3, with a steam feed rate nearly twice that of Run S-1, the fluidization velocity was 0.19 ft/s, but the char bed temperature was only 1280°F. Electrical heat input to the reactor tube, which was 16.30 kW, was insufficient to maintain higher temperatures in Run S-3 at steam feed rates required for gasification. The electrical heat input rate was limited because of a faulty reactor heater section which was repaired for the steam-oxygen gasification tests that followed.

Steam-oxygen gasification of Ireland mine bituminous coal char was conducted at a nominal pressure of 1000 psig in a fluidized bed of 3-1/2 feet and bed temperatures of 1650° to 1850°F. Fluidization velocities were in the range of 0.13 to 0.17 ft/s. In Run SO-7, at a maximum bed temperature of 1880°F, we attained a carbon gasification of 69%. To investigate the effect of char residence time on carbon gasification, tests were also performed in a 7-foot fluidized bed (Run SO-9 and SO-10). Because of low char bed temperatures, however, limited by faulty reactor heaters, carbon conversions were 53.5% in Run SO-9 and 28.4% in Run SO-10. In the steam-oxygen gasification tests through Run SO-10, steam and oxygen were fed to the reactor through a multiple-port feed-gas distributor, with ports on the side of the feed tube. Except for Run SO-9 (1650°F maximum temperature, and 0.145 ft/s fluidization velocity), some ash sintering, or slagging was experienced in tests with this feed-gas distribution. Slag normally formed just above the feed ports, but in Run SO-7 (1850 °F) it formed in the upper part of the 3-1/2 foot fluidized bed.

Starting with Run SO-11, a single vertical port feed-gas distributor with a cone above the port was used. Four tests were performed with this feed port. For Runs SO-11 and SO-12, the inlet port diameter was 9/32 inches. This port size was reduced to 7/32 inches for Runs SO-13 and SO-14 to obtain higher inlet port velocities. Higher velocities at the inlet port keep the bottom of the char bed sufficiently agitated and backmixed to inhibit ash slagging at this point. A higher velocity at the inlet port also results in bigger bubbles, which distribute oxygen (and the corresponding heat release) along a greater length of the reactor.

In Run SO-11, performed at a nominal pressure of 500 psig, a maximum bed temperature of 1555 °F, and a fluidization velocity of 0.298 ft/s, 47.6% of the carbon in the char was gasified. No ash sintering or slagging was observed. A carbon gasification of 74.4% was obtained in Run SO-12 at a nominal reactor pressure of 1000 psig and a maximum bed temperature of 1905 °F. However, slag formed on the reactor tube walls 6 to 12 inches above the gas-feed port. Fluidization velocity in this test was 0.17 ft/s. Slag-free operation was obtained in Run SO-14 with a fluidization velocity of 0.25 ft/s. In this test, performed at 1037 psig and a maximum bed temperature of 1750 °F, 54.1% of the carbon was gasified.

These tests in the 4-inch-diameter reactor served to establish char and steam conversion levels and, also, to define operating conditions for slag-free operation by using a properly designed steam-oxygen feed gas inlet system and by maintaining linear gas velocities through the char bed substantially above minimum velocities required for fluidization.

An analysis was made to compare the experimental results of the steam-oxygen gasification tests with predictions of an idealized kinetic model for char gasification previously developed at IGT. Because this model was developed from experimental gasification data obtained at temperatures below 1750 °F and for gas environments derived from steam-hydrogen feeds, its application to gasification with steam and oxygen at temperatures as high as 1840 °F is intended only to provide preliminary indications of the modifications which may be necessary to describe gasification kinetics at these more extreme conditions.

The model essentially consists of a quantitative correlation which defines the rates of char gasification in terms of carbon oxide and methane formation as functions of temperature, pressure, gas composition, carbon conversion, char temperature history, and char type. In any experimental system this information, along with a definition of the nature of gas and solid contacting, theoretically provides a basis for predicting the chemical behavior of that system. In this preliminary analysis, the following assumptions were made:

1) The gas in the experimental fluidized bed (4-inch-diameter balanced-pressure reactor) was perfectly mixed, implying that the uniform gas composition in the fluid bed is identical to the product gas composition.

2) All of the char particles fed to the reactor remained in it for an identical time period, prior to discharge.

3) The gas species in the fluidized bed were in equilibrium with respect to the water-gas shift reaction and were the same temperature as the fluidized bed.

4) Oxygen fed to the fluid bed reacted instantaneously with the char particles to form carbon dioxide, just prior to their discharge.

With these assumptions and using reasonable values for fluidized bed densities, the methane and carbon oxide formation rates were predicted for the four experimental tests conducted. The calculated and experimental rates are numerically compared in Table 4b-3, which also includes the test conditions, and are graphically compared in Figures 4b-16 and 4b-17.

Table 4b-3. COMPARISON OF CALCULATED AND EXPERIMENTAL GASIFICATION RATES

Run No.	SO-10	SO-9	SO-5	SO-7
Conditions				
Feed Gas, mole/mole feed carbon				
H_2O	1.326	1.347	1.009	1.200
O_2	0.173	0.159	0.147	0.216
Equivalent Kinetic Temp, °F	1520	1650	1750	1840
Pressure, atm	72.5	72.5	70.7	72.4
Solids Residence Time, min	30.5	33.1	16.4	18.3
Carbon Oxides, mole/mole feed carbon				
Experimental	0.234	0.445	0.482	0.602
Calculated	0.272	0.403	0.430	0.685
Methane, mole/mole feed carbon				
Experimental	0.047	0.094	0.079	0.086
Calculated	0.024	0.068	0.058	0.072

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Actual experimental data for the tests described in Table 4b-3 indicated that significant temperature gradients existed in certain portions of the fluidized bed. Although such temperature gradients can be literally interpreted in computing gasification rates with the idealized model, such a procedure is quite complicated and was not justified in this preliminary analysis. Therefore, a relatively simplified procedure was used to compute an "equivalent kinetic" temperature for each test — those values of temperature at which the integrated gasification rates are the same as would be obtained with the corresponding temperature gradient. The following equation represents an approximation; however, an indefinable degree of error in calculated gasification rates may accrue from use of the equation:

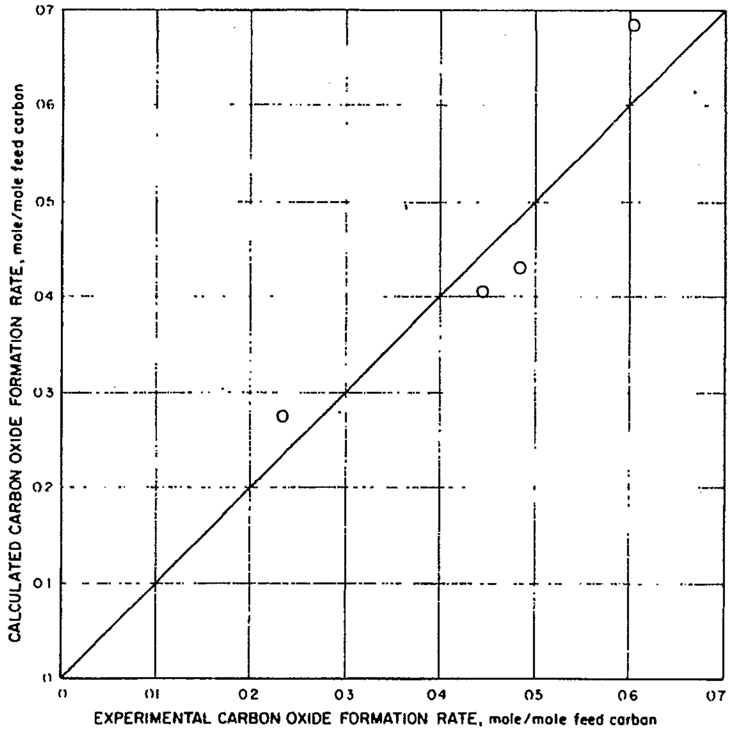

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Figure 4b-16. COMPARISON OF CALCULATED AND EXPERIMENTAL CARBON OXIDE FORMATION RATES

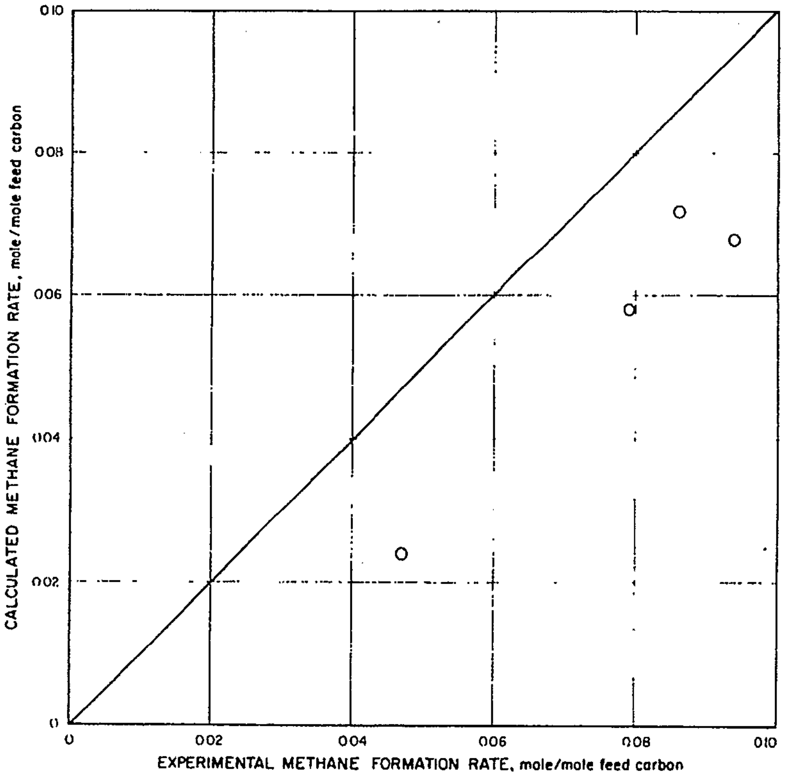

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Figure 4b-17. COMPARISON OF CALCULATED AND EXPERIMENTAL METHANE FORMATION RATES

$$\overline{T} = \text{equivalent kinetic temperature} = \frac{-E}{\ln\left(\int_0^L \frac{e^{-E/T}\,dz}{L}\right)}$$

where

z = distance above bottom of the fluid bed

T = temperature of fluid bed at z

L = total fluid bed height

E = representative temperature coefficient for the net gasification reaction

Some measure of confidence in the use of the computed temperatures given in Table 4b-3 can be obtained by comparing values of the water-gas shift reaction equilibrium constant corresponding to the computed temperatures, with the experimental-approach factors, $\frac{X_{CO_2} \cdot X_{H_2}}{X_{CO} \cdot X_{H_2O}}$ (where X_i = mole fraction of species i in the product gas). Such a comparison made in Table 4b-4 shows a reasonable consistency over a wide temperature range.

Table 4b-4. APPROACH TO WATER-GAS SHIFT EQUILIBRIUM

Run No.	SO-10	SO-9	SO-5	SO-7
Equivalent Kinetic Temperature, °F	1520	1650	1750	1840
Water-Gas Shift Equilibrium Constant	0.93	0.75	0.64	0.56
Experimental Approach Factor:				
$\frac{X_{CO_2} \cdot X_{H_2}}{X_{CO} \cdot X_{H_2O}}$	0.84	0.80	0.63	0.51

Figure 4b-16 shows that calculated and experimental values of carbon oxide formation rates are reasonably consistent for temperatures ranging from 1520° to 1840°F. Figure 4b-17, however, shows that experimental methane formation rates are about 50% greater than their calculated rates. Although methane formation rates are only about 15% of the total gasification rates, this trend appears to be systematic. This behavior is essentially the same as that observed in a previous analysis in which the predictions of the idealized model were compared with experimental gasification rates of Disco char, obtained with steam and oxygen in batch fluid-bed tests, as reported by May et al.[1] Those results, obtained at pressures ranging from 60 to 140 psia, also indicated that, although the predicted carbon oxide formation rates were reasonably consistent with experimental values, experimental methane formation rates were consistently greater than the calculated methane formation rates. This behavior appears to be related to the use of oxygen, since such trends have not been previously observed when only steam, or steam and hydrogen were used as gasifying agents.

4b. 3. 4 Gasifier Development Tests in 6-inch Diameter Reactor

4b. 3. 4. 1 Three-Feed Port Gas Distributor

4b. 3. 4. 1. 1 Gasification with Electric Heat Input

To assure adiabatic operation steam-oxygen gasification studies in the 6-inch diameter reactor were started using internal electrical heating. Direct current was applied to the metal electrode immersed in the fluidized char bed with a 1-1/2-inch diameter electrode of the same length. Resistance of the char bed to the current flow generated the heat for preheating the char bed and for balancing the heat losses during the gasification phase. In a shakedown test to determine reactor heat losses, the reactor was operated for several hours at 1000 psig and 1750°F, using only nitrogen to fluidized the bed. Thus, there were no exothermic or endothermic reactions, and the electrothermal power input was used in heating the feed nitrogen and to balance the reactor heat losses. It was determined, in this test, that about 5kW of power is necessary to balance the heat losses in steam-oxygen gasification tests.

A 3/4-inch diameter metal electrode was first used. The electrode was immersed for a length of 43 inches in a fluidized bed of 50 inches. This electrode was damaged because of high temperatures that developed at the tip, and was replaced after Run EGO-8 with a 1-1/2-inch diameter electrode of the same length. The larger diameter rod allowed for lower current densities and lessened the probability of damage.

In the limited number of gasification tests performed with internal electrical heat supply we attained a carbon gasification of 40. 4 percent, and a steam conversion of 17. 3 percent. These results were obtained in Run EGO-8, performed at 946 psig, a maximum char bed temperature of 1475°F, and with FMC char. Electrical power to the electrode was 7. 32 kW and the fluidization velocity was 0. 18 ft/s.

One of the major difficulties in operations with the electrode was the control of current flow. In periods of unsteady fluidization during test operations, the resultant low char bed resistance allowed a high current flow between the electrode and the wall. Electrical shorting at the tip of the electrode was also experienced. This led to the generation of high temperatures, that resulted in damage to the electrode, and to slagging of the char ash. Generally, electrode shorting occurred in unstable operating periods during start-up, and in periods of a loss of fluidization following the addition of steam to the reactor. In view of these difficulties internal electrical heating was not used in gasification tests after Run EGO-9. Preheated nitrogen was used to heat the char bed up to 850°F at which time oxygen was added to further raise the temperature to 1500°F before steam was added.

4b.3.4.1.2 Gasification with Heat Input from Carbon-Oxygen Reaction

The steam-oxygen gasification tests for synthesis gas production were designed to study operating conditions that would result in optimum carbon gasification and steam conversion. Related to this study, it was equally important to investigate the effect of fluidization velocity, char bed temperature, and oxygen concentration on the sintering of ash in the fluidized bed.

Gasification tests through Run EGO-17 were performed at a nominal reactor pressure of 1000 psig. At this pressure it was not possible to exceed a fluidization velocity of about 0.35 ft/s because of limitations on the steam feed rate and the unreacted steam condensing system. To attain higher fluidization velocities, we began performing additional tests at a reactor pressure of 500 psig, except for three tests that were performed at a pressure of 350 psig. The effect of char residence time on char gasification was studied by performing tests with 30, 34, 50 and 66 inch high fluidized beds. We also studied the effect of ash content of the char as to whether it sintered, or not, at a given temperature, in the fluidized bed. Previously ungasified FMC char had an ash content from 10 to 14 percent. By reusing the partically gasified FMC char with an ash content of from 20 to 50 percent we were able to study the effect of the higher ash content feed on possible sintering.

4b.3.4.1.2.1 FMC Char Gasification at 1000 psig

At 1000 psig we were able to attain sinter-free operation at fluidization velocities of 0.24 to 0.28 ft/s with char bed temperatures at 1610°F. (Runs EGO-13 and EGO-14) when gasifying FMC char. A carbon gasification up to 54 percent, and a steam conversion of 22 percent were obtained at these conditions. Additional tests at 1000 psig (Runs EGO-15, EGO-16 and EGO-17) indicated that the superficial gas velocity necessary to inhibit sintering increases with an increase in operating temperature; a velocity of 0.6 ft/s will prevent sintering up to a temperature of 1800°F, whereas one of 0.65 to 0.70 ft/s is required to attain 1850°F. These velocities are well above the minimum fluidization velocity (about 0.1 ft/s) and serve to promote good solids mixing in the bed, which prevents solids stagnation and subsequent sintering.

4b.3.4.1.2.2 Hydrogasified Ireland Mine Coal Gasification at 1000 psig

With hydrogasified Ireland mine bituminous coal having an ash content of 22.7 percent (Run EGO-16) we obtained practically sinter-free operation with a fluidization velocity of 0.312 ft/s and a maximum char bed temperature of 1690°F and a pressure of 1036 psig. Carbon gasification was 46.7 percent, and steam conversion was 10.1 percent of the steam fed.

4b.3.4.1.2.3 FMC Char Gasification at 500 psig

Fluidization velocities of 0.65 to 0.70 ft/s were obtained in tests performed with FMC char at a nominal pressure of 500 psig. In one of these tests, Run EGO-23, we gasified 64.0 percent of the carbon in the char, without any ash sintering at a maximum char bed temperature of 1830°F. Steam conversion was 27.5 percent of that fed. Hydrogen yield was 11.64 SCF/lb of char fed. The residue char had an ash content of 27.8 percent.

4b.3.4.1.2.4 FMC Char Residue Gasification at 500 psig

In other tests at 500 psig, we utilized partially gasified FMC char with an ash content greater than 20 percent to study the effect of ash content on sintering. These tests were performed at superficial velocities of 0.65 to 0.82 ft/s and at char bed temperatures of 1800° to 1860°F. Results of the tests indicate that with higher ash content chars that a slightly higher gas velocity, about 0.8 ft/s, is necessary to keep the ash from sintering. Tests with previously ungasified FMC char indicated that a superficial velocity of about 0.7 ft/s would be sufficient to overcome sinter formation. In one of the successful gasification tests with partially gasified FMC char (Run EGO-29) we gasified 74.9 percent of the carbon in the char at a temperature of 1840°F, and with a fluidization velocity of 0.82 ft/s. Hydrogen yield was 10.72 SCF/lb of char fed.

In the tests performed with the three-coned feed port gas distributor (9/32-inch diameter), we found that, although increased gas velocity promotes sinter-free operation, at the same time, it has resulted in decreased hydrogen production. This is due to the fact that larger gas bubbles are formed in the bed at the higher velocities. These bubbles rise very rapidly through the bed with short residence time and decreased oxygen utilization, giving rise to afterburning above the bed. Indications of afterburning have been noted with thermocouples in some of the tests. To overcome this problem, we redesigned the steam-oxygen injection ports increasing the number of ports from 3 to 6. This would result in smaller bubbles, longer resident time, and better oxygen utilization and heat release throughout the bed. The six port steam-oxygen injection feed system is illustrated in Figure 4b-15, referenced earlier. With the use of the 6-port feed distributor we have reduced the feed gas velocity from 30 ft/s to 20 ft/s in order to generate smaller bubbles than before. The smaller bubbles will give a higher reaction rate and will rise slower and give more conversion in the bottom of the bed.

4b.3.4.2 Six-Feed Port Gas Distributor

Gasification tests with the 6-port feed gas distributor were performed with FMC bituminous coal char, partially gasified FMC bituminous coal char, and with hydrogasified Ireland mine bituminous coal char. Except for a limited number of tests performed at 350 psig, all of the tests were performed at a nominal pressure of 500 psig. The effect of char residence time on char and steam conversion was studied by varying the fluidized char bed height. Tests were performed in fluidized beds of 30, 34, 50 and 66 inch heights.

4b.3.4.2.1 FMC Char Gasification at 500 psig

Initial tests with the 6-port feed gas distributor with FMC char, performed at 500 psig with a 50-inch fluidized bed, and maximum bed temperatures of 1925° to 1995°F (Runs EGO-33, EGO-34 and EGO-35) produced ash sintering at fluidization velocities of 0.60 to 0.865 ft/s. Carbon gasification in these tests ranged from 64.4 percent to 39.1 percent. However, in a later test (Run EGO-38) we obtained sinter-free operation at a fluidization velocity of 0.62 ft/s by starting the gasification with a 30-inch fluidized bed, and later increasing the bed height to 50 inches. Maximum temperature in this test was held to 1930°F with occasional peaks to 1990°F. Carbon gasification was 64.4 percent while operating with the shorter bed, and 67.0 percent during operation with the 50-inch bed.

We extended our tests with FMC char to gasification of the char in a 66-inch fluidized bed in order to increase char residence time and thus improve carbon conversion. In these series of tests we were able to demonstrate sinter-free operation by gasifying FMC char at maximum temperatures in the range of 1815° to 1900°F, and with fluidization velocities of 0.70 to 0.85 ft/s. Carbon conversions above 90 percent were obtained in a number of the tests. Highest carbon conversion was obtained in Run EGO-57 where 94.4 percent of the carbon was gasified. Steam conversion was highest in Run EGO-55 as 56 lb/hr of steam was converted, representing 24.9 percent of the steam fed. In addition to other factors, the amount of steam converted depended on the char feed rate and the total steam fed, generally increasing with an increase in both of the feed rates.

4b.3.4.2.2 FMC Char Residue Gasification at 500 psig and 350 psig

Gasification of partially gasified FMC char, having an ash content of from 19.2 to 23.0 percent, at 500 psig and in a 30-inch fluidized bed showed that fluidization velocities above 0.6 ft/s are necessary to keep the ash from sintering. Three tests (Runs EGO-40, EGO-41, and EGO-42) were performed with the residue char with maximum bed temperatures of 1830° to 1890°F. Sinter-free operation was obtained with the FMC residue char at a fluidization velocity of 0.79 ft/s in Run EGO-44. In this test, performed in a 50-inch fluidized, at a reactor pressure of 329 psig, we gasified 51.3 percent of the carbon at a maximum bed temperature of 1845°F.

4b.3.4.2.3 Hydrogasified Ireland Mine Coal Gasification at 500 psig

In two tests, Runs EGO-36 and EGO-37, we demonstrated successful steam-oxygen gasification of hydrogasified Pittsburgh steam bituminous coal from the Ireland mine. Ash content of the char was 21.2 to 23.2 percent. These two tests were performed at a nominal reactor pressure of 500 psig in a 50-inch fluidized bed. Highest carbon and steam conversions were obtained in Run EGO-37 at a maximum temperature of 1910°F as 73.3 percent of the carbon was gasified, and 33.5 lb/hr of steam was converted. The converted steam represents 28.4 percent of the steam fed. There was no ash sintering in either test with fluidization velocities of 0.62 ft/s in Run EGO-36, and 0.78 ft/s in Run EGO-37. Maximum char bed temperature in Run EGO-36 was 1930°F.

4b.3.4.3 Correlation of Experimental Data with Operating Variables

The steam-oxygen fluidized bed gasification studies performed in the 6-inch diameter were of sufficient number and range to allow for a reliable correlation of some of the key experimental results with operating parameters. These correlations have utility as guides for steam-oxygen fluid-bed gasifier operation at similar conditions, or, with limited extrapolation at other conditions. They are also applicable as a basis for the design of larger steam-oxygen gasifiers.

Steam conversion as a function of the average char bed temperature for two types of chars is shown in Figure 4b-18. One of the chars is an FMC Project COED char gasified as received, the other is an FMC Project COED char that was previously partially gasified with steam-oxygen in the 6-inch diameter reactor. The original coal of both chars was the same. The as-received char, with a typical ash content of 12 percent, was pyrolyzed at a temperature of about 1450°F when produced, and is, therefore, a low-temperature char. The partially gasified char, with an ash content greater than 20 percent, was gasified at temperatures of 1800° to 1900°F, resulting in a high-temperature char. Steam conversions are shown to increase with temperature for both chars. The rate of increase in steam conversion with temperature is greater for the low-temperature char than for the high-temperature char. Also, at any given temperature, steam conversions are larger with the low-temperature char. These results show that the high-temperature char, having been previously exposed to higher temperatures has a lower reactivity to steam gasification.

Gasified carbon appears in the product gas as carbon monoxide, carbon dioxide, and methane. The proportion of carbon appearing in each of these gaseous species is influenced by the char-bed gasification temperature as shown in Figure 4b-19. As the average bed temperature increases, the mole ratio of methane to the total carbon oxides decreases. The lower equilibrium methane concentration at higher temperatures is partially responsible for this. A contributing factor is the increase in carbon oxides formation associated with the increased carbon and steam conversions at higher temperatures. Figure 4b-19 also shows that the ratio of methane to carbon oxides formed by the carbon-steam reaction, $CH_4/CO_X - O_2$, decreases at a greater rate than the ratio of methane to total carbon oxides, CH_4/CO_X(total).

A typical temperature profile through the fluidized char bed is shown in Figure 4b-20 for a steam-oxygen gasification test Although the char bed is well fluidized, a gradient still exists between the bottom and the top of the char bed. This is explained by the differences in the predominant reactions taking place at the bottom of the bed and the top of the bed, and the different feed steam preheat requirements. At the bottom of the bed where the oxygen enters, there is a high heat release as the oxygen is rapidly consumed. Further up through the bed, the temperatures tend to moderate as the endothermic carbon-steam reaction continues in the absence of free oxygen. At the top of the bed the temperature is further lowered by the preheat requirements for the char entering the top of the reactor.

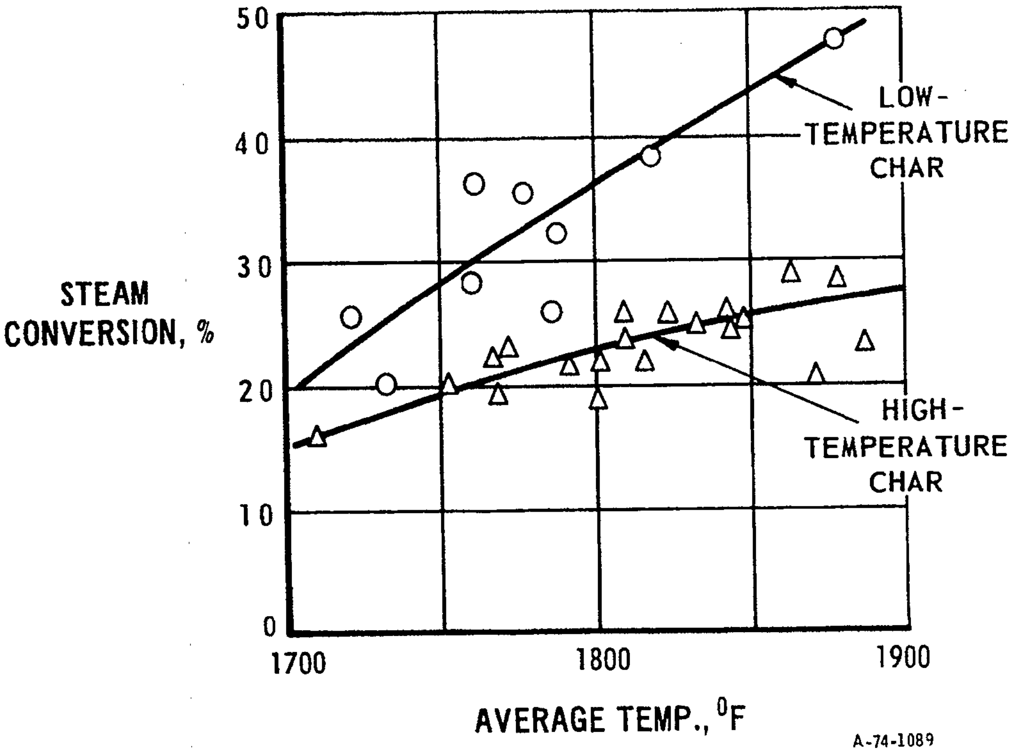

Figure 4b-18. STEAM CONVERSIONS IN A 6-INCH DIAMETER STEAM-OXYGEN FLUIDIZED-BED GASIFIER

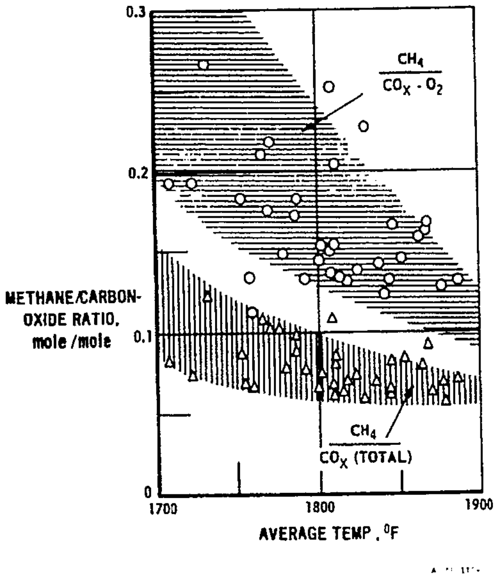

Figure 4b-19. CARBON DISTRIBUTION IN PRODUCT GAS FOR STEAM-OXYGEN CHAR GASIFICATION IN A 6-INCH DIAMETER FLUIDIZED REACTOR

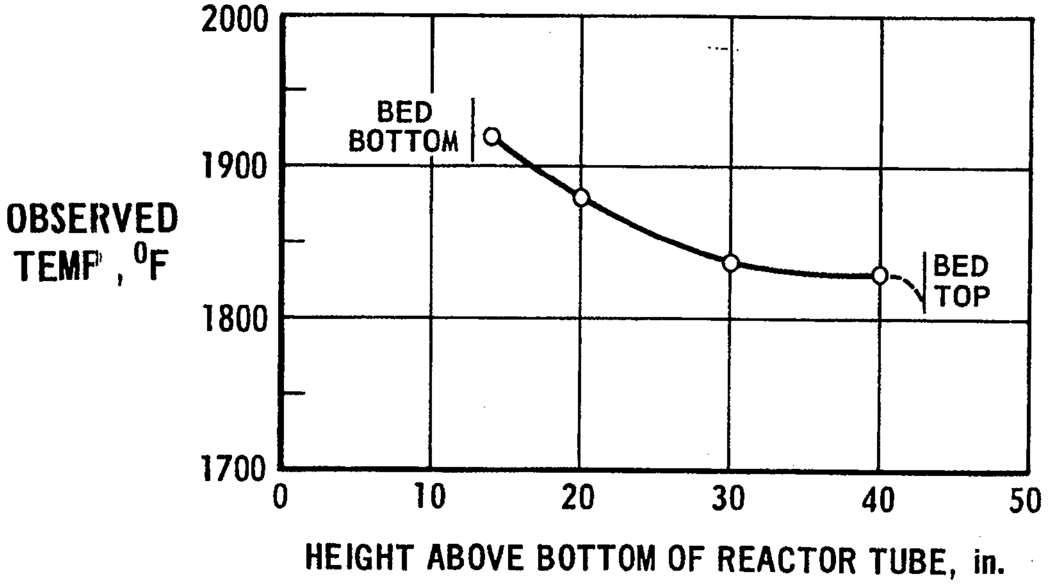

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Figure 4b-20. TYPICAL TEMPERATURE PROFILE THROUGH A FLUIDIZED CHAR BED FOR STEAM-OXYGEN GASIFICATION

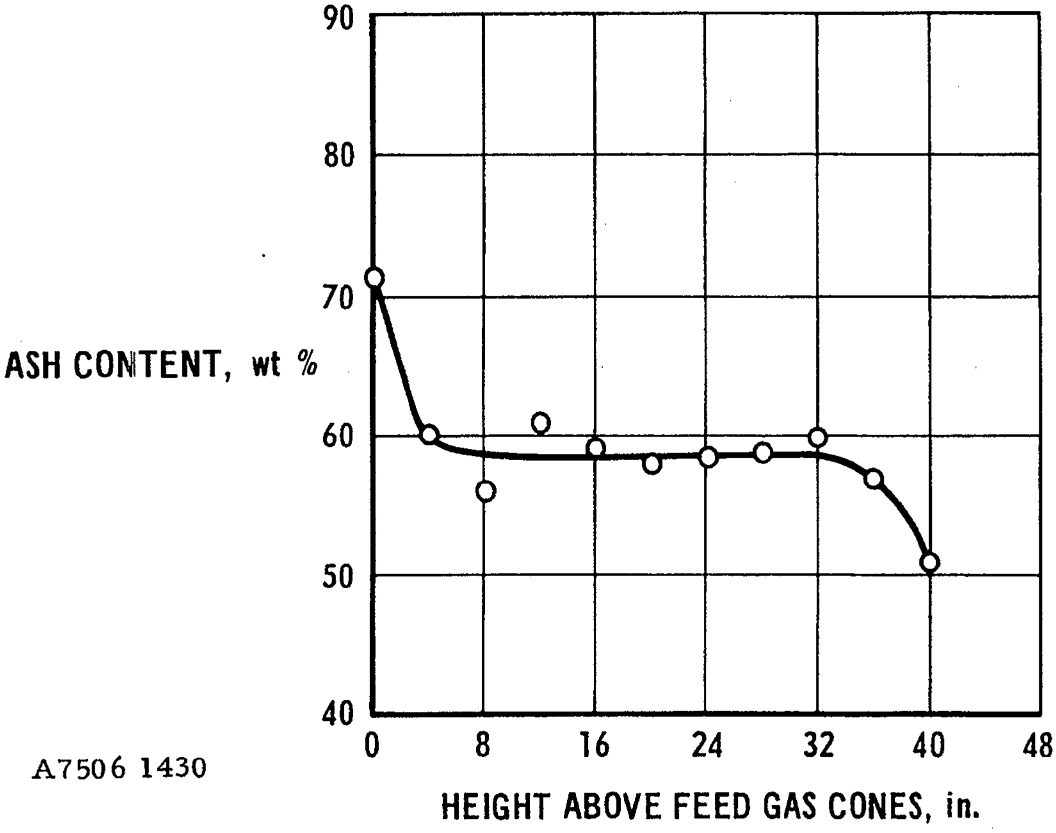

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Figure 4b-21. TYPICAL ASH DISTRIBUTION IN A FLUIDIZED BED FOR STEAM-OXYGEN CHAR GASIFICATION

From residue char samplings from various levels in the reactor bed we obtained analyses showing the variation of ash concentration through the char bed. An ash distribution in the fluidized bed after a typical steam-oxygen test is shown in Figure 4b-21. The uniformity of ash concentration through the bulk of the bed indicates a generally well mixed fluidized bed. However, there is an ash gradation at both the top and the bottom layers of the char bed. At the top, the ash concentration is lower since the feed char has not yet attained the average conversion level. At the bottom, the ash concentration is higher because of the somewhat higher reaction rates. The higher concentration of ash at the bottom indicates that a gasifier may be designed to preferentially discharge a high-ash, low-carbon content residue from the fluidized bed.

In Figure 4b-22 is shown a correlation between the maximum temperature in the char bed and the superficial fluidizing-gas velocity required for operation without sintering of the ash. Smooth operation with no ash sintering may be expected when operating in the area below the curve. The maximum temperature in this correlation is a temperature sensed by thermocouples in the char bed. In the steam-oxygen gasifier tests this temperature has generally been several hundred degrees (°F) lower than the ash-softening temperature as determined in the laboratory tests. However, since the unsensed temperatures of the char particles inside of gas bubbles may be higher than the measured and recorded temperatures, ash sintering may occur if the fluidization velocity is not sufficiently high. Also, as the temperature of the char particles increases, the inter-particle forces between the ash particles increase so that higher fluidization velocities are needed to counter the agglomerating tendency. The correlation of Figure 4b-22 is based on the gasification of FMC char and is applicable to operation with this char only. Even though other coals or chars may have ash softening temperatures similar to those of the FMC char, the behavior of the ash at gasification conditions could not be predicted from this correlation and a new relationship would have to be established for each char.

4b. 5 Reference Cited

1. May, W. G., Mueller, R. H. and Sweetser, S. B., "Carbon-Steam Reaction Kinetics From Pilot Plant Data," Ind. Eng. Chem. 50, 1289-96, (1958) September.

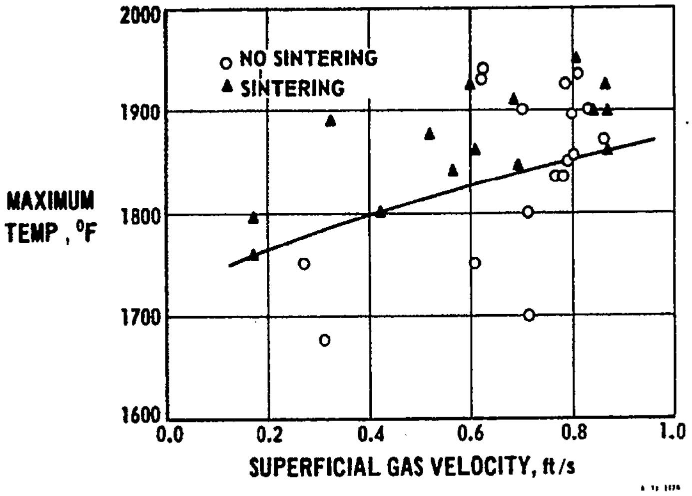

Figure 4b-22. DESIGN CURVE FOR SINTER-FREE STEAM-OXYGEN CHAR GASIFICATION

APPENDIX 4b-A

Steam-Oxygen Gasification Data Tabulated

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Table 4b-A 1 OPERATING CONDITIONS AND RESULTS OF SYNTHESIS GAS GENERATION STUDIES, WITHOUT OXYGEN FEED, IN A 4-INCH REACTOR TUBE OF BALANCE-PRESSURE HYDROGASIFICATION DEVELOPMENT UNIT (Runs S-1 and S-3)

Coal	Hydrogasified Ireland Mine Bituminous	
Source	Pittsburgh No. 8 Runs OH-1 through OH-7	
Sieve Size, USS	-10+80	-10+80
Run No.	S-1	S-3
Duration of Test, hr	3-1/4	3
Steady-State Operating Period, min[a]	123-189	61-127
OPERATING CONDITIONS		
Char Bed Height, ft	7.0	7.0
Reactor Pressure, psig	1009	1043
Reactor Temperature, °F[b]		
Inches From Bottom		
62-1/2	1295	1135
67-3/4	1485	1260
73	1625	1395
78-1/4	1465	1220
83-1/4	1550	1290
89	1470	1240
94-1/2	1485	1290
100	1590	1340
104	1600	1330
114	1535	1335
124-1/2	1465	1280
135	1560	1290
145	1450	1265
Average	1505	1280
Char Feed Rate, lb/hr[c]	19.62	22.36
Steam Rate, lb/hr	28.41	59.19
Steam/Char Ratio, lb/lb	1.448	2.647
Oxygen Rate, SCF/hr	None	None
Oxygen/Char Ratio, SCF/lb	None	None
Sweep Nitrogen, SCF/hr[d]	93.61	67.33
Purge Nitrogen, SCF/hr[e]	283.4	293.1
Char Space Velocity, lb/cu ft-hr	31.71	36.14
Char Residence Time, min[f]	42.6	36.19
Steam Residence Time, min[g]	0.987	1.820
Superficial Nitrogen + Steam Velocity, ft/s[h]	0.118	0.192
Electric Power Heat Input to Reactor,		
kW	15.00	16.30
Btu/hr	51,195	55,632

Continued

OPERATING RESULTS		
Product Gas Rate, nitrogen-free, SCF/hr	120.57	14.23
Product Gas Yield, SCF/lb	6.146	0.636
Hydrogen Yield, SCF/lb	2.925	0.391
Hydrocarbon Yield, SCF/lb	0.879	0.043
Carbon Oxides Yield, SCF/lb	2.341	0.173
Slagged Ash, lb/hr	--	--
Residue, lb/hr	16.19	21.22
Liquid Products, lb/hr[i]	24.39	58.88
Net MAF Char Hydrogasified, wt %[j]	14.12	1.41
Carbon Gasified, wt %	14.29	0.96
Steam Reacted, lb/hr[k]	4.02	0.307
Steam Concentration in Product Gas, mole %	81.0	98.9
Overall Material Balance, %	97.7	98.8
Carbon Balance, %	88.8	95.7
Hydrogen Balance, %	98.1	99.0
Oxygen Balance, %	99.0	99.3
PRODUCT GAS PROPERTIES		
Gas Composition, nitrogen-free, mole%		
Carbon Monoxide	6.2	9.1
Carbon Dioxide	31.9	18.1
Hydrogen	47.6	61.5
Methane	14.3	6.8
Hydrogen Sulfide	--	--
Total	100.0	100.0
Heating Value, Btu/SCF[l]	314	293
Specific Gravity (Air = 1.00)	0.660	0.499

a. From start of coal feed.

b. Tube wall temperatures. Bottom of coal bed at 62 in.

c. Operating conditions and results based on weight of dry feed.

d. Fed with steam to bottom of reactor.

e. Fed to top of reactor, above char bed.

f. (Char feed bulk density) X (Char bed volume)/Char feed rate.

g. Coal bed volume/(CF/min feed gas at reactor pressure and temperature).

h. (CF/s feed gas at reactor pressure and temperature)/cross-sectional area of reactor.

i. Unreacted steam. Difference between steam fed and reacted steam as computed from carbon oxides appearing in product gas.

j. 100 (wt of product gas-wt feed gas in-wt decomposed steam-wt nitrogen in/wt of moisture-, ash-free char).

k. Computed from carbon oxides appearing in product gas.

l. Gross, gas saturated at 60°F, 30-in. Hg pressure. SCF: dry gas volume in SCF at 60°F, 30-in. Hg pressure.

Table 4b-A 2 CHEMICAL AND SCREEN ANALYSES OF FEED AND RESIDUE OF SYNTHESIS GAS GENERATION STUDIES, WITHOUT OXYGEN FEED, IN A 4-INCH REACTOR TUBE (Runs S-1 and S-3)

	S-1		S-3	
Sample	**Feed**	**Residue**	**Feed**	**Residue**
Proximate Analysis, wt %				
Moisture	1.5	2.2	1.5	1.5
Volatile Matter	3.1	3.8	3.0	2.8
Fixed Carbon	70.6	61.9	70.8	69.7
Ash	24.8	32.1	24.7	26.0
Total	100.0	100.0	100.0	100.0
Ultimate Analysis (dry), wt %				
Carbon	71.5	64.5	71.2	71.1
Hydrogen	1.03	0.81	0.97	0.74
Nitrogen	0.58	0.48	0.59	0.51
Oxygen	0.00	0.00	0.28	0.00
Sulfur	1.99	1.44	1.91	1.77
Ash	25.20	32.77	25.05	26.40
Total	100.30	100.00	100.00	100.52
Screen Analysis, USS, wt %				
+20	19.8	24.7	20.3	23.3
+30	19.1	25.2	21.8	22.7
+40	16.3	19.6	18.8	18.3
+60	21.5	19.2	23.4	21.4
+80	10.4	6.5	10.7	9.0
+100	4.4	2.3	3.5	3.2
+200	6.5	1.9	1.1	1.5
+325	1.1	0.4	0.2	0.4
−325	0.9	0.2	0.2	0.2
Total	100.0	100.0	100.0	100.0

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Table 4b-A3 OPERATING CONDITIONS AND RESULTS OF SYNTHESIS GAS GENERATION STUDIES IN A 4-INCH REACTOR TUBE OF BALANCE-PRESSURE HYDROGASFICATION UNIT
(Runs SO-5, SO-7, and SO-9 through SO-14)

Coal	Hydrogasified Ireland Mine Bituminous	Hydrogasified Ireland Mine Bituminous	Hydrogasified Ireland Mine Bituminous	Hydrogasified Ireland Mine Bituminous	Gasified Ireland Mine Bituminous	Gasified Ireland Mine Bituminous	Gasified Ireland Mine Bituminous	Gasified Ireland Mine Bituminous
Source	Pittsburgh No. 8 Runs OH-1 through OH-7	Pittsburgh No. 8 Runs OH-1 through OH-7	Pittsburgh No. 8 Runs OH-1 through OH-7	Pittsburgh No. 8	Pittsburgh No. 8	Pittsburgh No. 8 Runs SO-1 through SO-9	Pittsburgh No. 8 Runs SO-1 through SO-10	Pittsburgh No. 8 Runs SO-1 through SO-12
Sieve Size, USS	-10+80	-10+80	-10+80	-10+80	-10+80	-10+80	-10+80	-10+80
Run No.	SO-5	SO-7	SO-9	SO-10	SO-11	SO-12	SO-13	SO-14
Duration of Test, hr	4-1/2	4	3-1/3	3-3/4	4-1/4	4-1/2	4-1/2	5
Steady-State Operating Period, min[a]	165-266	111-216	143-200	156-230	149-249	143-271	150-271	146-291
OPERATING CONDITIONS								
Char-Bed Height, ft	3.5	3.5	7.0	7.0	7.0	7.0	7.0	7.0
Reactor Pressure, psig	1026	1040	1050	1103	516	972	1018	1037
Reactor Temperature, °F[b]								
Inches From Bottom								
62-1/2	1615	1750	1380	1310	--	1420	1450	1445
67-3/4	1415	1840	1565	1540	1635	1685	1560	1640
73	1650	1880	1630	1640	1675	1760	1795	1750
78-1/4	1600	1650	1475	1405	1420	1540	1365	1525
83-1/4	1740	1825	1605	1550	--	--	--	--
89	1520	1660	1415	1355	1356	1480	1525	1470
94-1/2	1580	1670	1470	1425	1420	1520	1560	1510
100	1740	1810	1645	1555	1660	1730	1780	1715
104	1750	1825	1650	1525	1670	1735	1760	1705
114	None	None	1610	1515	1620	1690	1780	--
124-1/2	None	None	1410	1280	1365	1425	1450	1450
135	None	None	1490	1375	1485	1545	1495	1525
145	None	None	1430	1340	1445	1490	1460	1510
Average	1620	1770	1520	1445	1525	1585	1580	1570
Internal Bed Temperature, °F								
Inches from Bottom								
56-1/2	Not Measured	Not Measured	1130	1520	1060	--	--	--
62-1/2			900	1390	1095	--	--	--
65-1/2			--	--	--	1840	--	--
73-1/2			--	--	--	--	1885	1725
74-1/2			1670	--	1805	1905	--	--
85-1/2			--	--	--	1175	1850	1725
92-1/2			1040	980	1005	--	--	--
95-1/2			--	--	--	1515	--	--
97-1/2			--	--	--	--	1810	1705
115-1/2			--	--	--	--	1720	1465
116-1/2			1620	1520	1650	1705	--	--
135-1/2			--	--	--	--	1655	1665

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Char Feed Rate, lb/hr^c	27.83	26.17	23.49	24.13	22.91	23.0	23.7	21.4
Steam Rate, lb/hr	30.00	34.76	35.00	34.77	34.71	35.0	35.0	35.0
Steam/Char Ratio, lb/lb	1.078	1.328	1.490	1.441	1.515	1.52	1.31	1.64
Oxygen Rate, SCF/hr	91.40	131.5	86.59	95.14	79.64	99.4	117.3	101.7
Oxygen/Char Ratio, SCF/lb	3.28	5.03	3.69	3.94	3.48	4.33	4.95	4.75
Sweep Nitrogen, SCF/hr^d	29.15	40.26	53.44	110.12	87.99	68.5	92.3	628.8
Purge Nitrogen, SCF/hr^e	321.0	312.9	307.59	287.0	264.4	329	335	256
Char Space Velocity, lb/cu ft-hr	89.94	84.57	37.97	39.00	37.02	37.1	38.3	34.6
Char Residence Time, min^f	14.48	16.32	34.45	33.85	36.79	38.6	35.4	41.7
Steam Residence Time, min^g	0.436	0.343	0.804	0.820	0.391	0.70	0.70	0.46
Superficial Feed Gas Velocity, ft/s^h	0.134	0.170	0.145	0.142	0.298	0.17	0.17	0.25
Electric Power Heat Input to Reactor,								
kW	14.84	9.47	6.79	9.88	8.57	11.22	10.82	13.88
Btu/hr	50,649	32,334	23,174	33,729	29,254	38,292	36,929	47,372
OPERATING RESULTS								
Product Gas Rate, nitrogen-free, SCF/hr	553.6	675.5	470.8	247.6	392.7	610	634	444
Product Gas Yield, SCF/lb	19.89	25.81	20.04	10.26	17.14	26.5	26.8	20.7
Hydrogen Yield, SCF/lb	7.301	9.810	7.516	3.796	6.599	9.9	10.6	8.3
Hydrocarbon Yield, SCF/lb	1.751	2.014	2.184	1.067	1.131	2.34	1.85	1.43
Carbon Oxides Yield, SCF/lb	10.802	13.992	10.343	5.345	9.410	14.31	14.34	10.99
Slagged Ash, lb/hr	--	2.73	1.99	0.146	--	2.26	3.04	0
Residue, lb/hr^i	16.81	9.52^l	10.75	18.54	14.55	8.22	7.80	11.99
Liquid Products, lb/hr	16.53	17.67	22.50	28.31	25.63	19.84	20.10	25.29
Net MAF Char Hydrogasified, wt %^{j}	51.50	50.8	46.9	27.34	49.8	69.4	61.2	48.3
Carbon Gasified, wt %	54.19	69.00	53.5	28.38	47.6	74.4	70.5	54.1
Steam Reacted, lb/hr	13.47	17.09	12.50	6.46	9.07	15.16	14.90	9.71
Steam Concentration in Product Gas, mole	37.4	34.2	47.4	62.4	52.8	38.1	36.8	33.1
Overall Material Balance, %	99.5	95.7	97.1	95.5	99.7	98.9	97.8	98.4
Carbon Balance, %	100.9	99.8	94.5	97.0	99.1	102.9	99.2	97.2
Hydrogen Balance, %	97.9	95.3	98.1	99.6	98.3	98.3	98.3	100.2
Oxygen Balance, %	97.7	90.5	96.3	90.0	100.5	97.8	95.5	96.2
PRODUCT GAS PROPERTIES								
Gas Composition, nitrogen-free, mole %								
Carbon Monoxide	26.0	28.5	15.9	8.1	17.5	25.2	26.1	18.9
Carbon Dioxide	28.3	25.7	35.7	44.0	37.4	28.7	27.5	34.1
Hydrogen	36.7	38.0	37.5	37.0	38.5	37.3	39.5	40.1
Methane	8.8	7.8	10.9	10.4	6.6	8.8	6.9	6.9
Hydrogen Sulfide	0.2	--	--	0.5	0.02	0.03	0.03	0.0
Total	100.0	100.0	100.0	100.0	100.2	100.3	100.3	100.0
Heating Value, Btu/SCF^k	287	289	279	247	244	286	277	257
Specific Gravity (Air = 1.00)	0.761	0.738	0.786	0.840	0.804	0.757	0.738	0.770

a. From start of coal feed.
b. Tube wall temperatures. Bottom of coal bed at 62 inches.
c. Operating conditions and results based on weight of dry feed.
d. Fed with steam to bottom of reactor.
e. Fed to top of reactor, above char bed.
f. (Char-feed bulk density) X (Char-bed volume)/Char-feed rate.
g. Coal-bed volume/(CF/min feed gas at reactor pressure and temperature).
h. (CF/s feed gas at reactor pressure and temperature)/cross-sectional area of reactor.
i. By ash balance.
j. 100 (wt of product gas-wt feed gas in-wt decomposed steam-wt nitrogen in/wt of MAF char).
k. Gross, gas saturated at 60°F, 30-in. Hg pressure SCF: dry gas volume in SCF at 60°F, 30-in. Hg pressure.
l. Based on MAF Char gasified.

Table 4b-A 4 CHEMICAL AND SCREEN ANALYSES OF FEEDS AND RESIDUES OF SYNTHESIS GAS GENERATION STUDIES IN A 4-INCH REACTOR TUBE
(Runs SO-5, SO-7, and SO-9 through SO-14)

Run No.	SO-5		SO-7		SO-9		SO-10		SO-11		SO-12		SO-13		SO-14	
Sample	Feed	Residue	Feed	Residue	Feed	Residue	Feed	Residue	Feed	Residue	Feed	Residue	Feed	Residue	Feed	Residue
Proximate Analysis, wt %																
Moisture	1.5	0.2	1.9	1.2	1.8	1.0	1.5	1.8	1.2	0.3	1.4	0.3	1.5	0.6	2.7	0.5
Volatile Matter	3.2	3.2	3.7	2.6	3.5	3.3	3.5	4.3	3.6	2.3	3.5	2.8	4.3	4.3	4.2	2.3
Fixed Carbon	72.6	61.6	71.7	60.3	72.3	64.6	69.8	61.2	68.8	55.4	69.3	55.0	70.4	61.0	69.6	54.4
Ash	22.7	35.0	22.7	35.9	22.4	31.1	25.2	32.7	26.4	42.0	25.8	41.9	23.8	34.1	23.5	42.8
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
Ultimate Analysis (dry), %																
Carbon	73.5	62.1	73.6	62.2	74.3	66.7	71.7	64.0	70.2	56.9	71.0	56.6	72.8	63.3	72.8	56.0
Hydrogen	0.90	0.73	0.80	0.59	0.84	0.73	0.74	0.84	0.79	0.52	0.76	0.64	0.94	0.79	0.94	0.54
Nitrogen	0.54	0.42	0.53	0.29	0.48	0.33	0.47	0.34	0.48	0.20	0.48	0.28	0.42	0.40	0.42	0.19
Oxygen	0.24	0.00	0.37	0.00	0.00	0.00	0.00	0.61	0.35	0.00	0.00	0.00	0.52	0.0[illegible]	0.52	0.00
Sulfur	1.75	2.18	1.60	0.90	1.61	1.11	1.71	0.92	1.41	0.57	1.58	0.94	1.20	1.28	1.20	0.29
Ash	23.07	35.10	23.10	36.38	22.86	31.46	25.58	33.29	26.77	42.14	26.18	42.06	24.12	34.30	24.12	43.05
Total	100.00	100.53	100.00	100.36	100.09	100.33	100.00	100.00	100.00	100.00	100.00	100.52	100.00	100.07	100.00	100.07
Gross Heating Value, Btu/lb	--	--	--	--	11,140	9,940	10,750	9,530	10,641	8,517	10,965	8,459	11,010	9,530	11,010	8,310
Screen Analysis, USS, wt %																
+20	17.7	18.7	17.2	16.8	19.3	14.1	22.7	16.9	14.9	8.8	14.7	7.4	17.7	16.5	15.2	11.6
+30	19.0	24.5	17.2	20.1	20.8	17.0	23.5	22.1	22.2	19.5	19.4	19.4	24.0	25.6	21.3	22.4
+40	16.4	20.0	15.7	19.0	17.2	16.5	19.6	18.7	20.5	22.2	18.1	24.1	19.5	21.4	19.5	21.3
+60	23.1	23.2	23.5	23.8	22.8	27.8	21.5	23.3	24.9	27.6	23.4	28.2	18.3	18.8	25.1	23.6
+80	12.1	9.0	14.2	11.3	12.7	15.0	8.8	10.9	13.0	12.7	16.4	14.0	14.2	12.8	14.1	11.4
+100	4.8	2.8	6.0	4.4	4.8	5.6	2.7	4.2	3.6	4.1	5.2	3.8	3.5	2.6	4.1	4.3
+200	4.1	1.3	4.2	3.3	1.8	3.0	0.8	2.6	0.5	3.4	1.6	2.0	1.6	1.5	0.5	3.4
+325	1.3	0.3	1.0	0.5	0.2	0.4	0.2	0.5	0.2	0.7	0.3	0.1	0.6	0.5	0.0	0.9
−325	1.5	0.2	1.0	0.6	0.4	0.6	0.2	0.8	0.2	1.0	0.9	1.0	0.6	0.3	0.2	1.1
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

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Table 4b-A 5 OPERATING CONDITIONS AND RESULTS OF STEAM-OXYGEN GASIFICATION OF COAL CHAR IN A 6-INCH REACTOR TUBE OF ELECTROTHERMAL GASIFICATION DEVELOPMENT UNIT

(Runs EGO-7 through EGO-12)

Coal	Bituminous Coal Char	Bituminous Coal Char	Bituminous Coal Char	Bituminous Coal Char	Bituminous Coal Char	Bituminous Coal Char
Source	FMC, Project COED	FMC, Project COED	FMC, Project COED	FMC, Project COED	FMC, Project COED	FMC, Project COED
Sieve Size, USS	−10−80	−10−80	−10+80	−10−80	−10+80	−10+80
Run No.	EGO-7[j]	EGO-8	EGO-9	EGO-10	EGO-11	EGO-12
Duration of Test, hr	4-1/2	4-3/4	4	4	6-1/4	6
Steady-State Operating Period, min[a]	204-268	220-290	130-230	180-230	288-378	308-348
OPERATING CONDITIONS						
Electrode Diameter, in.	3/4	3/4	1-1/2	1-1/2	1-1/2	1-1/2
Electrode Tip, above gas feed cones, in.	12	12	12	12	12	12
Electrode Char Bed Immersion, in.	43-1/4	43-1/4	43-1/4	43-1/4	43-1/4	43-1/4
Char Bed Height, In.	50-1/4	50-1/4	50-1/4	50-1/4	50-1/4	50-1/4
Reactor Pressure, psig	1046	946	979	915	980	1023
Reactor Temperature, °F[b]						
Inches From Bottom						
8	1155	930	535	540	485	640
12	640	585	540	955	560	580
16	390	590	580	1105	745	525
18	910	800	1085	1000	915	895
22	1270	1100	875	1575	1325	1640
24	1015	940	1205	1205	1030	1300
26	1075	1475	--	--	--	--
28	1195	1245	--	--	--	--
30	1055	1015	1450	1255	1480	--
34	--	--	1085	1575	--	--
38	--	--	1455	1340	1440	1535
42	--	--	1485	1440	1500	1460
43	1000	845	--	--	--	--
45	990	1065	1325	1560	--	--
50	690	1350	1440	1475	--	--
60	1240	1217	1455	1440	1690	--
71	1095	--	1390	1560	--	--
75	1005	920	1365	1405	1585	1550
79	--	--	1365	1365	1655	1495
83		1060	--	--	--	--
Average Reaction Zone, °F[c]	1085	1320	1435	1525	1485	1545
Char-Feed Rate, lb/hr	48	52	50.0	50.8	45.4	44.4
Steam Rate, lb/hr	68.5	110	98.0	99.0	97.0	98.0
Steam/Char Ratio, lb/hr	1.43	2.12	1.96	1.95	2.14	2.21
Oxygen Rate, SCF/hr	156.0	207.4	125.1	248.0	290.8	298.3
Oxygen Char Ratio, SCF/lb	3.25	3.99	2.50	4.88	6.41	6.72
Fluidizing Nitrogen, SCF/hr	1,950	220	nil	917	134	1119
Purge Nitrogen, Shell, SCF/hr	362	400	430	422	395	375
Purge Nitrogen, Electrode, SCF/hr	152	185	192	126	161	166
Char Space Velocity, lb/cu ft-hr	59.7	65.6	65.6	66.6	56.9	58.2
Char Residence Time, min[d]	27.9	27.6	26.8	25.3	33.2	31.3
Steam Residence Time, min[e]	0.29	0.34	0.39	0.27	0.34	0.24

Continued

Superficial Feed Gas Velocity, ft/s[f]	0.21	0.18	0.155	0.254	0.179	0.250
Electric Power Input to Electrode,						
kW	Nil	7.32	12.27	nil	nil	nil
Btu/hr	Nil	24,968	41,865	nil	nil	nil
OPERATING RESULTS						
Product-Gas Rate, nitrogen-free, SCF/hr	826	844	646.1	618.7	937.9	892.7
Product-Gas Yield, SCF/lb	17.4	16.86	12.91	12.18	20.67	20.11
Hydrogen Yield, SCF/lb	No gas analysis	6.52	5.75	5.70	7.42	7.34
Hydrocarbon Yield, SCF/lb	No gas analysis	1.42	0.98	0.77	1.51	1.29
Carbon Oxides Yield, SCF/lb	No gas analysis	8.90	6.18	7.40	11.72	11.46
Residue, lb/hr[g]	42.7	29.9	36.05	37.37	21.89	24.05
Slagged Ash, lb/hr	Nil	Nil	nil	nil	0.894	nil
Condensed Liquids, lb/hr[h]	40.3	92.8	83.11	84.03	81.75	84.40
Net MAF Char Gasified, wt %	No gas analysis	38.8	27.6	30.2	51.2	50.3
Carbon Gasified, wt %	No gas analysis	40.4	27.7	30.2	51.6	49.7
Steam Reacted, lb/hr	No gas analysis	19.4	16.97	15.95	19.35	16.39
Steam Reacted, % of steam fed	No gas analysis	17.3	17.0	16.0	19.1	16.3
Steam Concentration in Product Gas, mol %	No gas analysis	69.8	73.0	74.0	64.7	66.5
Overall Material Balance, %	No gas analysis	92.7	95.1	95.8	95.4	97.7
Carbon Balance, %	No gas analysis	84.3	97.3	91.7	93.2	100.0
Hydrogen Balance, %	No gas analysis	100.0	100.0	95.8	101.2	101.5
Oxygen Balance, %	No gas analysis	97.2	93.6	93.2	95.4	97.0
PRODUCT GAS PROPERTIES						
Gas Composition, nitrogen-free, mol %						
Carbon Monoxide	No gas analysis	14.3	22.4	14.0	18.7	15.2
Carbon Dioxide	No gas analysis	38.5	25.4	46.8	38.0	41.8
Hydrogen	No gas analysis	38.7	44.5	32.8	35.9	36.5
Methane	No gas analysis	8.4	7.6	6.3	7.3	6.4
Argon	No gas analysis	0.1	0.1	0.1	0.05	0.1
Hydrogen Sulfide	No gas analysis	--	--	--	0.05	--
Total		100.0	100.0	100.0	100.0	100.0
Heating Value, Btu/SCF[i]	No gas analysis	252	287	212	246	228
Specific Gravity (Air 1.00)	No gas analysis	0.802	0.679	0.910	0.828	0.848

a. From start of char feed.
b. Tube wall temperatures. Bottom of char bed at 12-3/4 in.; top of char bed at 63 in.
c. Operating conditions and results based on weight of dry feed.
d. (Char-feed bulk density) X (Char bed volume)/Char-feed rate.
e. Char bed volume/(CF/min feed gas at reactor pressure and temperature).
f. Steam + oxygen + nitrogen. (CF/s feed gas at reactor pressure and temperature)/ cross-sectional area of reactor.
g. Based on weight residue recovered for Runs EGO-7 and EGO-10. Based on carbon gasified for Run EGO-8. Based on ash balance for Runs EGO-9, EGO-11 and EGO-12.
h. Based on weight liquid recovered, except Run EGO-9 which is based on 100% hydrogen balance.
i. Gross: gas saturated at 60°F, 30-in. Hg pressure. SCF: dry gas volume in SCF at 60°F, 30-in. Hg pressure.
j. Three cone feed-gas distributor. Feed ports 9/32 inch diameter. Used through Run EGO-32.

Table 4b-A 6 CHEMICAL AND SCREEN ANALYSES OF FEEDS AND RESIDUES OF STEAM-OXYGEN GASIFICATION OF COAL CHAR STUDIES IN ELECTROTHERMAL GASIFIER (Runs EGO-7 through EGO-12)

Run No.	EGO-7		EGO-8		EGO-9		EGO-10		EGO-11		EGO-12	
Sample	Feed	Residue	Feed	Residue	Feed	Residue	Feed	Residue	Feed	Residue	Feed	Residue
Proximate Analysis, wt %												
Moisture	4.4	8.3	4.1	3.1	4.0	1.4	1.9	2.0	8.3	4.1	5.9	6.5
Volatile Matter	5.4	4.0	3.9	2.5	4.8	4.4	2.9	2.7	3.6	2.5	4.4	1.6
Fixed Carbon	80.2	78.1	80.1	58.1	80.9	79.5	86.7	70.7	76.3	67.7	78.2	70.8
Ash	10.0	9.6	11.9	36.3	10.3	14.7	8.5	24.6	11.8	15.7	11.5	21.1
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
Ultimate Analysis (dry), wt %												
Carbon	82.0	83.6	81.1	59.7	82.0	79.2	85.8	70.9	81.3	70.1	81.4	75.5
Hydrogen	1.04	1.20	1.00	0.60	0.98	0.93	1.15	1.00	0.86	0.77	1.09	0.62
Nitrogen	1.46	1.46	1.33	0.52	1.46	1.18	1.38	0.98	1.42	0.57	1.44	0.47
Oxygen	3.15	2.40	3.12	1.28	3.60	2.76	2.56	1.76	2.99	1.69	2.67	0.73
Sulfur	1.93	0.86	1.09	0.44	1.21	1.01	0.44	0.28	0.52	0.11	1.17	0.11
Ash	10.42	10.48	12.36	37.46	10.75	14.92	8.67	25.08	12.91	26.76	12.23	22.57
Total	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 %												
+20	12.5	30.0	16.4	14.7	5.4	12.2	36.6	18.3	22.8	8.2	18.5	5.7
+30	13.8	16.6	14.0	14.7	9.5	13.2	18.0	16.5	15.8	14.1	15.0	12.1
+40	14.8	11.9	14.6	15.3	16.1	13.9	13.7	16.6	14.6	22.4	15.0	18.4
+60	25.0	17.7	25.4	22.3	32.6	22.5	18.1	24.0	21.1	33.0	23.7	30.5
+80	17.2	11.9	16.1	13.1	18.7	14.8	8.9	11.7	12.0	13.4	13.9	15.7
+100	8.8	5.5	6.8	6.3	8.7	8.2	3.2	4.9	5.2	4.8	6.8	6.9
+200	7.1	4.7	5.6	9.4	7.8	11.6	1.2	6.0	4.4	3.3	5.7	8.6
+325	0.4	0.9	0.7	2.0	0.8	2.3	0.1	1.1	1.6	0.4	0.8	1.1
−325	0.4	0.8	0.4	2.2	0.4	1.3	0.2	0.9	2.5	0.4	0.6	1.0
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

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Table 4b-A7, Part 1. OPERATING CONDITIONS AND RESULTS OF STEAM-OXYGEN GASIFICATION OF COAL CHAR IN A 6-INCH REACTOR-TUBE OF A GASIFICATION DEVELOPMENT UNIT (Runs EGO-13 through EGO-42, EGO-44 through EGO-60)

Coal	Bituminous Coal Char	Bituminous Coal Char	Bituminous Coal Char	Bituminous Coal Char	Hydrogasified Ireland Mine Bituminous	Bituminous Coal Char
Source	FMC, Project COED	FMC, Project COED	FMC, Project COED	FMC, Project COED	Pittsburgh No. 8 Seam	FMC, Project COED
Sieve Size, USS	−10+80	−10+80	−10+80	−10+80	−10+80	−10+80
Run No.	EGO-13A	EGO-13B	EGO-14	EGO-15	EGO-16	EGO-17
Duration of Test, hr	5-1/4	5-1/4	3-1/2	4-3/4	4-1/2	3
Steady-State Operating Period, min[a]	220-275	285-320	150-205	187-287	174-249	155-225
OPERATING CONDITIONS						
Char-Bed Height, in.	50-1/4	50-1/4	50-1/4	50-1/4	50-1/4	50-1/4
Reactor Pressure, psig	1015	1012	1028	998	1036	963
Reactor Temperature, °F[b]						
Inches From Bottom						
8	730	670	1080	535	880	1190
12	1120	1285	1410	1390	1055	1100
16	1370	1505	910	1490	1145	1205
18	--	--	--	--	1325	1555
22	1640	1640	1660	1640	1360	1090
24	1660	1665	1435	1630	1595	1415
30	--	--	--	--	1615	1725
34	--	--	--	--	1680	1505
38	1360	1360	1560	1370	1640	1700
42	1495	1505	1410	1485	1645	1705
45	--	--	--	--	1650	1650
56	--	--	--	--	1630	1715
60	--	--	--	--	1625	1730
71	--	--	--	--	1620	1781
75	1400	1445	1420	1630	1602	1470
79	1450	1460	1480	1645	1595	1460
Internal Bed Temperature, °F						
Inches From Bottom						
14	--	--	--	--	--	--
30	--	--	--	1765	1690	1805
40	--	--	--	--	--	--
45	--	--	--	1765	1670	1745
50	--	--	--	--	--	--
60	--	--	--	1745	1655	1452
77	1395	1430	1420	--	--	--
87	1280	1315	1230	1310	1660	1455
92	1230	1305	1245	--	--	--
Average Reaction Zone Temperature, °F	1595	1600	1610	1760	1670	1775
Char-Feed Rate, lb/hr[c]	55.4	55.4	63.1	58.2	66.1	102.3
Steam Rate, lb/hr	99.0	139	149	157	187.4	152.0
Steam/Char Ratio, lb/lb	1.79	2.51	2.36	2.62	2.86	1.49
Oxygen Rate, SCF/hr	303.6	312.1	344.2	397.7	430.3	486.4
Oxygen/Char Ratio, SCF/lb	5.48	5.63	5.45	6.64	6.51	4.75

Continued

Fluidizing Nitrogen, SCF/hr	1010	86.5	550	110	nil	nil
Purge Nitrogen, Shell, SCF/hr	350	373	392	395	40.5	342
Char Space Velocity, lb/cu ft-hr	68.7	68.7	78.2	72.1	81.9	126.8
Char Residence Time, min[d]	25.5	25.5	21.7	24.4	14.4	14.6
Steam Residence Time, min[e]	0.25	0.25	0.21	0.20	0.19	0.20
Superficial Feed Gas Velocity, ft/s[f]	0.239	0.238	0.281	0.293	0.312	0.296
OPERATING RESULTS						
Product-Gas Rate, nitrogen-free, SCF/hr	1187	1131	1450	1538	1594	2206
Product-Gas Yield, SCF/lb	21.40	20.49	22.97	26.43	16.77	21.57
Hydrogen Yield, SCF/lb	7.94	7.52	8.89	9.94	5.83	7.94
Hydrocarbon Yield, SCF/lb	1.91	2.01	1.98	2.38	1.22	1.88
Carbon Oxides Yield, SCF/lb	11.54	11.15	12.10	14.09	9.62	11.75
Residue Char, lb/hr[g]	26.56	29.53	28.29	25.49	40.37	51.94
Slagged Ash, lb/hr	nil	nil	nil	0.81	nil	nil
Bayonet Filter Fines, lb/hr	0.664	0.664	0.261	1.01	4.09	1.05
Sintered Ash, lb/hr	nil	nil	nil	0.810	0.182	4.60
Condensed Liquids, lb/hr[h]	79.2	110.3	123.0	122.1	169.5	99.8
Net MAF Char Gasified, wt %	50.8	47.5	52.8	62.5	46.1	52.8
Carbon Gasified, wt %	51.8	49.9	53.6	63.9	46.7	53.9
Steam Reacted, lb/hr	22.41	31.33	27.8	36.6	19.02	53.8
Steam Reacted, % of steam fed	22.1	22.1	18.4	23.1	10.1	35.0
Steam Concentration in Product Gas, mol %	58.4	67.1	64.1	62.5	76.3	48.7
Overall Material Balance, %	97.6	94.3	98.1	96.2	99.8	96.5
Carbon Balance, %	93.0	97.4	91.5	101.6	103.3	103.9
Hydrogen Balance, %	104.5	97.0	104.0	99.6	102.2	98.1
Oxygen Balance, %	99.2	93.1	99.7	94.5	98.4	93.1
PRODUCT GAS PROPERTIES						
Gas Composition, nitrogen-free, mol %						
Carbon Monoxide	17.8	14.7	17.2	18.6	8.8	24.3
Carbon Dioxide	36.1	38.7	35.5	34.7	48.6	30.2
Hydrogen	37.1	36.7	38.7	37.6	34.8	36.8
Methane	8.9	9.8	8.6	9.0	7.3	8.7
Argon	0.06	0.08	0.03	0.05	0.06	0.02
Hydrogen Sulfide	--	--	--	0.1	0.4	--
Total	99.96	99.98	100.03	100.05	99.96	100.02
Heating Value, Btu/SCF[i]	263	261	264	269	212	281
Specific Gravity (Air = 1.00)	0.800	0.815	0.784	0.787	0.899	0.771

a. From start of char feed.
b. Tube wall temperatures. Bottom of char bed at 12-3/4 inches; top of char bed at 63 in.
c. Operating conditions and results based on weight of dry feed.
d. (Char-feed bulk density) X (char bed volume)/char-feed rates.
e. Char bed volume/(CF/min feed gas at reactor pressure and temperature).
f. Steam + oxygen + nitrogen. (CF/s feed gas at reactor pressure and temperature)/cross-sectional area of reactor.
g. By ash balance.
h. Based on weight liquid recovered.
Gross: gas saturated at 60°F, 30-in. Hg pressure. SCF: dry gas volume in SCF at 60°F, 30-in. Hg pressure.

Table 4b-A7, Part 2. OPERATING CONDITIONS AND RESULTS OF STEAM-OXYGEN GASIFICATION OF COAL CHAR IN A 6-INCH REACTOR-TUBE OF A GASIFICATION DEVELOPMENT UNIT (Runs EGO-13 through EGO-42, EGO-44 through EGO-60)

Coal	Bituminous Coal Char	Bituminous Coal Char	Bituminous Coal Char	Bituminous Coal Char	Bituminous Coal Char	Bituminous Coal Char
Source	FMC, Project COED	FMC, Project COED	FMC, Project COED	FMC, Project COED	FMC, Project COED	FMC, Project COED
Sieve Size, USS	-10+80	-10+80	-10+80	-10+80	-10+80	-10+80
Run No.	EGO-18	EGO-19	EGO-20	EGO-21	EGO-22	EGO-23
Duration of Test, hr	4-3/4	3-3/4	4-1/4	4	3	4-1/2
Steady-State Operating Period, min[a]	168-268	240-293	160-260	170-245	110-180	220-280
OPERATING CONDITIONS						
Char-Bed Height, in.	50-1/4	50-1/4	50-1/4	50-1/4	50-1/4	50-1/4
Reactor Pressure, psig	480	631	512	482	493	470
Reactor Temperature, °F						
Tube Wall, Inches From Bottom[b]						
8	1435	810	1400	1355	1440	1270
12	990	920	1015	945	1055	990
16	1240	1380	1555	1430	1280	1505
18	1745	1475	1775	1800	1775	1795
22	1355	1505	1730	1735	1700	1750
24	1770	1700	1730	1750	1750	1755
30	1695	1645	1735	1800	1690	1750
34	1710	1790	1735	1710	1720	1760
38	1440	1690	1630	1650	1565	1705
42	1715	1715	1585	1760	1645	1721
45	995	775	780	--	--	--
56	1570	1760	1710	1770	1660	1740
60	1565	1725	1705	1775	1700	1740
71	1575	1775	1755	1910	1790	1830
75	1105	1510	1570	1730	1685	1615
79	1385	1495	1555	1725	1655	1580
Internal Bed Temperature, °F						
Inches From Bottom						
14	--	1570	1630	1745	1690	1615
30	1775	1755	1770	1835	1785	1815
40	--	--	--	--	--	--
45	1740	1775	1745	1920	1850	1650
50	--	--	--	--	--	--
60	1415	1570	1630	1755	1690	1670
77	--	--	--	--	--	--
87	1415	--	--	--	--	--
92	--	--	--	--	--	--
Average Reaction Zone Temperature, °F	1760	1765	1755	1880	1820	1760
Char-Feed Rate, lb/hr[c]	45.5	65.9	67.2	69.7	66.3	63.4
Steam Rate, lb/hr	74.5	73.5	80.5	75.5	86.4	90.3
Steam/Char Ratio, lb/lb	1.64	1.11	1.20	1.08	1.30	1.42
Oxygen Rate, SCF/hr	315.4	393.4	419.6	537.7	522.7	412.6
Oxygen/Char Ratio, SCF/lb	6.93	5.97	6.24	7.71	7.89	6.51
Oxygen Concentration in Feed Gas, mol %	16.8	10.4	9.8	13.0	11.5	9.9

Continued

Fluidizing Nitrogen, SCF/hr	1580	1840	2190	2025	2190	1870
Purge Nitrogen, Shell, SCF/hr	265	202	275	293	255	330
Char Space Velocity, lb/cu ft-hr	56.4	81.7	83.3	86.4	82.1	78.7
Char Residence Time, min[d]	31.6	20.9	23.9	22.4	23.4	19.1
Steam Residence Time, min[e]	0.20	0.13	0.094	0.088	0.084	0.089
Superficial Feed Gas Velocity, ft/s[f]	0.296	0.458	0.637	0.687	0.716	0.674
OPERATING RESULTS						
Product-Gas Rate, nitrogen-free, SCF/hr	1306	1340	1479	2154	1890	1822
Product-Gas Yield, SCF/lb	28.71	20.33	22.00	30.88	28.53	28.74
Hydrogen Yield, SCF/lb	11.80	7.38	7.92	11.55	10.35	11.64
Hydrocarbon Yield, SCF/lb	1.67	0.81	0.90	1.05	1.17	1.06
Carbon Oxides Yield, SCF/lb	15.22	12.11	13.16	18.25	16.94	15.98
Residue Char, lb/hr[g]	20.29	30.41	35.63	11.53	15.61	21.42
Bayonet Filter Fines, lb/hr	2.44	1.18	2.24	2.14	1.16	2.25
Sintered Ash, lb/hr	3.97	3.07	nil	5.24	5.00	nil
Condensed Liquids, lb/hr[h]	41.46	54.06	55.52	43.50	56.84	66.72
Net MAF Char Gasified, wt %	52.4	48.2	53.5	72.9	69.3	63.0
Carbon Gasified, wt %	53.1	49.5	54.7	74.6	70.6	64.0
Steam Reacted, lb/hr	33.6	21.4	29.3	35.5	33.2	25.4
Steam Reacted, % of steam fed	44.8	28.4	34.5	44.9	36.9	27.5
Steam Concentration in Product Gas, mol %	39.5	45.9	44.1	29.8	38.7	43.5
Overall Material Balance, %	95.0	96.0	98.0	96.2	96.5	101.1
Carbon Balance, %	99.7	95.9	100.0	91.9	94.5	95.4
Hydrogen Balance, %	94.7	103.1	96.9	105.7	102.6	111.6
Oxygen Balance, %	85.8	95.5	100.1	98.5	96.9	103.2
PRODUCT GAS PROPERTIES						
Gas Composition, nitrogen-free, mol %						
Carbon Monoxide	27.5	33.8	29.5	33.9	29.4	30.0
Carbon Dioxide	25.5	25.8	30.3	25.2	30.0	25.6
Hydrogen	41.1	36.3	36.0	37.4	36.3	40.5
Methane	5.8	4.0	4.1	3.4	4.1	3.7
Argon	0.06	0.1	0.1	0.1	0.1	0.09
Hydrogen Sulfide	--	0.02	--	--	0.1	0.07
Total	99.96	100.02	100.0	100.0	100.0	99.96
Heating Value, Btu/SCF[i]	276	263	249	260	250	261
Specific Gravity (Air = 1.00)	0.717	0.770	0.798	0.759	0.793	0.732

a. From start of char feed.
b. Tube wall temperatures. Bottom of char bed at 12-3/4 in.; top of char bed at 63 in.
c. Operating conditions and results based on weight of dry feed.
d. (Char-feed bulk density) X (char-bed volume)/char-feed rates.
e. Char-bed volume/(CF/min feed gas at reactor pressure and temperature).
f. Steam + oxygen + nitrogen. (CF/s feed gas at reactor pressure and temperature)/ cross-sectional area of reactor.
g. By ash balance, except Run EGO-20, by carbon balance.
h. Based on weight liquid recovered, except Run EGO-19, by hydrogen + oxygen balance.
i. Gross: gas saturated at 60°F, 30-in. Hg pressure. SCF: dry gas volume in SCF at 60°F, 30-in. Hg pressure.

Table 4b-A7, Part 3. OPERATING CONDITIONS AND RESULTS OF STEAM-OXYGEN GASIFICATION OF COAL CHAR IN A 6-INCH REACTOR-TUBE OF A GASIFICATION DEVELOPMENT UNIT (Runs EGO-13 through EGO-42, EGO-44 through EGO-60)

Coal	Partially Gasified FMC Bituminous Coal Char						
Source	Residue. Runs EGO-6 to EGO-15	Residue. Runs EGO-9 to EGO-15	Residue. Runs EGO-9 to EGO-15	Residue. Runs EGO-9 to EGO-15	Residue. Runs EGO-25 to EGO-27	Residue. Runs EGO-18 to EGO-20	Residue Runs EGO-19 to EGO-[illegible]
Sieve Size, USS	−10+80	−10+80	−10+80	−10+80	−10+80	−10+80	−10+80
Run No.	EGO-24	EGO-25	EGO-26	EGO-27	EGO-28	EGO-29	EGO-[illegible]
Duration of Test, hr	3-1/4	4	5-1/4	4	3-3/4	5	[illegible]
Steady-State Operating Period, min[a]	121-186	160-220	225-310	159-207	148-278	193-303	197-292
OPERATING CONDITIONS							
Char-Bed Height, in.	50-1/4	50-1/4	50-1/4	50-1/4	50-1/4	50-1/4	50-1/4
Reactor Pressure, psig	456	457	451	450	444	541	585
Reactor Temperature, °F							
Tube Wall, inches from bottom[b]							
8	1475	1180	1390	1360	1360	1395	1495
12	1140	795	850	885	960	950	940
16	1550	1405	1375	1310	1555	1470	1285
18	1760	1725	1775	1740	1745	1775	1760
22	1710	1760	1735	1745	1710	1725	1690
24	1720	1760	1745	1655	1725	1735	1685
30	1710	1680	1760	1725	1725	1785	1740
34	1725	1760	1750	1770	1750	1765	1710
38	1675	1690	1710	1790	1740	1710	1610
42	1565	1710	1710	1645	1690	1770	1605
45	--	--	--	--	--	--	--
56	1700	1530	1645	1695	1765	--	1695
60	1710	1675	1660	1710	1725	1755	1755
71	1800	1800	1805	1800	1835	1820	1770
75	1565	1635	1685	1610	1670	--	1655
79	1580	1650	1600	1600	1635	1710	1670
Internal , inches from bottom							
14	1880	1660	1600	1670	1700	1835	1865
30	1775	1800	1800	1790	1850	1820	1815
40	1455	1815	1825	1825	1840	1850	1790
50	1645	1655	1640	1680	1695	1835	1690
Average Reaction Zone Temperature, °F	1830	1800	1815	1805	1845	1840	1825
Char-Feed Rate, lb/hr[c]	70.5	33.9	53.3	58.9	49.0	58.5	68.6
Steam Rate, lb/hr	89.4	86.4	87.7	85.8	85.9	124.0	139.1
Steam/Char Ratio, lb/lb	1.27	2.55	1.65	1.46	1.75	2.12	2.03
Oxygen Rate, SCF/hr	388.0	325.0	376.3	360.8	351.2	515.3	530.2
Oxygen/Char Ratio, SCF/lb	5.50	9.60	7.06	6.12	7.16	8.81	7.73
Oxygen Concentration in Feed Gas, mol %	9.5	8.5	9.4	9.6	9.20	9.15	8.84
Fluidizing Nitrogen, SCF/hr	1825	1699	1782	1601	1662	2513	2545
Purge Nitrogen, shell, SCF/hr	283	286	275	254	252	260	287
Char Space Velocity, lb/cu ft-hr	87.4	42.0	66.0	73.0	60.8	72.5	84.9
Char Residence Time, min[d]	19.0	33.9	23.4	19.6	23.0	21.4	18.6

Continued

Steam Residence Time, min[e]	0.086	0.092	0.087	0.093	0.089	0.074	0.075
Superficial Feed Gas Velocity, ft/s[f]	0.690	0.650	0.687	0.647	0.675	0.820	0.804
OPERATING RESULTS							
Product-Gas Rate, nitrogen-free, SCF/hr	1287	962	1160	1077	1121	1736	1906
Product-Gas Yield, SCF/lb	18.26	28.40	21.77	18.29	22.86	29.69	27.79
Hydrogen Yield, SCF/lb	6.83	10.39	8.01	6.58	8.71	10.72	10.00
Hydrocarbon Yield, SCF/lb	0.767	1.02	0.784	0.731	0.80	1.13	1.19
Carbon Oxides Yield, SCF/lb	10.63	16.92	12.95	10.93	13.30	17.81	16.53
Residue Char, lb/hr[g]	40.70	10.64	25.84	32.04	21.29	17.25	26.01
Bayonet Filter Fines, lb/hr	1.68	1.13	1.08	2.03	1.65	1.64	1.53
Sintered Ash, lb/hr	nil	0.788	nil	2.22	2.88	nil	nil
Condensed Liquids, lb/hr[h]	75.91	66.18	68.59	64.36	65.38	92.35	105.7
Net MAF Char Gasified, wt %	49.6	72.1	53.9	46.4	60.4	73.3	70.2
Carbon Gasified, wt %	49.8	73.1	54.6	46.9	61.1	74.9	71.1
Steam Reacted, lb/hr	18.2	20.4	20.0	22.2	20.5	32.5	35.4
Steam Reacted, % of steam fed	19.4	23.6	22.6	25.6	23.9	26.0	25.1
Steam Concentration in Product Gas, mol %	55.3	59.1	55.4	55.7	55.1	52.8	53.8
Overall Material Balance, %	99.9	94.6	96.5	95.8	96.4	96.9	99.2
Carbon Balance, %	99.7	96.3	96.1	101.9	99.2	94.4	100.0
Hydrogen Balance, %	107.5	97.6	102.0	98.2	100.6	100.0	100.8
Oxygen Balance, %	99.7	93.5	95.9	92.8	94.4	97.4	98.8
PRODUCT GAS PROPERTIES							
Gas Composition, nitrogen-free, mol %							
Carbon Monoxide	25.0	22.7	26.0	25.1	26.3	26.2	25.5
Carbon Dioxide	33.2	36.9	33.5	34.7	31.9	33.8	34.0
Hydrogen	37.4	36.6	36.8	36.0	38.1	36.1	36.0
Methane	4.2	3.6	3.6	4.0	3.5	3.8	4.3
Argon	0.13	0.1	0.1	0.1	0.1	0.1	0.15
Hydrogen Sulfide	0.1	0.06	0.03	0.1	0.1	0.08	0.07
Total	100.03	99.96	100.03	100.0	100.0	100.08	100.02
Heating Value, Btu/SCF[i]	240	224	236	234	240	236	238
Specific Gravity (Air = 1.00)	0.802	0.832	0.811	0.823	0.790	0.818	0.818

a. From start of char feed.

b. Tube wall temperatures. Bottom of char bed at 12-3/4 inches; top of char bed at 63 inches.

c. Operating conditions and results based on weight of dry feed.

d. (Char-feed bulk density) X (char-bed volume)/char-feed rates.

e. Char bed volume/(CF/min feed gas at reactor pressure and temperature).

f. Steam + oxygen + nitrogen. (CF/s feed gas at reactor pressure and temperature)/cross-sectional area of reactor.

g. By ash balance.

h. Based on weight liquid recovered.

i. Gross: gas saturated at 60°F, 30-in Hg pressure. Dry gas volume in SCF at 60°F and 30-in. Hg pressure.

Table 4b-A7, Part 4. OPERATING CONDITIONS AND RESULTS OF STEAM-OXYGEN GASIFICATION OF COAL CHAR IN A 6-INCH REACTOR-TUBE OF A GASIFICATION DEVELOPMENT UNIT (Runs EGO-13 through EGO-42, EGO-44 through EGO-60)

Coal	Partially Gasified FMC Bituminous Coal Char	Bituminous Coal Char				Hydrogasified Ireland Mine Bituminous		Bituminous Coal Char	
Source	Residue, Runs EGO-27, EGO-28, and EGO-30	FMC, Project COED				Pittsburgh No. 8 Seam		FMC, Project COED	
Sieve Size, USS	−10 +80	−10 +80	−10+80	−10+80	−10+80	−10+80	−10+80	−10+80	−10+80
								EGO-38	
Run No.	EGO-31	EGO-32	EGO-33[j]	EGO-34	EGO-35	EGO-36	EGO-37	Part A	Part B
Duration of test, hr	3-3/4	3-1/2	3-1/2	4	3-3/4	4	4-1/4		
Steady-State Operating Period, min[a]	151-211	152-182	160-210	150-240	123-218	175-235	180-255	122-192	207-263
OPERATING CONDITIONS									
Char-Bed Height, in.	50-1/4	50-1/4	50-1/4	50-1/4	50-1/4	50-1/4	50-1/4	30-1/4	50-1/4
Reactor Pressure, psig	578	545	446	502	573	492	564	506	508
Reactor Temperature, °F									
Tube Wall, inches from bottom[b]									
8	1450	1330	1295	1420	1320	1280	1340	1345	1470
12	700	715	650	1065	1135	1030	1245	1160	1260
16	1170	845	1225	1210	1715	1545	1590	1540	1575
18	1755	1610	1730	1780	1745	1730	1790	1750	1745
22	1650	1550	1655	1680	1715	1725	1765	1730	1715
24	1680	1550	1685	1715	1740	1730	1770	1735	1720
30	1735	1516	1715	1700	1730	1730	1790	1760	1740
34	1675	1480	1715	1755	1755	1740	1795	1750	1740
38	1465	1375	1680	1710	1725	1700	1740	1705	1730
42	1460	1565	1670	1700	1760	1700	1730	1705	1680
45	--	--	--	--	--	--	--	--	--
56	1730	1560	1660	1710	1765	1700	1760	1635	1675
60	1750	--	1690	1665	1725	1630	1670	--	--
71	1685	1520	1600	1380	1590	1595	1717	1605	1650
75	1685	1535	1585	1430	1630	1605	1715	1575	1605
79	1690	1540	1600	1445	1635	1555	1675	1510	1530
Internal, inches from bottom									
14	1860	1735	1930	1925	1995	1930	1910	1930	1905
30	1815	1720	1835	1815	1860	1810	1830	1830	1800
40	1825	1670	1810	1795	1805	--	1850	--	--
50	1785	1620	1750	1710	1755	1700	1770	--	--
Average Reaction Zone Temperature, °F	1835	1710	1860	1845	1885	1870	1865	1880	1850
Char-Feed Rate, lb/hr[c]	69.6	49.3	90.2	80.4	69.68	48.77	65.28	60.31	67.61
Steam Rate, lb/hr	134.1	115.3	128.9	83.3	116.7	89.07	116.86	89.55	90.14
Steam/Char Ratio, lb/lb	1.93	2.34	1.43	1.04	1.68	1.83	1.79	1.48	1.33
Oxygen Rate, SCF/hr	547.3	446.8	449.0	353.8	478.9	334.6	518.5	359.9	379.0
Oxygen/Char Ratio, SCF/lb	7.86	9.07	4.98	4.40	6.87	6.86	7.94	5.97	5.61
Oxygen Concentration in Feed Gas, mol %	9.23	8.14	9.20	9.29	8.80	8.79	9.37	9.11	9.59
Fluidizing Nitrogen, SCF/hr	2568	2616	1724	1703	2511	1602	2560	1709	1679
Purge Nitrogen, shell, SCF/hr	196	267	282	177	279	198	218	213	215
Char Space Velocity, lb/cu ft-hr	74.3	52.6	96.2	85.7	74.3	52.02	69.62	106.9	72.11

Continued

Char Residence Time, min[d]	20.4	32.5	18.3	21.4	23.6	23.9	16.72	15.8	23.5
Steam Residence Time, min[e]	0.086	0.091	0.081	0.117	0.091	0.113	0.089	0.067	0.114
Superficial Feed Gas Velocity, ft/s[f]	0.808	0.765	0.865	0.599	0.765	0.617	0.783	0.625	0.615
OPERATING RESULTS									
Product Gas Rate, nitrogen-free, SCF/hr	1805	994.8	1864	1270	1759	1192	1860	1358	1534
Product Gas Yield, SCF/lb	25.92	20.19	20.66	15.80	25.24	24.44	28.49	22.52	22.69
Hydrogen Yield, SCF/lb	9.75	5.27	8.08	6.24	9.41	9.66	11.14	8.47	8.53
Hydrocarbon Yield, SCF/lb	1.04	0.969	0.847	0.727	1.03	1.10	1.28	0.901	1.09
Carbon Oxides Yield, SCF/lb	15.11	13.93	11.71	8.96	14.74	13.49	16.04	13.09	13.00
Residue Char, lb/hr[g]	24.98	20.39	42.05	52.03	29.34	20.80	24.80	27.22	29.90
Bayonet Filter Fines, lb/hr	4.05	1.50	4.40	1.46	1.56	1.63	2.69	1.44	1.61
Sintered Ash, lb/hr	3.14	nil	2.73	0.40	1.05	nil	nil	nil	nil
Condensed Liquids, lb/hr[h]	102.0	97.7	94.0	63.4	90.46	71.36	84.43	65.75	64.92
Net MAF Char Gasified, wt %	66.1	58.4	50.8	39.0	63.1	65.7	70.9	55.7	56.1
Carbon Gasified, wt %	67.2	60.6	51.8	39.1	64.4	67.0	73.3	55.8	56.2
Steam Reacted, lb/hr	33.2	18.0	35.8	20.5	26.70	18.39	33.49	25.47	27.10
Steam Reacted, % of steam fed	24.5	15.6	27.7	24.4	22.8	20.49	28.4	27.9	29.4
Steam Concentration in Product Gas, mol %	54.3	67.4	51.4	51.2	58.2	55.7	48.8	50.4	47.1
Overall Material Balance, %	97.7	96.2	97.6	98.3	100.6	99.1	98.7	97.1	97.9
Carbon Balance, %	94.5	94.6	96.8	100.9	99.6	98.6	100.1	95.9	95.4
Hydrogen Balance, %	101.6	96.7	101.5	104.8	104.5	105.7	103.3	100.2	102.8
Oxygen Balance, %	96.3	96.8	97.6	96.4	101.0	98.6	98.4	97.2	98.8
PRODUCT GAS PROPERTIES									
Gas Composition nitrogen-free, mol%									
Carbon Monoxide	24.4	19.7	28.1	26.6	27.4	21.8	22.3	26.7	27.7
Carbon Dioxide	33.9	49.3	28.6	29.1	31.0	33.4	34.0	31.4	29.6
Hydrogen	37.6	26.1	39.1	39.5	37.3	39.5	39.1	37.6	37.6
Methane	4.0	4.8	4.1	4.6	4.1	4.5	4.5	4.0	4.8
Argon	0.1	0.1	0.1	0.07	0.10	0.09	0.10	0.10	0.11
Hydrogen Sulfide	0.03	--	--	0.12	0.12	0.72	--	0.24	0.19
Total	100.03	100.0	100.0	99.99	100.02	100.01	100.00	100.04	100.00
Heating Value, Btu/SCF[i]	237	193	254	256	247	240	240	244	255
Specific Gravity (Air = 1.00)	0.804	0.990	0.760	0.757	0.790	0.784	0.789	0.791	0.777

a. From start of char feed.
b. Bottom of char bed at 12-3/4 in.; top of char bed at 63 in.
c. Operating conditions and results based on weight of dry feed.
d. (Char-feed bulk density) X (char-bed volume)/char-feed rates.
e. Char-bed volume/(CF/min feed gas at reactor pressure and temperature).
f. Steam + oxygen + nitrogen. (CF/s feed gas at reactor pressure and temperature)/cross-sectional area of reactor. Cross-sectional area = 0.2239 sq ft.
g. By ash balance.
h. Based on weight liquid recovered.
i. Gross: gas saturated at 60°F, 30-in. Hg pressure. Dry gas volume in SCF at 60°F and 30-in. Hg pressure.
j. Six-cone feed gas distributor. Feed ports 23/64 inch diameter. Installed for Run EGO-33. Used in all subsequent tests.

Table 4b-A7, Part 5. OPERATING CONDITIONS AND RESULTS OF STEAM-OXYGEN GASIFICATION OF COAL CHAR IN A 6-INCH REACTOR-TUBE OF A GASIFICATION DEVELOPMENT UNIT (Runs EGO-13 through EGO-42, EGO-44 through EGO-60)

Coal	Bituminous Coal Char	Partially Gasified FMC Bituminous Coal Char	Partially Gasified FMC Bituminous Coal Char	Partially Gasified FMC Bituminous Coal Char	Partially Gasified FMC Bituminous Coal Char	Partially Gasified FMC Bituminous Coal Char
Source	FMC, Project COED	Residue, Runs EGO-32 to EGO-34	Residue, Runs EGO-39 to EGO-34	Residue, Runs EGO-31, EGO-39 and EGO-40	Residue. Runs EGO-38 and EGO-39	Residue, Runs EGO-38 and EGO-39
Sieve Size, USS	−10 +80	−10 +80	−10+80	−10+80	−10+80	−10+80
Run No.	EGO-39	EGO-40	EGO-41	EGO-42	EGO-44	EGO-45
Duration of Test, hr	4-1/4	3-3/4	4	4-1/4	4-1/4	4-1/4
Steady-State Operating Period, min[a]	204-259	165-225	190-235	193-253	195-260	185-255
OPERATING CONDITIONS						
Char-Bed Height, in.	30-1/4	30-1/4	30-1/4	30-1/4	50-1/4	66-1/4
Reactor Pressure, psig	501	511	500	499	329	375
Reactor Temperature, °F						
Tube Wall, inches from bottom[b]						
8	1435	1275	--	--	1230	1355
12	1170	1085	1185	1145	1210	1230
16	1635	1540	1545	1125	1560	1655
18	1745	1440	1575	1680	1675	1645
22	1715	1535	1645	1670	1645	1630
24	1735	1610	1625	1660	1645	1655
30	1735	1700	1640	1710	1685	1665
34	1725	1730	1705	1700	1695	1640
38	1690	1670	1530	1540	1675	1625
42	1690	1640	1530	1580	1645	1620
45	--	--	--	--	--	--
56	1575	1580	1515	1665	1680	1625
60	--	1605	--	--	1630	1615
71	1460	1500	1440	1620	1585	1575
75	1490	1460	1380	1585	1540	1570
79	1495	1465	1385	1590	1535	1570
Internal, inches from bottom						
10	--	--	--	--	--	1845
14	1940	1790	1890	1830	1845	--
20	1860	1720	1790	1820	1795	--
25	--	--	--	--	--	1750
30	1805	1855	1765	1785	1785	--
40	1795	1790	1785	1805	1780	--
45	--	--	--	--	--	1725
Average Reaction Zone Temperature, °F	1870	1810	1810	1810	1802	1755
Char Feed Rate, lb/hr[c]	68.81	41.96	48.04	53.57	57.5	57.2
Steam Rate, lb/hr	108.0	94.50	85.78	119.3	140.2	103.5
Steam/Char Ratio, lb/lb	1.57	2.25	1.79	2.23	2.44	1.81
Oxygen Rate, SCF/hr	409.9	246.0	219.3	343.9	333	326
Oxygen/Char Ratio, SCF/lb	5.96	5.86	4.57	6.42	5.79	5.69

Continued

Oxygen Concentration in Feed Gas, mol %	9.50	9.56	10.85	9.00	10.17	13.03
Fluidizing Nitrogen, SCF/hr	1635	440.6	nil	971.0	nil	nil
Purge Nitrogen, shell, SCF/hr	211	247	254	243	170	246
Char Space Velocity, lb/cu ft-hr	121.9	74.7	85.12	94.91	61.3	46.29
Char Residence Time, min^{d}	14.5	22.7	21.0	17.9	25.8	35.2
Steam Residence Time, min^{e}	0.061	0.101	0.130	0.0687	0.088	0.177
Superficial Feed Gas Velocity, ft/s^{f}	0.685	0.418	0.323	0.612	0.793	0.519
OPERATING RESULTS						
Product Gas Rate, nitrogen-free, SCF/hr	1696	769	702	1294	1152	1125
Product Gas Yield, SCF/lb	24.65	18.31	14.61	24.15	20.03	19.66
Hydrogen Yield, SCF/lb	9.88	7.31	5.70	9.52	7.87	7.59
Hydrocarbon Yield, SCF/lb	1.23	0.86	0.88	1.09	0.84	0.98
Carbon Oxides Yield, SCF/lb	13.51	10.13	8.02	13.50	11.28	11.07
Residue Char, lb/hr^{g}	29.05	24.09	28.90	22.10	34.13	26.45
Bayonet Filter Fines, lb/hr	1.45	0.380	0.518	1.096	1.38	0.928
Sintered Ash, lb/hr	0.228	0.471	1.481	1.483	nil	5.24
Condensed Liquids, lb/hr^{h}	80.00	79.64	73.96	94.50	111.2	83.75
Net MAF Char Gasified, wt %	59.4	45.5	38.8	63.9	50.5	55.9
Carbon Gasified, wt %	58.5	46.0	39.3	64.4	51.3	53.4
Steam Reacted, lb/hr	30.5	15.41	12.95	26.6	30.15	21.03
Steam Reacted, % of steam fed	27.6	16.21	14.9	22.0	21.3	20.1
Steam Concentration in Product Gas, mol %	49.8	68.5	68.9	62.5	67.0	61.0
Overall Material Balance, %	97.4	95.1	96.2	96.6	95.0	97.1
Carbon Balance, %	98.5	96.2	95.4	95.2	103.7	97.1
Hydrogen Balance, %	102.1	100.3	102.0	100.2	95.7	103.3
Oxygen Balance, %	96.7	94.0	95.2	96.4	92.2	96.5
PRODUCT GAS PROPERTIES						
Gas Composition, nitrogen-free, mol %						
Carbon Monoxide	25.4	22.6	22.8	22.8	23.5	22.0
Carbon Dioxide	29.4	32.7	32.1	33.1	32.8	34.3
Hydrogen	40.1	39.9	39.0	39.4	39.3	38.6
Methane	5.0	4.7	6.0	4.5	4.2	5.0
Argon	0.08	0.09	0.05	0.08	0.07	0.07
Hydrogen Sulfide	0.00	0.00	0.05	0.12	0.13	0.06
Total	99.98	99.99	100.00	100.00	100.00	100.00
Heating Value, Btu/SCF^{i}	258	246	256	243	242	243
Specific Gravity (Air = 1.00)	0.752	0.773	0.773	0.781	0.782	0.793

a. From start of char feed.
b. Bottom of char bed at 8 inches; top of char bed at 62 inches. Run EGO-45: Bottom of char bed at 8 inches; top of char bed at 74 inches.
c. Operating conditions and results based on weight of dry feed.
d. Six-cone feed-gas distributor; feed ports have 23/64-inch diameter.
e. (Char-feed bulk density) X (char-bed volume)/char-feed rates.
f. Char bed volume/(CF/min feed gas at reactor pressure and temperature).
g. Steam oxygen nitrogen. (CF/s feed gas at reactor pressure and temperature)/cross-sectional area of reactor.
h. By ash balance.
i.

Table 4b-A7, Part 6. OPERATING CONDITIONS AND RESULTS OF STEAM-OXYGEN GASIFICATION OF COAL CHAR IN A 6-INCH REACTOR-TUBE OF A GASIFICATION DEVELOPMENT UNIT (Runs EGO-13 through EGO-42, EGO-44 through EGO-60)

Coal	Partially Gasified FMC Bituminous Coal Char Residue, Runs EGO-41 and EGO-42	Bituminous Coal Char			
Source		FMC, Project COED			
Sieve Size, USS	−10+80	−10+80	−10+80	−10+80	−10+80
Run No.	EGO-46	EGO-47	EGO-48	EGO-49	EGO-50
Duration of Test, hr	4	3	2	4-1/2	4
Steady-State Operating Period, min[a]	170-240	128-158	93-123	170-265	200-245
OPERATING CONDITIONS					
Char-Bed Height, in.	66-1/4	66-1/4	66-1/4	66-1/4	66-1/4
Reactor Pressure, psig	344	521	531	564	511
Reactor Temperature, °F					
Tube Wall, inches from bottom[b]					
8	1300	620	655	815	765
12	1145	1390	1435	1550	1635
16	1335	1515	1480	1635	1655
18	1675	1580	1570	1690	1755
22	1665	1605	1590	1710	1775
24	1690	1620	1600	1710	1775
30	1750	1625	1605	1705	1765
34	1720	1630	1605	1710	1765
38	--	1630	1610	1710	1760
45	--	1635	1610	1705	1755
56	--	1600	1565	1655	1705
60	1680	--	--	1625	1680
71	1600	--	--	1625	1665
75	1580	--	--	1615	1625
78	1565	--	--	1605	1515
Internal, inches from bottom					
10	1845	1720	1630	1785	1870
16	--	1665	1650	1735	1855
25	1730	1645	1635	1720	1785
40	--	1650	1635	1720	1760
45	1840	--	--	--	--
55	--	1645	1635	1705	1740
70	1785	--	--	--	--
73	--	1585	1565	1670	1735
Average Reaction Zone Temperature, °F	1800	1650	1625	1720	1790
Char-Feed Rate, lb/hr[c]	51.37	46.27	55.77	52.41	75.09
Steam Rate, lb/hr	132.30	71.12	118.1	112.8	121.9
Steam/Char Ratio, lb/lb	2.58	1.54	2.12	2.15	1.62
Oxygen Rate, SCF/hr	349.2	273.6	341.8	543.0	556.9
Oxygen/Char Ratio, SCF/lb	6.80	5.91	6.13	10.36	7.42
Oxygen Concentration in Feed Gas, mol %	11.16	6.28	6.41	10.13	9.97
Fluidizing Nitrogen, SCF/hr	nil	2586	2505	2447	2465
Purge Nitrogen, shell, SCF/hr	232	225	263	261	217

Continued

Purge Nitrogen, top pressure tap, SCF/hr	--	--	nil	60.5	55.0
Char Space Velocity, lb/cu ft-hr	41.56	37.43	45.05	42.40	60.75
Char Residence Time, min[d]	37.5	47.9	43.05	41.46	27.95
Steam Residence Time, min[e]	0.133	0.152	0.128	0.129	0.109
Superficial Feed Gas Velocity, ft/s[f]	0.694	0.605	0.716	0.712	0.842
OPERATING RESULTS					
Product-Gas Rate, nitrogen-free, SCF/hr	1118	774.8	868	1481	1947
Product-Gas Yield, SCF/lb	21.75	16.74	15.56	28.26	25.93
Hydrogen Yield, SCF/lb	8.46	-- [j]	5.01	10.34	9.88
Hydrocarbon Yield, SCF/lb	0.805	-- [j]	0.51	1.22	1.01
Carbon Oxides Yield, SCF/lb	12.46	-- [j]	10.02	16.65	15.02
Residue Char, lb/hr[g]	26.93	26.71	30.78	18.67	24.51
Bayonet Filter Fines, lb/hr	1.38	1.53	3.316[k]	2.129[l]	3.089
Sintered Ash, lb/hr	1.66	nil	nil	nil	5.897
Condensed Liquids, lb/hr[h]	109.3	63.33	95.86	84.87	87.76
Net MAF Char Gasified, wt %	61.2	48.8	48.1	75.1	65.7
Carbon Gasified, wt %	62.1	48.9	51.0	79.2	68.8
Steam Reacted, lb/hr	24.27	8.35	23.54	28.73	36.23
Steam Reacted, % of steam fed	18.2	11.65	19.7	25.3	29.2
Steam Concentration in Product Gas, mol %	67.3	63.2	69.9	54.6	48.6
Overall Material Balance, %	96.8	100.2	93.6	94.8	97.7
Carbon Balance, %	103.9	-- [j]	98.1	101.9	100.1
Hydrogen Balance, %	98.5	-- [j]	91.5	100.0	100.4
Oxygen Balance, %	94.9	-- [j]	92.8	92.8	97.3
PRODUCT GAS PROPERTIES					
Gas Composition, nitrogen-free, mol %					
Carbon Monoxide	22.3	-- [j]	18.9	20.0	24.0
Carbon Dioxide	35.0	-- [j]	45.5	38.9	33.9
Hydrogen	38.9	-- [j]	32.2	36.6	38.1
Methane	3.7	-- [j]	3.3	4.3	3.9
Argon	0.05	-- [j]	0.12	0.11	0.10
Hydrogen Sulfide	--	-- [j]	0.00	0.09	0.00
Total	99.95	-- [j]	100.02	100.00	100.00
Heating Value, Btu/SCF[i]	232	-- [j]	195	223	236
Specific Gravity (Air = 1.00)	0.799	0.830	0.921	0.840	0.800

a. From start of char feed.
b. Bottom of char bed at 8-3/4 in.; top of char bed at 75 in.
c. Operating conditions and results based on weight of dry feed.
d. (Char-feed bulk density) X (char-bed volume)/char-feed rates.
e. Char bed volume/(CF/min feed gas at reactor pressure and temperature).
f. Steam + oxygen + nitrogen. (CF/s feed gas at reactor pressure and temperature)/cross-sectional area of reactor.
g. By ash balance.
h. Based on weight liquid recovered.
i. Gross: gas saturated at 60°F, 30-in Hg pressure. Dry gas volume in SCF at 60°F and 30-in. Hg pressure.
j. No product gas sample available.
k. Filter bottom at 1.615 lb/hr; filter top at 1.521 lb/hr.
l. Filter bottom at 0.398 lb/hr; filter top at 1.731 lb/hr.

Table 4b-A7, Part 7. OPERATING CONDITIONS AND RESULTS OF STEAM-OXYGEN GASIFICATION OF COAL CHAR IN A 6-INCH REACTOR-TUBE OF A GASIFICATION DEVELOPMENT UNIT (Runs EGO-13 through EGO-42, EGO-44 through EGO-60)

Coal	Bituminous Coal Char	Bituminous Coal Char	Bituminous Coal Char	Bituminous Coal Char	Bituminous Coal Char	Bituminous Coal Char
Source	FMC, Project COED	FMC, Project COED	FMC, Project COED	FMC, Project COED	FMC, Project COED	FMC, Project COED
Sieve Size, USS	−10+80	−10+80	−10+80	−10+80	−10+80	−10+80
Run No.	EGO-51	EGO-52	EGO-53	EGO-54	EGO-55	EGO-56
Duration of Test, hr	4-1/4	4-1/4	4	3-3/4	4-3/4	5-1/4
Steady-State Operating Period, min[a]	188-258	216-256	170-235[k]	200-218	225-288	180-300[k]
OPERATING CONDITIONS						
Char-Bed Height, in.	66-1/4	66-1/4	34-1/4	66-1/4	66-1/4	66-1/4
Reactor Pressure, psig	557	698	471	465	490	488
Reactor Temperature, °F						
Tube Wall, inches from bottom[b]						
8	800	670	760	885	580	560
12	1450	1455	1105	1390	1490	1315
16	1550	1545	1490	1390	--	1270
18	1720	1750	1740	1660	1690	1685
22	1740	1750	1745	1675	1725	1710
24	1745	1765	1765	1680	1720	1710
30	1750	1750	1775	1685	1745	1735
34	1750	1750	1775	1685	1745	1730
38	1755	1765	1780	1685	1745	1730
45	1755	1750	1780	1685	1740	1730
56	1700	1695	1740	1635	1700	1660
60	1665	--	1610	1580	1640	1635
71	1620	--	1620	1580	1640	1610
75	1610	--	1490	1570	1630	1515
78	1435	--	1505	1475	1485	1425
Internal, inches from bottom						
10	1900	1840	1860	1830	1875	1865
16	1820	1840	1855	1790	1855	1825
25	1755	1810	1805	1710	1775	1755
40	1735	1775	1800	1705	1765	1750
55	1735	1745	1790	1695	1745	1730
73	1695	1715	1710	1665	1705	1690
Average Reaction Zone Temperature, °F	1780	1780	1830	1730	1785	1770
Char-Feed Rate, lb/hr[c]	78.68	61.62	41.17	65.36	69.79	55.89
Steam Rate, lb/hr[d]	114.4	119.5	174.9	226.5	224.1	219.2
Steam/Char Ratio, lb/lb	1.45	1.94	4.25	3.46	3.21	3.92
Oxygen Rate, SCF/hr	498.3	509.0	534.5	536.6	587.7	555.8
Oxygen/Char Ratio SCF/lb	6.33	8.26	12.98	8.21	8.42	9.94
Oxygen Concentration in Feed Gas, mol %	9.83	9.99	10.30	10.14	11.10	10.77
Fluidizing Nitrogen, SCF/hr	2166	2076	979	nil	nil	nil
Purge Nitrogen, shell, SCF/hr	227	232	223	214	350	336

Continued

Purge Nitrogen, top pressure tap, SCF/hr	54	59	62	62	59	72
Char Space Velocity, lb/cu ft-hr	63.6	49.9	64.4	52.9	56.5	45.2
Char Residence Time, min[e]	30.2	33.8	94.0	33.5	29.75	151.0
Steam Residence Time, min[f]	0.132	0.163	0.0552	0.107	0.110	0.114
Superficial Feed Gas Velocity, ft/s[g]	0.698	0.566	0.861	0.852	0.829	0.806
OPERATING RESULTS						
Product-Gas Rate, nitrogen-free, SCF/hr	1803	1812	1433	1958	2636	1976
Product-Gas Yield, SCF/lb	22.92	29.41	29.17[m]	29.96	37.77	28.07[m]
Hydrogen Yield, SCF/lb	9.14	11.94	11.93[m]	12.25	15.90	11.59[m]
Hydrocarbon Yield, SCF/lb	0.963	1.41	0.963[m]	1.917	1.964	1.516[m]
Carbon Oxides Yield, SCF/lb	12.77	15.94	16.16[m]	15.61	19.75	14.82[m]
Residue Char, lb/hr[h]	37.63	13.26	5.349	18.81	13.94	12.53
Bayonet Filter Fine, lb/hr	3.50	2.72	2.23	5.68	3.66	3.59
Sintered Ash, lb/hr	nil	5.90	4.18	nil	nil	nil
Condensed Liquids, lb/hr[i]	75.25	81.56	148.5	184.1	169.18	178.60
Net MAF Char Gasified, wt %	59.9	72.5	75.9[n]	72.6	87.0	84.7[q]
Carbon Gasified, wt %	62.5	76.3	80.1[p]	76.7	91.2	88.5[r]
Steam Reacted, lb/hr	40.84	38.59	26.92	43.40	56.09	41.41
Steam Reacted, % of steam fed	35.2	32.1	15.3	19.1	24.9	18.8
Steam Concentration in Product Gas, mol %	46.7	48.6	68.5	66.4	57.4	65.5
Overall Material Balance, %	94.1	93.2	95.4	96.2	99.2	97.2
Carbon Balance, %	100.6	97.6	98.6	97.1	99.7	96.6
Hydrogen Balance, %	96.2	100.5	101.1	100.9	101.7	101.2
Oxygen Balance, %	91.6	92.2	94.5	95.5	99.3	96.5
PRODUCT GAS PROPERTIES						
Gas Composition, nitrogen-free, mol %						
Carbon Monoxide	23.7	22.1	14.8	15.8	16.3	14.7
Carbon Dioxide	32.0	32.1	40.6	36.3	36.0	38.1
Hydrogen	39.9	40.6	40.9	40.9	42.1	41.3
Methane	4.2	4.8	3.3	6.4	5.2	5.4
Argon	0.07	0.07	0.08	0.06	0.05	0.05
Hydrogen Sulfide	0.09	0.36	0.29	0.56	0.32	0.41
Total	99.96	100.03	99.97	100.02	99.97	99.96
Heating Value, Btu/SCF[j]	244	247	210	244	238	232
Specific Gravity (Air = 1.00)	0.771	0.764	0.815	0.779	0.770	0.789

a. From start of char feed.
b. Bottom of char bed at 8-3/4 inches; top of char bed at 75 inches.
c. Operating conditions and results based on weight of dry feed.
d. Six-cone feed gas distributor. Feed ports have a 23/64-inch diameter.
e. (Char-feed bulk density) X (char-bed volume)/char-feed rates.
f. Char bed volume/(CF/min feed gas at reactor pressure and temperature).
g. Steam + oxygen + nitrogen. (CF/s feed gas at reactor pressure and temperature)/ cross-sectional area of reactor.
h. By ash balance.
i. Based on weight liquid recovered.
j. Gross: gas saturated at 60°F, 30-in. Hg pressure. Dry gas volume in SCF at 60°F and 30-in. Hg pressure.
k. No residue discharge during steady-state operation.
m. Based on hourly char-feed rate plus char in reactor at start of steady-state operation.
n. Based on hourly MAF char-feed rate plus MAF in reactor at start of steady-state operation. Based on char feed rate of 41.17 lb/hr, net MAF char gasified is 84.8%.
p. Based on hourly carbon-feed rate plus carbon in reactor at start of steady-state operation. Based on char feed rate of 41.17 lb/hr, 90.8% of the carbon is gasified.
q. Based on hourly MAF char-feed rate plus MAF char in reactor at start of steady-state operation. Based on char feed rate of 55.89 lb/hr, net MAF char gasified is 87.4%.
r. Based on hourly carbon-feed rate plus carbon in reactor at start of steady-state operation. Based on char-feed rate of 55.89 lb/hr, 91.6% carbon is gasified.

Table 4b-A7, Part 8. OPERATING CONDITIONS AND RESULTS OF STEAM-OXYGEN GASIFICATION OF COAL CHAR IN A 6-INCH REACTOR-TUBE OF A GASIFICATION DEVELOPMENT UNIT (Runs EGO-13 through EGO-42, EGO-44 through EGO-60)

Coal	Bituminous Coal Char			
Source	FMC, Project COED			
Sieve Size, USS	−10+80	−10+80	−10+80	−10+80
Run No.	EGO-57	EGO-58	EGO-59	EGO-60
Duration of Test, hr	4-1/4	4-1/2	5-1/2	4-1/4
Steady-State Operating Period, min[a]	184-259	190-255	255-330	195-255
OPERATING CONDITIONS				
Char-Bed Height, in.	66-1/4	66-1/4	66-1/4	66-1/4
Reactor Pressure, psig	491	501	520	508
Reactor Temperature, °F				
Tube Wall, inches from bottom[b]				
8	610	515	760	625
12	1510	1420	1450	1405
16	--	--	--	1500
18	1660	1650	1730	1565
22	1695	1670	1715	1575
24	1695	1675	1715	1685
30	1720	1715	1740	1710
34	1725	1715	1745	1715
38	1725	1720	1740	1725
45	1705	--	1710	--
56	1650	1645	1670	--
60	1630	1625	1655	1630
71	1575	1555	1620	1615
75	1415	1385	1525	1595
78	1420	1405	1540	1600
Internal, inches from bottom				
10	1815	1830	1850	1835
16	1805	1835	1820	1800
25	1755	1740	1770	1755
40	1740	1735	1760	1750
55	1720	1720	1745	1730
73	1680	1640	1700	1685
Average Reaction Zone Temperature, °F	1765	1770	1775	1760
Char-Feed Rate, lb/hr[c]	64.18	66.04	61.71	69.94
Steam Rate, lb/hr[d]	222.0	225.2	227.6	223.5
Steam/Char Ratio, lb/lb	3.46	3.41	3.69	3.20
Oxygen Rate, SCF/hr	551.5	508.9	596.2	575.0
Oxygen/Char Ratio, SCF/lb	8.59	7.71	9.66	8.22
Oxygen Concentration in Feed Gas, mol %	10.57	9.71	11.09	10.91
Fluidizing Nitrogen, SCF/hr	nil	nil	nil	nil
Purge Nitrogen, shell, SCF/hr	380	384	224	298

Continued

Purge Nitrogen, top pressure tap, SCF/hr	70	57	69	61
Char Space Velocity, lb/cu ft-hr	51.9	53.4	49.9	56.6
Char Residence Time, min[e]	40.8	33.1	32.8	28.85
Steam Residence Time, min[f]	0.114	0.115	0.116	0.117
Superficial Feed Gas Velocity, ft/s[g]	0.808	0.799	0.791	0.787
OPERATING RESULTS				
Product-Gas Rate, nitrogen-free, SCF/hr	2139	2288	2150	2419
Product-Gas Yield, SCF/lb	33.32	34.65	34.84	34.59
Hydrogen Yield, SCF/lb	13.49	14.10	14.53	14.32
Hydrocarbon Yield, SCF/lb	1.93	1.87	1.986	2.006
Carbon Oxides Yield, SCF/lb	17.76	18.47	18.26	18.19
Residue Char, lb/hr[h]	16.62	15.26	14.59	13.05
Bayonet Filter Fine, lb/hr	4.63	4.01	3.51[k]	3.16[m]
Sintered Ash, lb/hr	nil	nil	nil	nil
Condensed Liquids, lb/hr[i]	174.3	172.3	184.3	171.0
Net MAF Char Gasified, wt %	89.0	86.7	83.1	82.4
Carbon Gasified, wt %	94.2	92.2	88.0	86.0
Steam Reacted, lb/hr	48.52	53.8	43.92	52.51
Steam Reacted, % of steam fed	21.8	23.8	19.2	23.5
Steam Concentration in Product Gas, mol %	63.1	61.3	64.3	59.8
Overall Material Balance, %	97.5	98.9	97.2	96.9
Carbon Balance, %	102.2	99.7	99.1	97.1
Hydrogen Balance, %	101.7	99.4	102.5	100.9
Oxygen Balance, %	97.1	97.5	96.9	97.0
PRODUCT GAS PROPERTIES				
Gas Composition, nitrogen-free, mol %				
Carbon Monoxide	15.6	14.6	15.0	15.8
Carbon Dioxide	37.7	38.7	37.4	36.8
Hydrogen	40.5	40.7	41.7	41.4
Methane	5.8	5.4	5.7	5.8
Argon	0.05	0.06	0.07	0.06
Hydrogen Sulfide	0.30	0.58	0.15	0.17
Total	99.95	100.04	100.02	100.03
Heating Value, Btu/SCF[j]	236	230	237	240
Specific Gravity (Air = 1.00)	0.792	0..799	0.780	0.779

a. From start of char feed.

b. Bottom of char bed at 8-3/4 inches; top of char bed at 75 inches.

c. Operating conditions and results based on weight of dry feed.

d. Six-cone feed-gas distributor; feed ports have 23/64-inch diameter.

e. (Char-feed bulk density) X (char-bed volume)/ char-feed rates.

f. Char-bed volume/(CF/min gas at reactor pressure and temperature).

g. Steam + oxygen + nitrogen. (CF/s feed gas at reactor pressure and temperature)/cross-sectional area of reactor.

h. By ash balance.

i. Based on weight liquid recovered.

j. Gross: gas saturated at 60°F, 30-in. Hg pressure. Dry gas volume in SCF at 60°F and 30-in. Hg pressure.

k. Filter bottom at 0.89 lb/hr; filter top at 2.62 lb/hr.

m. Filter bottom: 0.88 lb/hr; filter top: 2.28 lb/hr.

Table 4b-A 8,Part 1. CHEMICAL AND SCREEN ANALYSES OF FEEDS AND RESIDUES OF STEAM-OXYGEN GASIFICATION OF COAL CHAR STUDIES IN A 6-INCH REACTOR TUBE OF A GASIFICATION DEVELOPMENT UNIT

(Runs EGO-13 through EGO-42, EGO-44 through EGO-60)

Run No.	EGO-13 (Part A)		EGO-13 (Part B)		EGO-14		EGO-15		EGO-16			EGO-17		
Sample	Feed	Residue	Feed	Residue	Feed	Residue	Feed	Residue	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines
Proximate Analysis, wt %														
Moisture	4.5	1.9	4.5	1.9	2.8	1.4	2.9	2.9	1.7	0.7	2.1	2.5	4.8	7.8
Volatile Matter	3.2	2.6	3.2	2.5	2.7	2.4	3.5	2.9	2.3	2.5	4.1	3.5	2.9	3.2
Fixed Carbon	80.6	72.5	80.6	73.0	83.2	70.9	81.2	69.1	73.6	60.3	70.0	80.4	74.8	74.0
Ash	11.7	23.0	11.7	22.6	11.3	25.3	12.4	25.1	22.4	36.5	23.8	13.6	17.5	15.0
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	100.0	100.0
Ultimate Analysis (dry), wt %														
Carbon	82.3	70.8	82.3	73.3	83.3	70.4	81.8	70.4	73.7	61.0	71.5	80.3	77.5	79.4
Hydrogen	1.15	0.83	1.15	0.83	1.15	0.92	1.22	0.68	1.06	0.79	1.17	1.14	1.11	0.85
Nitrogen	1.45	0.24	1.45	0.15	1.45	0.76	1.46	0.89	0.52	0.30	0.57	1.32	0.83	0.97
Oxygen	2.38	2.46	2.38	2.62	2.06	1.86	2.14	1.90	0.00	0.57	1.55	2.66	1.96	2.07
Sulfur	0.46	0.08	0.46	0.08	0.44	0.18	0.65	0.24	2.62	0.57	0.89	0.59	0.17	0.45
Ash	12.26	25.59	12.26	23.02	11.60	25.88	12.73	15.89	22.74	36.77	24.32	13.99	18.43	16.26
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.64	100.00	100.00	100.00	100.00	100.00
Screen Analysis, USS, wt %														
-20	27.2	16.3	27.2	16.9	30.9	27.9	20.4	19.2	16.4	16.6	0.4	18.6	17.5	2.0
-30	21.0	21.2	21.0	24.9	19.4	22.3	15.2	16.3	17.7	18.2	0.3	18.8	14.8	0.8
-40	19.4	18.7	19.4	20.3	15.9	18.2	16.6	16.6	16.4	14.7	0.5	19.0	16.3	0.6
-60	21.0	22.1	21.0	20.8	19.7	20.3	24.9	25.1	21.5	16.6	1.1	25.2	25.9	1.1
-80	7.8	9.7	7.8	8.9	9.0	7.0	13.4	13.1	[illegible]	8.0	2.0	11.9	14.0	3.2
-100	2.5	4.3	2.5	4.0	3.4	2.4	5.7	5.1	5.0	3.8	20.4	4.3	5.9	5.6
-200	0.9	5.1	0.9	3.2	1.3	1.1	2.9	3.8	[illegible]	9.9	30.7	1.8	4.0	25.0
-325	0.1	0.8	0.1	0.4	0.1	0.1	0.4	0.4	2.3	5.3	3.5	0.2	0.6	19.0
−325	0.1	1.8	0.1	0.6	0.3	0.7	0.5	0.4	[illegible]	6.9	41.1	0.2	1.0	42.7
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	[illegible]	100.0	100.0	100.0	100.0	100.0
Heating Value, Btu/lb, dry basis	--	--	--	--	--	--	--	--	11,730	--	--	12,231	--	--

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Table 4b -A 8,Part 2.

Run No.	EGO-18			EGO-19			EGO-20			EGO-21			EGO-22			EGO-23		
Sample	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines
Proximate Analysis, wt %																		
Moisture	1.3	0.8	0.7	2.9	0.3	0.7	6.0	0.4	0.7	5.4	0.9	0.7	5.2	0.5	0.7	2.7	0.3	0.7
Volatile Matter	3.0	2.8	2.0	4.0	3.5	4.2	4.5	2.7	4.9	4.5	2.8	4.2	4.5	2.9	3.8	3.7	3.0	4.1
Fixed Carbon	82.7	86.5	80.2	82.0	81.8	78.4	77.9	65.0	77.6	78.8	73.1	75.5	78.5	77.8	71.0	83.8	69.0	75.7
Ash	13.0	9.9	17.1	11.1	14.4	16.7	11.6	31.9	16.8	11.3	23.2	19.6	11.8	18.8	24.5	9.8	27.7	19.5
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	100.0	100.0
Ultimate Analysis (dry), wt %																		
Carbon	82.1	85.7	77.5	82.8	80.4	77.9	81.6	64.9	78.2	82.1	73.5	74.9	81.4	77.3	70.6	84.5	69.0	75.5
Hydrogen	1.26	0.87	0.92	1.23	1.05	0.99	1.14	0.61	0.98	0.97	0.67	0.96	0.94	0.77	0.76	1.12	0.70	0.86
Nitrogen	1.55	1.15	1.37	0.74	1.43	1.47	1.51	0.54	1.32	1.55	0.74	1.22	1.39	1.06	0.98	1.47	0.96	1.27
Oxygen	1.40	2.07	2.28	2.31	2.15	1.85	2.46	1.68	1.60	2.47	1.58	2.24	2.88	1.48	2.10	2.26	1.26	2.03
Sulfur	0.51	0.20	0.68	1.50	0.51	0.81	0.91	0.18	0.95	1.01	0.12	0.95	0.98	0.55	0.89	0.57	0.31	0.66
Ash	13.18	10.01	17.25	11.42	14.46	16.98	12.38	32.09	16.95	11.90	23.39	19.73	12.41	18.84	24.67	10.08	27.77	19.68
Total	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	100.00	100.00
Screen Analysis, USS, wt %																		
-20	24.9	17.6	0.1	32.7	35.5	0.5	24.1	25.7	0.2	21.4	82.6	0.1	18.9	34.4	1.5	38.4	39.5	0.2
+30	22.0	19.5	0.0	20.5	21.4	0.1	19.3	20.3	0.0	19.5	6.9	0.1	19.5	27.9	3.6	21.3	22.9	0.2
+40	19.2	19.3	0.0	17.5	16.7	0.1	16.8	15.7	0.1	19.3	4.2	0.1	21.2	20.5	6.7	15.7	16.2	0.3
+60	22.3	26.3	0.3	18.8	17.7	0.4	18.6	19.2	1.0	23.6	3.0	2.4	29.2	13.9	17.3	16.6	13.6	2.5
+80	9.2	11.7	2.8	6.9	6.6	1.9	7.4	8.8	3.1	8.2	1.0	5.5	9.8	2.2	15.8	5.8	4.0	8.0
+100	1.8	3.2	3.7	2.1	1.3	2.1	2.3	3.0	2.4	2.0	0.4	3.5	0.9	0.3	5.4	1.1	1.0	5.7
+200	0.3	1.6	10.2	1.0	0.3	6.7	5.1	3.4	11.1	2.4	0.7	11.0	0.3	0.3	7.9	0.7	1.5	16.5
+325	0.0	0.4	12.3	0.2	0.2	16.5	2.7	1.4	20.5	1.0	0.3	14.8	0.1	0.2	7.9	0.2	0.6	16.6
-325	0.3	0.4	70.6	0.3	0.3	71.7	3.7	2.5	61.6	2.6	0.9	62.5	0.1	0.3	33.9	0.2	0.7	50.0
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	100.0	100.0	100.0	100.0	100.0	100.0
Heating Value (dry basis), Btu/lb	--	--	--	--	--	--	12,346	--	--	--	--	--	12,372	--	--	12,788	--	--

Table 4b -A 8, Part 3

Run No.	EGO-24			EGO-25			EGO-26			EGO-27			EGO-28			EGO-29			EGO-30		
Sample	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines
Proximate Analysis, wt %																					
Moisture	6.3	0.7	0.7	2.0	0.2	0.7	1.6	7.5	0.7	1.2	0.4	0.7	0.8	0.7	0.7	1.4	0.1	0.7	2.9	0.2	0.7
Volatile Matter	3.2	2.0	3.2	2.6	1.6	3.4	2.6	2.2	3.4	2.4	2.3	2.5	2.2	2.4	2.8	2.9	1.6	2.2	3.2	1.4	3.6
Fixed Carbon	73.3	66.7	73.1	77.4	50.8	62.6	80.0	60.9	65.1	79.7	74.7	61.5	73.8	58.8	64.4	80.0	47.2	66.2	78.0	56.1	63.8
Ash	17.2	30.6	23.0	18.0	47.4	33.3	15.8	29.4	30.8	16.7	22.6	35.3	23.2	38.1	32.1	15.7	51.1	30.9	15.9	42.3	31.9
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	100.0	100.0	100.0	100.0	100.0
Ultimate Analysis (dry), wt %																					
Carbon	77.5	66.7	72.7	77.9	50.7	62.5	79.8	65.5	64.8	78.9	73.9	61.4	73.3	59.4	64.1	80.2	46.7	66.0	79.1	56.5	63.5
Hydrogen	0.79	0.66	0.89	0.78	0.49	0.79	0.81	0.56	0.74	0.82	0.74	0.61	0.68	0.60	0.63	0.90	0.57	0.76	0.87	0.56	0.64
Nitrogen	0.91	0.81	0.99	0.95	0.34	0.59	1.17	0.76	0.72	1.06	0.80	0.65	0.84	0.48	0.57	1.10	0.47	0.57	1.02	0.53	0.72
Oxygen	2.01	0.76	1.64	1.69	0.89	1.98	1.75	1.14	2.11	1.88	1.48	1.29	1.36	1.00	1.89	1.36	0.85	1.23	2.14	0.84	2.49
Sulfur	0.47	0.29	0.53	0.36	0.12	0.67	0.42	0.24	0.54	0.39	0.40	0.39	0.40	0.18	0.42	0.47	0.22	0.34	0.45	0.16	0.55
Ash	18.32	30.78	23.25	18.32	47.46	33.47	16.05	31.80	31.09	16.95	22.68	35.66	23.42	36.34	32.39	15.97	51.19	31.10	16.42	41.41	32.10
Total	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	100.00	100.00	100.00	100.00	100.00
Screen Analysis, USS, wt %																					
+20	21.6	38.2	0.1	19.2	10.1	0.4	20.3	17.9	0.1	22.6	24.1	0.0	16.0	14.2	0.3	19.6	18.6	0.0	27.6	18.5	0.1
+30	18.8	22.2	0.3	21.0	17.0	0.3	19.2	18.4	0.1	21.7	22.8	0.1	20.7	20.2	0.5	21.2	22.3	0.4	22.6	22.3	0.1
+40	18.2	16.1	0.3	19.7	20.5	0.3	18.4	17.8	0.1	18.9	19.1	0.1	20.1	20.6	0.8	18.8	18.8	0.5	18.4	18.8	0.2
+60	25.7	16.0	3.1	26.2	30.6	3.1	26.3	25.4	3.9	22.8	21.4	3.2	26.4	27.1	4.9	25.8	24.3	7.4	20.7	21.7	3.0
+80	10.9	4.7	10.4	10.3	13.8	13.5	11.7	12.5	14.3	9.4	7.8	13.5	12.9	12.2	16.4	10.6	10.1	21.2	8.3	10.2	11.8
+100	2.6	0.9	8.0	1.9	3.7	10.9	2.3	3.4	8.0	2.3	1.9	10.2	2.5	3.2	12.5	2.8	3.1	15.8	1.5	3.3	9.0
+200	1.6	0.9	18.0	1.1	2.8	19.0	1.2	3.1	14.6	1.4	1.5	19.2	1.0	1.6	15.0	0.8	1.8	20.7	0.5	3.2	14.6
+325	0.3	0.5	13.9	0.2	0.5	9.8	0.3	0.7	10.4	0.4	0.7	11.1	0.2	0.3	8.0	0.1	0.4	8.5	0.1	0.8	12.0
−325	0.3	0.5	45.9	0.4	1.0	41.8	0.3	0.8	48.5	0.5	0.7	42.6	0.2	0.6	41.6	0.3	0.6	25.5	0.3	1.2	49.2
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	100.0	100.0	100.0	100.0	100.0
Heating Value (dry basis), Btu/lb	11,358	--	--	11,680	--	--	11,954	--	--	12,080	--	--	10,912	--	--	12,050	--	--	11,948	--	--

Table 4b-A 8, Part 4

Run No.	EGO-31			EGO-32			EGO-33			EGO-34			EGO-35			EGO-36		
Sample	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines
Proximate Analysis, wt %																		
Moisture	1.5	0.3	0.7	0.7	0.3	0.7	0.9	0.3	0.7	0.8	0.2	0.7	0.6	2.7	0.7	1.4	0.7	0.7
Volatile Matter	2.8	1.9	2.8	3.4	2.6	4.4	2.1	1.7	4.6	3.2	1.8	3.3	3.6	1.8	3.3	2.9	2.7	4.1
Fixed Carbon	76.0	48.4	58.2	79.7	59.7	68.9	77.7	67.3	72.3	79.1	73.2	73.4	78.8	60.5	73.5	72.8	45.2	60.0
Ash	19.7	49.4	38.3	16.2	37.4	26.0	18.3	30.7	22.4	16.9	24.8	22.6	17.0	35.0	22.5	22.9	51.4	35.2
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	100.0	100.0
Ultimate Analysis (dry), wt %																		
Carbon	76.2	48.5	58.3	78.0	59.0	68.3	76.9	66.6	72.4	77.3	71.8	72.3	77.7	61.0	73.2	69.1	46.4	61.1
Hydrogen	0.85	0.55	0.68	1.07	0.89	1.10	1.04	0.72	1.10	1.07	0.65	0.88	1.16	0.48	0.86	1.19	0.50	0.74
Nitrogen	1.01	0.44	0.59	1.47	0.88	1.11	1.37	0.80	1.05	1.42	0.66	1.10	1.48	0.59	0.98	0.50	0.22	0.38
Oxygen	1.44	0.77	1.44	2.58	1.34	2.62	1.78	0.90	2.10	2.71	1.83	2.36	2.03	1.79	2.13	3.25	0.10	0.76
Sulfur	0.49	0.22	0.37	0.55	0.34	0.66	0.46	0.23	0.77	0.48	0.16	0.61	0.48	0.12	0.52	2.71	1.05	1.45
Ash	20.01	49.52	38.62	16.33	37.55	26.21	18.45	30.75	22.58	17.02	24.90	22.75	17.15	36.02	22.31	23.25	51.73	35.57
Total	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	100.00	100.00
Screen Analysis, USS, wt %																		
+20	17.1	18.7	0.0	24.2	11.3	0.1	29.1	27.6	5.2	27.3	30.5	0.1	29.7	15.6	0.5	15.1	13.2	0.2
+30	20.2	24.5	0.1	21.0	15.6	0.1	20.1	22.5	2.5	20.0	19.2	0.1	19.0	18.4	0.2	20.5	21.7	0.0
+40	19.6	24.5	0.1	18.6	18.6	0.1	17.2	19.1	2.7	17.7	15.8	0.1	16.4	19.8	0.2	19.8	18.2	0.2
+60	26.8	4.4	3.0	21.7	18.9	2.1	10.6	19.2	7.0	21.2	19.1	2.6	20.0	27.1	3.1	25.9	18.1	3.9
+80	12.8	5.5	11.6	9.3	14.9	7.0	8.1	6.6	10.1	8.6	8.4	7.7	8.6	10.8	9.8	11.2	7.6	12.5
+100	2.5	1.1	8.9	3.7	7.2	6.9	3.4	2.9	10.1	3.8	4.4	11.1	4.2	5.0	14.2	5.1	4.6	13.7
+200	0.6	0.6	12.9	1.1	3.1	13.4	1.1	1.6	12.5	1.2	2.0	17.6	1.7	2.4	23.3	1.8	7.3	20.7
+325	0.2	0.2	9.5	0.1	0.2	11.9	0.2	0.1	7.2	0.1	0.2	9.8	0.2	0.3	9.3	0.3	4.0	13.5
−325	0.2	0.5	53.9	0.3	0.2	58.4	0.2	0.4	42.7	0.1	0.4	50.9	0.2	0.6	39.4	0.3	5.3	35.3
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	100.0	100.0
Heating Value (dry basis), Btu/lb	11,344	--	--	12,034	--	--	11,307	--	--	11,974	--	--	11,953	--	--	11,320	--	--

Table 4b-A 8, Part 5

Run No.	EGO-37				EGO-38			
Sample	Feed	Residue	Top Filter Fines	Bottom Filter Fines	Feed A and B	Residue A	Residue B	Filter Fines A and B
Proximate Analysis, wt %								
Moisture	1.6	1.0	0.7	0.7	2.7	0.3	0.5	0.7
Volatile Matter	2.6	3.1	2.6	5.7	4.1	1.4	1.6	2.4
Fixed Carbon	74.9	44.1	63.0	65.8	79.1	68.1	67.1	65.4
Ash	20.9	51.8	33.7	27.8	14.1	30.2	30.8	31.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Ultimate Analysis (dry), wt %								
Carbon	75.0	46.0	63.5	67.5	79.6	67.3	67.1	65.1
Hydrogen	1.17	0.73	2.75	0.94	1.07	0.68	0.61	0.70
Nitrogen	0.59	0.29	0.33	0.46	1.43	0.68	0.44	0.80
Oxygen	0.00	0.00	0.51	1.64	2.89	0.73	0.80	1.68
Sulfur	2.35	1.54	1.06	1.55	0.58	0.28	0.10	0.61
Ash	21.23	52.35	33.85	27.91	14.43	30.33	30.95	31.11
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Screen Analysis, USS, wt %								
+20	17.7	12.8	0.3	0.2	20.4	5.5	26.4	0.2
+30	22.8	20.1	0.0	0.0	17.9	11.1	27.3	0.0
+40	20.6	19.6	0.0	0.2	16.8	15.8	19.3	0.2
+60	24.1	23.9	1.3	4.7	22.6	32.2	15.9	1.9
+80	9.0	9.4	7.6	13.4	10.7	19.4	5.0	8.1
+100	3.8	4.5	13.2	14.1	5.4	9.7	2.6	12.9
+200	1.6	5.6	27.9	22.0	2.8	4.9	2.1	22.4
+325	0.3	2.2	16.0	14.6	0.8	0.6	0.5	14.2
−325	0.1	1.9	33.7	30.8	2.6	0.8	0.9	40.1
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Heating Value (dry basis), Btu/lb	11,570	--	--	--	12,287	--	--	--

Table 4b-A 8, Part 6

Run No.	EGO-39			EGO-40			EGO-41			EGO-42			EGO-44			EGO-45		
Sample	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines
Proximate Analysis, wt %																		
Moisture	3.4	0.3	0.7	1.3	0.4	0.7	2.3	0.5	0.7	2.7	0.4	0.7	2.1	0.3	0.7	2.2	0.8	0.7
Volatile Matter	9.0	1.6	4.0	3.2	2.0	3.2	3.5	2.4	4.0	3.9	1.9	3.6	3.0	2.0	3.9	3.2	1.5	4.7
Fixed Carbon	76.6	73.4	68.7	76.3	66.2	66.4	71.2	63.8	62.6	71.1	50.1	67.0	74.4	63.9	62.9	71.2	66.9	63.2
Ash	11.0	24.7	26.6	19.2	31.4	29.7	23.0	33.3	32.7	22.3	47.6	28.7	20.5	33.8	32.5	23.4	30.8	31.4
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	100.0	100.0
Ultimate Analysis (dry), wt %																		
Carbon	80.0	72.5	68.1	75.8	65.2	66.3	71.8	63.2	62.6	71.9	50.0	67.2	74.9	63.6	63.0	71.6	66.9	63.9
Hydrogen	1.56	0.78	0.91	1.05	0.75	0.85	1.02	0.75	0.87	0.99	0.66	0.95	0.83	0.58	0.82	0.89	0.66	1.00
Nitrogen	1.46	0.87	1.08	1.23	0.78	0.79	1.21	0.69	1.00	1.11	0.50	0.93	1.03	0.40	0.80	0.73	0.50	0.78
Oxygen	5.01	0.77	2.73	2.08	1.53	1.74	2.08	1.76	2.15	2.74	0.97	1.72	1.94	1.45	2.13	2.41	0.81	2.09
Sulfur	0.61	0.28	0.53	0.36	0.22	0.43	0.37	0.17	0.51	0.36	0.07	0.29	0.40	0.07	0.43	0.40	0.10	0.57
Ash	11.36	24.80	26.65	19.48	31.52	29.89	23.52	33.43	32.87	22.90	47.80	28.91	20.90	33.90	32.82	23.97	31.03	31.66
Total	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	100.00	100.00
Screen Analysis, USS, wt %																		
+20	35.5	11.6	0.1	22.9	20.8	0.4	19.4	21.1	0.2	20.9	18.4	0.1	14.4	10.4	0.1	14.2	11.9	0.3
+30	20.5	17.5	0.0	22.5	21.8	0.0	20.3	20.6	0.0	21.7	23.4	0.0	19.3	18.1	0.2	20.8	22.1	0.0
+40	16.0	17.5	0.1	19.1	18.4	0.2	19.2	18.0	0.0	20.2	20.9	0.1	19.0	18.9	0.4	19.6	22.0	0.2
+60	16.6	28.8	1.7	21.7	20.3	2.2	24.9	22.6	1.7	23.5	22.8	3.6	26.6	27.6	3.3	27.0	25.4	2.4
+80	6.5	12.6	6.2	9.1	8.8	10.5	10.8	9.8	7.3	9.2	8.5	12.6	13.1	12.1	8.9	12.4	10.1	9.0
+100	3.0	6.0	9.2	3.6	4.9	14.1	4.2	4.7	8.9	3.2	3.5	12.8	5.5	6.2	11.4	4.5	4.6	10.5
+200	1.2	2.5	16.5	0.7	3.1	15.2	0.8	1.8	11.1	0.9	1.5	14.2	1.4	4.4	16.3	0.9	2.7	15.2
+325	0.3	0.1	12.3	0.1	0.4	8.3	0.1	0.3	10.3	0.2	0.3	11.1	0.3	1.0	12.1	0.3	0.5	12.9
−325	0.4	0.3	53.9	0.3	1.5	49.1	0.3	1.1	60.5	0.2	0.7	45.5	0.4	1.3	47.3	0.3	0.7	49.5
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	100.0	100.0
Heating Value (dry basis), Btu/lb	12,256	--	--	11,526	--	--	10,911	--	--	10,844	--	--	11,290	--	--	10,770	--	--

Table 4b-A 3, Part 7

Run No.	EGO-46			EGO-47			EGO-48				EGO-49				EGO-50		
									Filter Fines				Filter Fines				
Sample	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Bottom	Top	Feed	Residue	Bottom	Top	Feed	Residue	Filter Fines
Proximate Analysis, wt %																	
Moisture	2.5	2.9	0.7	1.2	1.0	0.7	2.2	1.1	0.7	0.7	1.5	0.4	0.7	0.7	2.7	0.8	0.7
Volatile Matter	2.6	1.7	3.0	2.9	2.6	5.9	3.9	2.5	5.0	8.3	3.0	2.4	5.6	5.1	3.2	2.5	5.4
Fixed Carbon	66.5	49.3	60.5	74.6	61.3	60.7	66.2	48.8	65.1	56.5	73.4	38.7	70.3	55.2	74.5	63.3	62.7
Ash	28.4	46.1	35.8	21.3	35.1	32.7	27.7	47.6	29.2	34.5	22.1	58.5	23.4	39.0	19.6	33.4	31.2
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	100.0
Ultimate Analysis (dry) wt %																	
Carbon	67.8	50.9	60.6	72.6	60.8	61.3	65.6	49.8	64.4	58.3	71.6	39.1	68.8	56.0	73.9	62.8	62.9
Hydrogen	0.82	0.52	0.72	0.99	0.80	0.89	1.02	0.65	0.85	0.72	0.94	0.45	1.02	0.75	1.16	0.74	0.85
Nitrogen	0.87	0.34	0.64	1.04	0.57	0.80	0.86	0.31	0.84	0.88	1.05	0.29	1.01	0.50	1.05	0.56	0.70
Oxygen	1.14	0.68	1.63	1.42	0.43	1.83	0.82	0.44	2.09	3.21	1.12	0.00	2.15	1.74	0.99	0.55	1.61
Sulfur	0.28	0.07	0.35	2.38	1.92	2.22	3.37	0.72	2.43	2.19	2.90	1.80	3.43	1.77	2.77	1.70	2.49
Ash	29.09	47.49	36.06	21.57	35.48	32.96	28.33	48.08	29.39	34.70	22.39	58.70	23.59	39.24	20.13	33.65	31.45
Total	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	100.00
Screen Analysis, USS, wt %																	
+20	13.0	14.0	0.2	8.6	3.3	2.1	6.5	7.8	0.4	0.0	11.6	37.4	0.5	2.6	15.6	33.0	0.7
+30	20.9	25.8	0.3	13.2	4.6	0.3	11.9	16.3	0.0	0.0	16.4	27.9	0.3	1.3	16.3	22.7	0.2
+40	20.6	24.1	0.5	16.9	7.8	0.3	17.0	17.6	0.1	0.1	17.5	17.5	0.1	1.5	16.2	16.0	0.2
+60	27.0	24.3	3.9	30.5	29.2	0.6	31.8	25.6	0.6	1.2	26.1	12.4	2.3	4.1	25.9	16.4	1.3
+80	12.8	7.7	11.2	16.9	27.6	3.6	17.3	11.3	2.8	3.8	15.0	2.1	6.3	6.3	14.0	5.9	6.4
+100	4.2	2.4	13.0	8.9	16.5	8.5	9.9	5.9	6.2	7.5	8.5	0.7	9.0	9.2	7.4	2.7	11.8
+200	0.9	1.0	14.6	4.1	10.1	17.9	5.2	8.3	17.6	17.9	4.0	0.6	18.6	25.0	3.6	1.9	22.8
+325	0.2	0.2	8.9	0.4	0.6	14.2	0.1	3.3	17.8	17.0	0.3	0.3	17.4	13.7	0.3	0.6	13.5
−325	0.4	0.5	47.4	0.5	0.3	52.5	0.3	3.9	54.5	52.5	0.6	1.1	45.5	36.3	0.7	0.8	43.1
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	100.0
Heating Value (dry basis), Btu/lb	10,130	--	--	11,193	--	--	10,121	--	--	--	10,900	--	--	--	11,389	--	--

Table 4b-A 8, Part 8

Run No.	EGO-51			EGO-52			EGO-53			EGO-54			EGO-55			EGO-56		
Sample	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines
Proximate Analysis, wt %																		
Moisture	2.1	0.8	0.7	1.1	0.5	0.7	1.3	0.3	0.7	1.6	2.8	0.7	1.9	0.2	0.7	1.4	0.3	0.7
Volatile Matter	3.4	1.6	5.0	3.2	3.2	8.4	3.3	1.6	5.1	2.9	2.7	5.8	3.0	1.1	5.0	3.1	1.1	4.0
Fixed Carbon	70.6	50.4	58.1	74.2	60.6	52.7	73.1	20.7	50.3	74.0	28.4	67.8	76.8	18.3	46.1	73.0	12.2	42.3
Ash	23.9	47.2	36.2	21.5	35.7	38.2	22.3	77.4	43.9	21.5	66.1	25.7	18.3	80.4	48.2	22.5	86.4	53.0
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	100.0	100.0	100.0	100.0	100.0	100.0
Ultimate Analysis (dry), wt %																		
Carbon	69.7	50.1	58.4	72.2	59.6	55.1	71.4	21.5	51.5	72.5	31.0	67.3	75.6	19.9	47.6	71.3	13.7	43.5
Hydrogen	1.05	0.54	0.70	1.01	0.77	0.87	1.04	0.35	0.82	1.00	0.42	1.04	1.09	0.38	0.74	1.07	0.07	0.50
Nitrogen	0.96	0.36	0.58	0.97	0.78	0.65	0.97	0.29	0.50	1.02	0.24	0.82	1.09	0.10	0.44	1.07	0.09	0.39
Oxygen	1.16	0.24	1.04	1.10	0.27	2.73	0.55	0.00	1.06	0.93	0.00	2.44	0.92	0.00	1.19	1.16	0.00	1.22
Sulfur	2.74	1.16	2.83	3.01	2.73	2.23	3.40	0.26	1.89	2.71	0.56	2.50	2.66	0.09	1.44	2.55	0.13	0.97
Ash	24.39	47.60	36.45	21.71	35.85	38.42	22.64	77.68	44.23	21.84	68.05	25.90	18.64	80.57	48.59	22.85	86.66	53.42
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.08	100.00	100.00	100.27	100.00	100.00	101.04	100.00	100.00	100.65	100.00
Screen Analysis, USS, wt %																		
+20	8.1	10.4	2.5	12.9	8.6	0.7	15.1	14.6	3.0	15.1	19.2	1.0	16.2	8.7	2.8	10.9	3.1	1.0
+30	13.1	15.9	0.5	14.2	17.5	0.2	16.6	15.6	0.2	18.9	21.3	0.4	17.7	14.5	0.8	15.3	3.7	0.3
+40	17.8	17.7	0.4	15.6	21.3	0.2	17.0	17.1	0.2	18.4	18.5	0.3	17.7	17.0	0.5	18.6	7.3	0.3
+60	33.3	27.5	1.2	18.0	30.4	0.9	24.4	26.0	1.1	25.3	20.6	0.6	24.2	26.6	0.8	29.9	21.5	0.6
+80	16.0	13.4	3.8	15.8	11.6	2.9	12.9	12.9	3.5	11.9	8.2	0.8	12.4	12.5	1.5	15.1	17.5	1.3
+100	7.8	7.3	7.6	8.5	5.1	5.3	7.0	6.7	6.7	6.3	4.3	1.4	7.0	6.8	4.2	7.3	13.4	3.5
+200	3.3	6.0	21.4	4.0	3.7	18.1	4.7	5.9	23.8	3.1	5.5	14.0	3.5	9.1	22.8	2.4	26.0	21.3
+325	0.3	0.8	16.9	0.3	1.0	18.3	0.9	0.6	14.6	0.4	1.3	28.0	0.5	2.3	16.0	0.2	4.5	16.8
−325	0.3	1.0	45.7	0.7	0.8	53.4	1.4	0.6	46.9	0.6	1.1	53.5	0.8	2.5	50.6	0.3	3.0	54.9
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	100.0	100.0
Heating Value (dry basis), Btu/lb	10,752	--	--	11,182	--	--	10,970	--	--	11,140	--	--	11,690	--	--	11,000	--	--

Table 4b-A 8, Part 9

Run No.	EGO-57			EGO-58			EGO-59				EGO-60			
									Filter Fines				Filter Fines	
Sample	Feed	Residue	Filter Fines	Feed	Residue	Filter Fines	Feed	Residue	Bottom	Top	Feed	Residue	Bottom	Top
Proximate Analysis, wt %														
Moisture	1.3	0.2	0.7	1.2	0.1	0.7	0.9	0.2	0.7	0.7	1.0	0.7	0.7	0.7
Volatile Matter	3.6	1.3	4.1	3.2	1.0	5.2	3.0	1.3	5.4	4.9	3.9	3.6	7.7	7.9
Fixed Carbon	67.8	2.7	55.9	72.0	7.4	49.8	74.9	21.0	55.9	45.7	75.6	27.9	57.8	45.3
Ash	27.3	95.8	39.3	23.6	91.5	44.3	21.2	77.5	38.0	48.7	19.5	67.8	33.8	46.1
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
Ultimate Analysis (dry), wt %														
Carbon	66.3	4.5	57.1	70.0	9.4	50.9	73.0	22.3	56.3	47.8	74.5	31.4	61.1	49.3
Hydrogen	0.81	0.04	0.70	0.81	0.13	0.77	0.95	0.18	0.63	0.59	1.03	0.45	0.87	0.59
Nitrogen	0.94	0.04	0.54	0.99	0.05	0.52	0.98	0.11	0.63	0.47	1.11	0.23	0.65	0.47
Oxygen	1.18	0.00	0.71	0.84	0.00	1.41	0.30	0.00	2.32	0.90	1.37	0.00	1.89	1.62
Sulfur	3.06	0.06	1.41	3.50	0.07	1.74	3.35	0.19	1.88	1.20	2.27	0.25	1.46	1.59
Ash	27.71	95.97	39.54	23.86	91.55	44.66	21.42	77.70	38.24	49.04	19.72	68.29	34.03	46.43
Total	100.00	100.61	100.00	100.00	101.20	100.00	100.00	100.48	100.00	100.00	100.00	100.62	100.00	100.00
Screen Analysis, USS, wt %														
+20	8.9	8.0	0.4	17.7	16.1	1.2	17.3	5.4	0.2	1.5	20.2	15.2	0.3	4.2
+30	12.7	15.1	0.1	16.9	18.3	0.3	19.6	10.0	0.1	0.1	22.2	17.4	0.1	0.4
+40	17.6	20.3	0.1	16.4	19.0	0.3	18.9	14.0	0.1	0.1	20.0	19.8	0.1	0.3
+60	33.0	28.8	0.3	25.1	22.7	0.6	24.9	27.0	0.8	0.4	21.4	25.6	1.0	0.8
+80	16.9	10.2	2.1	13.6	7.8	2.5	11.1	15.9	3.7	2.7	9.0	10.1	4.2	3.0
+100	7.8	4.6	5.8	6.7	4.1	5.4	4.8	9.7	6.9	6.2	4.1	5.1	7.5	6.5
+200	2.7	7.1	23.7	2.4	6.8	21.7	2.3	14.0	24.0	20.9	1.8	4.9	23.0	19.8
+325	0.1	2.8	17.9	0.4	2.7	17.2	0.4	2.3	18.2	14.0	0.4	0.8	18.5	13.5
−325	0.3	3.1	49.6	0.8	2.5	50.8	0.7	1.7	46.0	54.1	0.9	1.1	45.3	51.5
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
Heating Value (dry basis), Btu/lb	10,330	--	--	10,819	--	--	11,200	--	--	--	11,466	--	--	--

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PART 4c

Steam-Iron Gasification

TABLE OF CONTENTS, PART 4c

LIST OF FIGURES, PART 4c

LIST OF TABLES, PART 4c

4c.0 Summary of Steam-Iron Gasification

A summary of this work appears in section 4.0.

4c.1 Introduction

4c.1.1 Equilibrium Considerations

The steam-iron reactions are based on reversible, cyclic reduction and oxidation of iron oxides. Three iron phases enter into these reactions — magnetite (Fe_3O_4), Wustite (FeO) and metallic iron (Fe). The highest oxidation form, Fe_2O_3 (hematite) is not produced in the system.

The following reactions describe the steam-iron system:

Reduction

1. $Fe_3O_4 + H_2 \rightarrow 3FeO + H_2O$ (1)
2. $Fe_3O_4 + CO \rightarrow 3FeO + CO_2$ (2)
3. $FeO + H_2 \rightarrow Fe + H_2O$ (3)
4. $FeO + CO \rightarrow Fe + CO_2$ (4)

Oxidation

5. $Fe + H_2O \rightarrow FeO + H_2$ (5)
6. $3FeO + H_2O \rightarrow Fe_3O_4 + H_2$ (6)

Note that reactions 5 and 6 are the reverse of reactions 3 and 1, respectively.

The equilibrium constants for the steam-iron process reactions are shown in Figure 4c-1 as a function of temperature in the range of 1050°F and 1800°F. It can be seen that, as oxidation progresses and the H_2O/H_2 ratio decreases, the oxidation of Wustite ceases before the oxidation of metallic iron. In like manner, as reduction progresses and the H_2O/H_2 and CO_2/CO ratios increase, the reduction of Wustite ceases before the reduction of magnetite.

For steady cyclic operations, the moles of elemental iron (Fe), oxidized by steam, must be formed by reduction of Wustite (FeO) by CO and H_2. Also, the moles of magnetite (Fe_3O_4) formed in the oxidizer by reaction 6 must be reduced by reactions 1 and 2 in the reductor.

The problems of equilibrium and conversion connected with operation of the steam-iron process will now be considered.

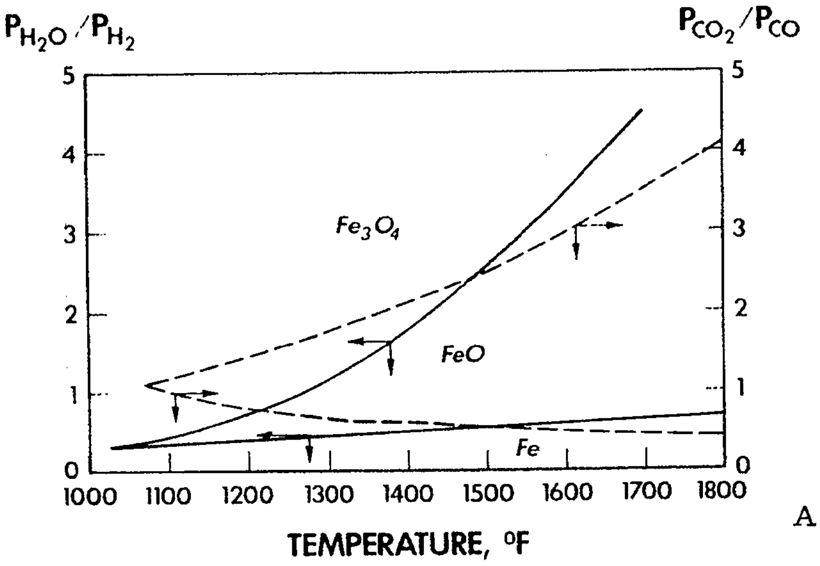

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Figure 4c-1. EQUILIBRIUM CONSTANTS FOR STEAM-IRON PROCESS REACTIONS

Table 4c-1 summarizes oxygen transfer and resulting gas conversions for the system operating under isothermal conditions when using a typical reducing gas ($CO_2 + H_2O/CO + H_2$ ratio of 0.25). As shown, production of Fe stops when the H_2O/H_2 ratio exceeds 0.52 at 1500°F, and production of FeO stops at a H_2O/H_2 ratio of 2.52. This corresponds to 2.6 atoms of oxygen transferred by reactions 1 and 2 for each atom of oxygen transferred by reactions 3 and 4.

Table 4c-1. CYCLIC COUNTERCURRENT CONVERSIONS (Isothermal Operation at 1500°F)

Reduction	Reducing Gas	FeO → Fe	Fe_3O_4 → FeO
H_2 + CO, mol	5.6	4.6	2.0
$H_2O + CO_2$, mol	1.4	2.4	5.0
Oxygen Transferred, mol	--	1.0	2.6
$H_2O + CO_2/H_2 + CO$	0.25	0.52	2.52
Gas Conversion, %	0	18	64

Oxidation	Steam	FeO → Fe_3O_4	Fe → FeO
H_2, mol	0	2.6	3.6
H_2O, mol	9.2	6.6	5.6
Oxygen Transferred, mol	--	2.6	1.0
H_2/H_2O		0.40	0.64
Steam Conversion, %	0	28	39

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In subsequent oxidation at 1500 °F, this stoichiometry, rather than the thermodynamics, is limiting. To maintain cyclic material balances, the feed steam must add 2.6 atoms of oxygen to the iron solids by reaction 6 before 28% conversion of the steam is attained. Because the Fe content of the feed solids is sufficient to transfer only 1 atom of oxygen by reaction 5, maximum steam conversion is 39%, not 66% as the equilibrium ratio of 1.92 would indicate.

The only way to balance the stoichiometry so that both reducing and oxidizing gases can achieve equilibrium conversion is to operate the reducer at a higher temperature than the oxidizer. For example, if reduction is carried out at 1750 °F and oxidation at 1350 °F, near-equilibrium conversions of 80 and 60% can be achieved for the reducing and oxidizing gases. This requires manipulating reaction zone temperatures, which is difficult because of the large recirculating stream of solids and their relatively large heat-carrying capacity. However, several schemes can be used for this purpose which would normally be applied where high steam conversion is desired, such as for the production of hydrogen.

For the HYGAS process, it is not necessary to attain high steam conversion, because the process requires only about 40-45% hydrogen in the feed steam for thermal and kinetic balance. In this application, then, the steam-iron process is designed to attain high reducing gas conversion to maximize total carbon utilization in the process, while at the same time only 40 to 45% steam conversion is attained in the oxidizer.

Because of the cyclic nature of the process chemistry, one may note, the recirculating solids stream tends, after several cycles, toward a high FeO concentration. Once steady-state chemistry is achieved, all Fe and Fe_3O_4 produced are subsequently consumed in their respective reverse reactions. Furthermore, process kinetics and thermal requirements dictate that the amounts of Fe and Fe_3O_4 produced be very small relative to the FeO content; for example, only about 10% of the total iron content is converted to Fe in actual cyclic operation.

4c.1.2 Summary of Experimental Results

During the 1960's, IGT investigated all types of iron solids, ranging from raw ores to high-temperature sinters, to determine their kinetic behavior in cyclic reduction and oxidation. As expected, most of these solids were unsuitable for the process, although several were found to be acceptable from a kinetic standpoint. These included commercial ammonia synthesis catalysts, raw and sintered siderite ores (iron carbonates), and several different iron ore sinters. In addition to kinetic activity, IGT investigated the attrition resistance of the various solids and the tendency of these solids to agglomerate at the operating temperatures necessary for the process. These criteria are summarized in Table 4c-2 for several different types of iron solids tested.

As shown in Table 4c-2, the most suitable solid for the process is the siderite sinter which has high chemical activity, will not cause excessive fines production, and does not agglomerate at steam-iron process operating temperatures. Siderite, in its natural form, is iron carbonate which decomposes to wustite and carbon dioxide upon heating. This decomposition results in high porosity which probably leads to a high kinetic activity. The particular presintered siderite ore used contains a sufficient concentration of gangue to prevent sticking at operating temperature, and presintering at high temperature also produces a high, attrition-resistant material.

Table 4c-2. CHEMICAL AND PHYSICAL BEHAVIOR OF VARIOUS IRON SOLIDS IN THE STEAM-IRON PROCESS

Solids	Kinetic Activity	Initial Agglomerating Temp, °F	Attrition Resistance
Ammonia Catalysts	High	1500	Good
Magnetite Ores	Low	1100	Good
Raw Siderite Ores	High	1800	Poor
Siderite Sinter	High	1800	Good

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Other types of iron solids can be used in the process. The above three properties should be considered, however, before final selection is made. We believe, for example, that magnetite ores can be chemically promoted to produce ideal solids for the steam-iron process using techniques already developed for making ammonia synthesis catalysts.

Additional work at IGT in the 1960's included the operation of large bench-scale reactors to separately test the reduction and oxidation reactions batchwise. Cyclic operation was achieved by refeeding the solids reduced in one test to a subsequent oxidation test. Thus, about 1 week was required to complete a reaction cycle.

In later operations, the bench reactor was modified to include solids recirculation between separate reducing and oxidizing zones. This unit was operated at 1000 psi at solids recirculation rates up tc 1000 lb/hr producing up to 10 complete cycles per hour.

4c.1.3 Pilot Plant Design

Figure 4c-2 is a diagram of the major equipment in the pilot facility now (1974) being designed and built for steam-iron system development. It includes a high-pressure slurry heater, a fluidized-bed steam-iron reactor. Char-grinding and slurry-mixing equipment, product-gas quench and disposal systems, and spent-char pressure letdown and disposal units are not shown in Figure 4c-2.

Initially, all gases including the make hydrogen will be incinerated. In later operations with stockpiled HYGAS char, the make hydrogen will be fed back to the HYGAS reactor so that integrated operation can be demonstrated.

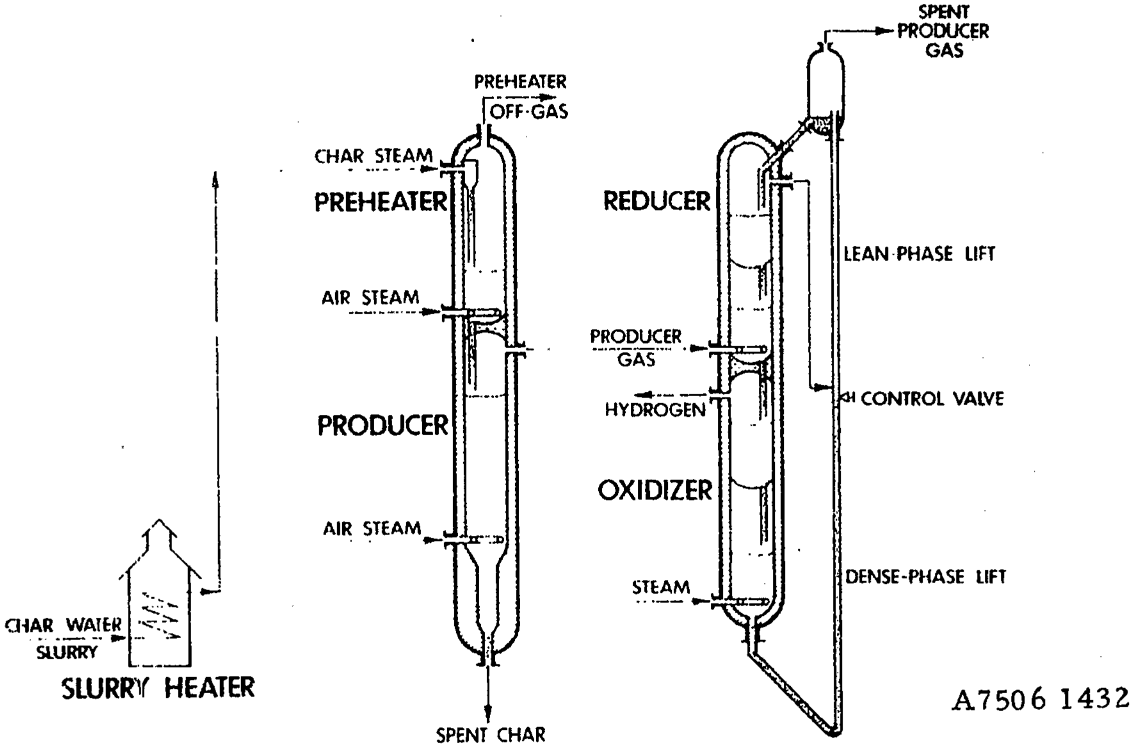

Figure 4c-2. STEAM-IRON PILOT PLANT REACTOR SYSTEM

In operation, a char-water slurry containing from 35 to 50% char will be heated in a direct-fired furnace to produce a lean-phase mixture of char and steam. The steam will serve to vapor-lift the char to the top of the producer, where the char will be fed, essentially dry, to the upper-stage preheat bed. This bed, fluidized with air and steam, will combust about 10% of the feed char, thus raising its temperature from 600° to 1750°F — the typical operating temperature of the high-temperature bed in the HYGAS reactor. This step is necessary to avoid an unusual heat load on the producer which, in integrated operation, would receive 1750°F char solids.

The preheated char next enters the producer bed, where it is essentially completely gasified at about 2000°F with air and steam to produce a high-quality reducing gas, which has a $CO + H_2/CO_2 + H_2O$ ratio of at least 4:1. Spent char is cooled with additional steam (not shown in Figure 4c-2) and is discharged at about 1000°F from the bottom of the producer.

The make producer gas, at a temperature ranging from 1900° to 2000°F, enters the steam-iron reactor as feed to the lower reducer stage, where, because of its high reducibility, FeO is converted to Fe. Because of its high temperature, the producer gas also serves as a heat source for the endothermic reduction reactions. The producer gas reaches a conversion level of about 20% in the lower stage before entering the upper stage, where the bulk of the final conversion level of the producer gas (65%) is attained by the conversion of Fe_3O_4 to FeO. The pressure energy in the spent gas is further used to maintain circulation of the iron solids in the upper, lean-phase portion of the solids lift system. Countercurrent operation in the reducer permits production of Fe in the lower reducer stage and conversion of Fe_3O_4 in the upper stage. Thus, high reducing gas conversion is attained, and sufficient metallic iron is produced to ensure the necessary hydrogen production.

Steam fed to the lower oxidizer stage converts FeO to Fe_3O_4. Steam conversion in this bed is limited to about 30% by equilibrium. Further conversion (above 30%) in the upper oxidizer stage, must be effected by conversion of Fe to FeO. Although the equilibrium limit of about 66% steam conversion is possible, conversion is limited by the amount of Fe formed in the lower reducer stage. For use as feed to the HYGAS reactor, the production of Fe is controlled to produce a final steam conversion of about 45%

Overall, four fluidized beds are used in the steam-iron process to avhieve full countercurrent operation. Also, because of other considerations, the reducing stages are located above the oxidizing stages with external recirculation of the Fe_3O_4-rich solids from the bottom to the top of the vessel. This configuration avoids dual, vertical solids transport that would be required if the oxidizing and reducing stages were located side by side; also, Fe, the most reactive species, is rapidly transferred to the oxidizer and not contacted by undesirable lift gases.

Because of pressure differentials created in the system, a large part of the solids conveying is effected in a dense phase with steam prior to adding the spent reducing gas for lean-phase solids conveying near the middle of the lift pipe. IGT investigated several alternative schemes for solids transfer and decided that this method is most desirable because it minimizes solids reaction (usually opposite to that desired) in the lift system. This configuration is very similar to Model IV FCC units, which utilize combined dense- and lean-phase solids transfer. The major difference, of course, is that the steam-iron process operates at elevated pressures.

4c.2 Present Program Status

IGT and the Blaw-Knox Division of Dravo are now working on the process design details for the steam-iron pilot facility. Process flow sheets have been completed and work is in progress on piping and instrumentation diagrams. Initial efforts were directed toward design of the reactor system so that orders for long-delivery items (principally reactor vessels) could be placed with a fabricator as soon as possible. A contract has been awarded Belmas Corporation for the fabrication of both the producer and steam-iron reactors, and delivery is anticipated in early 1975 (as of August, 1974).

Details of all steam-iron contract work to date – including process flow sheets – may be found in the U.S. Department of the Interior, Office of Coal Research, R&D Report No. 95, Interim Report No. 1, Development of the Steam-Iron System for Production of Hydrogen for the HYGAS Process, Washington, D.C. 1974. Orientation regarding the application of the Steam-Iron Process with relation to more recent HYGAS operations may be obtained by studying HYGAS: 1972 to 1974, Pipeline Gas From Coal – Hydrogenation, OCR, R&D Report No. 110, Interim Report No. 1. In preparation, for publication during 1975.

APPENDIX 4c-A

Steam-Iron Patents Based on Work Performed at IGT and Assigned to Consolidation Coal Co. As Agent for Fuel Gas Associates

May 6 1969 J. HUEBLER ET AL **3,442,619**

PRODUCTION OF HYDROGEN VIA THE STEAM-IRON PROCESS UTILIZING
DUAL SOLIDS RECYCLE
Filed March 27, 1968

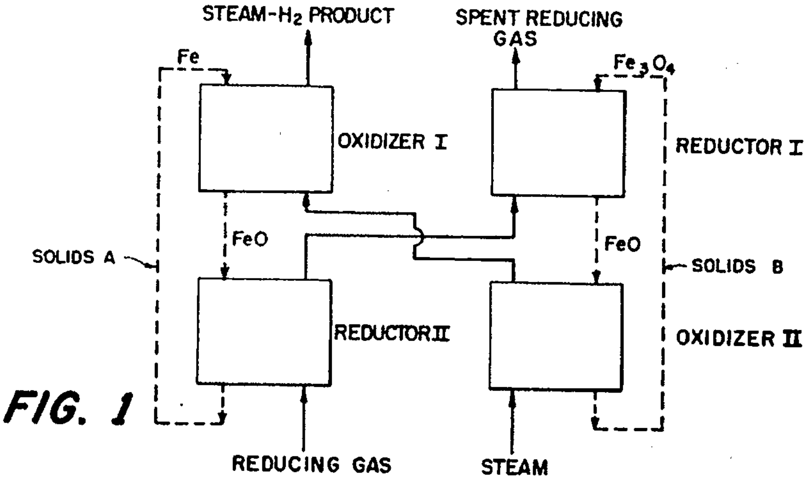

FIG. 1

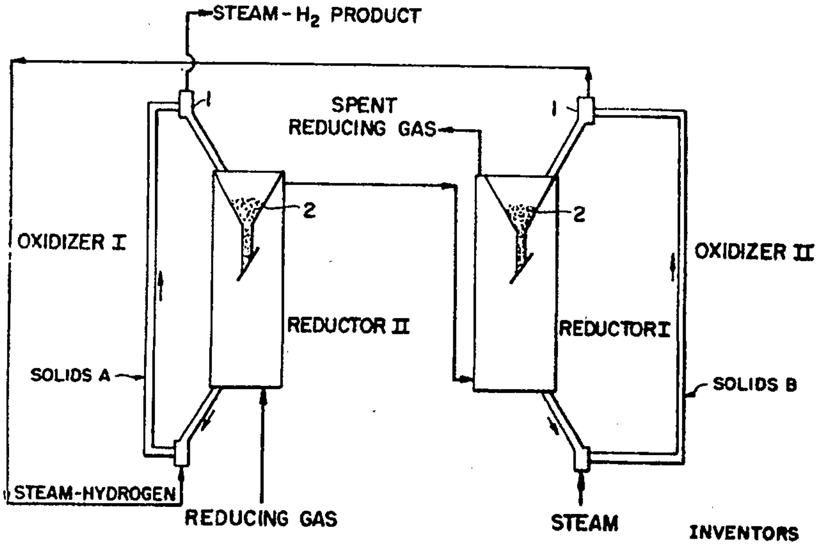

FIG. 2

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United States Patent Office

3,442,619
Patented May 6, 1969

3,442,619

PRODUCTION OF HYDROGEN VIA THE STEAM-IRON PROCESS UTILIZING DUAL SOLIDS RECYCLE

Jack Huebler, Deerfield, James L. Johnson, Oak Park, Frank C. Schora, Jr., Palatine, and Paul B. Tarman, Elmhurst, Ill., assignors to Consolidation Coal Company, Pittsburgh, Pa., a corporation of Delaware

Continuation-in-part of application Ser. No. 477,512, Aug. 5, 1965. This application Mar. 27, 1968, Ser. No. 716,569
Int. Cl. C01b 1/08
U.S. Cl. 23—214 13 Claims

ABSTRACT OF THE DISCLOSURE

An improved process for making hydrogen by the steam-iron reaction in which a dual solids system is used to effect the oxidation of Fe to Fe_3O_4 in two oxidation steps, namely Fe to FeO and FeO to Fe_3O_4, and also the reduction of the resulting oxides in two separate steps.

This application is a continuation-in-part of our copending application Ser. No. 477,512 filed Aug. 5, 1965, now abandoned.

This invention relates to the production of hydrogen and steam-hydrogen mixtures for use in synthesis processes, such as the production of ammonia, methane, or other products of hydrogenation processes. In particular, this invention relates to the production of hydrogen by an improved dual cycle steam-iron process wherein hydrogen is produced efficiently and in maximized yields.

The art has sought methods of producing hydrogen gas in large quantities for use in processes as noted above. For example, at present, hydrogen is obtained in most instances by reforming methane (natural gas) with steam. However, methane reformation is not so attractive for hydrogen production since the product gases contain not only hydrogen but also carbon monoxide, carbon dioxide, methane, and steam, which gases must be treated in conventional carbon monoxide shift and carbon dioxide removal equipment to achieve a final gas product rich in hydrogen.

There are also known processes for producing hydrogen which use the steam-iron reaction wherein steam is reacted with elemental iron or lower oxides of iron to produce hydrogen and iron oxides. The resultant iron oxides are then reduced with a reducing gas, usually containing carbon monoxide and hydrogen, to produce elemental iron and lower oxides. There have been proposed various fixed and fluidized bed cyclic processes, all of which suffer from poor hydrogen conversion due to improper design from thermodynamic and equilibrium considerations.

For example, Parsons in U.S. Patent 1,658,939 describes a process wherein elemental iron is oxidized by steam to form FeO; and the formation of Fe_3O_4 is specifically avoided by low temperature operation. This process results in unduly low hydrogen production and is commercially unattractive.

Marshall in U.S. Patent 2,182,747 describes a steam-iron process using as an oxidizing agent liquid water under pressure at 450° to 700° F. High hydrogen yields are not commercially feasible with this process because of equilibrium limitations in the operation of a liquid-gas phase system.

Benson et al. in U.S. Patent 3,031,287 describe a steam-iron process for making synthesis gas containing hydrogen which ultilizes as an oxidizing agent a gaseous mixture of carbon dioxide and steam at relatively low pressures.

This process is for the production of gas mixtures containing primarily H_2, CO, and mixtures thereof.

It is thus an object of this invention to produce hydrogen by a dual solids cycle steam-iron process wherein there is effected a high ultilization of the reducing gas in reduction of the iron oxide solids.

It is a further object of this invention to produce hydrogen by a dual solids cycle steam-iron process wherein the oxidation and reduction phases of the process are effected at relatively high pressure to attain high reaction rates and rapid approaches to equilibrium.

It is yet another object of this invention to produce hydrogen by a dual solids cycle steam-iron process wherein the oxidation and reduction phases of the process are effected separately and continuously at conditions which provide nearly equilibrium conversions of steam and reducing gas.

It is yet another object of this invention to produce hydrogen by a dual solids cycle steam-iron process wherein the oxidation and reduction phases are effected continuously in separate reactors in which the oxidation and reduction phases each occur in step-wise fashion in two distinct reactors wherein gas-solids contact is either countercurrent or cocurrent.

Other objects will become apparent as the invention is more fully described hereinafter. In the drawings:

FIGURE 1 is a diagram showing the process of one embodiment of the invention illustrating countercurrent gas-solids contact; and

FIGURE 2 is a diagram showing the process of another embodiment of the invention illustrating part countercurrent, part cocurrent gas-solids contact.

In the process of this invention, hydrogen is produced by oxidation of reduced iron solids with steam. The resulting product gas, hydrogen and unreacted steam, is essentially free of other contaminants. The steam used in the oxidation phase may also be admixed with noncondensable gases such as nitrogen or carbon dioxide. The oxidation is effected in two separate reactors with one oxidation stage occurring in each reactor; in the first stage, elemental iron is oxidized to FeO, and in the second stage, FeO is oxidized to Fe_3O_4. In this disclosure we denote the lower oxide of iron as FeO. As is well known in the art, the ratio of Fe to O in this oxide is slightly less than one, and this ratio will vary depending on the gas composition with which it is in equilibrium. Iron solids in the oxidation reactors can be contacted either cocurrently or countercurrently with gases as hereinafter more fully described. A continuous supply of reduced iron solids for the oxidation stages is provided by subsequent reduction of the oxidized iron solids with a reducing gas. Reduction is also effected in two separate reactors with one reduction stage occurring in each reactor. In the first stage, Fe_3O_4 is reduced to FeO, and in the second stage, FeO is reduced to elemental iron. Iron solids in the reduction reactors can be contacted either countercurrently or cocurrently with gases as hereinafter more fully described.

Thus, the essence of our invention is the separation of the solids phase reactions described above to yield higher reducing gas and steam conversions.

The reducing gas used in the reduction reaction need only contain carbon monoxide and/or hydrogen in sufficient quantities to reduce oxidized iron solids. The presence of other constituents in the reducing gas such as nitrogen, steam, carbon dioxide, methane, etc., does not affect the quality of hydrogen produced in the oxidation step. Thus, the reducing gas can be obtained from the least expensive and/or the most convenient source, such as the partial oxidation of coal, methane, shale oil, or other hydrocarbons with air or a mixture of steam and air, or with such gases as may be obtained by retorting oil shale. The air or air-steam mixture may also contain carbon dioxide. In addition, we have found that it is advantageous for the reducing gas to contain small quantities of sulfur compounds which inhibit formation of free carbon. A suitable tail gas from other plant operations can be used as the reducing gas.

In carrying out the process of this invention, there are employed four reaction vessels: a first and second oxidizer, where reduced iron solids are contacted with oxidizing gas; and a first and second reductor, where the oxidized iron solids are contacted with reducing gas. For continuous operation, it is necessary to recycle the iron solids from the oxidizers to the reductors. The equipment required for the transfer of solids can be of any type, mechanical or pneumatic, available to all industrial processes. When employing the embodiment as illustrated in FIGURE 2, the solids recycle lines serve as the oxidizers.

In solids recycle systems, such as is utilized here, it is essential that cyclic solids conversion be exactly balanced with respect to all solids phases. If not balanced, the solids will tend to yield high reduction or high oxidation levels which limit solids reaction rates and gas conversions in the oxidizer or reductor.

Hydrogen production via cyclic steam-iron processes has been used in the past with fixed, fluidized, moving, and free-fall beds. Both cocurrent and countercurrent gas-solids contact systems have been employed. However, in all cases heretofore, only one solids stream has been utilized. Because of thermodynamics of the steam-iron process, this single solids stream is composed of three separate solids phases, elemental iron (Fe), wustite (FeO), and magnetite (Fe_3O_4). Therefore, six different reactions are possible, four in reduction and two in oxidation:

(1) $Fe_3O_4+H_2=3FeO+H_2O$ $K_1=PH_2O/PH_2$
(2) $Fe_3O_4+CO=3FeO+CO_2$ $K_2=PCO_2/PCO$
(3) $FeO+H_2=Fe+H_2O$ $K_3=PH_2O/PH_2$
(4) $FeO+CO=Fe+CO_2$ $K_4=PCO_2/PCO$
(5) $Fe+H_2O=FeO+H_2$ $K_5=PH_2/PH_2O$
(6) $3FeO+H_2O=Fe_3O_4+H_2$ $K_6=PH_2/PH_2O$

Reactions (1) and (2) favor high-reducing gas conversion and reaction (5) favors high-steam conversion. To insure high-gas conversion and a sufficient feed supply of metallic iron to the oxidizer and magnetite to the reductor, it is necessary that countercurrent gas-solids contact be employed in single solids systems. Furthermore, if reactions (1) and (2) occur at low reducing gas conversions [where the H_2O/H_2 and CO_2/CO ratios are below the respective equilibrium values for reactions (3) and (4)], the supply of elemental iron to the oxidizer will be limited. This is true because the amount of reducing gas converted by reactions (3) and (4) has been proportionately decreased. If in oxidation, reaction (5) occurs at low steam conversions [below the equilibrium value for reaction (6)], the supply of magnetite to the reductor will be curtailed. These stoichiometric limitations can significantly decrease reducing gas and/or steam conversions.

There is described in our copending application Ser. No. 477,511, filed Aug. 5, 1965 and now abandoned, a cyclic system utilizing two reactors where countercurrent contact of gas and solids is required. There is also described in our aforementioned application the equilibrium and thermodynamic details of above reactions (1) to (6) with equilibrium constants and diagrams set out. The details thereof apply as well to the process of this invention, and the disclosure regarding equilibrium considerations is thus incorporated by reference herein.

The novel use of a dual solids system described in this application overcomes the limitations of using only a single solids cycle system, and allows high gas conversions in either cocurrent or countercurrent operation. The dual solids system effects separation of the three solids phases of iron such that one system (called solids system A,

herein) contains elemental iron (Fe) and wustite (FeO), and the other system (called solids system B, herein) contains wustite (FeO) and magnetite (Fe_3O_4). Preferably, each of the two solids systems consists essentially of the solids specified. However, as a practical matter, other reactive or nonreactive solids may be present without seriously affecting the practice of our invention. It is essential that the principal reactive constituents of the designated system be the solids specified. Each solids system utilizes a reductor and an oxidizer as shown in FIGURE 1, i.e. solids system A utilizes Reductor II and Oxidizer I, and solids system B utilizes Reductor I and Oxidizer II. In Reductor II, reducing gas contacts solids A to attain equilibrium with respect to Fe-FeO (low reducing gas conversion), and in Reductor I, the reducing gas is contacted with solids B where high reducing gas conversion is attained due to the reduction of magnetite. In Oxidizer II, steam contacts solids B to attain equilibrium with respect to FeO-Fe_3O_4 (low steam conversion), and in Oxidizer I, the steam-hydrogen mix is contacted with solids A where high steam conversion is attained due to the presence of elemental iron. Thus, principally reactions (3) and (4) occur in Reductor II, reactions (1) and (2) in Reductor I, reaction (6) in the Oxidizer II and reaction (5) in Oxidizer I.

Because of the separation of phases, one essential solids phase reaction occurs in each reactor: $Fe\rightleftarrows FeO$ in solids system A, and $FeO\rightleftarrows Fe_3O_4$ in solids system B. There can, therefore, be little or no loss of elemental iron production due to the reduction of magnetite to wustite in Reductor II. This separation also provides a means of more efficient design. Each reactor can be sized according to known kinetics of the particular solids phase reaction taking place. In single solids cycle systems, the oxidizer and reductor must be sized to accommodate the complicated kinetic mechanisms for two different solids phase changes.

Although countercurrent gas-solids contact is illustrated in FIGURE 1, full or partial cocurrent operation is just as efficient, because the separation of solids phases insures sufficient feeds of elemental iron and magnetite to Oxidizer I and Reductor I, respectively.

FIGURE 2 illustrates an embodiment of the process of the invention wherein reduction is effected countercurrently in Reductors I and II and oxidation is effected cocurrently in the solids recycle lines indicated as Oxidizers I and II. Gas streams are fed into and out of the oxidizers and reductors as shown in FIGURE 2. Solids A are recycled between Reductor II and Oxidizer I, and solids B are recycled between Reductor I and Oxidizer II. The solids in Oxidizers I and II are transported up through the oxidation zones by steam-hydrogen and steam, respectively, so that the gas and solids are transported in cocurrent relation. At the top of the oxidizers are separators 1, shown diagrammatically, such as cyclone separators by which the gas and solids are disengaged. Solids are then fed to hoppers 2 for subsequent further reacting in the respective reductors.

We have found several types of iron-bearing solids suitable for this system, such as siderite, magnetite, and hemetite ores (either raw or beneficiated), ammonia synthesis catalysts, iron ore sinters, as well as other commercially available iron compounds. The preferable particle size range for this process is from 10 to 325 mesh, preferably 40 to 100 mesh.

With these iron-bearing solids, particle residence times in the range of 5 to 180 seconds, preferably 10 to 45 seconds, are sufficient to effect the necessary gas and solids conversions in each reactor. Operating temperature significantly affects reducing gas conversion in Reductor I and steam conversion in Oxidizer II, but has only slight effect on gas conversions in solids system A. Therefore, operation of solids system B at a higher temperature than solids system A can be beneficial to gas conversions. However, it may be necessary, in this type of operation, to adjust the temperature of the feed gases to the first stage reactors so that the steam-hydrogen fed to Oxidizer I will not oxidize wustite and the reducing gas mixture fed to Reductor I will not reduce wustite. Otherwise, the two-phase solids system would be destroyed. We have found that temperatures in the range of 1000° to 2000° F. allow sufficiently high reaction rates so that high steam and reducing gas conversions will result. More preferable ranges are 1000° to 1500° F. for oxidation and 1300° to 2000° F. for reduction. Higher reduction temperatures can cause agglomeration of some iron-bearing solids, especially those high in total iron content, such as ammonia synthesis catalysts. For these types of solids, the solids free-fall bed is best suited since low solids densities in the range of 2 to 30 lbs./cu. ft. can be used effectively. With non-agglomerating solids, any type of bed can be used, and for all solids, either cocurrent or countercurrent operation is suitable.

Solids/gas ratios in the range of 0.1 to 5 lbs. solids/s.c.f. active gas are adaptable to this process, but this ratio does depend upon the reaction rates obtained and upon the heat requirements of the individual solids system. More preferable solids/gas ratios are 0.3 to 2 lbs. solids/s.c.f. active gas. Incremental solids conversions most beneficial to this process range from 0.25 to 15, preferably from 0.5 to 10 lbs. oxygen transferred per 100 lbs. solids fed to each reactor.

We have found that reaction rates increase with pressure up to about 200 p.s.i.g. Therefore, operation above this pressure, say 200 to 2500 p.s.i.g., can significantly decrease the required size of each reactor. In addition, gas residence time increases with pressure and in countercurrent, solids free-fall reactors, the residence time of the solids is increased due to the lower terminal velocity of particles in denser gases.

An example is given in the following table of operating conditions and results for conversion of a typical reducing gas. The various gas and solids stream compositions noted are for a system as shown in FIGURE 1, the solids used being a commercial ammonia synthesis catalyst of 40–100 mesh.

TABLE I.—GAS COMPOSITIONS AND FLOW RATES

	Reductor			Oxidizer		
Gas	Stage II Feed	Stage I Feed	Spent Gas	Stage II Feed	Stage I Feed	Steam-H_2 Product
Temperature, ° F.	1,500	1,500	1,500	1,100	1,200	1,500
S.c.f./hr.	10,000	10,000	10,000	4,130	4,130	4,130
Composition, mole percent:						
CO	21.4	17.0	7.8			
CO_2	4.5	8.9	18.1			
H_2	20.2	17.2	7.9		44.7	62.5
H_2O	6.0	9.0	18.3	100.0	55.3	37.5
N_2	47.9	47.9	47.9			
Total	100.0	100.0	100.0	100.0	100.0	100.0
	To Stage II		To Stage I	To Stage II		To Stage I
Solids, moles/hr.:						
Fe_3O_4			8.8	3.0		
FeO*	57.8			18.3		55.9
Fe						1.8
Temperature, ° F.	1,500		1,500	1,200		1,500

*Assumed as $Fe_{.95}O$.

In the system embodiment, shown in FIGURE 2, the steam and reducing gas flow patterns could have been interchanged, that is, countercurrent oxidation and cocurrent reduction could have been used. However, it is known that the rate of oxidation is faster than the rate of reduction and since lift flow rates (both gas and solids) are usually maintained high to yield smooth operation, residence times are necessarily low. Thus, the faster oxidation reactions should preferably be carried out in the lift-reactors.

This latter system variation has several other advantages. For instance, total reactor heights are about half those for the system shown in FIGURE 1. Thus, differential lift pressures are smaller, hence solids legs are also shorter.

We have found that the addition of methane to the reducing gas can increase its reducing potential by the following probable reactions:

$$CH_4+H_2O=CO+3H_2 \quad (7)$$

$$CH_4+Fe_3O_4=3FeO+CO+2H_2 \quad (8)$$

The temperature of the feed reducing gas can be increased to supply the endothermic heat of these reactions if methane is added to the reductors. Product gases can also be burned with air injected at the top of Reductor I for this purpose. The heat of combustion can thus be used to impart heat to the incoming solids and thereby maintain Reductor I temperature.

We have also found that the addition of sulfur compounds, such as hydrogen sulfide, to the feed reducing gas is beneficial to the process. Hydrogen sulfide concentrations of 0.1 to 0.5 percent inhibit the formation of free carbon thus eliminating subsequent loss in reducing quality of the reducing gas.

In actual commercially sized equipment, some heat losses from the system can be expected. Reasonable equipment design should limit these losses to less than 5 percent of the heat input to the system, In this case the enthalpy input of the feed gas streams. Therefore, to maintain optimum temperature gradients in the reactors, higher inlet gas temperatures can be used as a convenient source of additional enthalpy. However, only enough additional enthalpy to balance heat losses should be provided, otherwise higher than optimum operating temperatures will result.

There are other possible variations of this system, as can be seen by those skilled in the art. All, however, should be considered within the scope of this invention which is limited solely by the appended claims.

We claim:

1. Process for producing hydrogen comprising:

(1) reacting Fe_3O_4 with a reducing gas in a first reduction zone, and FeO with a reducing gas in a second reduction zone, whereby Fe_3O_4 is reduced to FeO in said first reduction zone and FeO is reduced to Fe in said second reduction zone, and

(2) reacting the resultant reduced solid products from each of said reduction zones separately with steam at a temperature from 1000° to 2000° F., whereby Fe is oxidized to FeO in a first oxidation zone, and FeO is oxidized to Fe_3O_4 in a second oxidation zone; and

wherein two separate solids systems are utilized in such a manner that one system (solids B) containing FeO and Fe_3O_4 is recycled between the first reduction zone and the second oxidation zone, and the other system (solids A) containing Fe and FeO is recycled between the second reduction zone and the first oxidation zone; wherein in step (1) fresh reducing gas is contacted with solids A containing FeO in said second reduction zone to produce Fe and the resulting gas is contacted with solids B containing Fe_3O_4 in said first reduction zone of produce FeO; and wherein in step (2) feed steam is contacted with solids B containing FeO in said second oxidation zone to produce Fe_3O_4 and the resulting gas is contacted with solids A containing Fe in said first oxidation to produce FeO, thereby producing hydrogen.

2. Process for producing hydrogen comprising:

(1) reacting Fe_3O_4 with a reducing gas in a first reduction zone, and FeO with a reducing gas in a second reduction zone, whereby Fe_3O_4 is reduced to FeO in said first reduction zone and FeO is reduced to Fe in said second reduction zone, and

(2) reacting the resultant reduced solid products from each of said reduction zones separately with steam at a temperature from 1000° to 2000° F., whereby Fe is oxidized to FeO in a first oxidation zone, and FeO is oxidized to Fe_3O_4 in a second oxidation zone; and

wherein two separate solids systems are utilized in such a manner that one system (solids B) containing principally FeO and Fe_3O_4 is recycled between the first reduction zone and the second oxidation zone, and the other system (solids A) containing principally Fe and FeO is recycled between the second reduction zone and the first oxidation zone; wherein in step (1) fresh reducing gas is contacted with solids A containing FeO in said second reduction zone to produce Fe and the resulting gas is contacted with solids B containing Fe_3O_4 in said first reduction zone to produce FeO; and wherein in step (2) feed steam is contacted with solids B containing FeO in said second oxidation zone to produce Fe_3O_4 and the resulting gas is contacted with solids A containing Fe in said first oxidation zone to produce FeO, thereby producing hydrogen.

3. Process of claim 2 wherein the residence time of solids in each zone is 5 to 180 seconds.

4. Process of claim 2 wherein flow between solids and gases in at least one of the zones is countercurrent.

5. Process of claim 4 wherein said countercurrent flow is conducted using a free-fall bed.

6. Process of claim 2 wherein flow between solids and gases in at least one of the zones is cocurrent.

7. Process of claim 2 wherein the reducing gas contains carbon monoxide and hydrogen.

8. Process of claim 7 wherein said reducing gas also contains methane.

9. Process of claim 7 wherein said reducing gas also contains sulfur compounds in sufficient quantity to inhibit the formation of free carbon.

10. Process of claim 8 wherein air is injected into the first reduction reactor to combust a portion of the spent reducing gas to supply the necessary additional heat to offset the endothermic methane consuming reactions.

11. Process of claim 2 wherein the temperature of the oxidation zones is between 1000 and 1500° F. and the temperature of the reduction zones is between 1300 and 2000° F.

12. Process of claim 2 wherein steps (1) and (2) are conducted at a pressure minimally 200 p.s.i.g.

13. Process of claim 2 wherein the solids system B is maintained at a higher temperature than solids system A.

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EDWARD STERN, *Primary Examiner.*

U.S. Cl. X.R.

23—150, 200, 204

May 6, 1969 J. HUEBLER ET AL **3,442,620**

PRODUCTION OF HYDROGEN VIA THE STEAM-IRON PROCESS

Filed April 18, 1968 Sheet 1 of 2

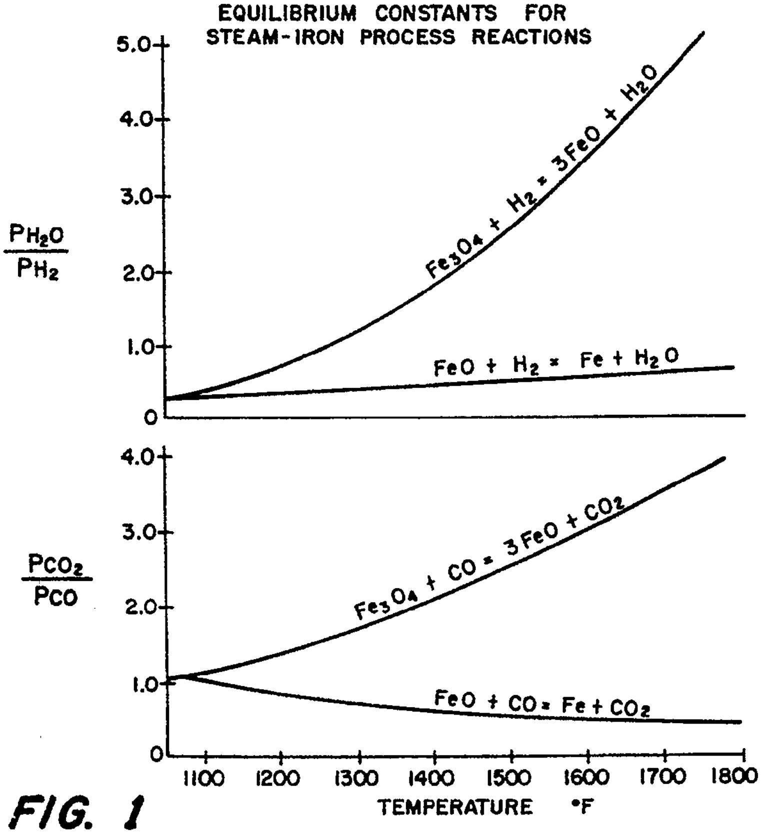

FIG. 1

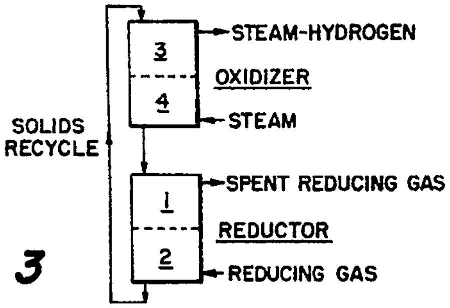

FIG. 3

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PRODUCTION OF HYDROGEN VIA THE STEAM-IRON PROCESS

Filed April 18, 1968 Sheet 2 of 2

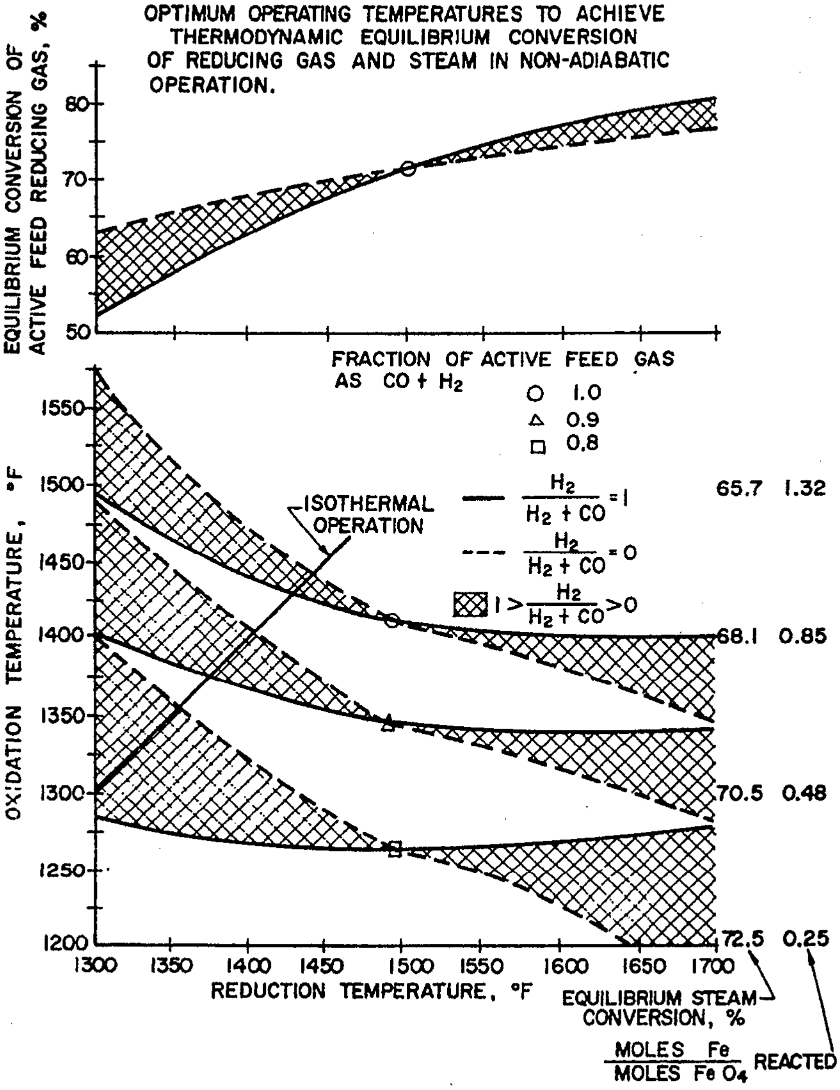

FIG. 2

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3,442,620

PRODUCTION OF HYDROGEN VIA THE STEAM-IRON PROCESS

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Continuation-in-part of application Ser. No. 477,511, Aug. 5, 1965. This application Apr. 18, 1968, Ser. No. 722,389

Int. Cl. C01b *1/08*

U.S. Cl. 23—214 **10 Claims**

ABSTRACT OF THE DISCLOSURE

A process for making hydrogen by the steam-iron reaction utilizing countercurrent gas-solids contact, wherein oxidation of Fe to Fe_3O_4 is conducted in two zones, one principally for the Fe to FeO reaction and the other principally for the FeO to Fe_3O_4 reaction: and the reduction of the Fe_3O_4 to Fe is also conducted in two zones for the same reactions in the reverse direction.

This application is a continuation-in-part of our copending application, Ser. No. 477,511, filed Aug. 5, 1965, now abandoned.

This invention relates to the production of hydrogen and steam-hydrogen mixtures for use in synthesis processes, such as the production of ammonia, methane, or other products of hydrogenation processes. In particular, this invention relates to the production of hydrogen by an improved steam-iron process wherein hydrogen is produced efficiently and in maximized yields.

The art has sought methods of producing hydrogen gas in large quantities for use in processes as noted above. For example, at present, hydrogen is obtained in most instances by reforming methane (natural gas) with steam. However, methane reformation is not so attractive for hydrogen production since the product gases contain not only hydrogen but also carbon monoxide, carbon dioxide, methane, and steam, which gases must be treated in conventional carbon monoxide shift and carbon dioxide removal equipment to achieve a final gas product rich in hydrogen.

There are also known processes for producing hydrogen which use the steam-iron reaction wherein steam is reacted with elemental iron or lower oxides of iron to produce hydrogen and iron oxides. The resultant iron oxides are then reduced with a reducing gas, usually containing carbon monoxide and hydrogen, to produce elemental iron and lower oxides. There have been proposed various fixed and fluidized bed cyclic processes, all of which suffer from poor hydrogen conversion due to improper design from thermodynamic and equilibrium considerations.

For example, Parsons, in U.S. Patent No. 1,658,939, describes a process wherein elemental iron is oxidized by steam to form FeO; and the formation of Fe_3O_4 is specifically avoided by low temperature operation. This process results in unduly low hydrogen production and is commercially unattractive.

Marshall, in U.S. Patent No. 2,182,747, describes a steam-iron process using, as oxidizing agent, liquid water under pressure at 450° to 700° F. High hydrogen yields are not commercially feasible with this process because of equilibrium limitations in the operation of a liquid-gas phase system.

Benson et al., in U.S. Patent No. 3,031,287, describe a steam-iron process for making synthesis gas containing hydrogen which utilizes, as an oxidizing agent, a gaseous mixture of carbon dioxide and steam at relatively low pressures. This process is for the production of gas mixtures containing primarily H_2, CO, and/or methane. Other patents which are illustrative of the state of the art include the following: U.S. Patents Nos. 2,772,954; 2,864,688; 2,996,373; and 3,076,702.

It is thus an object of this invention to produce hydrogen by the steam-iron process wherein there is effected a high utilization of the reducing gas in reduction of the iron oxide solids.

It is a further object of this invention to produce hydrogen by the steam-iron process wherein the oxidation and reduction phases of the process are effected at relatively high pressure to attain high reaction rates and rapid approaches to equilibrium.

It is yet another object of this invention to produce hydrogen by the steam-iron process wherein the oxidation and reduction phases of the process are effected separately and continuously at conditions which provide nearly equilibrium conversions of steam and reducing gas.

It is yet another object of this inveniton to produce hydrogen by the steam-iron process wherein the oxidation and reduction phases are effected continuously in separate reactors in which oxidation and reduction occur in each of the respective reactors in step-wise fashion in two distinct reaction zones.

Other objects will become apparent as the invention is more fully described hereinafter. In the drawings:

FIGURE 1 is a graph showing equilibrium constants as a function of temperature for the various chemical reactions involved in the invention;

FIGURE 2 is a graph showing various relationships of process parameters, including the relationship of oxidation and reduction temperatures to composition of reducing gas feed; and

FIGURE 3 is a diagram showing the process steps of the invention.

In the process of this invention, hydrogen is produced by oxidation of reduced iron solids with steam. The resulting product gas, hydrogen and unreacted steam, is essentially free of other contaminants. The steam used in the oxidation process may also be admixed with noncondensable gases such as nitrogen or carbon dioxide. The oxidation is effected in a reaction zone wherein the oxidation step occurs in substantially two stages: in the first stage, elemental iron is oxidized to FeO, and in the second stage, FeO is oxidized to Fe_3O_4. In this disclosure, we denote the lower oxide of iron as FeO. As is well known in the art, the ratio of Fe to O in this oxide is slightly less than one, and this ratio will vary depending upon the gas composition with which it is in equilibrium. The first reaction stage occurs in a distinct subzone, preferably located above a subzone in which the second stage occurs, the solid materials being contacted countercurrently with gases as hereinafter more fully described. A continuous supply of reduced iron solids for the oxidation step is provided by subsequent reduction of the oxidized iron solids with a reducing gas. Reduction is also effected in a reaction zone wherein the reduction step occurs in substantially two stages: in the first stage, Fe_3O_4 is reduced to FeO, and in the second stage, FeO is reduced to elemental iron. The first reduction stage occurs in a distinct subzone, preferably located above a subzone in which the second stage occurs, the solid materials being contacted countercurrently with gases as hereinafter more fully described.

We have found that temperatures in the range of 1000° to 2000° F. generally allow sufficiently high reaction rates in both the oxidation and the reduction zones so that high steam and reducing gas conversions will result. More preferably ranges are 1000° to 15000° F. for oxidation and 1300° to 2000° F. for reduction. We have also found that reaction rates increase with pressure up to about

200 p.s.i.g. Therefore, operation about this minimal pressure, say 200 to 2500 p.s.i.g., can significantly decrease the required size of each reactor.

The essence of our invention is in providing that the oxidation and reduction reactions occur in reaction zones wherein both the oxidation and reduction steps are carried out in two stages in separate subzones of the oxidizer and reductor. The two-stage reactions are more fully described hereinafter.

The reducing gas used in the reduction reaction need only contain carbon monoxide and/or hydrogen in sufficient quantities to reduce oxidized iron solids. The presence of other constituents such as nitrogen, steam, carbon dioxide, methane, etc., does not affect the quality of hydrogen produced in the oxidation step. Thus, the reducing gas can be obtained from the least expensive and/or the most convenient source, such as the partial oxidation of coal, methane, shale oil or other hydrocarbons with air or a mixture of steam and air or with such gases as may be obtained by retorting oil shale. The air or air-steam mixture may also contain carbon dioxide. In addition, we have found that it is advantageous for the reducing gas to contain small quantities of sulfur which inhibit formation of iron carbides and free carbon. A suitable tail gas from other plant operations might be used as the reducing gas.

In carrying out the process of the invention, there are employed two reaction vessels: the oxidizer, where reduced iron solids are contacted with steam; and the reductor, where the oxidized iron solids are contacted with reducing gas. For continuous operation, it is necessary to recycle the iron solids from the oxidizer to the reductor. The equipment required for the transfer of solids can be of any type, mechanical or pneumatic, which are availble to all industrial processes.

In a solids recycle system, such as is utilized here, it is essential that cyclic solids conversion be exactly balanced with respect to all solids phases. If not balanced, the solids will tend to yield high reduction or high oxidation levels which limit solids reaction rates and gas conversions in the oxidizer or reductor.

The reactions pertinent to the cyclic reduction and oxidation of iron can be summarized:

(1) $Fe+H_2O \rightarrow FeO+H_2$ $K_1=PH_2/PH_2O$
(2) $3FeO+H_2O \rightarrow Fe_3O_4+H_2$ $K_2=PH_2/PH_2O$
(3) $Fe_3O_4+H_2 \rightarrow 3FeO+H_2O$ $K_3=PH_2O/PH_2$
(4) $Fe_3O_4+CO \rightarrow 3FeO+CO_2$ $K_4=PCO_2/PCO$
(5) $FeO+H_2 \rightarrow Fe+H_2O$ $K_5=PH_2O/PH_2$
(6) $FeO+CO \rightarrow Fe+CO_2$ $K_6=PCO/PCO$

The first two reactions occur in the oxidizer and the last four in the reductor. Thus, for steady cyclic operations, the moles of elemental iron (Fe), oxidized with steam by reaction (1), must in turn be formed by reduction of wustite (FeO) with carbon monoxide and/or hydrogen by reactions (5) and (6). Also, the moles of magnetite (Fe_3O_4), formed in the oxidizer by reaction (2), must be reduced by carbon monoxide and/or hydrogen in the reductor by reactions (3) and (4).

The equilibrium constants for these reactions are shown in FIGURE 1 as a function of temperature in the range of 1050° F. to 1800° F. It can be seen that, as oxidation progresses and the H_2O/H_2 ratio decreases, the oxidation of wustite ceases before the oxidation of metallic iron. Likewise, as reduction progresses and the H_2O/H_2 and CO_2/CO ratios increase, the reduction of wustite ceases before the reduction of magnetite.

We will first consider and discuss the problems of equilibrium and conversion connected with operation of the steam-iron process. As an example, if the reductor is maintained at 1490° F., the formation of iron by reactions (5) and (6) can occur only in the lower subzone of the reductor where the H_2O/H_2 and CO_2/CO ratios are below 0.52. This corresponds to about 27 percent conversion of the carbon monoxide plus hydrogen in a typical reducing gas where the carbon monoxide plus hydrogen is about 90 percent of the total active gases (CO, CO_2, H_2, H_2O). The maximum equilibrium conversion of the $CO+H_2$ in this typical reducing gas is about 68 percent at 1490° F. (H_2O/H_2 and CO_2/CO ratios of 2.52 for the reduction of magnetite). Therefore, the incremental reducing gas conversion from 27 to 68 percent can be effected by reaction (3) and (4) only. To obtain equilibrium reducing gas conversions at this temperature, the amount of magnetite reduced in the upper subzone by reactions (3) and (4) must, therefore, be about 1.5 times the amount of iron formed in the lower subzone by reactions (5) and (6). Since steady cyclic operation is necessary, the oxidation must in turn form 1.5 times as much magnetite by reaction (2) than iron oxidized by reaction (1). This magnetite can only be formed in the lower subzone of the oxidizer where H_2/H_2O ratios are less than the equilibrium value for reaction (2). At 1490° F., this corresponds to only about 28 percent steam conversion.

Thus, to insure sufficient magnetite, the steam feed to the oxidizer must be about 1.5 times the carbon monoxide plus hydrogen fed to the reductor. As a result of this imbalance in active gas feeds, maximum steam conversion will be only 45 percent: 28 percent in the lower subzone by reaction (2), and 17 percent in the upper subzone by reaction (1). Thus, the lack of sufficient elemental iron in the solids feed to the oxidizer limits steam conversion to values far below the thermodynamic equilibrium value of 68 percent at 1490° F. Thus, it is seen that improper isothermal operation can seriously limit either the steam or reducing gas conversion; the reducing gas conversion would be decreased at lower steam/reducing gas ratios since the production of magnetite would be limiting.

Equilibrium conversion of both feed gases can only be obtained by isothermal operation at specific temperatures or by operation of the reductor and oxidizer at specific temperature differences. For instance, operation of the oxidizer at about 1350° F. and the reductor at 1490° F. would allow the steam conversion to reach 41 percent in the lower subzone before the equilibrium for reaction (2) was exceeded. Thus, steam fed to the oxidizer could equal the carbon monoxide plus hydrogen fed to the reductor and maximum thermodynamic steam conversion of 68 percent could be obtained: 41 percent in lower subzone by reaction (2), and 27 percent in upper subzone by reaction (1).

The above example is cited to stress the importance of maintaining proper temperature differences between the oxidizer and reductor to achieve equilibrium steam and reducing gas conversions. The corresponding operating temperatures to attain these conversions are given in FIGURE 2 over a range of 1300° F. to 1700° F. for different reducing gas qualities (reducing gas quality is herein defined as the fraction of carbon monoxide and hydrogen in the total active gases). FIGURE 2 shows that, for any given reduction temperature and reducing gas quality, the proper oxidation temperature depends only on the fraction of hydrogen in the carbon monoxide plus hydrogen feed. Thus, for any particular reducing gas and reductor temperature, the specific oxidation temperature can easily be determined from FIGURE 2.

Consider, as an example, a feed reducing gas containing 90 percent of its active gas as carbon monoxide plus hydrogen. We see that isothermal operation is only possible for such gas in the range of about 1375° F. to 1405° F., depending upon the ratio of hydrogen to the carbon monoxide plus hydrogen fed to the reductor. Low ratios of hydrogen to carbon monoxide plus hydrogen require operation proportionately closer to 1405° F. as shown in FIGURE 2 by the fact that the dotted lines represent 100 percent carbon monoxide—0 percent hydrogen. Operation of the reductor at temperatures higher than the isothermal temperature requires operation of the oxidizer at lower than the isothermal temperatures, and vice-versa. Operation of the reductor at 1600° F., for instance, with a reducing gas quality of 90 percent, requires oxidation temperatures in the range of about 1320° F. to 1345° F., depending upon the ratio of hydrogen to carbon monoxide plus hydrogen in the feed reducing gas.

FIGURE 2 also shows the equilibrium steam and reducing gas conversions obtained at the different sets of operating temperatures. The equilibrium steam conversion is shown along the vertical scale at the right side of FIGURE 2. Equilibrium reducing gas conversion is shown by the plot in the upper portion of FIGURE 2. Equilibrium reducing gas conversion, Y_T, in this plot is expressed as conversion of total active gases fed and, as such, is independent of gas quality. The conversion of carbon monoxide plus hydrogen fed, Y, is easily obtained for any particular reducing gas quality, Q, as follows:

$$Y = \frac{Y_T + Q - 100}{Q}$$

As shown, reducing gas conversions increase appreciably with reductor temperature, and steam conversion decreases slightly with oxidation temperatures. Thus, high reduction and low oxidation temperatures are more beneficial if large temperature differences can be practically maintained. FIGURE 2 also shows (along the right-hand vertical scale) the molar ratio of iron to magnetite reacted at the various oxidation temperatures.

We have found, according to our invention, that the gas conversions shown in FIGURE 2 are possible only when the gas and solids are contacted countercurrently in both the oxidizer and reductor. This ensures that the solids of the highest elemental iron content exiting the reductor are fed to the top of the oxidizer, and that the solids of the highest magnetite content exiting the oxidizer are fed to the top of the reductor.

In most large process equipment, heat additions or removals from reaction zones to control reactor temperatures is both difficult and expensive. For this reason, large reactors are usually operated essentially adiabatically; the heat inputs and outputs are those associated with the inlet and exit streams and reactor heat losses. In this process, oxidation is exothermic and reduction endothermic, except for reduction reaction (6) which is slightly exothermic. Therefore, temperature gradients will be imposed across each reaction zone. These gradients depend upon the gas and solids flow rates, heat capacities, and inlet and exit temperatures, and, also, upon the amount of solids reacted in each reaction zone. Thus, it is seen that oxidation and reduction temperatures cannot be chosen arbitrarily, but will be dictated as a result of the many variables involved. It is, therefore, highly unlikely that both equilibrium conversions can be simultaneously obtained because of these restrictions. However, it is possible to determine the optimum operating conditions (flow rates, temperatures, solids conversions, etc.) to yield maximum steam and reducing gas conversions for reducing gas compositions typical of those available for this process. It should be understood that the optimum operating conditions do depend on the composition of reducing gas, and will, therefore, vary accordingly.

EXAMPLE 1

As an example, the process of the invention was operated using a reducing gas of the following composition:

Composition:	Mole percent
CO	17.2
CO_2	1.3
H_2	35.0
H_2O	4.6
CH_4	0.8
N_2	41.1

The solids material used was a commercial ammonia synthesis catalyst of 40–100 mesh size. The solids residence time was 20 seconds in the oxidizer, 30 seconds in the reductor. The gas composition above noted is typical of that produced by the adiabatic partial oxidation of methane at 1900° F. The optimum operating conditions to achieve maximum reducing gas and steam conversion are shown in Table I.

TABLE I.—GAS COMPOSITIONS AND FLOW RATES

Gas	Reducing Gas	Spent Reducing Gas	Steam	Steam-H_2
Temperature, ° F.	1,380	1,550	1,100	1,405
Moles/hr.	5.2	5.2	3.4	3.4
Composition, Mole percent:				
CO	17.2	5.6		
CO_2	1.3	12.9		
H_2	35.0	11.2		53.3
H_2O	4.6	28.3	100.0	46.7
CH_4	0.8	0.8		
N_2	41.1	41.1		
Total	100.0	100.0	100.0	100.0

	From Oxidizer	From Reductor
Solids (moles/hr.):		
Fe_3O_4	3.26	1.92
FeO*		3.55
Fe		0.70
Temperature, ° F	1,550	1,405

*Assumed as $Fe_{0.95}O$.

Note that solids compositions, gas compositions, inlet and exit temperatures (and internal reactor temperature gradients not shown in Table I), and the ratios of solids to gas flow rates are fixed for the particular reducing gas fed to the reductor. Changes in the independent operating variables, viz, feed gas temperatures and the ratio of solids to gas flow rates, will decrease either the reducing gas or steam conversion. For instance, higher steam or reducing gas inlet temperatures will result in higher solids temperatures in the reductor and oxidizer. These higher temperatures will effect slight increases in the reducing gas conversion, but a relatively larger decrease in steam conversion will result and the net hydrogen production per mole of reducing gas and steam fed will be decreased. It should be understood that the values listed for gas and solids flow rates are for illustrative purposes only. Larger throughput rates are, of course, possible. However, these rates should be increased proportionate to those listed in Table I for the particular feed reducing gas.

According to the invention as shown diagrammatically in FIGURE 3, the reductor has upper and lower subzones 1 and 2. As hereinbefore described, the reduction occurs in the two subzones, the reduction of Fe_3O_4 to FeO occurring in subzone 1, and the reduction of FeO to elemental iron occurring in subzone 2. Similarly, the oxidizer has two subzones 3 and 4, the oxidation of elemental iron to FeO occurring in subzone 3, and the oxidation of FeO to Fe_3O_4 occurring in subzone 4. Solids are recycled as shown in FIGURE 3 from the bottom of subzone 2 to the top of subzone 3. Gases are introduced and exhausted from the oxidizer and reductor zones as indicated in FIGURE 3.

As mentioned previously, gas-solids contacting must be countercurrent to achieve optimum gas conversions. This contact may be effected in a moving, fluidized or solids free-fall bed. In particular, there may be used a free-fall bed where the solids fall through the upwardly moving gas and tend to reach their terminal downward velocity. Also, there may be employed a hindered free-fall bed wherein downwardly falling solids are baffled in their fall by means of a suitable baffle. One such baffled system consists of a 17-foot long by 2-inch I.D. oxidizer, and a 25-foot long by 2-inch I.D. reductor; both containing a spined baffle. These baffles consisted of vertical ⅜-inch diameter center support rods in which ¼-inch diameter spines were horizontally mounted. The spines were ½ inch apart (24 per foot of support rod) and located in such a manner that the entire cross-section of the reactor was covered by the

24 spines. Thus, each vertically falling particle of solids strikes at least one baffle each foot of reactor length. There may also be used a fluidized bed of high length/diameter ratio where the overall solids movement is countercurrent to gas flow. In the alternative, there may be used staged fluidized beds wherein there exists two distinct fluidized beds in each reactor.

The kind of bed used, fluidized or free-falling, depends to some extent on the nature of the solids. For example, we have found that some iron solids, such as ammonia synthesis catalysts, become "tacky" at temperatures above about 1000° F., and the solids free-fall bed is best suited to handle such solids since lower particle densities can be effectively utilized in the reactors. The rates of solids reaction, both oxidation and reduction, are also favored in solids free-fall beds, since the maximum differential velocity (terminal settling velocity of the particle) between gas and particles is obtained independent of linear gas velocity in the reactor. Thus, net reaction rates are not hindered by relatively low gas diffusion rates, as is often the case in fluidized and moving beds where gas velocities are normally maintained substantially below particle terminal velocities.

We have found that the process of our invention can effectively utilize several types of iron-bearing solids such as ammonia synthesis catalysts (an activated form of iron oxide), several types of iron ores such as siderites and magnetites (both raw and beneficiated), several types of ore sinters, and other similar iron compounds. The rates of reaction, both oxidation and reduction, measured in our work show that temperatures in excess of 900° F., preferably 1300° F. to 1700° F. are sufficient to effect conversions with solids residence times in each reaction zone on the order of 5 to 180 seconds, preferably 30 to 60 seconds in the reduction zone, and from 15 to 60 seconds in the oxidation zone using particles ranging in size from 10 to 320 mesh, preferably 40 to 100 mesh. The ratio of elemental iron to magnetite reacted in the oxidation zone is 0.12:1 to 1.85:1, preferably 0.3:1 to 0.5:1. The ratio of active gas to total iron in the system is between 0.18:1 and 9.0:1. The corresponding solids conversions (100 percent conversion equals 27.6 pounds oxygen transferred per 100 pounds solids fed) for these operating conditions are 2 to 30 percent, preferably 10 to 20 percent. Linear gas velocities (based on actual operating conditions and empty reactor dimensions) between 0.1 and 6 feet/second, preferably 2 to 3 feet/second, can be utilized with solids free-fall bed densities as high as 40 pounds/cubic foot, preferably 5 to 15 pounds/cubic foot. Operation with fluidized bed densities of 125 to 175 pounds/cubic foot, requires high length to diameter ratios, above about 5. Thus, solids backmixing is minimized, and true countercurrent operation is more closely approached. Staged bed fluidization techniques commonly employed in industry can also be used for this purpose, as previously mentioned.

We have found that reaction rates increase substantially with pressure increases in the range of 0 to about 200 p.s.i.g. Therefore, the process of our invention should operate in excess of about 200 p.s.i.g. to take full advantage of these higher reaction rates. The use of higher pressures, say 200 to 2500 p.s.i.g., preferably about 500 to 1500 p.s.i.g., may be advantageous, depending on the subsequent use of the hydrogen-steam mixture. For instance, pressures of 1000 to 1500 p.s.i.g. are favorable for hydrogasification of carbonaceous materials to produce methane. Further, if the product hydrogen is to be used in ammonia manufacture, it is advantageous to operate at pressures of up to 2500 p.s.i.g., at which pressure the hydrogen can be fed directly into the ammonia synthesis equipment. Higher pressure also increases solids residence time in a solids-free-fall reactor since the terminal settling velocity of particles decreases with increases in pressure.

We have also found that additions of methane to the

feed reducing gas can increase its reducing quality by the following probable reactions.

$$CH_4+H_2O=3H_2+CO \tag{7}$$

$$CH_4+Fe_3O_4=3FeO+CO+2H_2 \tag{8}$$

The water for this reaction (7) is usually available in the raw feed gas and is also produced internally by the hydrogen reduction reactions. Since these reactions are endothermic, the heat of reaction must be supplied to the reductor to maintain proper reactor temperatures. This can be accomplished with higher inlet gas temperatures or by combustion of some of the spent reducing gas at the top of the reductor by the admission of air to this portion of the reductor.

We have also found that the addition of sulfur or sulfur compounds to the feed reducing gas is beneficial to the process. For example, hydrogen sulfide concentrations of 0.1 to 0.5 percent in the feed reducing gas inhibit the possible formation of free carbon; the formation of the unwanted products decreases the reducing quality of the reducing gases and causes the formation of carbon oxides in the oxidizer.

In commercially sized equipment, some heat losses from the system can be expected. Reasonable equipment design should limit these losses to less than 5 percent of the heat input to the system, in this case the enthalpy of the feed gas streams. Therefore, to maintain optimum temperature gradients in the reactors, higher inlet gas temperatures can be used as a convenient source of additional enthalpy. However, only enough additional enthalpy to balance heat losses should be provided, otherwise higher than optimum operating temperatures will result.

In our process, loss of solids temperature is detrimental to reducing gas conversion. Therefore, the most favorable reactor orientation with respect to temperature profiles is that which insures high inlet solids temperature to the reductor. For this reason, in one embodiment of our invention, the oxidizer should be mounted directly atop the reductor so that hot solids can be rapidly transferred from oxidizer bottom to reductor top as shown diagrammatically in FIGURE 3.

In such a reactor system, freshly reduced solids pass downwardly through the oxidizer through two reaction subzones indicated as 3 and 4, and exit at the bottom directly into the top of the reductor, subzone 1, with minimum heat loss. In subzone 3 there occurs predominantly reaction (1) hereinbefore described. In subzone 4 there occurs predominantly reaction (2). Freshly oxidized solids pass downwardly through the reductor through two reaction subzones indicated as 1 and 2, exiting into the bottom of a suitable lift means, e.g., a pneumatic lift where they are carried to the top of the oxidizer completing the cycle. In subzone 1, the predominant reactions are reactions (3) and (4); in subzone 2, reactions (5) and (6).

Any conventional reaction chambers and equipment can be used as oxidizer and reductor. For example, we have employed a 17-foot long oxidizer mounted directly atop a 25-foot long reductor, both with 2-inch internal diameters and both baffled, as discussed previously. A 6-inch I.D. hopper about 3 feet in length was mounted above the oxidizer, and a receiver of similar size was mounted below the reductor. The hopper contained a screw feeder for solids flow rate control so that excess solids were always stored directly above the screw. Solids were fed from the hopper at controlled rates and fell through the oxidizer, then through the reductor into the receiver from which the solids discharged into the bottom of the penumatic lift where they were entrained by the lift gas and carried to the top of the unit where the solids were disengaged from the lift gas and discharged into the hopper. Feed steam at controlled pressure and temperature enters at the bottom of the oxidizer, flows upwardly, contacts the solids countercurrently, and exits at the top of the oxidizer as product hydrogen and unreacted steam.

Feed reducing gas at controlled pressure and temperature enters the bottom of the reductor where it flows upwardly countercurrent to the solids, exiting at the top of the reductor. Both product gas streams are processed as required in conventional process equipment.

In this embodiment of the invention, feed reducing gas at controlled temperature and pressure is used in the pneumatic lift to transport solids from the bottom of the reductor to the top of the oxidizer. The gas entrains the solids, carries them upwardly through a conduit to a gas-solid separator, for example, a centrifugal separator where the solids are disengaged and fed into the oxidizer. Transport gas is then returned to the bottom of the reductor.

The following further examples illustrate the invention. In both Examples 2 and 3, the solids material and reactor residence times are the same as in Example 1.

EXAMPLE 2.—GAS COMPOSITIONS AND FLOW RATES

Gas	Reducing Gas	Spent Reducing Gas	Steam	Steam-H_2
Temperature, ° F	1,600	1,550	1,100	1,428
Moles/hr	2.21	2.21	1.69	1.69
Composition, Mole percent:				
CO	14.7	4.6		
CO_2	1.6	11.7		
H_2	40.7	12.6		50.1
H_2O	6.7	34.8	100.0	49.9
CH_4	1.2	1.2		
N_2	34.4	34.4		
Ar	0.7	0.7		
Total	100.0	100.0	100.0	100.0

	From Oxidizer	From Reductor
Solids (moles/hr.):		
Fe_3O_4	1.58	0.92
FeO*		1.81
Fe		0.27
Temperature, ° F	1,550	1,428

*Assumed as $Fe_{.95}O$.

EXAMPLE 3.—GAS COMPOSITIONS AND FLOW RATES

Gas	Reducing Gas	Spent Reducing Gas	Steam	Steam-H_2
Temperature, ° F	1,500	1,500	1,100	1,430
Moles/hr	3.65	3.65	2.02	2.02
Composition, Mole percent:				
CO	21.4	7.8		
CO_2	4.5	18.1		
H_2	20.2	8.0		46.7
H_2O	6.0	18.2	100.0	53.3
N_2	47.8	47.8		
H_2S	0.1	0.1		
Total	100.0	100.0	100.0	100.0

	From Oxidizer	From Reductor
Solids (moles/hr.):		
Fe_3O_4	3.00	2.50
FeO*		1.05
Fe		.50
Temperature	1,500	1,430

*Assumed as $Fe_{.95}O$.

The above description has served to illustrate a specific application of this invention. Other modifications of equipment and operating conditions can easily be made by those skilled in the art to utilize more advantageously a specific type of feed reducing gas or type of iron-bearing solids and is considered within the scope of this invention.

We claim:

1. A continuous steam-iron process utilizing countercurrent gas-solids contact for producing hydrogen comprising the following steps:

(1) reacting Fe_3O_4 with a reducing gas at a temperature from 1000° F. to 2000° F. in a reduction zone wherein said Fe_3O_4 is reduced to FeO in a first subzone and said FeO is reduced to elemental iron in a second subzone, and

(2) reacting the resultant reduced solids product with steam at a temperature from 1000° F. to 2000° F. in an oxidation zone wherein said elemental iron is oxidized to FeO in a third subzone and said FeO is oxidized to Fe_3O_4 in a fourth subzone,

step (1) being caused to occur countercurrently such that fresh reducing gas is contacted with substantially FeO to produce elemental iron and the resultant gas is contacted with substantially Fe_3O_4 to produce FeO, and step (2) being caused to occur countercurrently such that feed steam is contacted with substantially FeO to produce Fe_3O_4 and the resultant gas is contacted with substantially elemental iron to produce FeO, thereby producing hydrogen, and said steps (1) and (2) being operated at a pressure of minimally 200 p.s.i.g.

2. Process of claim 1 wherein the ratio of elemental iron to Fe_3O_4 reacted in the oxidation subzones is 0.12:1 to 1.85:1.

3. Process of claim 1 wherein the solids discharged from the fourth subzone, comprising substantially Fe_3O_4, are fed to the first subzone.

4. Process of claim 1 wherein the third and fourth subzones of step (2) are located above the first and second subzones of step (1) and wherein the solids discharged from the fourth subzone, comprising substantially Fe_3O_4, are fed directly to the first subzone whereby temperature loss between the first and fourth subzones is minimized.

5. Process of claim 1 wherein countercurrent flow between solids and gases in said reduction zone is attained by free-fall of solids downwardly through upwardly rising gas.

6. Process of claim 1 wherein countercurrent flow between solids and gases in said oxidation zone is attained by free-fall of solids downwardly through upwardly rising gas.

7. Process of claim 1 wherein countercurrent flow between solids and gases in said reduction zone is attained in a fluidized bed.

8. Process of claim 1 wherein countercurrent flow between solids and gases in said oxidation zone is attained in a fluidized bed.

9. Process of claim 1 wherein air is injected at the top of the first subzone to combust a portion of the spent reducing gas.

10. Process of claim 1 wherein the reducing gas contains carbon monoxide and hydrogen.

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U.S. Cl. X.R.

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STEAM-IRON PROCESS FOR AMMONIA SYNTHESIS GAS PRODUCTION

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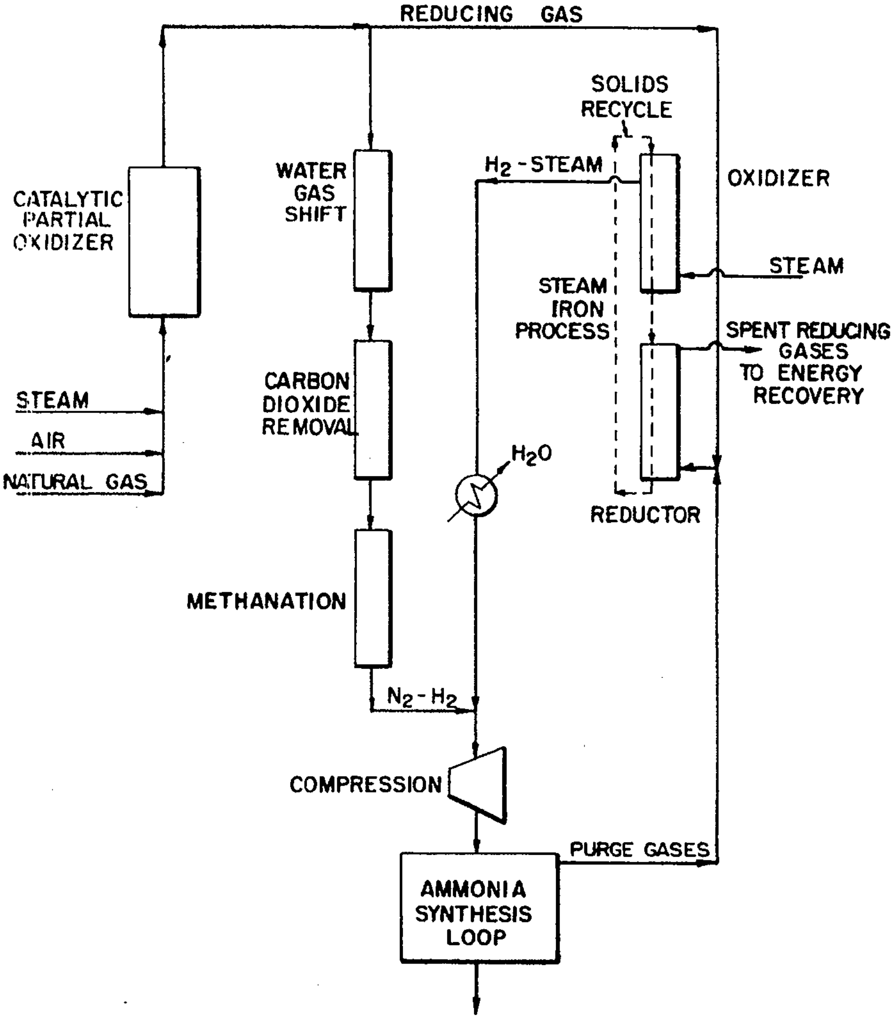

FIG. 1

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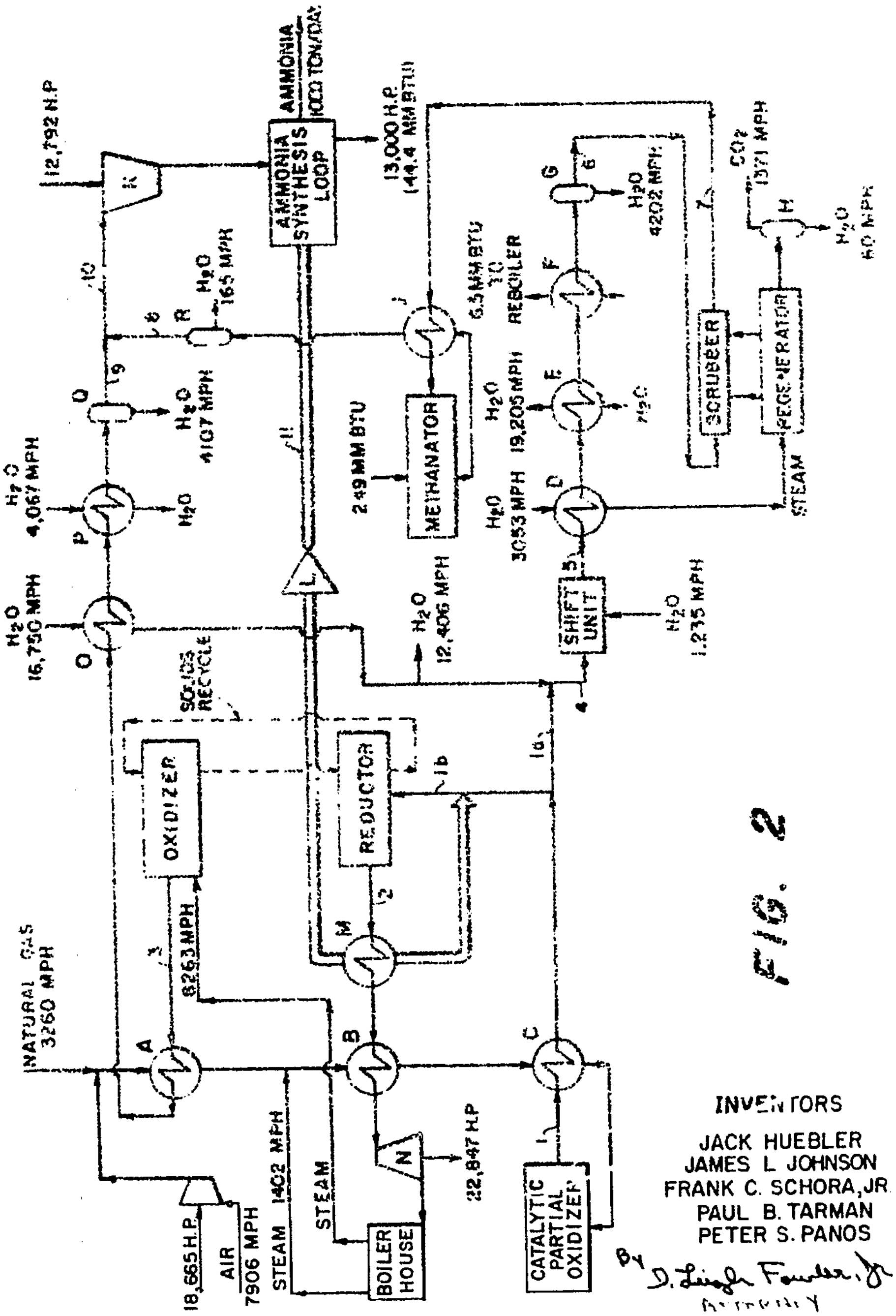

FIG. 2

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STEAM-IRON PROCESS FOR AMMONIA SYNTHESIS GAS PRODUCTION

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Continuation-in-part of abandoned application Ser. No. 477,769, Aug. 6, 1965. This application Mar. 7, 1968, Ser. No. 711,379
Int. Cl. C01b *1/08;* C01c *1/04;* B01j *9/00*
U.S. Cl. 23—199 6 Claims

ABSTRACT OF THE DISCLOSURE

In an ammonia synthesis wherein part of the requisite hydrogen is supplied by the steam-iron process, the improvement which comprises using purge gases from the ammonia synthesis to assist in the reduction step of the steam-iron process.

This application is a continuation-in-part of our copending application, Ser. No. 477,769, filed Aug. 6, 1965, now abandoned.

This invention relates to the production of ammonia via the steam-iron process. In particular, this invention relates to methods for improving the overall process efficiency of ammonia production wherein the feed hydrocarbon requirements are reduced and the process is thereby rendered more economical.

Ammonia synthesis gas, i.e. gas containing nitrogen and hydrogen in the proper ratio for conversion to ammonia, is conventionally produced by steam reforming of methane, wherein natural gas (methane) is reacted with air and steam in a catalytic reformer to produce a gas consisting of carbon monoxide, carbon dioxide, hydrogen, water, nitrogen, argon, and residual methane. These gases are further treated by water gas shift, carbon dioxide removal, and methanation equipment to produce ammonia synthesis gas substantially free of carbon monoxide, carbon dioxide, and water.

The process is known for producing ammonia synthesis gas which uses the steam-iron process for producing hydrogen which serves as an adjunct to the nitrogen and hydrogen produced by the partial oxidation of natural gas (see U.S. Pat. No. 2,014,757). The steam-iron process uses a reducing gas to reduce iron oxides which then are reacted with steam to produce hydrogen.

The ammonia synthesis gas, however produced, is then reacted in a conventional ammonia synthesis loop at elevated pressures to produce ammonia. Because of the recycle nature of ammonia synthesis, the loop system must be continuously purged to prevent accumulation of residual gases, such as argon and methane. These purge gases contain considerable amounts of nitrogen and hydrogen which must be discarded and, as a result, the overall efficiency of the process is decreased.

Recent advances in ammonia synthesis have resulted in lowering of ammonia loop operating pressures from about 5000 p.s.i.a. to substantially lower pressures with a net decrease in operating costs because of decreased compression expenses. However, the savings are offset to a degree by a necessary increase in the volume of purge bled from the synthesis loop. For example, at 2300 p.s.i.g. an amount of gas equivalent to about 10% of the feed synthesis gases is purged from the loop.

These purge gases comprise about 69 percent hydrogen, 23 percent nitrogen, 6 percent methane, 2 percent argon, traces of ammonia and other impurities, and would be considered a low quality heating value gas (about 280 B.t.u./s.c.f.). Purge gases are normally burned to recoup their thermal energy in a conventional plant.

In accordance with our invention, these purge gases are used in the steam-iron process to effect a more efficient operation when using such process for ammonia synthesis gas production. In the preferred embodiment of the steam-iron process, two reactors are used: a reductor to produce reduced iron oxides by reaction of a suitable reducing gas with iron oxides, and an oxidizer to produce hydrogen by reaction of steam with the reduced iron oxides. Admission of the ammonia loop purge gases to the reductor increases the production of reduced iron oxides and subsequently increases the hydrogen production in the oxidizer. Since the spent reducing gas is not used as a portion of ammonia synthesis gas in this invention, there can be no additional accumulation in the synthesis loop of undesirable residual gases, such as argon. In fact, methane in the purge gases can react in the reductor to form additional hydrogen and carbon monoxide and increase the reducing potential of the reducing gas resulting in even further increases in hydrogen production in the oxidizer. Increases in hydrogen production are reflected as decreases in feedstock requirements to the partial oxidizer in the production of the reducing gas. This is an important economic consideration because the feedstock material is the principal operating expense in ammonia manufacture.

Thus, it is the essence of this invention to produce ammonia by combining the partial oxidation of natural gas, other hydrocarbons, or carbonaceous fuels with the steam-iron process to effect substantial economic savings by injecting the ammonia synthesis loop purge gases into the reductor of the steam-iron process.

It is an object of this invention to produce ammonia by the steam-iron process wherein the pressure energy of the ammonia loop purge gases is more efficiently recovered by injecting these gases into the reductor of the steam-iron process.

It is yet another object of this invention to produce ammonia using the steam-iron process wherein methane in the ammonia loop purge gases reacts in the reductor of the steam-iron process to substantially decrease natural gas feed requirements.

Other objects of this invention will become apparent as the invention is more fully described hereinafter.

In the drawings:

FIG. 1 is a flow diagram showing the process steps of this invention.

FIG. 2 is a detailed flow diagram for a 1000 ton/day ammonia plant using the improved process of the invention.

In the process of the invention as shown broadly in FIG. 1, natural gas, air, and steam enter the catalytic partial oxidizer wherein high quality reducing gas (high carbon monoxide plus hydrogen content) is produced. Such process and apparatus effecting it are well known in the art. As an alternative to natural gas feedstock, higher hydrocarbons may be used as the hydrocarbon feed. It is also possible to produce this high quality reducing gas by partial oxidation of coal or other carbonaceous materials. The product reducing gas stream is then split, some used in the reductor of the steam-iron process for reducing iron oxide, the rest used to supply the necessary nitrogen for the ammonia synthesis loop. The latter stream is passed through conventional water gas shift, carbon dioxide removal, and methanation equipment as shown diagrammatically in FIG. 1, yielding nitrogen, hydrogen, and residuals, such as methane and argon. Additional hydrogen to obtain the proper stoichiometric mixture of hydrogen and nitrogen for the ammonia synthesis loop is obtained from the steam-iron process wherein reducing gas reacts with the iron oxide solids in the reductor to produce a reduced form of iron oxide (elemental iron and ferrous oxide). The reduced form of iron oxide is recirculated to the oxidizer and contacted with steam to produce the necessary hydrogen. The steam-hydrogen mixture is then cooled to condense steam and the residual hydrogen is mixed with gas from the methanator and fed to the ammonia synthesis loop.

Because the spent reducing gases from the reductor do not enter the synthesis loop, any inert gases added to the feed reducing gas will not accumulate in the system. This addition of the loop purge gases to the reducing gas feed to the reductor subsequently decreases feedstock requirements to the partial oxidizer. Thus, as shown in FIG. 1, the purge gases are fed to the steam-iron process reductor and are used as supplemental reducing gas to augment the reducing gas from the partial oxidizer.

A detailed flow diagram of a 1000 ton/day ammonia plant using the process of our invention is shown in FIG. 2. All the necessary energy required for process operation is developed within the process. When using the process of this invention—utilizing the loop purge gases in the reductor—there is required only 29,600 s.c.f. natural gas/ton ammonia as compared to requirements of 32,000 to 42,000 s.c.f. natural gas/ton ammonia for conventional ammonia plants now in operation. Thus, the natural gas requirements, which account for almost two-thirds of total manufacturing costs of a 1000 ton/day ammonia plant, can be reduced 15 to 30 percent by use of the process described herein. In conventional operation, about 17 percent of the feed natural gas is required to maintain reformer temperatures. The economic advantage to be had with this process is self-evident.

The following description of the invention should be read in conjunction with Table I which describes the various gas streams identified in FIG. 2. The moles of material fed, or formed, in the process are shown in FIG. 2, and indicated by the letters m.p.h., i.e. moles per hour.

to 1500° F., and then split into two streams, one for the reductor, the other for the water gas shift unit. The smaller portion is admixed with water, which flashes to steam, and is fed to the water gas shift reactor to convert the carbon monoxide by reaction with steam and carbon dioxide to hydrogen.

These product gases pass through exchangers D, E, F and water knockout pot G, and enter the carbon dioxide removal system which consists of a scrubber, regenerator and water knockout pot H. The scrubbed gases pass through exchanger J and enter the methanator where the residual carbon oxides are almost completely removed by formation of methane to prevent poisoning of the ammonia synthesis catalyst in the ammonia synthesis loop. The methanated gases are (1) passed through exchanger J, (2) passed through water knockout pot R, (3) admixed with hydrogen from the steam-iron process, and (4) compressed in compressor K to ammonia synthesis loop pressure at 2300 p.s.i.a. in this example.

The ammonia loop system, here illustrated, produces 1000 tons/day of ammonia and 1,189 moles/hour of purge gas at 100° F. The purge gases are reduced in pressure from 2300 to 470 p.s.i.a. in pressure reducer L. Because of the small volumetric flow rate, pressure energy is not recovered in this pressure reduction. The purge gases are then heated in exchanger M to 1500° F. and admixed with the larger portion of reducing gases from the catalytic partial oxidizer to improve the reducibility of the feed gases to the reductor of the steam-iron process.

In the reductor, the improved reducing gases are contacted countercurrently with downwardly moving iron oxide solids reducing them to lower oxide forms (elemental iron plus ferrous oxide). The spent reducing gases pass through exchangers M and B and expander N generating about 23,000 H.P. The expanded gases are further utilized in the boiler house to generate steam which is used for process feed steam. Of the total energy extracted from the spent reducing gases, over 10 percent results from the purge gases added to the feed reducing gas. Thus, in contrast to conventional operation, about 80 percent of the pressure energy in the purge gases is recovered by admixing them with the reducing gas feed.

TABLE I.—STREAM VOLUMES AND COMPOSITION

Stream No.	H_2	CO	CO_2	CH_4	N_2	A	H_2O	Gas flow	
								Moles/hr.	MMs.c.f./hr.
1	37.25	16.54	1.74	0.68	35.86	0.46	7.47	17,192	6.51
1a	37.25	16.54	1.74	0.68	35.86	0.46	7.47	7,561	2.87
1b	40.70	14.72	1.55	1.22	34.43	0.73	6.65	10,800	4.09
2	12.85	4.65	11.71	1.22	34.43	0.73	34.51	10,800	4.09
3	50.08						49.92	8,263	3.13
4	23.68	10.51	1.11	0.43	22.80	0.29	41.18	11,925	4.51
5	30.92	0.06	10.47	0.30	20.66	0.26	37.24	13,160	4.98
6	45.42	0.00	15.38	0.88	30.35	0.39	7.79	8,958	3.39
7	57.75	0.12	0.10	0.73	38.58	0.49	2.23	7,047	2.67
8	67.63			0.97	30.68	0.51	0.21	6,852	2.59
9	99.80						0.20	4,147	1.57
10	74.14			0.61	24.72	0.32	0.21	10,989	4.16
11	68.60			5.60	22.88	2.92		1,189	0.45

In the operation of the process, air is compressed to 470 p.s.i.a., mixed with natural gas to attain 395° F., and heated in heat exchanger A to 860° F., exchanger B to 1125° F., and exchanger C to 1520° F. Because of the combustibility of the gas air premix, premix velocities in the exchanger coils should exceed about 40 feet/sec. in A for temperatures up to about 900° F., 100 feet/sec. in B and 200 feet/sec. in C. Steam is added to the premix before it enters exchanger B to inhibit combustion and carbon deposition reactions in the higher temperature exchangers. These gases are converted to reducing gases in the catalytic partial oxidizer which operates at a nominal temperature of 1500° F. to 2200° F. and a pressure of 470 p.s.i.a. If desired, the natural gas, air, and steam can be separately heated to 1520° F., mixed and fed to the catalytic partial oxidizer.

The product reducing gases from the catalytic partial oxidizer pass through heat exchanger C and are cooled

The reduced iron oxides from the reductor enter the oxidizer and are contacted with steam to produce a steam-hydrogen product mixture. This mixture is passed through exchanger A, and through exchanger O which heats water for the water gas shift system. The mixture is further cooled in exchanger P and water is removed in knockout pot Q. The pure hydrogen remaining is then admixed with the methanated gases to yield a proper stoichiometric ratio of hydrogen and nitrogen for ammonia synthesis.

The above example shown diagrammatically in FIG. 2 serves to illustrate a specific application of this invention. Modifications of equipment and operating conditions can easily be made by those skilled in the art to utilize more advantageously a specific type of feedstock material and are considered within the scope of this invention.

We claim:

1. In an ammonia synthesis loop which is supplied with

supplemental hydrogen by the steam-iron process, the improvement which comprises using purge gases from said ammonia synthesis loop to reduce iron oxides formed in said steam-iron process.

2. In the process for producing ammonia in an ammonia synthesis loop from a synthesis gas obtained by the partial oxidation of a hydrocarbonaceous feedstock, wherein the hydrogen content of said synthesis gas is supplemented by hydrogen supplied by a steam-iron system containing an oxidizer and reductor, the improvement which comprises feeding purge gases from said ammonia synthesis loop to said reductor of said steam-iron system.

3. In a process for producing ammonia comprising the following steps:

(a) reacting air with a hydrocarbonaceous feedstock either with or without the addition of steam to produce reducing gas comprising carbon monoxide, hydrogen, nitrogen, steam, carbon dioxide, and residuals such as methane, argon, and other impurities;

(b) reacting a portion of the reducing gas from step (a) by water gas shift reaction, carbon dioxide removal and by methanation reaction to remove residual carbon oxides, thereby producing a synthesis gas comprising essentially nitrogen and hydrogen; and

(c) producing hydrogen-rich gas by the steam-iron process for admixture with said synthesis gas for feeding to an ammonia synthesis loop,

the improvement which comprises feeding purge gases from said ammonia synthesis loop to the reductor of said steam-iron process to increase the efficiency of the reductor reducing gas in said steam-iron process.

4. Process for producing ammonia from synthesis gas containing hydrogen and nitrogen in required stoichiometric ratio comprising the following steps:

(a) reacting air with a hydrocarbonaceous feedstock, either with or without the addition of steam, by catalytic partial oxidation to produce reducing gas comprising carbon monoxide, hydrogen, nitrogen,

steam, carbon dioxide and residual methane and argon;

(b) feeding a portion of said gas produced in step (a) successively to water gas shift reactor, carbon dioxide removal apparatus and methanation reactor to remove residual carbon oxides, thereby producing a gas essentially composed of nitrogen and hydrogen;

(c) feeding the balance of gas from step (a) to the reductor reactor of a steam-iron process apparatus, and withdrawing hydrogen from the oxidizer reactor of said apparatus;

(d) admixing hydrogen from step (c) with gas resulting from step (b) to produce the required stoichiometric ratio for ammonia synthesis and feeding said admixture to an ammonia synthesis loop; and

(e) feeding purge gas from said synthesis loop to the reductor of said steam-iron process apparatus whereby said purge gas augments the reducing gas requirements in step (c) and substantially reduces the requirement for hydrocarbonaceous feedstock in step (a).

5. Process of claim 4 wherein said hydrocarbonaceous feedstock in step (a) is natural gas.

6. Process of claim 5 wherein catalytic partial oxidation of step (a) is effected at a pressure above 300 p.s.i.g., and a temperature between 1500° and 2200° F.

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U.S. Cl. X.R.

23—214, 289

United States Patent

[11] 3,619,142

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[21] Appl. No. **798,334**
[22] Filed **Feb. 11, 1969**
[45] Patented **Nov. 9, 1971**
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[54] **CONTINUOUS STEAM-IRON PROCESS**
8 Claims. 5 Drawing Figs.

[52] **U.S. Cl.** **23/214,** 23/200, 23/212, 23/284, 48/197
[51] **Int. Cl.** **C01b 1/07,** C01b 1/02
[50] **Field of Search** 23/214, 212, 210, 200

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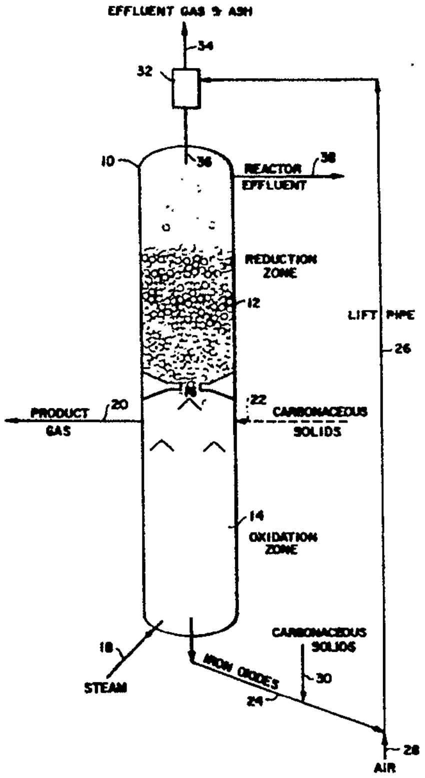
ABSTRACT: In a continuous steam-iron process wherein finely divided iron oxides are reduced in a reduction zone and the reduced iron oxides are reacted with steam in an oxidation zone to make hydrogen, the reduction of the iron oxides is effected by means of a continuously recirculating stream of hot, finely divided carbonaceous solids which are mixed with the iron oxides in a downwardly moving bed under reducing conditions, and heat is supplied to the reduction zone by the carbonaceous solids which are heated by partial combustion outside the reduction zone. In the preferred embodiment of the process, the mixture of reduced iron oxides and carbonaceous solids from the reduction zone is separated in a fluidized separation zone into a stream of reduced iron oxides and a stream of carbonaceous solids. The stream of reduced iron oxides is conducted to the oxidation zone where the reduced iron oxides fall through a fluidized bed of hydrocarbonaceous solids in countercurrent flow relationship to steam, whereby a product gas is produced which contains methane by virtue of the reaction of the hydrogen (produced by the steam-iron reaction) with the hydrocarbonaceous solids



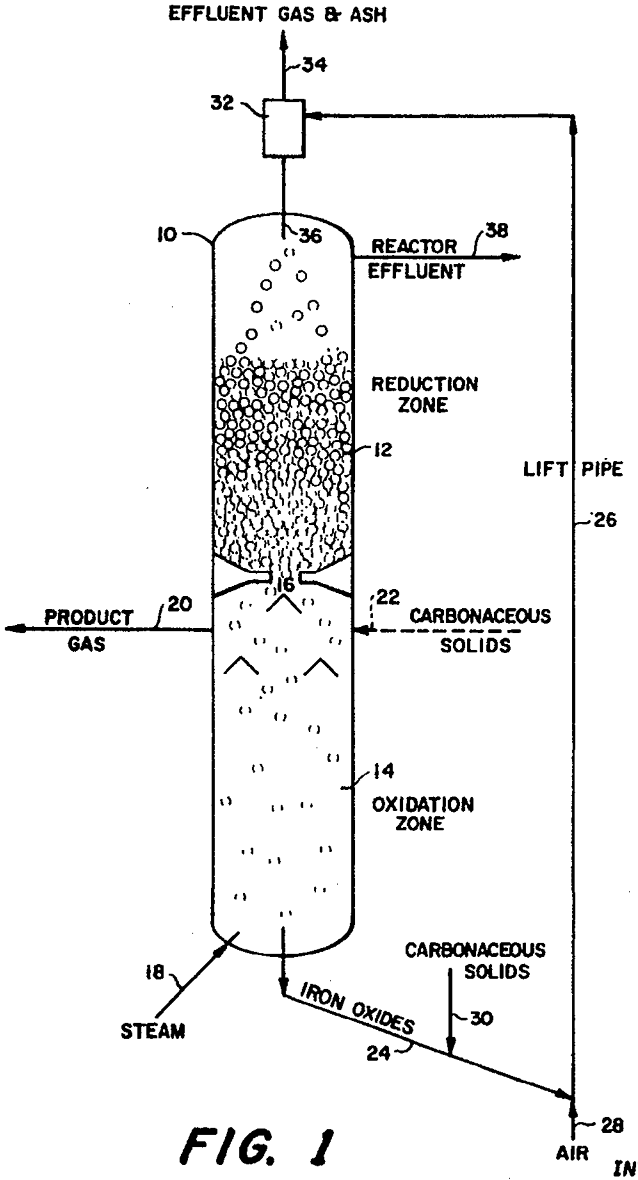


FIG. 1

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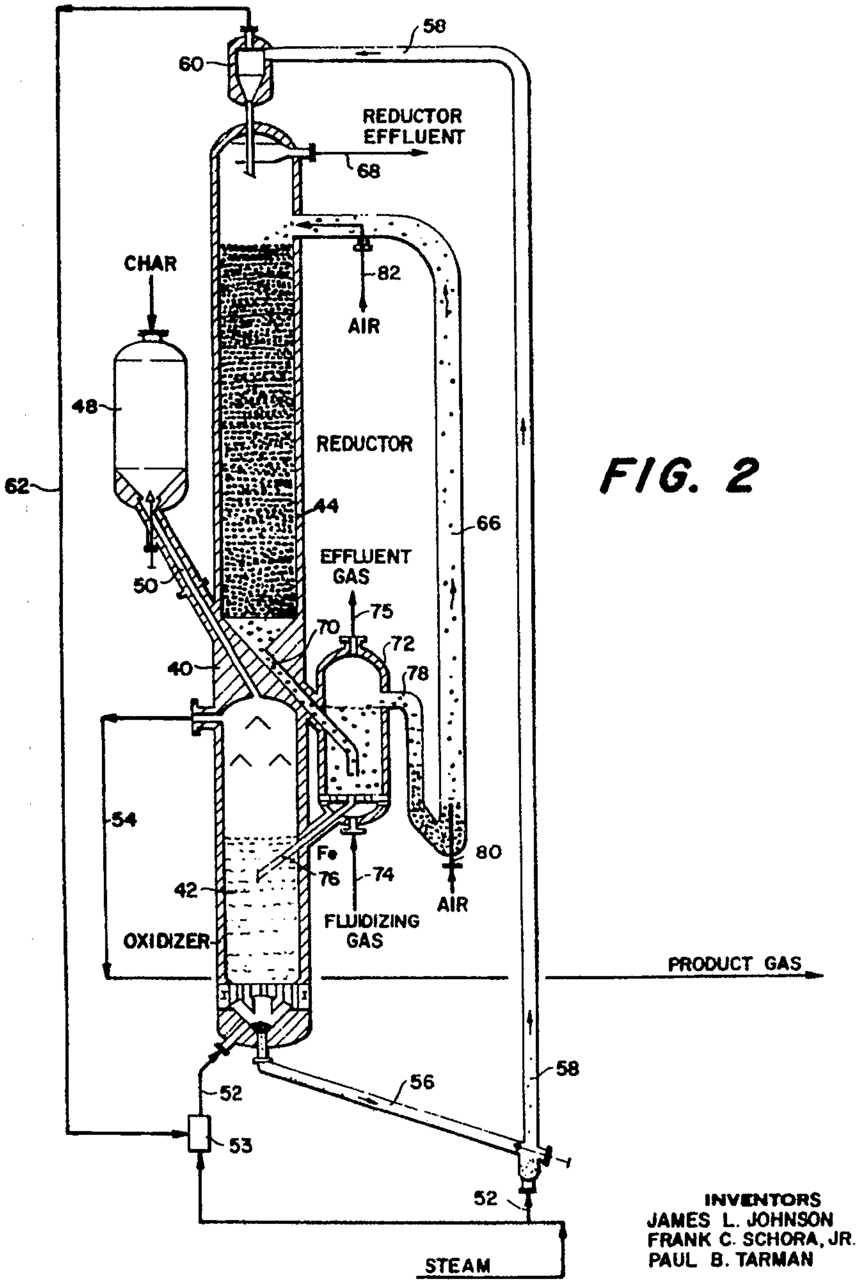

FIG. 2

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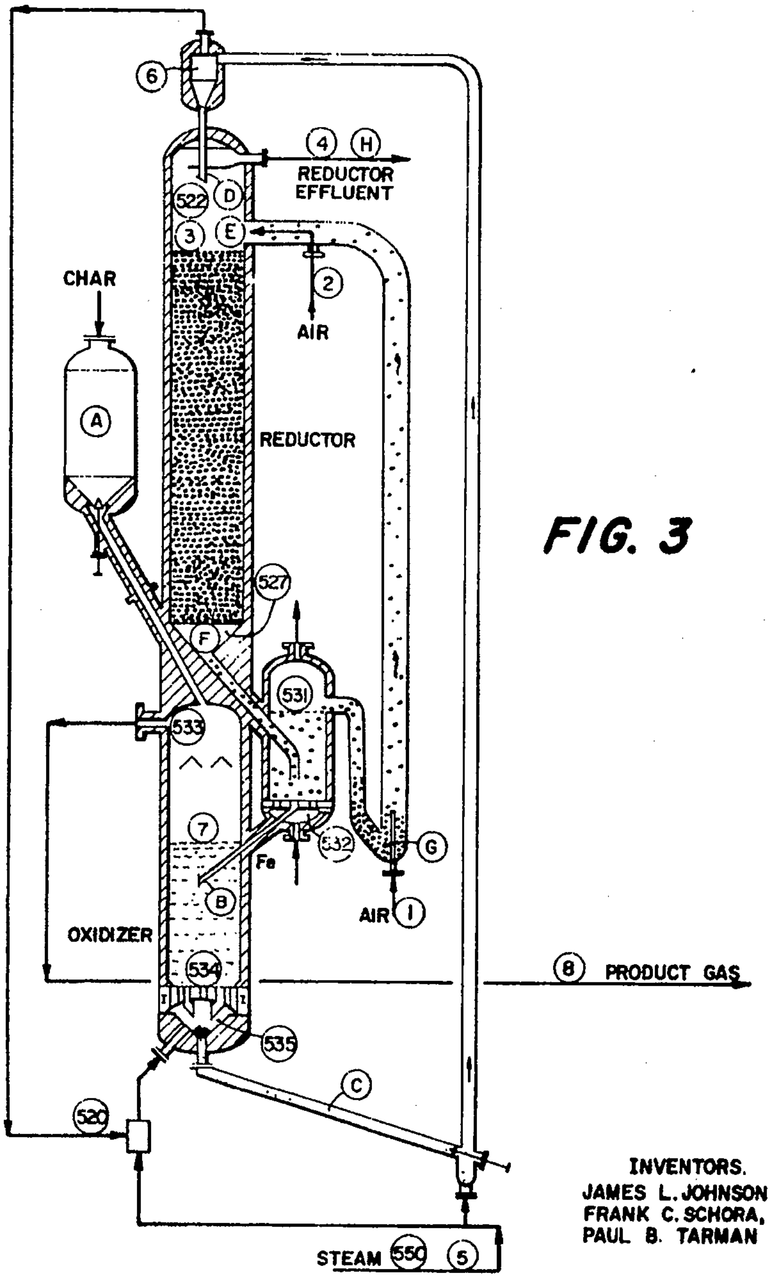

FIG. 3

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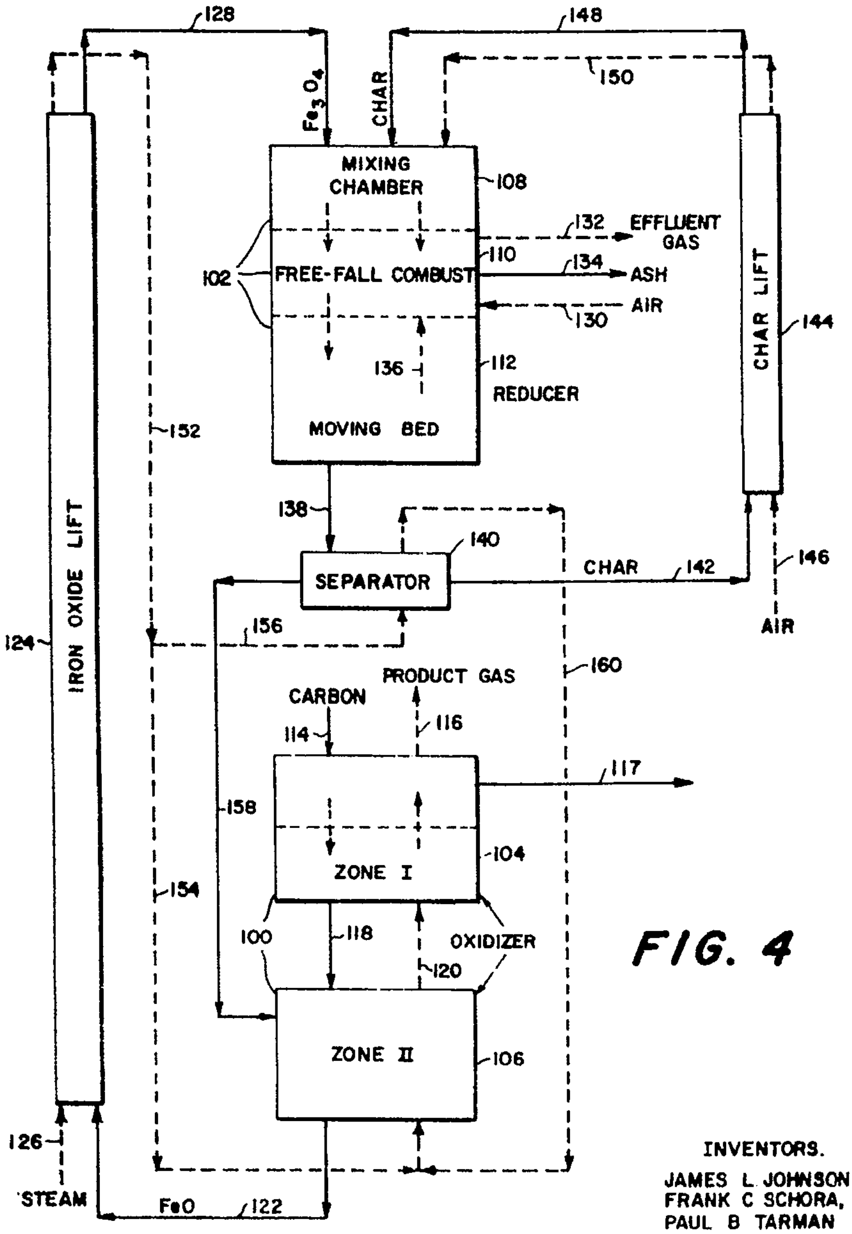

FIG. 4

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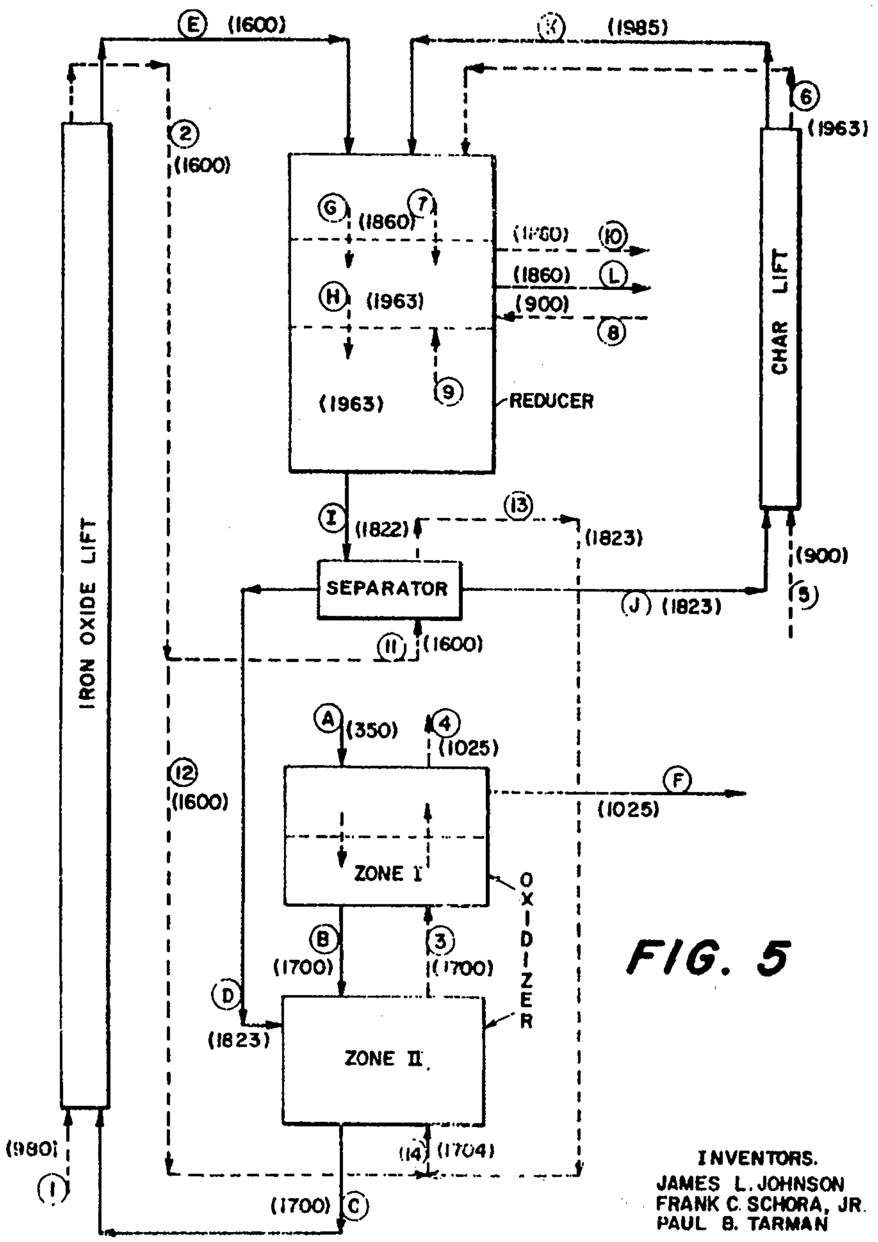

FIG. 5

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CONTINUOUS STEAM-IRON PROCESS

This invention relates to an improvement in the steam-iron process for making hydrogen or fuel gas.

The steam-iron process is a process for making hydrogen by the reaction of steam with either elemental iron or a lower iron oxide, for example, FeO. The reaction produces higher oxides of iron, for example, Fe_3O_4, which may be reduced to repeat the cycle.

Despite the apparent simplicity of the steam-iron process and despite the fact that it has been known and worked on for over 100 years, to the best of our knowledge no technically and economically feasible embodiment of a continuous steam-iron process has been developed which is now practiced commercially. Perhaps the principal reason for the failure of the steam-iron process to achieve commercial success is the difficulty involved in making it a continuous process. To do so requires subjecting a continuously flowing recirculatory stream of iron oxides to two different reactions, namely oxidation and reduction, under optimum conditions for each reaction, including optimum input and distribution of the heat required in the process.

Prior continuous steam-iron processes have favored the use of gaseous reductants for reducing the iron oxides (see, by way of illustration, U.S. Pat. No. 2,198,560). However, the production of a suitable gaseous reductant is expensive, and renders the overall process uneconomical. Furthermore, because of the limitations imposed by the thermodynamic equilibrium during the reduction of Fe_3O_4 and FeO to FeO and Fe with reducing gases containing hydrogen and carbon monoxide, the off-gas from once-through reduction contains considerable unreacted hydrogen and carbon monoxide. Thus, such a process tends to be wasteful of reducing gas.

In the copending application of Homer E. Benson, Ser. No. 598,072, filed Nov. 30, 1966 and assigned to the assignee of the present invention, the reducing gas is made *in situ* by reacting air and carbonaceous solids in the presence of the iron oxides. Such a process has many advantages but requires careful control to minimize reconversion of elemental iron to higher oxides by contact with air.

Continuous steam-iron processes have been proposed which utilize either a solids in gas dispersion or the fluidized solids technique in the oxidation zone and the reduction zone (see, by way of illustration, U.S. Pat. Nos. 2,602,809 and 3,017,250). Reducing systems employing a dispersion of powdered iron oxide in a suspending gas call for large reactors and costly gas-solids separators. All attempts to operate with the iron oxide in a fluidized condition have failed to become sufficiently attractive for commercial adoption because a fluidized mass is of uniform composition throughout whereas a composition gradient is generally desired.

In accordance with the present invention we have provided an improved continuous steam-iron process which uses not only a recirculatory stream of particulate iron oxides, but also uses a recirculatory stream of particulate carbonaceous solids to effect reduction of the iron oxides and to supply process heat requirements. In the practice of the process of this invention, reduced iron oxides comprising principally FeO and Fe are oxidized by steam in an oxidation zone, and iron oxides comprising principally Fe_3O_4 and FeO are reduced in a reduction zone. By "principally" we mean that at least 50 percent by weight of any mixture of oxidizable or reducible iron compounds, as the case may be, consists of the indicated compounds, and the actual percentage approaches 100 percent under equilibrium conditions. The relative amounts of FeO and Fe in the oxidizable mixture, and the relative amounts of Fe_3O_4 and FeO in the reducible mixture are functions largely of the temperature, pressure, and residence time maintained in the respective reaction zones. The oxidation of FeO and Fe (sometimes simply referred to herein as reduced iron oxides) is accomplished by passing steam in reactive relationship with the reduced iron oxides in an oxidation zone. The reduction of Fe_3O_4 and FeO is accomplished by subjecting them to direct contact with the recirculatory stream of hot carbonaceous solids in a downwardly moving bed in the reduction zone. No oxygen-(molecular) containing gases are introduced into the moving bed in the reduction zone. The reduction conditions are selected to insure that only partial carbon depletion is effected during the passage of the carbonaceous solids through the reduction zone, while however, the desired reduction of the iron oxides to Fe and FeO is effected. Heat is supplied to meet the requirements of the process by partial combustion of the carbonaceous solids in a combustion zone located outside the reduction zone. The amount of partial burning is controlled to raise the temperature of the carbonaceous solids sufficiently high to supply adiabatically the heat required.

In the preferred embodiment of the process, a separation zone is interposed between the reduction zone and the oxidation zone to effect separation of the carbonaceous solids from the reduced iron oxides leaving the reduction zone. Separation is effected by passing a gas through the mixture of carbonaceous solids and reduced iron oxides at a velocity which permits ready separation by virtue of the difference in densities of the iron compounds and carbonaceous solids. A fluidized separation zone is especially preferred wherein the fluidized bed consists essentially of the lighter carbonaceous solids from which the heavier iron compounds may be withdrawn and sent to the oxidation zone. The oxidation zone in the preferred embodiment comprises a fluidized bed of fresh carbonaceous solids into which the reduced iron oxides are fed. Hydrogen is produced by the relatively fast reaction of steam and reduced iron oxides, and in turn reacts with the carbonaceous solids to form methane. The separated carbonaceous solids from the separation zone are recirculated through the combustion zone back to the reduction zone.

The process operates continuously and efficiently to yield hydrogen or a methane-rich gas. The improvement in economics of the process as compared with prior steam-iron processes is due to the efficient use of low cost, finely divided carbonaceous solids for 1 the reduction of iron oxides, 2 the supply of process heat, and 3 in the preferred embodiment, the production of methane in a relatively simple two-vessel system. The gain in efficiency in the reduction zone arises from the thermal gradient established in the downwardly moving bed and from the lack of back-mixing of reduced iron. Thus, maximum reaction rates result from the countercurrent flow relationship of the upwardly flowing reducing gases (generated *in situ*) and the downwardly flowing fresh iron oxides. The absence of molecular oxygen-containing gases assures no loss of desired reduction as a result of competing reactions. The flow of gases and solids in the oxidizer is most efficiently conducted in a fluidized bed for the particular reactions involved, to thereby minimize temperature gradients and to provide for an efficient balance between exothermic and endothermic reactions. Thus, in summary, the improved process provides for the maintenance of the optimum conditions for the reduction of Fe_3O_4 to FeO to Fe, and for the oxidation of the reduced iron oxides with steam.

For a better understanding of our invention, its objects and advantages, reference should be had to the following description and accompanying drawings in which

FIG. 1 is a diagrammatic drawing of our invention in its broadest aspects,

FIG. 2 is a diagrammatic drawing of the preferred embodiment of our invention,

FIG. 3 is the same diagrammatic drawing of FIG. 2 but showing the locations of different points in the solids and gas streams to aid in understanding the material balance run reported in Table I of the specification,

FIG. 4 is a schematic drawing of a modification of the preferred embodiment of FIG. 2, and

FIG. 5 is the same schematic drawing of FIG. 4 but showing the locations of different points in the solids and gas streams to aid in understanding the material balance run reported in Table II of the specification.

Referring to FIG. 1 of the drawings, the numeral 10 designates a suitable vessel for housing a reduction zone 12 and an oxidation zone 14. The reduction zone consists essentially of a downwardly moving bed of solids which flows by gravity through an opening 16 into the oxidation zone. The downwardly moving bed of solids in the reduction zone consists essentially of a mixture of two recirculatory streams of solids moving in substantially concurrent flow relationship. The first stream of solids contains iron oxides which are principally Fe_3O_4 and FeO. The second stream of solids contains carbonaceous solids which serve not only to effect reduction of the iron oxides, but also to provide adiabatically the heat required for the reduction reaction. The primary reactions which occur in the reduction zone are as follows:

1. $CO+Fe_3O_4 \rightarrow 3FeO+CO_2$
2. $CO+FeO \rightleftarrows Fe+CO_2$
3. $CO_2+C \rightarrow 2\,CO$

The temperature maintained in the reduction zone is between 1000° and 2600° F. The pressure may be atmospheric or superatmospheric. The size consist of the iron oxides may suitably be in the range of 325 to 2 Tyler Standard screen. The size consist of the carbonaceous solids may also suitably by in the range of 325 to 2 Tyler Standard screen. The residence time of both solids in the reduction zone is generally between 15 seconds and 60 minutes

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The carbonaceous solids in the reduction zone may conveniently be a solid carbonaceous fuel that is noncaking under the conditions of the reduction zone. Suitable solids of this kind are noncaking coals, lignite, coke, char which is the solid product obtained by the pyrolysis of coal or lignite, or coals rendered noncaking by preoxidation. Such solids are generally ash-containing, and as will be shown later, provision must be made for discharging ash from the overall system to prevent its buildup beyond a given point. Actually, up to a point, the ash serves as a heat carrier for maintaining the desired temperature in the reduction zone. In general, the carbon content of the carbonaceous solids in the reduction zone is at least 20 percent by weight. The weight ratio of carbon to iron oxide in the reduction zone must be sufficient to assure the required conversion of Fe_3O_4 and FeO to FeO and Fe during the passage through the reduction zone. In the broadest aspect of this invention, the reduced iron oxides, together with carbon-depleted carbonaceous solids, flow into the oxidation zone without any attempt to separate the two solids systems. This is not the preferred procedure as will be seen in the description of the preferred embodiment. However, in the case of very reactive carbonaceous solids, such as some lignites, it is feasible for them even in a carbon depleted state to react with steam in the oxidation zone, even in the presence of iron or FeO. The less reactive carbonaceous solids in a carbon-depleted state would generally constitute a mass of relatively inert solids, thus reducing the effective throughput in the oxidation zone.

In the oxidation zone, steam is introduced through a steam inlet 18 and is circulated in reactive relationship to the reduced iron oxides. The reaction of steam with Fe and with FeO is extremely rapid and exothermic. The reactions are as follows:

4. $H_2O+Fe \rightarrow FeO+H_2$
5. $H_2O+3FeO \rightarrow Fe_3O_4+H_2$

Any gas-solids system may be used in the oxidation zone to make hydrogen because of the high rate of reaction of steam and the reduced iron oxides. If a fuel gas is the desired product, then the best system is determined by the reactivity of the carbonaceous solids fed to the oxidation zone or by the extent of carbon gasification desired. For example, a free-fall system in which solids have a relatively short residence time may be used for highly reactive carbonaceous solids or in those instances where a relatively small amount of carbon gasification is desired for less reactive carbonaceous solids. Where significant carbon gasification is desired with less reactive carbonaceous solids, a fluidized bed system may be used. The temperature maintained in the oxidation zone is generally between 1000° and 2000° F. The pressure may be atmospheric or superatmospheric. The residence time of the solids in the oxidation zone may be between 30 seconds and 200 minutes. The higher pressures and longer residence times favor methane production and the shorter residence times are sufficient for hydrogen production.

In addition to the reaction of steam with the reduced iron oxides to make hydrogen, there will be some reaction of steam with any carbonaceous solids that are present to produce CO and H_2, as well as some CO_2. More importantly, the hydrogen produced by the steam-Fe, steam-FeO, or steam-carbon reaction will react with the carbonaceous solids to produce methane, particularly at elevated pressures. If desired, fresh carbonaceous solids may be introduced into the oxidation zone through a conduit 22 to increase the content of methane in the product gas. The mixture of gases is discharged as product gas through a conduit 20 for direct use or for further treatment or purification, as may be desired.

The solid product of the oxidation zone, principally FeO and Fe_3O_4, along with unreacted carbonaceous solids, are withdrawn from the oxidation zone through a pipe 24 to a lift pipe 26 for recirculation to the reduction zone. The lift pipe 26 constitutes an elongated combustion zone for partially burning the carbonaceous solids with air introduced through an air feed pipe 28. Additional fresh carbonaceous solids may also be introduced through a feed pipe 30 to replenish the carbon consumed in the oxidation and reduction zones, as well as in the combustion lift pipe 26. The conditions maintained in the combustion lift pipe are such as to insure partial combustion of the carbonaceous solids to raise the temperature of the upwardly flowing mass of solids to a temperature sufficiently high to provide the necessary heat for the reduction reaction. As the carbonaceous solids recirculate through the recirculatory system, there is a buildup of ash. This ash may be separated from the main stream of recirculatory solids from the lift pipe 26 in a cyclone separator 32 or by other suitable means. The flue gas, plus such ash, is discharged through a pipe 34 while the mixture of hot iron oxides and carbonaceous solids drops through pipe 36 onto the downwardly moving bed in the reduction zone. The effluent gas from the latter is withdrawn separately through a pipe 38.

The preferred embodiment shown diagrammatically in FIG. 2 is adapted to produce a methane-containing gas that may be converted by conventional means to a high B.t.u. gas. Fresh hydrocarbonaceous solids containing both fixed carbon and volatile carbon are continuously fed to the oxidation zone, labeled Oxidizer in the drawing and also designated by the numeral 42. The oxidation zone is contained in the lower part of a vessel 40, the upper part of which confines the reduction zone 44, sometimes called Reductor. The fresh, hydrocarbonaceous solids fed to the Oxidizer are high in total carbon content, in the range of 50 to 90 percent by weight. Preferably we use either char, the noncaking solid product resulting from pyrolysis of coal or lignite at low temperature, or a raw coal which has been rendered noncaking, if necessary, by preoxidation. The char, or raw coal (and hereafter reference is made only to char for convenience), is introduced by a pipe 46 into a continuous hopper 48 from which valve-regulated amounts of char are fed by a pipe 50 into the open space above the oxidation zone.

The char is maintained in a dense fluidized phase which serves as the oxidation zone. Elemental Fe and FeO substantially free of carbonaceous solids are introduced directly into the interior of the fluidized bed from a source and a manner to be later described. The elemental Fe and FeO being of greater density than the fluidized char, descend in the bed in countercurrent flow relationship to steam which is introduced by a steam pipe 52 after being compressed by a jet compressor 53. Under the temperature and pressure conditions maintained in the oxidation zone, the steam reacts preferentially and rapidly with the elemental Fe and FeO as set forth in equations 4 and 5 above to form hydrogen. At least some of the latter reacts with the char in the fluidized bed to form methane. The methane is discharged together with unused steam through an effluent gas pipe 54 for suitable treatment to recover a high B.t.u. gas.

The conditions maintained in the oxidation zone of the preferred embodiment are as follows: temperature, 1400° to 1800° F., pressure, 100 to 1500 p.s.i.; and residence time of char, 1 to 200 minutes, with the higher pressures and longer residence times being preferred for methane production.

The mixture of iron oxides, mostly Fe_3O_4 and FeO, along with carbon-depleted char, is withdrawn from the oxidation zone through a pipe **56**. This mixture is lifted to the reduction zone through a lift pipe **58** by means of steam from the steam feed pipe **52**. In recycling to the reduction zone, the solids pass through a cyclone separator **60** which separates the steam from the solids. The steam is returned through a conduit **62** to the oxidation zone after being compressed to the desired pressure, together with the rest of the inlet steam in the compressor **53**. The solids drop out of the cyclone **60** into the space above the moving bed and thence onto the moving bed in the reduction zone.

The reduction zone, as in the case of the embodiment shown in FIG. 1, consists essentially of a downwardly moving bed of two substantially concurrently flowing streams of solids. The recycled iron oxides are mixed with the hot stream of carbonaceous solids entering the vessel from a lift pipe **66** whose function will be more fully described below. The gas produced in the reduction zone is discharged through a pipe **68**. The conditions maintained in the reduction zone of the preferred embodiment are as follows: temperature, 1500° to 2100° F., pressure, 100 to 1500 p.s.i., residence time, 1 to 30 minutes, carbon depletion per pass, 1 to 10 percent of the carbon in the carbonaceous solids, and weight ratio of char to iron oxides, 0.5 to 5 lb./lb.

The mixture of reduced iron oxides, principally Fe and FeO, along with partially carbon-depleted carbonaceous solids drops by gravity through an outlet conduit **70** to a separator **72**. The latter is adapted to confine the mixture of solids in a fluidized state, the fluidizing gas being introduced by a pipe **74**. The fluidizing gas may be essentially inert, or it may contain some steam. If it does contain steam, then some hydrogen may be generated, in which case the effluent gas from the separator may be conducted to the Oxidizer. Otherwise, the effluent gas may be discharged conveniently through conduit **75**. Because of the different densities of the carbonaceous solids and the iron compounds, fluidization conditions can be selected to permit the iron compounds to settle out of the bed to be discharged through a conduit **76** into the oxidation zone **42**. The fluidized char overflows into a pipe **78** which leads to the previously mentioned lift pipe **66**. Air is introduced into the foot of the lift pipe through a pipe **80** not only to lift the solids back to the reductor, but also to burn part of the carbonaceous solids under controlled conditions to raise the temperature of the solids sufficiently high to provide the heat required in the reduction zone. Additional air may be introduced into the space above the reduction zone through a pipe **82** to effect combustion of the carbon monoxide generated in the reduction zone, as well as some of the carbonaceous solids from the lift pipe **66**.

The following example illustrates the operation of the preferred embodiment.

The conditions maintained and results obtained in a material balance run are set forth in the following table I wherein the conditions and compositions of the various gas and solids streams are tabulated. The gas streams are designated by numerals 1 to 8 inclusive, and the solids streams by letters A to H inclusive. The so designated streams are shown in FIG. 3 by the encircled numerals or letters, as the case may be. In addition, the pressures in pounds per square inch are shown by the encircled 3-digit numbers at several points throughout the system.

A modification of the preferred embodiment is shown in FIG. 4. Numerals **100** and **102** designate the Oxidizer and the Reducer respectively. The Oxidizer consists of two superimposed fluidized zones, Zone I and Zone II, designated by the numerals **104** and **106** respectively. Zone I is intended to serve primarily for the reaction of carbonaceous solids with hydrogen to make methane, while Zone II is intended to serve primarily for the reaction of steam and Fe or FeO to make hydrogen. The Reducer **102** consists of three superimposed zones, designated by the numerals **108**, **110**, and **112** respectively. Zone **108** is a mixing chamber wherein incoming Fe_3O_4 and FeO and carbonaceous solids are mixed. Zone **110** is a combustion zone where carbon monoxide and/or the carbonaceous solids, while falling freely in admixture with the iron oxides, are partially burned to supply heat. Zone **112** is the reduction zone itself, consisting of a downwardly moving bed of the mixture of iron oxides and carbonaceous solids.

The operation of the process illustrated in FIG. 4 is as follows. Solid lines indicate solids streams and dotted lines, gas streams. Hydrocarbonaceous solids (identified as "carbon") containing a volatile hydrocarbonaceous component and a fixed carbon component are fed continuously through **114** into the Zone I of the Oxidizer **100**. A fluidized bed of the hydrocarbonaceous solids is maintained at a temperature between 1400° and 1800° F. and at a pressure between 100 and 1500 p.s.i. in order to optimize the reaction between the hydrocarbonaceous solids and hydrogen. The product gas comprising principally methane and hydrogen is withdrawn through a conduit **116**, after being freed of solids and condensibles which are shown schematically as discharged through conduit **117**. The partially reacted carbonaceous solids from Zone I are conducted by gravity down through a conduit **118** to the lower Zone II. In this zone, a fluidized bed of carbonaceous solids is maintained at a temperature between 1400° and 1800° F. and at a pressure between 100 and 1500 p.s.i. The gaseous product from this zone contains principally hydrogen and unreacted steam, with some CO, CO_2, and CH_4, and is conducted through a conduit **120** to the upper Zone II to serve as fluidizing reactant in Zone I.

The mixture of iron oxides from Zone II is withdrawn therefrom through a conduit **122** to an iron oxide lift pipe **124** wherein the mixture of oxides is lifted by steam introduced through a conduit **126**. The temperature in the lift pipe is maintained, by suitable regulation of the temperature of the

TABLE 1.—GAS STREAMS

	Number							
	1	2	3	4	5	6	7	8
	Moles/hour							
	2.93	1.47	1.82	6.72	6.98	6.99	7.02	8.78
	Pressure, p.s.i.a.							
			822	822	880	821	828	830
Temperature, ° F.	842	842	1,871	1,866	1,165	1,166 1656	1,780	1,347
Composition, percent volume								
O_2	20.99	20.99						0.81
N_2	79.01	79.01		79.62				
CO			35.62				11.85	10.18
CO_2			64.38	20.38			9.26	8.34
CH_4							20.42	20.84
H_2						18.25	27.06	32.36
H_2O					100.00	81.75	31.66	26.49
H_2S								1.26

SOLIDS STREAMS

	Number							
	A	B	C	D	E	F	G	H
	Lb./hr.							
	100	666	732	753	1,862	2,236	1,869	17
Temperature, ° F.	350	1,795	1,700	1,656	1,908	1,795	1,770	1,866
Composition, wt. percent								
C	70.35		3.96	3.85	45.31	31.99	45.57	11.40
H	3.93							
N	1.24							
O	5.60							
S	2.86							
Ash	16.03		2.06	2.00	54.69	38.21	54.43	88.60
Fe		11.03				3.29		
$Fe_{1-x}O$		88.97	93.98	47.03		26.51		
Fe_3O_4				47.12				

steam and iron oxides, between 1300° and 1800° F., thereby promoting the reaction of the steam with FeO in the feed to the lift pipe to form Fe_3O_4. The latter is separated from the effluent gases by any suitable means at the top of the lift pipe. The iron oxides comprising principally Fe_3O_4 and FeO are carried by a conduit **128** to the mixing chamber **108** at the top of the Reducer vessel where they are mixed with char entering the mixing chamber from conduit **148**.

The iron oxides and char which are intimately mixed in the mixing chamber **108** are then allowed to fall freely through the combustion zone **110**. The latter is suitably supplied with air through a conduit **130**, in sufficient quantity to partially burn the char and thereby raise the temperature of the mixture of solids to that required for reduction of the iron oxides. Effluent gas and ash are discharged from the combustion zone by any suitable means, schematically shown in the figure as two conduits **132** and **134** respectively.

FeO formed by the reaction of steam and Fe or FeO in the Separator, is conducted to Zone II via conduit **158** from the Separator. The effluent gas from the Separator, including any hydrogen formed by the reaction of steam and Fe or FeO in the Separator, is conducted to Zone II by a conduit **160**, joining up with conduit **154** at the inlet to Zone II.

The following example illustrates the operation of the modification of the preferred embodiment shown in FIG. 4.

The conditions maintained and results obtained in a material balance run are set forth in the following Table II wherein the conditions and compositions of the various gas and solids streams are tabulated. The gas streams are designated by numerals 1 to 14 inclusive, and the solids streams by letters A to L inclusive. The so designated streams are shown in FIG. 5 by the encircled corresponding numerals or letters. In addition, the temperatures in ° F. of the several streams are shown by the 4-digit numbers in parentheses.

TABLE II.—GAS STREAMS—POUND MOLES/HOUR /C

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
CO			.0097	.1746					.0733					
CO_2			.0851	.1585	.0001	.1001	.1001	.0001	.1986	.4058				
H_2		.2300	.5778	.6473					.0029		.1150	.1150	.365	.480
H_2O	1.4660	1.2350	.7161	.5811		.0069	.0069		.0157	.0281	.6180	.6180	.368	.966
CH_4			.0962	.2516										
C_2H_6				.0057										
C_3H_8				.0016										
N_2				.0063	.3848	.3848	.3848	.2837		.6685				
H_2S			.0016	.0150										
O_2					.1035			.0763						
COS						.0001	.0001			.0003				
A					.0046	.0046	.0046	.0034		.0060				

C₂H₆

→ Solids Streams – lb. moles/hr.

	A	B	C	D	E	F	G	H	I	J	K	L
C	1.0580	.7150	.4350		.4350	.0173	9.9213	9.8552	9.5864	9.5864	9.4863	.0291
H_2	.3399	.0495	.0301		.0301	.0073	.6567	.6821	.6635	.6635	.6566	.0020
O	.0870					.0012						
N_2	.0078	.0015	.0015		.0016		.0930	.0915	.0915	.0915	.0915	.0015
S*	.0132											
FeS*	.0057	.0055	.0039		.0039		.2220	.2182	.2182	.2182	.2181	.0036
Fe*		.0002	.0018		.0018		.1296	.1276	.1276	.1276	.1277	.0021
Ash**	1.8546	1.8546	1.8546		1.8546		88.1493	86.2947	86.2947	86.2947	86.2947	1.8546
Fe									.23675			
$Fe_{.947}O$			1.4667	1.4667	.5911		.5911	.5911	1.2167			
Fe_3O_4					.2764		.2764	.2764				
MgO			.7598	.7598	.7598		.7598	.7598	.7598			
SiO_2			.3550	.3550	.3550		.3550	.3550	.3550			

*Associated with the ash content of the char.
**Given in Lbs./hr.

88.1493

The hot mixture of iron oxides and char is dropped onto the top of downwardly moving bed **112** wherein the iron oxides are reduced to Fe and FeO. The only gases present in the moving bed are those generated in situ as schematically illustrated by the dotted arrow **136**. The solid product from the reduction zone is removed through a conduit **138** to a Separator **140**. A fluidized bed is maintained in this Separator as described before, and the velocity of the fluidizing gas is so regulated that the reduced iron oxides drop down while the char remains in a fluidized state and overflows through a separate discharge conduit **142**. The char is recycled to the Reducer through a lift pipe **144** by means of air introduced through conduit **146**. The air also serves, as before, to burn part of the char for process heat. The hot solids are conducted from the top of the lift pipe through a conduit **148** to the mixing chamber **108**. The effluent gas from the lift pipe **144** is also conducted to the mixing chamber and is shown schematically, in order to show all gas streams as well as solids streams, as being conducted through a separate conduit **150**, although it would normally not be handled separately.

The gas stream issuing from the top of the iron oxide lift pipe **124**, as stated before, comprises principally hydrogen and unreacted steam. This gas stream is carried by conduits **152** and **154** to Zone II; and, if desired, a slip stream may be conducted to the Separator **140** by means of a conduit **156**. Thus, it may serve as the fluidizing gas in the Separator; but, in that case, in the course of passing in contact with the reduced iron oxide, will reoxidize at least some of the Fe to FeO, which in turn will react, at least to some extent, with the steam to form hydrogen. The mixture of reduced iron oxides, including any

We claim:

1. A continuous process for making hydrogen which comprises:

a. passing a stream of particulate iron oxides comprising principally Fe_3O_4 and FeO and a stream of particulate carbonaceous solids concurrently and downwardly into the top of a reduction zone,

b. subjecting said stream of particulate iron oxides to direct reactive contact with said stream of particulate carbonaceous solids in a downwardly moving bed in said reduction zone, there being no molecular oxygen-containing gas introduced into the moving bed in the reduction zone,

c. maintaining the following conditions in said reduction zone: temperature, 1000° to 2600° F.; pressure, atmospheric or superatmospheric; residence time of said solids, 15 seconds to 60 minutes; carbon depletion per pass, 1 to 10 percent of the carbon in said carbonaceous solids; and a carbon content of said carbonaceous solids which is at least 20 percent by weight, whereby the iron oxides are reduced to a mixture comprising principally FeO and Fe,

d. partially burning carbon-depleted carbonaceous solids from step *b* outside the reduction zone to raise the temperature of said carbonaceous solids sufficiently high to supply adiabatically the heat required in said reduction zone,

e. returning said partially burned carbonaceous solids from step *d* to said reduction zone,

- f. adding carbonaceous solids to replenish the carbonaceous solids consumed in the process,
- g. reacting reduced iron oxides from step *b* with steam in an oxidation zone,
- h. maintaining the following conditions in said oxidation zone: temperature, 1000° to 2000° F.; pressure, atmospheric or superatmospheric, and residence time of solids, 0.5 to 200 minutes, whereby hydrogen is formed and a mixture of iron oxides comprising principally Fe_3O_4 and FeO is produced, and
- i. returning said mixture of iron oxides from step *g* to said reduction zone of step a to repeat the cycle.

2. The process according to claim 1 in which the reduction zone is maintained at a temperature between 1500° and 2100° F. and a pressure between 100 and 1500 p.s.i.; and the oxidation zone is maintained at a temperature between 1400° and 1800° F. and a pressure between 100 and 1500 p.s.i.

3. A continuous process for making hydrogen which comprises:

- a. passing a stream of particulate iron oxides comprising principally Fe_3O_4 and FeO and a stream of particulate carbonaceous solids concurrently and downwardly into the top of a reduction zone,
- b. subjecting said stream of particulate iron oxides to direct reactive contact with said stream of particulate carbonaceous solids in a downwardly moving bed in said reduction zone, there being no molecular oxygen-containing gases introduced into said moving bed in said reduction zone,
- c. maintaining the following conditions in said reduction zone: temperature, 1000° to 2600° F.; pressure, atmospheric or superatmospheric, residence time of solids, aa.i 15 seconds to 60 minutes; carbon depletion of p.s.i.; carbonaceous solids per pass through said reduction zone, 1 to 10 percent of the carbon in said carbonaceous solids; and a carbon content of said carbonaceous solids which is at least 20 percent by weight, whereby said iron oxides are reduced to a mixture comprising principally FeO and Fe,
- d. withdrawing the mixture of carbon-depleted carbonaceous solids and reduced iron oxides from said reduction zone and transferring said mixture to a separation zone,
- e. passing a gas through said mixture of carbon-depleted carbonaceous solids and reduced iron oxides in said separation zone at a velocity sufficient to effect separation by virtue of the difference in densities of the reduced iron oxides and carbonaceous solids;
- f. withdrawing carbon-depleted carbonaceous solids from said separation zone and partially burning same outside said reduction zone to raise the temperature of said carbonaceous solids sufficiently high to supply adiabatically the heat required in said reduction zone,
- g. returning said partially burned carbonaceous solids to said reduction zone,
- h. withdrawing iron oxides from said separation zone and reacting same with steam in an oxidation zone,
- i. maintaining the following conditions in said oxidation zone: temperature, 1000 to 2000° F.; pressure, atmospheric or superatmospheric; and residence time of the solids, 30 seconds to 200 minutes, whereby hydrogen is formed and a mixture of iron oxides comprising principally Fe_3O_4 and FeO is produced,
- j. returning said mixture of iron oxides from said oxidation zone to said reduction zone, and
- k. adding carbonaceous solids to replenish the carbonaceous solids consumed in the process.

4. The process according to claim 3 in which the reduction zone is maintained at a temperature between 1500° and 2100° F. and a pressure between 100 and 1500 p.s.i.; and the oxidation zone is maintained at a temperature between 1400° and 1800° F. and a pressure between 100 and 1500 p.s.i.

5. A continuous process for making hydrogen which comprises:

- a. passing a stream of particulate iron oxides comprising principally Fe_3O_4 and FeO and a stream of particulate carbonaceous solids concurrently and downwardly into the top of a reduction zone,
- b. Subjecting said stream of particulate iron oxides to direct reactive contact with said stream of particulate carbonaceous solids in a downwardly moving bed in said reduction zone, there being no molecular oxygen-containing gases introduced into said moving bed in said reduction zone,
- c. maintaining the following conditions in said reduction zone: temperature, 1000° to 2600° F., pressure, atmospheric or superatmospheric; residence time of solids, 15 seconds to 60 minutes; carbon depletion of said carbonaceous solids per pass through said reduction zone, 1 to 10 percent of the carbon in said carbonaceous solids, and a carbon content of said carbonaceous solids which is at least 20 percent by weight, whereby said iron oxides are reduced to a mixture comprising principally FeO and Fe,
- d. withdrawing the mixture of carbon-depleted carbonaceous solids and reduced iron oxides from said reduction zone and transferring said mixture to a separation zone,
- e. Passing a fluidizing gas through said mixture of carbon-depleted carbonaceous solids and reduced iron oxides in said separation zone at such a velocity that a fluidized bed of said carbonaceous solids is established and maintained from which said iron oxides and said carbonaceous solids may be separately withdrawn,
- f. withdrawing carbon-depleted carbonaceous solids from said fluidized separation zone and partially burning same outside said reduction zone to raise the temperature of said carbonaceous solids sufficiently high to supply adiabatically the heat required in said reduction zone,
- g. returning said partially burned carbonaceous solids to said reduction zone,
- h. withdrawing iron oxides from said separation zone and reacting same with steam in an oxidation zone,
- i. maintaining the following conditions in said oxidation zone: temperature, 1000° to 2000° F.; pressure, atmospheric or superatmospheric; and residence time of the solids, 30 seconds to 200 minutes, whereby hydrogen is formed and a mixture of iron oxides comprising principally Fe_3O_4 and FeO is produced,
- j. returning said mixture of iron oxides from said oxidation zone to said reduction zone, and
- k. adding carbonaceous solids to replenish the carbonaceous solids consumed in the process.

6. The process according to claim 5 in which the reduction zone is maintained at a temperature between 1500° and 2100° F. and a pressure between 100 and 1500 p.s.i.; and the oxidation zone is maintained at a temperature between 1400° and 1800° F. and a pressure between 100 and 1500 p.s.i.

7. The process according to claim 5 in which the fluidizing gas used in the separation zone is an inert gas.

8. The process according to claim 5 in which the fluidizing gas used in the separation zone contains steam.

* * * * *

Oct. 24, 1972 J. L. JOHNSON ET AL 3,700,421

APPARATUS FOR CONDUCTING A CONTINUOUS STEAM-IRON PROCESS

Original Filed Feb. 11, 1969 2 Sheets-Sheet 1

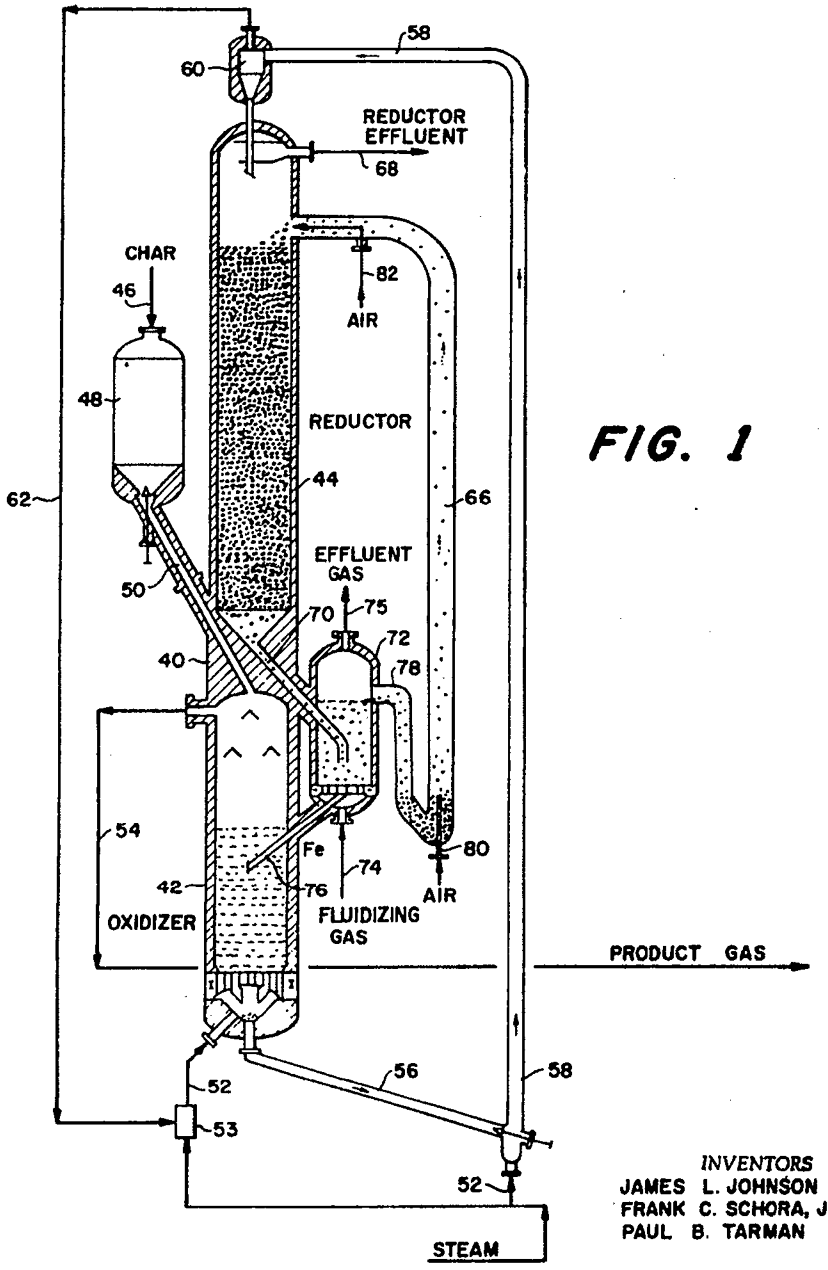

FIG. 1

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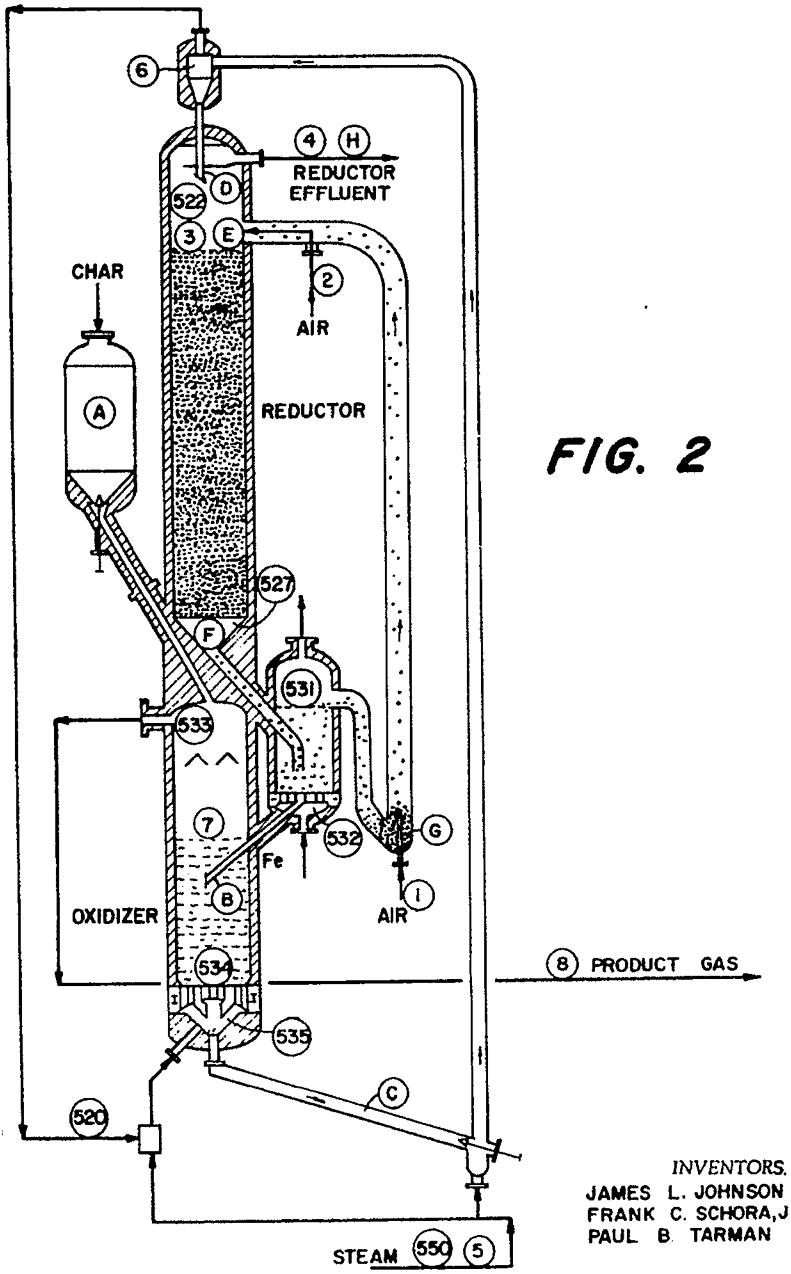

FIG. 2

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APPARATUS FOR CONDUCTING A CONTINUOUS STEAM-IRON PROCESS

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Original application Feb. 11, 1969, Ser. No. 798,334. Divided and this application Feb. 17, 1971, Ser. No. 116,051

The portion of the term of the patent subsequent to Nov. 9, 1988, has been disclaimed

Int. Cl. C10j *3/20*
U.S. Cl. 48—73 **2 Claims**

ABSTRACT OF THE DISCLOSURE

Apparatus is provided for conducting a continuous steam-iron process wherein finely divided iron oxides are reduced in a reduction vessel and the reduced iron oxides are reacted with steam in an oxidation vessel to make hydrogen. The reduction of the iron oxides is effected by means of a continuously recirculating stream of hot, finely divided carbonaceous solids which are mixed with the iron oxides in a downwardly moving bed under reducing conditions, and heat is supplied by the carbonaceous solids which are heated by partial combustion outside the reduction vessel. The mixture of reduced iron oxides and carbonaceous solids from the reduction vessel is separated in a separation vessel into a stream of reduced iron oxides and a stream of carbonaceous solids. The stream of reduced iron oxides is conducted to the oxidation vessel where the reduced iron oxides react with steam to reoxidize the reduced iron oxides. The latter are returned to the reduction vessel. The carbonaceous solids separated in the separation vessel are returned to the reduction vessel after passage through a partial combustion zone.

REFERENCE TO RELATED APPLICATION

This application is a division of copending application, Ser. No. 798,334, filed Feb. 11, 1969, now Pat. No. 3,619,142, issued Nov. 9, 1971 and assigned to the assignee of the present invention.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to an apparatus for conducting an improved steam-iron process for making hydrogen or fuel gas.

The steam-iron process is a process for making hydrogen by the reaction of steam with either elemental iron or a lower iron oxide, for example, FeO. The reaction produces higher oxides of iron, for example, Fe_3O_4, which may be reduced to repeat the cycle.

Despite the apparent simplicity of the steam-iron process and despite the fact that it has been known and worked on for over one hundred years, to the best of our knowledge no technically and economically feasible embodiment of a continuous steam-iron process has been developed which is now practiced commercially. Perhaps the principal reason for the failure of the steam-iron process to achieve commercial success is the difficulty involved in making it a continuous process. To do so requires subjecting a continuously flowing recirculatory stream of iron oxides to two different reactions, namely oxidation and reduction, under optimum conditions for each reaction, including optimum input and distribution of the heat required in the process.

Description of the prior art

Prior continuous steam-iron processes have favored the use of gaseous reductants for reducing the iron oxides (see, by way of illustration, U.S. Pat. No. 2,198,560). However, the production of a suitable gaseous reductant is expensive, and renders the overall process uneconomical. Furthermore, because of the limitations imposed by the thermodynamic equilibrium during the reduction of Fe_3O_4 and FeO to FeO and Fe with reducing gases containing hydrogen and carbon monoxide, the off-gas from once-through reduction contains considerable unreacted hydrogen and carbon monoxide. Thus, such a process tends to be wasteful of reducing gas.

In U.S. Pat. No. 3,503,724 of Homer E. Benson, issued Mar. 31, 1970, the reducing gas is made in situ by reacting air and carbonaceous solids in the presence of the iron oxides. Such a process has many advantages but requires careful control to minimize reconversion of elemental iron to higher oxides by contact with air.

Continuous steam-iron processes have been proposed which utilize either a solids in gas dispersion or the fluidized solids technique in the oxidation zone and the reduction zone (see, by way of illustration, U.S. Pats. Nos. 2,602,809 and 3,017,250). Reducing systems employing a dispersion of powdered iron oxide in a suspending gas call for large reactors and costly gas-solids separators. All attempts to operate with the iron oxide in a fluidized condition have failed to become sufficiently attractive for commercial adoption because a fluidized mass is of uniform composition throughout whereas a composition gradient is generally desired.

SUMMARY OF THE INVENTION

In accordance with the present invention we have provided apparatus for conducting an improved continuous steam-iron process which uses not only a recirculatory stream of particulate iron oxides, but also uses a recirculatory stream of particulate carbonaceous solids to effect reduction of the iron oxides and to supply process heat requirements. In the practice of the process of this invention, reduced iron oxides comprising principally FeO and Fe are oxidized by steam in an oxidation zone, and iron oxides comprising principally Fe_3O_4 and FeO are reduced in a reduction zone. By "principally" we mean that at least fifty percent by weight of any mixture of oxidizable or reducible iron compounds, as the case may be, consists of the indicated compounds, and the actual percentage approaches 100 percent under equilibrium conditions. The relative amounts of FeO and Fe in the oxidizable mixture, and the relative amounts of Fe_3O_4 and FeO in the reducible mixture are functions largely of the temperature, pressure, and residence time maintained in the respective reaction zones. The oxidation of FeO and Fe (sometimes simply referred to herein as reduced iron oxides) is accomplished by passing steam in reactive relationship with the reduced iron oxides in an oxidation zone. The reduction of Fe_3O_4 and FeO is accomplished by subjecting them to direct contact with the recirculatory stream of hot carbonaceous solids in a downwardly moving bed in the reduction zone. No oxygen-(molecular) containing gases are introduced into the moving bed in the reduction zone. The reduction conditions are selected to insure that only partial carbon depletion is effected during the passage of the carbonaceous solids through the reduction zone, while however, the desired reduction of the iron oxides to Fe and FeO is effected. Heat is supplied to meet the requirements of the process by partial combustion of the carbonaceous solids in a combustion zone located outside the reduction zone. The amount of partial burning is controlled to raise the temperature of the carbonaccous solids sufficiently high to supply adibatically the heat required.

A separation zone is interposed between the reduction zone and the oxidation zone to effect separation of the carbonaceous solids from the reduced iron oxides leaving the reduction zone. Separation is effected by passing a gas through the mixture of carbonaceous solids and reduced iron oxides at a velocity which permits ready separation by virtue of the difference in densities of the iron compounds and carbonaceous solids. A fluidized separation zone is especially preferred wherein the fluidized bed consists essentially of the lighter carbonaceous solids from which the heavier iron compounds may be with drawn and sent to the oxidation zone. The oxidation zone in the preferred embodiment comprises a fluidized bed of fresh carbonaceous solids into which the reduced iron oxides are fed. Hydrogen is produced by the relatively fast reaction of steam and reduced iron oxides, and in turn reacts with the carbonaceous solids to form methane. The separated carbonaceous solids from the separation zone are recirculated through the combustion zone back to the reduction zone.

The process operates continuously and efficiently to yield hydrogen or a methane-rich gas. The improvement in economics of the process as compared with prior steam-iron processes is due to the efficient use of low cost, finely divided carbonaceous solids for (1) the reduction of iron oxides, (2) the supply of process heat, and (3) in the preferred embodiment, the production of methane in a relatively simple two-vessel system. The gain in efficiency in the reduction zone arises from the thermal gradient established in the downwardly moving bed and from the lack of back-mixing of reduced iron. Thus, maximum reduction rates result from the countercurrent flow relationship of the upwardly flowing reducing gases (generated in situ) and the downwardly flowing fresh iron oxides. The absence of molecular oxygen-containing gases assures no loss of desired reduction as a result of competing reactions. The flow of gases and solids in the oxidizer is most efficiently conducted in a fluidized bed for the particular reactions involved, to thereby minimize temperature gradients and to provide for an efficient balance between exothermic and endothermic reactions. Thus, in summary, the improved process provides for the maintenance of the optimum conditions for the reduction of Fe_3O_4 to FeO to Fe, and for the oxidation of the reduced iron oxides with steam.

BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding of our invention, its objects and advantages, reference should be had to the following description and accompanying drawings in which

FIG. 1 is a diagrammatic drawing of the preferred embodiment of our invention; and

FIG. 2 is the same diagrammatic drawing of FIG. 1 but showing the locations of different points in the solids and gas streams to aid in understanding the material balance run reported in Table I of the specification.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The preferred embodiment shown diagrammatically in FIG. 1 is adapted to produce a methane-containing gas that may be converted by conventional means to a high B.t.u. gas. Fresh hydrocarbonaceous solids containing both fixed carbon and volatile carbon are continuously fed to the oxidation zone, labeled Oxidizer in the drawing and also designated by the numeral **42**. The oxidation zone is contained in the lower part of a vessel **40**, the upper part of which confines the reduction zone **44**, sometimes called Reductor. The fresh, hydrocarbonaceous solids fed to the Oxidizer are high in total carbon content, in the range of fifty to ninety percent by weight. Preferably we use either char, the noncaking product resulting from pyrolysis of coal or lignite at low temperature, or a raw coal which has been rendered noncaking, if necessary, by preoxidation. The char, or raw coal (and hereafter reference is made only to char for convenience), is introduced by a pipe **46** into a continuous hopper **48** from which valve-regulated amounts of char are fed by a pipe **50** into the open space above the oxidation zone.

The char is maintained in a dense fluidized phase which serves as the oxidation zone. Elemental Fe and FeO substantially free of carbonaceous solids are introduced directly into the interior of the fluidized bed from a source and in a manner to be later described. The elemental Fe and FeO being of greater density than the fluidized char, descend in the bed in countercurrent flow relationship to steam which is introduced by a steam pipe **52** after being compressed by a jet compressor **53**. Under the temperature and pressure conditions maintained in the oxidation zone, the steam reacts preferentially and rapidly with the elemental Fe and FeO to form hydrogen. At least some of the latter reacts with the char in the fluidized bed to form methane. The methane is discharged together with unused steam through an effluent gas pipe **54** for suitable treatment to recover a high B.t.u. gas.

The conditions maintained in the oxidation zone of the preferred embodiment are as follows: temperature, 1400 to 1800° F.; pressure, 100 to 1500 p.s.i.; and residence time of char, 1 to 200 minutes, with the higher pressures and longer residence times being preferred for methane production.

The mixture of iron oxides, mostly Fe_3O_4 and FeO, along with carbon-depleted char is withdrawn from the oxidation zone through a pipe **56**. This mixture is lifted to the reduction zone through a lift pipe **58** by means of steam from the steam feed pipe **52**. In recycling to the reduction zone, the solids pass through a cyclone separator **60** which separates the steam from the solids. The steam is returned through a conduit **62** to the oxidation zone after being compressed to the desired pressure, together with the rest of the inlet steam in the compressor **53**. The solids drop out of the cyclone **60** into the space above the moving bed and thence onto the moving bed in the reduction zone.

The reduction zone consists essentially of a downwardly moving bed of two substantially concurrently flowing streams of solids. The recycled iron oxides are mixed with the hot stream of carbonaceous solids entering the vessel from a lift pipe **66** whose function will be more fully described below. The gas produced in the reduction zone is discharged through a pipe **68**. The conditions maintained in the reduction zone of the preferred embodiment are as follows: temperature, 1500 to 2100° F.; pressure, 100 to 1500 p.s.i.; residence time, 1 to 30 minutes; carbon depletion per pass, 1 to 10 percent of the carbon in the carbonaceous solids: and weight ratio to char to iron oxides, 0.5 to 5 lb./lb.

The mixture of reduced iron oxides, principally Fe and FeO, along with partially carbon-depleted carbonaceous solids drops by gravity through an outlet conduit **70** to a separator **72**. The latter is adapted to confine the mixture of solids in a fluidized state, the fluidizing gas being introduced by a pipe **74**. The fluidizing gas may be essentially inert, or it may contain some steam. If it does contain steam, then some hydrogen may be generated, in which case the effluent gas from the separator may be conducted to the Oxidizer. Otherwise, the effluent gas may be discharged conveniently through conduit **75**. Because of the different densities of the carbonaceous solids and the iron compounds, fluidization conditions can be selected to permit the iron compounds to settle out of the bed to be discharged through a conduit **76** into the oxidation zone **42**. The fluidized char overflows into a pipe **78** which leads to the previously mentioned lift pipe **66**. Air is introduced into the foot of the lift pipe through a pipe **80** not only to lift the solids back to the Reductor, but also to burn part of the carbonaceous solids under controlled conditions to raise the temperature of the solids sufficiently high to provide the heat required in the reduction zone. Additional air may be introduced into the space above the reduction zone through a pipe **82** to effect combustion of the carbon monoxide generated in the reduction zone, as well as some of the carbonaceous solids from the lift pipe **66**.

The following example illustrates the operation of the preferred embodiment.

The conditions maintained and results obtained in a material balance run are set forth in the following Table I wherein the conditions and compositions of the various gas and solids streams are tabulated. The gas streams are designated by numerals 1 to 8 inclusive, and the solids streams by letters A to H inclusive. The so designated streams are shown in FIG. 2 by the encircled numerals or letters, as the case may be. In addition, the pressures in pounds per square inch are shown by the encircled 3-digit numbers at several points throughout the system.

TABLE I

GAS STREAMS

No.	1	2	3	4	5	6	7	8
Moles/hr	2.93	1.47	1.62	5.72	6.99	6.99	7.02	8.78
Pressure, p.s.i.a.			522	522	550	521	533	530
Temperature, ° F	812	812	1,971	1,866	1,165	1,656	1,700	1,317
Composition, percent vol.:								
O_2	20.99	20.99						
N_2	79.01	79.01		60.62				0.51
CO			35.62				11.55	10.18
CO_2			64.38	39.38			9.26	8.31
CH_4							20.49	20.84
H_2						18.25	27.06	32.36
H_2O					100.00	81.75	31.65	26.49
H_2S								1.29

SOLIDS STREAMS

No.	A	B	C	D	E	F	G	H
Lb./hr	100	666	732	753	1,562	2,236	1,569	17
Temperature, ° F.	350	1,705	1,700	1,656	1,948	1,795	1,770	1,866
Composition, wt. percent:								
C	70.55		3.96	3.85	45.31	31.99	48.57	11.40
H	3.93							
N	1.24							
O	5.69							
S	3.58							
Ash	16.03		2.05	2.00	54.69	38.21	51.43	88.60
Fe		11.03				3.29		
$Fe_{.95}O$		88.97	93.99	47.03		26.51		
Fe_3O_4				47.12				

According to the provisions of the patent statutes, we have explained the principle, preferred construction and mode of operation of our invention and have illustrated and described what we now consider to represent its best embodiment. However, we desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically illustrated and described.

We claim:

1. Apparatus for the production of hydrogen or methane comprising, in combination:

(a) two interconnected vessels, the first vessel being adapted to confine a downwardly moving stream of iron oxide and carbonaceous solids under iron oxide reducing conditions, the second being adapted to confine a steam-iron reaction zone,

(b) means for feeding carbonaceous solids,

(c) a separation vessel interconnected to said first vessel and said second vessel for receiving the solids from said first vessel and adapted to confine a separation zone,

(d) means for introducing a gas into the bottom of said separation vessel at a velocity sufficient to carry the carbonaceous solids out of the vessel, but not the iron oxides,

(e) means for transferring iron oxides from the separation vessel to the second vessel,

(f) means for introducing steam into the second vessel in oxidative relationship to reduced iron oxides received from said separation vessel,

(g) means for removal of the gas product,

(h) means for returning iron oxides discharged from the second vessel to the first vessel, and

(i) means for returning carbonaceous solids from the separator through a combustion zone to said first vessel.

2. Apparatus for the production of hydrogen or methane comprising, in combination:

(a) two interconnected vessel, one at a higher level than the other, the first and higher vessel being adapted to confine a downwardly moving bed of iron oxides and carbonaceous solids under iron oxide reducing conditions, the second and lower vessel being adapted to confine a steam-iron reaction zone,

(b) means for feeding carbonaceous solids,

(c) a separation vessel interconnected to said first vessel and said second vessel for receiving by gravity flow solids from said first vessel and adapted to confine a separation zone,

(d) means for introducing a gas into the bottom of said separation vessel at a velocity sufficient to carry the carbonaceous solids out of the vessel, but not the iron oxides,

(e) means for transferring iron oxides from the separation vessel to the second vessel,

(f) means for introducing steam into the second vessel in oxidative relationship to reduced iron oxides received from said separation vessel,

(g) means for removal of the gas product,

(h) means for returning iron oxides discharged from the second vessel up to the top of the first vessel, and

(i) means for returning carbonaceous solids from the separator through a combustion zone to the first vessel.

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3,222,147	12/1965	Benson	23—214 X
3,503,724	3/1970	Benson	23—214 X

JOSEPH SCOVRONEK, Primary Examiner

U.S. Cl. X.R.

23—284

Oct. 24, 1972 J. L. JOHNSON ET AL **3,700,422**

CONTINUOUS STEAM-IRON PROCESS FOR MAKING FUEL GAS

Original Filed Feb. 11, 1969 5 Sheets-Sheet 1

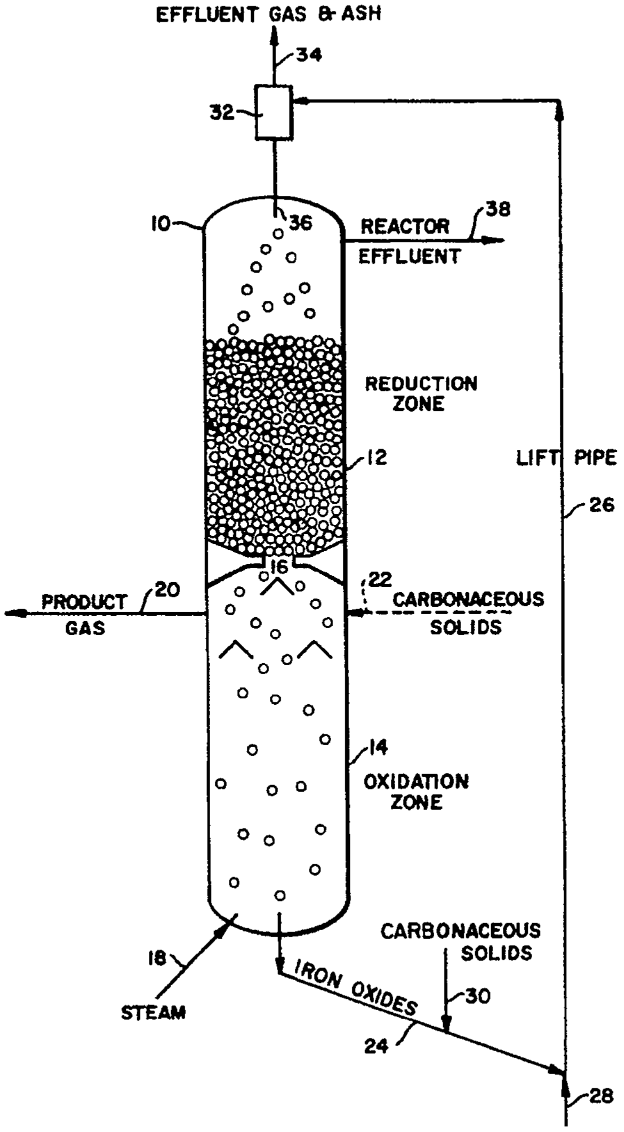

FIG. 1

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CONTINUOUS STEAM-IRON PROCESS FOR MAKING FUEL GAS

Original Filed Feb. 11, 1969 5 Sheets-Sheet 2

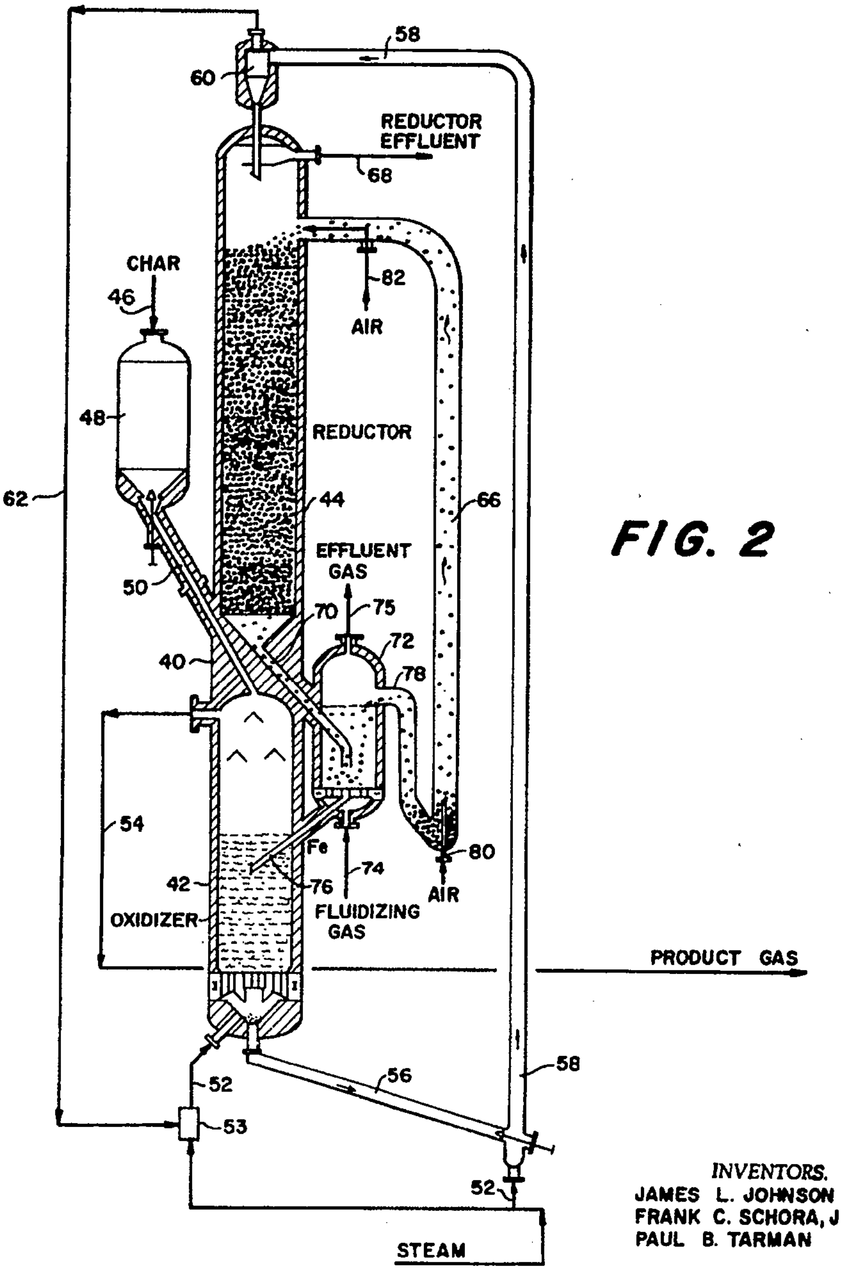

FIG. 2

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CONTINUOUS STEAM-IRON PROCESS FOR MAKING FUEL GAS

Original Filed Feb. 11, 1969 5 Sheets-Sheet 3

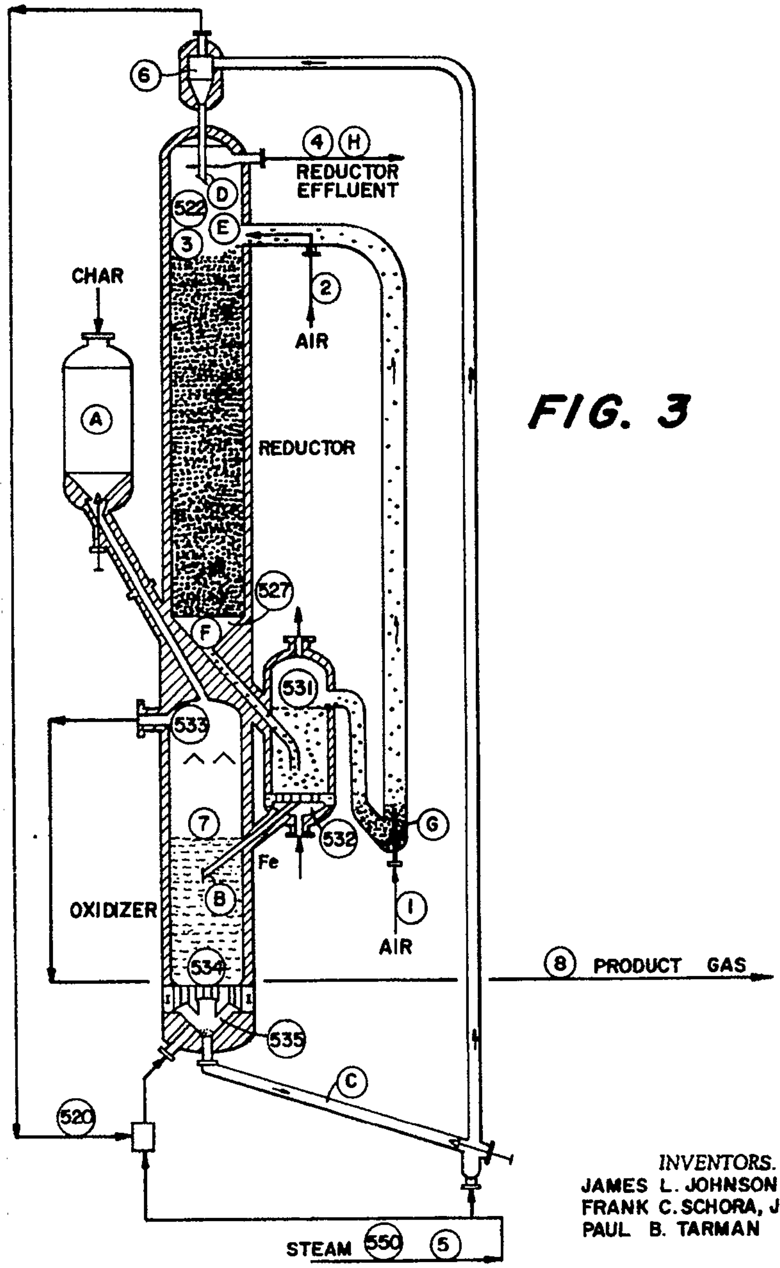

FIG. 3

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CONTINUOUS STEAM-IRON PROCESS FOR MAKING FUEL GAS

Original Filed Feb. 11, 1969 5 Sheets-Sheet 4

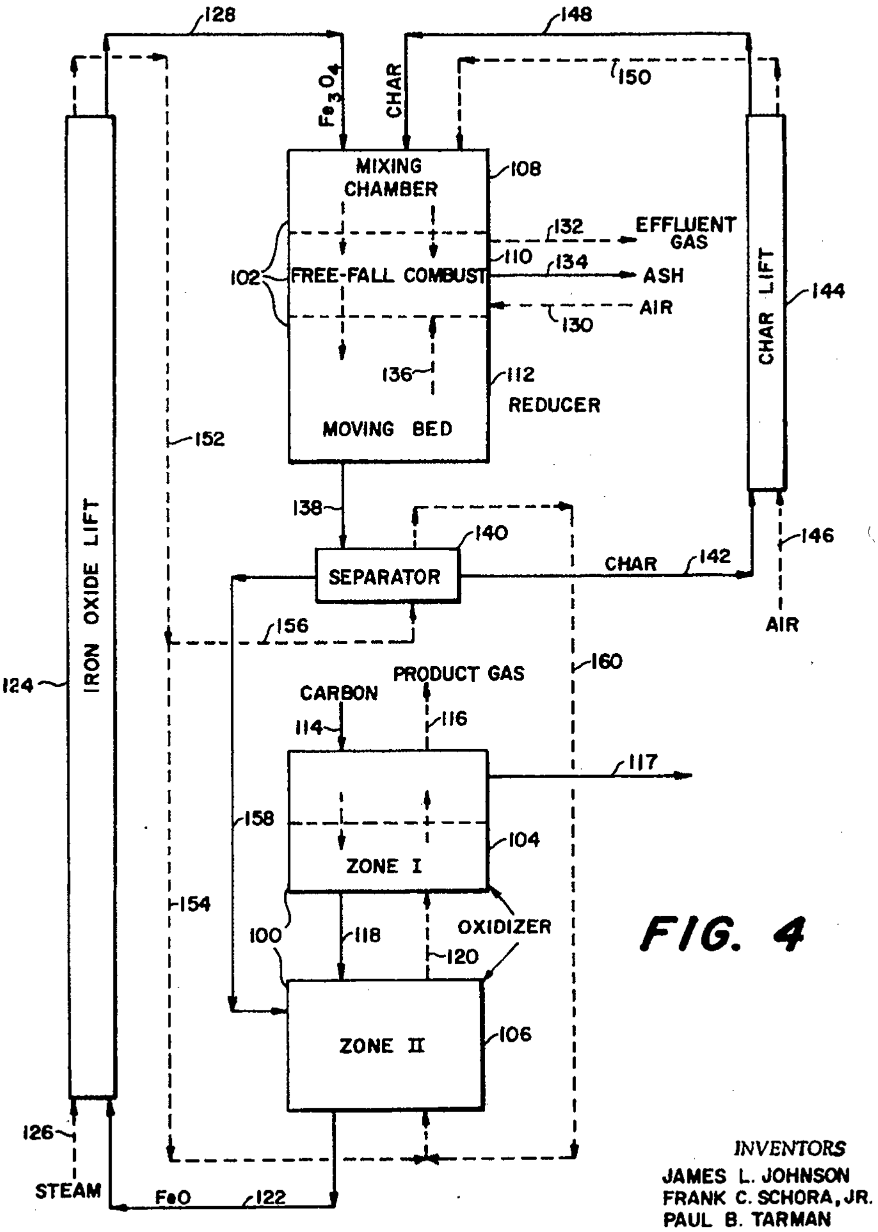

FIG. 4

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CONTINUOUS STEAM-IRON PROCESS FOR MAKING FUEL GAS

Original Filed Feb. 11, 1969 5 Sheets-Sheet 5

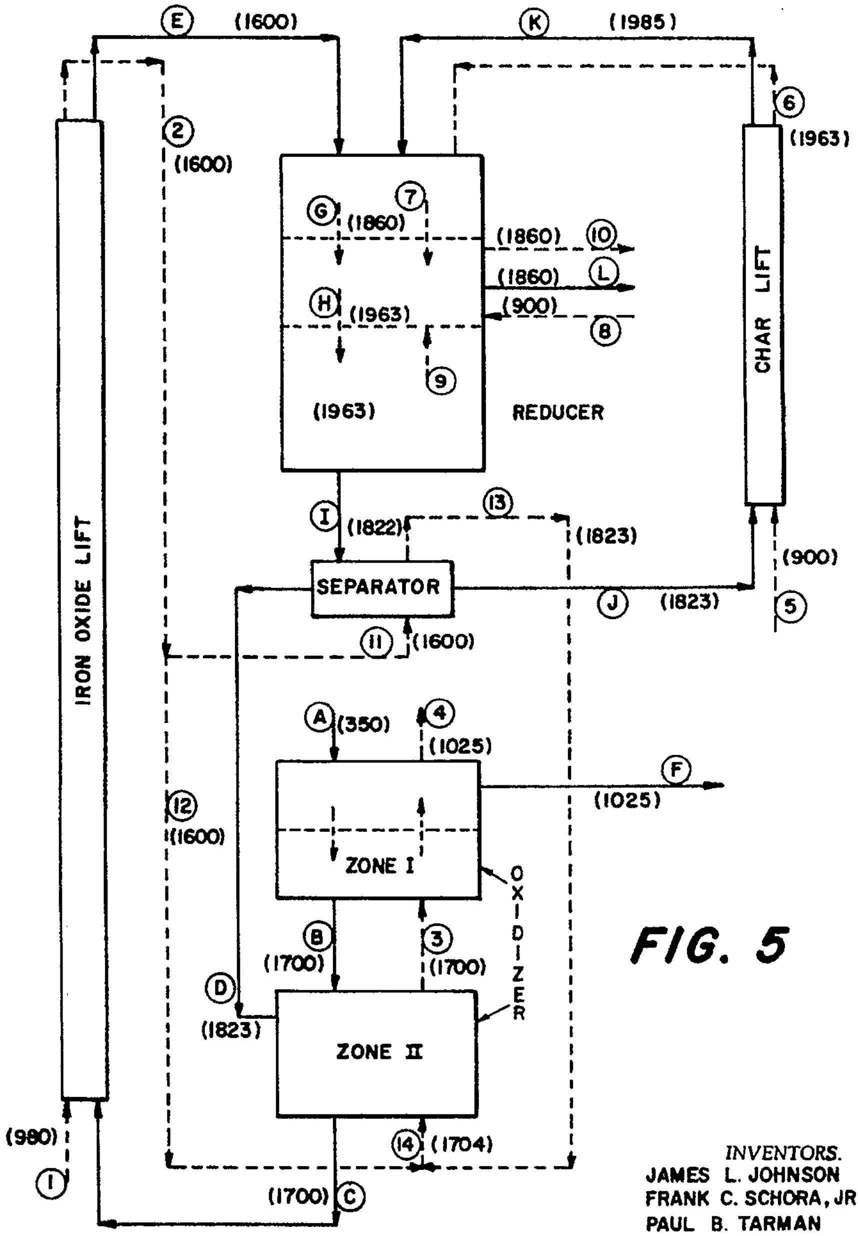

FIG. 5

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United States Patent Office

3,700,422
Patented Oct. 24, 1972

3,700,422

CONTINUOUS STEAM-IRON PROCESS FOR MAKING FUEL GAS

James L. Johnson, Oak Park, Frank C. Schora, Jr., Palatine, and Paul B. Tarman, Elmhurst, Ill., assignors to Consolidation Coal Company, Pittsburgh, Pa.

Original application Feb. 11, 1969, Ser. No. 798,334. Divided and this application Feb. 17, 1971, Ser. No. 116,054
The portion of the term of the patent subsequent to Nov. 9, 1988, has been disclaimed
Int. Cl. C10j *3/20*
U.S. Cl. 48—197 R **10 Claims**

ABSTRACT OF THE DISCLOSURE

In a continuous steam-iron process wherein finely divided iron oxides are reduced in a reduction zone and the reduced iron oxides are reacted with steam and hydrocarbonaceous solids in an oxidation zone to make fuel gas, the reduction of the iron oxides is effected by means of a continuously recirculating stream of hot, finely divided carbonaceous solids which are mixed with the iron oxides in a downwardly moving bed under reducing conditions, and heat is supplied to the reduction zone by the carbonaceous solids which are heated by partial combustion outside the reduction zone. In the preferred embodiment of the process, the mixture of reduced iron oxides and carbonaceous solids from the reduction zone is separated in a fluidized separation zone into a stream of reduced iron oxides and a stream of carbonaceous solids. The stream of reduced iron oxides is conducted to the oxidation zone where the reduced iron oxides fall through a fluidized bed of hydrocarbonaceous solids in countercurrent flow relationship to steam, whereby a product gas is produced which contains methane by virtue of the reaction of the hydrogen (produced by the steam-iron reaction) with the hydrocarbonaceous solids.

REFERENCE TO RELATED APPLICATION

This application is a division of copending application, Ser. No. 798,334, filed Feb. 11, 1969, now Pat. No. 3,619,142 issued Nov. 9, 1971, and assigned to the assignee of the present invention.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to an improvement in the steam-iron process for making fuel gas.

The steam-iron process is a process for making hydrogen by the reaction of steam with either elemental iron or a lower iron oxide, for example, FeO. The reaction produces higher oxides of iron, for example, Fe_3O_4, which may be reduced to repeat the cycle.

Despite the apparent simplicity of the steam-iron process and despite the fact that it has been known and worked on for over one hundred years, to the best of our knowledge no technically and economically feasible embodiment of a continuous steam-iron process has been developed which is now practiced commercially. Perhaps the principal reason for the failure of the steam-iron process to achieve commercial success is the difficulty involved in making it a continuous process. To do so requires subjecting a continuously flowing recirculatory stream of iron oxides to two different reactions, namely oxidation and reduction, under optimum conditions for each reaction, including optimum input and distribution of the heat required in the process.

Description of the prior art

Prior continuous steam-iron processes have favored the use of gaseous reductants for reducing the iron oxides (see, by way of illustration, U.S. Pat. No. 2,198,560). However, the production of a suitable gaseous reductant is expensive, and renders the overall process uneconomical. Furthermore, because of the limitations imposed by the thermodynamic equilibrium during the reduction of Fe_3O_4 and FeO to FeO and Fe with reducing gases containing hydrogen and carbon monoxide, the off-gas from once-through reduction contains considerable unreacted hydrogen and carbon monoxide. Thus, such a process tends to be wasteful of reducing gas.

In U.S. Pat. No. 3,503,724 of Homer E. Benson, issued Mar. 31, 1970, the reducing gas is made in situ by reacting air and carbonaceous solids in the presence of the iron oxides. Such a process has many advantages but requires careful control to minimize reconversion of elemental iron to higher oxides by contact with air.

Continuous steam-iron processes have been proposed which utilize either a solids in gas dispersion or the fluidized solids technique in the oxidation zone and the reduction zone (see, by way of illustration, U.S. Pat. Nos. 2,602,809 and 3,017,250). Reducing systems employing a dispersion of powdered iron oxide in a suspending gas cell for large reactors and costly gas-solids separators. All attempts to operate with the iron oxide in a fluidized condition have failed to become sufficiently attractive for commercial adoption because a fluidized mass is of uniform composition throughout whereas a composition gradient is generally desired.

SUMMARY OF THE INVENTION

In accordance with the present invention, we have provided an improved continuous steam-iron process for making fuel gas which uses not only a recirculatory stream of particulate iron oxides, but also uses a recirculatory stream of particulate carbonaceous solids to effect reduction of the iron oxides and to supply process heat requirements. In the practice of the process of this invention, reduced iron oxides comprising principally FeO and Fe are oxidized by steam in an oxidation zone, and iron oxides comprising principally Fe_3O_4 and FeO are reduced in a reduction zone. By "principally" we mean that at least fifty percent by weight of any mixture of oxidizable or reducible iron compounds, as the case may be, consists of the indicated compounds, and the actual percentage approaches 100 percent under equilibrium conditions. The relative amounts of FeO and Fe in the oxidizable mixture, and the relative amounts of Fe_3O_4 and FeO in the reducible mixture are functions largely of the temperature, pressure, and residence time maintained in the respective reaction zones. The oxidation of FeO and Fe (sometimes simply referred to herein as reduced iron oxides) is accomplished by passing steam in reactive relationship with the reduced iron oxides in an oxidation zone. The reduction of Fe_3O_4 and FeO is accomplished by subjecting them to direct contact with the recirculatory stream of hot carbonaceous solids in a downwardly moving bed in the reduction zone. No oxygen (molecular) containing gases are introduced into the moving bed in the reduction zone. The reduction conditions are selected to insure that only partial carbon depletion is effetced during the passage of the carbonaceous solids through the reduction zone, while however, the desired reduction of the iron oxides to Fe and FeO is effected. Heat is supplied to meet the requirements of the process by partial combustion of the carbonaceous solids in a combustion zone located outside the reduction zone. The amount of partial burning is controlled to raise the temperature of the carbonaceous solids sufficiently high to supply adiabatically the heat required.

In the preferred embodiment of the process, a separation zone is interposed between the reduction zone and the oxidation zone to effect separation of the carbonaceous solids from the reduced iron oxides leaving the reduction zone. Separation is effected by passing a gas through the mixture of carbonaceous solids and reduced iron oxides at a velocity which permits ready separation by virtue of the difference in densities of the iron compounds and carbonaceous solids. A fluidized separation zone is especially preferred wherein the fluidized bed consists essentially of the lighter carbonaceous solids from which the heavier iron compounds may be withdrawn and sent to the oxidation zone. The oxidation zone in the preferred embodiment comprises a fluidized bed of fresh carbonaceous solids into which the reduced iron oxides are fed. Hydrogen is produced by the relatively fast reaction of steam and reduced iron oxides, and in turn reacts with the carbonaceous solids to form methane. The separated carbonaceous solids from the separation zone are recirculated through the combustion zone back to the reduction zone.

The process operates continuously and efficiently to yield a methane-rich gas. The improvement in economics of the process as compared with prior steam-iron processes is due to the efficient use of low cost, finely divided carbonaceous solids for (1) the reduction of iron oxides, (2) the supply of process heat, and (3) the production of methane in a relatively simple two-vessel system. The gain in efficiency in the reduction zone arises from the thermal gradient established in the downwardly moving bed and from the lack of back-mixing of reduced iron. Thus, maximum reaction rates result from the counter-current flow relationship of the upwardly flowing reducing gases (generated in situ) and the downwardly flowing fresh iron oxides. The absence of molecular oxygen-containing gases assures no loss of desired reduction as a result of competing reactions. The flow of gases and solids in the oxidizer is most efficiently conducted in a fluidized bed for the particular reactions involved, to thereby minimize temperature gradients and to provide for an efficient balance between exothermic and endothermic reactions. Thus, in summary, the improved process provides for the maintenance of the optimum conditions for the reduction of Fe_3O_4 to FeO to Fe, and for the oxidation of the reduced iron oxides with steam.

BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding of our invention, its objects and advantages, reference should be had to the following description and accompanying drawings in which

FIG. 1 is a diagrammatic drawing of our invention in its broadest aspects,

FIG. 2 is a diagrammatic drawing of the preferred embodiment of our invention,

FIG. 3 is the same diagrammatic drawing of FIG. 2 but showing the locations of different points in the solids and gas streams to aid in understanding the material balance run reported in Table I of the specification,

FIG. 4 is a schematic drawing of a modification of the preferred embodiment of FIG. 2; and

FIG. 5 is the same schematic drawing of FIG. 4 but showing the locations of different points in the solids and gas streams to aid in understanding the material balance run reported in Table II of the specification.

DESCRIPTION OF FIGURE 1

Referring to FIG. 1 of the drawings, the numeral **10** designates a suitable vessel for housing a reduction zone **12** and an oxidation zone **14**. The reduction zone consists essentially of a downwardly moving bed of solids which flows by gravity through an opening **16** into the oxidation zone. The downwardly moving bed of solids in the reduction zone consists essentially of a mixture of two recirculatory streams of solids moving in substantially concurrent flow relationship. The first stream of solids contains iron

oxides which are principally Fe_3O_4 and FeO. The second stream of solids contains carbonaceous solids which serve not only to effect reduction of the iron oxides, but also to provide adiabatically the heat required for the reduction reaction. The primary reactions which occur in the reduction zone are as follows:

$$CO+Fe_3O_4 \rightarrow 3\ FeO+CO_2 \tag{1}$$

$$CO+FeO \rightarrow Fe+CO_2 \tag{2}$$

$$CO_2+C \rightarrow 2\ CO \tag{3}$$

The temperature maintained in the reduction zone is between 1000 and 2600° F. The pressure may be atmospheric or superatmospheric. The size consist of the iron oxides may suitably be in the range of 325 to 2 Tyler Standard screen. The size consist of the carbonaceous solids may also suitably be in the range of 325 to 2 Tyler Standard screen. The residence time of both solids in the reduction zone is generally between fifteen seconds and 60 minutes.

The carbonaceous solids in the reduction zone may conveniently be a solid carbonaceous fuel that is noncaking under the conditions of the reduction zone. Suitable solids of this kind are noncaking coals, lignite, coke, char which is the solid product obtained by the pyrolysis of coal or lignite, or coals rendered noncaking by preoxidation. Such solids are generally ash-containing, and as will be shown later, provision must be made for discharging ash from the overall system to prevent its build-up beyond a given point. Actually, up to a point, the ash serves as a heat carrier for maintaining the desired temperature in the reduction zone. In general, the carbon content of the carbonaceous solids in the reduction zone is at least twenty percent by weight. The weight ratio of carbon to iron oxide in the reduction zone must be sufficient to assure the required conversion of Fe_3O_4 and FeO to FeO and Fe during the passage through the reduction zone.

In the broadest aspect of this invention, the reduced iron oxides, together with carbon-depleted carbonaceous solids, flow into the oxidation zone without any attempt to separate the two solids systems. This is not the preferred procedure as will be seen in the description of the preferred embodiment. However, in the case of very reactive carbonaceous solids such as some lignites, it is feasible for them even in a carbon-depleted state to react with steam in the oxidation zone, even in the presence of iron or FeO. The less reactive carbonaceous solids in a carbon-depleted state would generally constitute a mass of relatively inert solids, thus reducing the effective throughput in the oxidation zone.

In the oxidation zone, steam is introduced through a steam inlet **18** and is circulated in reactive relationship to the reduced iron oxides. The reaction of steam with Fe and with FeO is extremely rapid and exothermic. The reactions are as follows:

$$H_2O+Fe \rightarrow FeO+H_2 \tag{4}$$

$$H_2O+3\ FeO \rightarrow Fe_3O_4+H_2 \tag{5}$$

Any gas-solids system may be used in the oxidation zone to make hydrogen because of the high rate of reaction of steam and the reduced iron oxides. If a fuel gas is the desired product, then the best system is determined by the reactivity of the carbonaceous solids fed to the oxidation zone or by the extent of carbon gasification desired. For example, a free-fall system in which solids have a relatively short residence time may be used for highly reactive carbonaceous solids, or in those instances where a relatively small amount of carbon gasification is desired for less reactive carbonaceous solids. Where significant carbon gasification is desired with less reactive carbonaceous solids, a fluidized bed system may be used. The temperature maintained in the oxidation zone is generally between 1000 and 2000° F. The pressure may be atmospheric or superatmospheric. The residence time of the solids in the oxidation zone may be between 30 seconds and 200 minutes. The higher pressures and longer residence times favor methane production, and the shorter residence times are sufficient for hydrogen production.

In addition to the reaction of steam with the reduced iron oxides to make hydrogen, there will be some reaction of steam with any carbonaceous solids that are present to produce CO and H_2, as well as some CO_2. More importantly, the hydrogen produced by the steam-Fe, steam-FeO, or steam-carbon reaction will react with the carbonaceous solids to produce methane, particularly at elevated pressures. If desired, fresh carbonaceous solids may be introduced into the oxidation zone through a conduit **22** to increase the content of methane in the product gas. The mixture of gases is discharged as product gas through a conduit **20** for direct use or for further treatment or purification, as may be desired.

The solid product of the oxidation zone, principally FeO and Fe_3O_4, along with unreacted carbonaceous solids, are withdrawn from the oxidation zone through a pipe **24** to a lift pipe **26** for recirculation to the reduction zone. The lift pipe **26** constitutes an elongated combustion zone for partially burning the carbonaceous solids with air introduced through an air feed pipe **28**. Additional fresh carbonaceous solids may also be introduced through a feed pipe **30** to replenish the carbon consumed in the oxidation and reduction zones, as well as in the combustion lift pipe **26**. The conditions maintained in the combustion lift pipe are such as to insure partial combustion of the carbonaceous solids to raise the temperature of the upwardly flowing mass of solids to a temperature sufficiently high to provide the necessary heat for the reduction reaction. As the carbonaceous solids recirculate through the recirculatory system there is a build-up of ash. This ash may be separated from the main stream of recirculatory solids from the lift pipe **26** in a cyclone separator **32** or by other suitable means. The flue gas, plus such ash, is discharged through a pipe **34** while the mixture of hot iron oxides and carbonaceous solids drops through pipe **36** onto the downwardly moving bed in the reduction zone. The effluent gas from the latter is withdrawn separately through a pipe **38**.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The preferred embodiment shown diagrammatically in FIG. 2 is adapted to produce a methane-containing gas that may be converted by conventional means to a high B.t.u. gas. Fresh hydrocarbonaceous solids containing both fixed carbon and volatile carbon are continuously fed to the oxidation zone, labeled Oxidizer in the drawing and also designated by the numeral **42**. The oxidation zone is contained in the lower part of a vessel **40**, the upper part of which confines the reduction zone **44**, sometimes called Reductor. The fresh, hydrocarbonaceous solids fed to the Oxidizer are high in total carbon content, in the range of fifty to ninety percent by weight. Preferably we use either char, the noncaking solid product resulting from pyrolysis of coal or lignite at low temperature, or a raw coal which has been rendered noncaking, if necessary, by preoxidation. The char, or raw coal (and hereafter reference is made only to char for convenience), is introduced by a pipe **46** into a continuous hopper **48** from which valve-regulated amounts of char are fed by a pipe **50** into the open space above the oxidation zone.

The char is maintained in a dense fluidized phase which serves as the oxidation zone. Elemental Fe and FeO substantially free of carbonaceous solids are introduced directly into the interior of the fluidized bed from a source and in a manner to be later described. The elemental Fe and FeO being of greater density than the fluidized char, descend in the bed in countercurrent flow relationship to steam which is introduced by a steam pipe **52** after being compressed by a jet compressor **53**. Under the temperature and pressure conditions maintained in the oxidation zone, the steam reacts preferentially and rapidly with the elemental Fe and FeO as set forth in Equations 4 and 5 above, to form hydrogen. At least some of the latter reacts with the char in the fluidized bed to form methane. The methane is discharged together with unused steam through an effluent gas pipe **54** for suitable treatment to recover a high B.t.u. gas.

The conditions maintained in the oxidation zone of the preferred embodiment are as follows: temperature, 1400 to 1800° F.; pressure, 100 to 1500 p.s.i.; and residence time of char, 1 to 200 minutes, with the higher pressures and longer residence times being preferred for methane production.

The mixture of iron oxides, mostly Fe_3O_4 and FeO, along with carbon-depleted char, is withdrawn from the oxidation zone through a pipe **56**. This mixture is lifted to the reduction zone through a lift pipe **58** by means of steam from the steam feed pipe **52**. In recycling to the reduction zone, the solids pass through a cyclone separator **60** which separates the steam from the solids. The steam is returned through a conduit **62** to the oxidation zone after being compressed to the desired pressure, together with the rest of the inlet steam in the compressor **53**. The solids drop out of the cyclone **60** into the space above the moving bed and thence onto the moving bed in the reduction zone.

The reduction zone, as in the case of the embodiment shown in FIG. 1, consists essentially of a downwardly moving bed of two substantially concurrently flowing streams of solids. The recycled iron oxides are mixed with the hot stream of carbonaceous solids entering the vessel from a lift pipe **66** whose function will be more fully described below. The gas produced in the reduction zone is discharged through a pipe **68**. The conditions maintained in the reduction zone of the preferred embodiment are as follows: temperature, 150 to 2100° F.; pressure, 100 to 1500 p.s.i.; residence time, 1 to 30 minutes; carbon depletion per pass, 1 to 10 percent of the carbon in the carbonaceous solids; and weight ratio of char to iron oxides, 0.5 to 5 lb./lb.

The mixture of reduced iron oxides, principally Fe and FeO, along with partially carbon-depleted carbonaceous solids drops by gravity through an outlet conduit **70** to a separator **72**. The latter is adapted to confine the mixture of solids in a fluidized state, the fluidizing gas being introduced by a pipe **74**. The fluidizing gas may be essentially inert, or it may contain some steam. If it does contain steam, then some hydrogen may be generated, in which case the effluent gas from the separator may be conducted to the Oxidizer. Otherwise, the effluent gas may be discharged conveniently through conduit **75**. Because of the different densities of the carbonaceous solids and the iron compounds, fluidization conditions can be selected to permit the iron compounds to settle out of the bed to be discharged through a conduit **76** into the oxidation zone **42**. The fluidized char overflows into a pipe **78** which leads to the previously mentioned lift pipe **66**. Air is introduced into the foot of the lift pipe through a pipe **80** not only to lift the solids back to the reductor, but also to burn part of the carbonaceous solids under controlled conditions to raise the temperature of the solids sufficiently high to provide the heat required in the reduction zone. Additional air may be introduced into the space above the reduction zone through a pipe **82** to effect combustion of the carbon monoxide generated in the reduction zone, as well as some of the carbonaceous solids from the lift pipe **66**.

The following example illustrates the operation of the preferred embodiment.

The conditions maintained and results obtained in a material balance run are set forth in the following Table I wherein the conditions and compositions of the various gas and solids streams are tabulated. The gas streams are designated by numerals 1 to 8 inclusive, and the solids streams by letters A to H inclusive. The so designated streams are shown in FIG. 3 by the encircled numerals or letters, as the case may be. In addition, the pressures in pounds per square inch are shown by the encircled 3-digit numbers at several points throughout the system.

TABLE I

GAS STREAMS

No.	1	2	3	4	5	6	7	8
Moles/hr.	2.93	1.47	1.02	5.72	6.99	6.99	7.02	8.78
Pressure, p.s.i.a.			623	622	650	621	633	630
Temperature, ° F.	842	842	1,971	1,866	1,165	1,656	1,700	1,347
Composition, percent vol.:								
O_2	20.99	20.99						
N_2	79.01	79.01		60.62				0.51
CO			35.62				11.55	10.18
CO_2			64.38	39.38			9.26	8.34
CH_4							20.49	20.84
H_2						18.25	27.06	32.36
H_2O					100.00	81.75	31.65	26.49
H_2S								1.28

SOLIDS STREAMS

No.	A	B	C	D	E	F	G	H
Lb./hr.	100	666	732	753	1,562	2,236	1,569	17
Temperature, ° F.	350	1,795	1,700	1,656	1,948	1,795	1,770	1,866
Composition, wt. percent:								
C	70.65		3.96	3.85	45.31	31.99	45.57	11.40
H	3.93							
N	1.24							
O	5.60							
S	3.56							
Ash	15.03		2.05	2.00	51.69	34.21	54.43	88.60
Fe		11.03				3.29		
$Fe_{.947}O$		88.97	93.99	47.03		26.51		
Fe_3O_4				47.12				

A modification of the preferred embodiment is shown in FIG. 4. Numerals **100** and **102** designate the Oxidizer and the Reducer respectively. The Oxidizer consists of two superimposed fluidized zones, Zone I and Zone II, designated by the numerals **104** and **106** respectively. Zone I is intended to serve primarily for the reaction of carbonaceous solids with hydrogen to make methane, while Zone II is intended to serve primarily for the reaction of steam and Fe or FeO to make hydrogen. The Reducer **102** consists of three superimposed zones, designated by the numerals **108**, **110** and **112** respectively. Zone **108** is a mixing chamber wherein incoming Fe_3O_4 and FeO and carbonaceous solids are mixed. Zone **110** is a combustion zone where carbon monoxide and/or the carbonaceous solids, while falling freely in admixture with the iron oxides, are partially burned to supply heat. Zone **112** is the reduction zone itself, consisting of a downwardly moving bed of the mixture of iron oxides and carbonaceous solids.

The operation of the process illustrated in FIG. 4 is as follows. Solid lines indicate solids streams and dotted lines, gas streams. Hydrocarbonaceous solids (identified as "carbon") containing a volatile hydrocarbonaceous component and a fixed carbon component are fed continuously through **114** into the Zone I of the Oxidizer **100**. A fluidized bed of the hydrocarbonaceous solids is maintained at a temperature between 1400 and 1800° F. and at a pressure between 100 and 1500 p.s.i. in order to optimize the reaction between the hydrocarbonaceous solids and hydrogen. The product gas comprising principally methane and hydrogen is withdrawn through a conduit **116**, after being freed of solids and condensibles which are shown schematically as discharged through conduit **117**. The partially reacted carbonaceous solids from Zone I are conducted by gravity down through a conduit **118** to the lower Zone II. In this zone, a fluidized bed of carbonaceous solids is maintained at a temperature between 1400 and 1800° F. and at a pressure between 100 and 1500 p.s.i. The gaseous product from this zone contains principally hydrogen and unreacted steam, with some CO, CO_2, and CH_4, and is conducted through a conduit **120** to the upper Zone II to serve as fluidizing reactant in Zone I.

The mixture of iron oxides from Zone II is withdrawn therefrom through a conduit **122** to an iron oxide lift pipe **124** wherein the mixture of oxides is lifted by steam introduced through a conduit **126**. The temperature in the lift pipe is maintained, by suitable regulation of the temperature of the steam and iron oxides, between 1300 and 1800° F., thereby promoting the reaction of the steam with FeO in the feed to the lift pipe to form Fe_3O_4. The latter is separated from the effluent gases by any suitable means at the top of the lift pipe. The iron oxides comprising principally Fe_3O_4 and FeO are carried by a conduit **128** to the mixing chamber **108** at the top of the Reducer vessel where they are mixed with char entering the mixing chamber from conduit **148**.

The iron oxides and char which are intimately mixed in the mixing chamber **108** are then allowed to fall freely through the combustion zone **110**. The latter is suitably supplied with air through a conduit **130**, in sufficient quantity to partially burn the char and thereby raise the temperature of the mixture of solids to that required for reduction of the iron oxides. Effluent gas and ash are discharged from the combustion zone by any suitable means, schematically shown in the figure as two conduits **132** and **134** respectively.

The hot mixture of iron oxides and char is dropped onto the top of downwardly moving bed **112** wherein the iron oxides are reduced to Fe and FeO. The only gases present in the moving bed are those generated in situ as schematically illustrated by the dotted arrow **136**. The solid product from the reduction zone is removed through a conduit **138** to a Separator **140**. A fluidized bed is maintained in this Separator as described before, and the velocity of the fluidizing gas is so regulated that the reduced iron oxides drop down while the char remains in a fluidized state and overflows through a separate discharge conduit **142**. The char is recycled to the Reducer through a lift pipe **144** by means of air introduced through conduit **146**. The air also serves, as before, to burn part of the char for process heat. The hot solids are conducted from the top of the lift pipe through a conduit **148** to the mixing chamber **108**. The effluent gas from the lift pipe **144** is also conducted to the mixing chamber and is shown schematically, in order to show all gas streams as well as solids streams, as being conducted through a separate conduit **150**, although it would normally not be handled separately.

The gas stream issuing from the top of the iron oxide lift pipe **124**, as stated before, comprises principally hydrogen and unreacted steam. This gas stream is carried by conduits **152** and **154** to Zone II, and, if desired, a slip stream may be conducted to the Separator **140** by means of a conduit **156**. Thus, it may serve as the fluidizing gas in the Separator; but, in that case, in the course of passing in contact with the reduced iron oxide, will reoxidize at least some of the Fe to FeO, which in turn will react, at least to some extent, with the steam to form hydrogen. The mixture of reduced iron oxides, including any FeO formed by the reaction of steam and Fe or FeO in the Separator, is conducted to Zone II via conduit **158** from the Separator. The effluent gas from the Separator, including any hydrogen formed by the reaction of steam and Fe or FeO in the Separator, is conducted to Zone II by a conduit **160**, joining up with conduit **154** at the inlet to Zone II.

The following example illustrates the operation of the modification of the preferred embodiment shown in FIG. 4.

The conditions maintained and results obtained in a material balance run are set forth in the following Table II wherein the conditions and compositions of the various gas and solids streams are tabulated. The gas streams are designated by numerals **1** to **14** inclusive, and the solids streams by letters A to L inclusive. The so designated streams are shown in FIG. 5 by the encircled corresponding numerals or letters. In addition, the temperatures in ° F. of the several streams are shown by the 4-digit numbers in parentheses.

TABLE II

GAS STREAMS—LB. MOLES/HR.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
CO			.0997	.1746					.0733					
CO_2			.0851	.1585	.0001	.1001	.1001	.0001	.1955	.4058				
H_2		.2300	.5773	.6173					.0020		.1150	.1150	.365	.480
H_2O	1.4660	1.2360	.7161	.5811		.0069	.0069		.0157	.0281	.6180	.6180	.368	.986
CH_4			.0952	.2516										
C_2H_6				.0057										
C_3H_8				.0016										
N_2				.0063	.3818	.3848	.3848	.2837		.6685				
H_2S			.0016	.1050										
O_2					.1035			.0703						
COS						.0001	.0001			.0003				
A					.0046	.0046	.0046	.0034		.0090				

SOLIDS STREAMS—LB. MOLES/HR.

	A	B	C	D	E	F	G	H	I	J	K	L
C	1.0580	.7150	.4350		.4350	.0173	9.9213	9.8552	9.5864	9.5861	9.4903	.0291
H_2	.3399	.0495	.0301		.0301	.0073	.6867	.6821	66.35	.6635	.6566	.0020
O	.0879					.0012						
N_2	.0078	.0015	.0015		.0015		.0930	.0915	.0915	.0915	.0915	.0015
S [1]	.0132											
FeS [1]	.0057	.0055	.0039		.0039		.2220	.2182	.2182	.2182	.2181	.0036
Fe [1]		.0002	.0018		.0018		.1295	.1276	.1276	.1276	.1277	.0021
Ash [2]	1.8546	1.8546	1.8546		1.8546		88.1493	86.2947	86.2917	86.2917	86.2947	1.8516
Fe									.23675			
$Fe_{.947}O$			1.4667	1.4667	.5911		.5911	.5911	1.2167			
Fe_3O_4					.2761		.2764	.2761				
MgO			.7598	.7598	.7598		.7598	.7598	.7598			
SiO_2			.3550	.3550	.3550		.3550	.3550	.3550			

[1] Associated with the ash content of the char.

[2] Given in lbs./hr.

According to the provisions of the patent statutes, we have explained the principle, preferred construction and mode of operation of our invention and have illustrated and described what we now consider to represent its best embodiment. However, we desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically illustrated and described.

We claim:

1. A process for the gasification of hydrocarbonaceous solids which comprises:
   - (a) passing a stream of particulate iron oxides comprising principally Fe_3O_4 and FeO and a stream of particulate carbonaceous solids concurrently and downwardly into the top of a reduction zone,
   - (b) subjecting said stream of particulate iron oxides to direct reactive contact with said stream of particulate carbonaceous solids in a downwardly moving bed in said reduction zone, there being no molecular oxygen-containing gas introduced into the moving bed in the reduction zone,
   - (c) maintaining the following conditions in said reduction zone: temperature, 1000 to 2600° F.; pressure, atmospheric or superatmospheric; residence time of said solids, 15 seconds to 60 minutes; carbon depletion per pass, 1 to 10 percent of the carbon in said carbonaceous solids; and a carbon content of said carbonaceous solids which is at least twenty percent by weight, whereby the iron oxides are reduced to a mixture comprising principally FeO and Fe,
   - (d) partially burning carbon-depleted carbonaceous solids from step (b) outside the reduction zone to raise the temperature of said carbonaceous solids sufficiently high to supply adiabatically the heat required in said reduction zone,
   - (e) returning said partially-burned carbonaceous solids from step (d) to said reduction zone,
   - (f) reacting reduced iron oxides from step (b) with steam in the presence of hydrocarbonaceous solids in an oxidation zone,
   - (g) maintaining the following conditions in said oxidation zone: temperature, 1000 to 2000° F.; and pressure, atmospheric or superatmospheric, whereby hydrogen and methane are formed and a mixture of iron oxides comprising principally Fe_3O_4 and FeO is produced, and
   - (h) returning said mixture of iron oxides from step (f) to said reduction zone of step (a) to repeat the cycle.

2. The process according to claim 1 in which the reduction zone is maintained at a temperature between 1500 and 2100° F. and a pressure between 100 and 1500 p.s.i.; and the oxidation zone is maintained at a temperature between 1400 and 1800° F. and a pressure between 100 and 1500 p.s.i.

3. A process for the gasification of hydrocarbonaceous solids which comprises:
   - (a) passing a stream of particulate iron oxides comprising principally Fe_3O_4 and FeO and a stream of particulate carbonaceous solids concurrently and downwardly into the top of a reduction zone,
   - (b) subjecting said stream of particulate iron oxides to direct reactive contact with said stream of particulate carbonaceous solids in a downwardly moving bed in said reduction zone, there being no molecular oxygen-containing gases introduced into said moving bed in said reduction zone,

(c) maintaining the following conditions in said reduction zone: temperature, 1000 to 2600° F.; pressure, atmospheric or superatmospheric; residence time of solids, 15 seconds to 60 minutes; carbon depletion of said carbonaceous solids per pass through said reduction zone, 1 to 10 percent of the carbon in said carbonaceous solids; and a carbon content of said carbonaceous solids which is at least twenty percent by weight, whereby said iron oxides are reduced to a mixture comprising principally FeO and Fe,

(d) withdrawing the mixture of carbon-depleted carbonaceous solids and reduced iron oxides from said reduction zone and transferring said mixture to a separation zone,

(e) passing a gas through said mixture of carbon-depleted carbonaceous solids and reduced iron oxides in said separation zone at a velocity sufficient to effect separation by virtue of the difference in densities of the reduced iron oxides and carbonaceous solids,

(f) withdrawing carbon-depleted carbonaceous solids from said separation zone and partially burning same outside said reduction zone to raise the temperature of said carbonaceous solids sufficiently high to supply adiabatically the heat required in said reduction zone,

(g) returning said partially-burned carbonaceous solids to said reduction zone,

(h) withdrawing iron oxides from said separation zone and reacting same with steam in the presence of hydrocarbonaceous solids in an oxidation zone,

(i) maintaining the following conditions in said oxidation zone: temperature, 1000 to 2000° F.; and pressure, atmospheric or superatmospheric, whereby hydrogen and methane are formed and a mixture of iron oxides comprising principally Fe_3O_4 and FeO is produced, and

(j) returning said mixture of iron oxides from said oxidation zone to said reduction zone.

4. The process according to claim 3 in which the reduction zone is maintained at a temperature between 1500 and 2100° F. and a pressure between 100 and 1500 p.s.i.; and the oxidation zone is maintained at a temperature between 1400 and 1800° F. and a pressure between 100 and 1500 p.s.i.

5. A process for the gasification of hydrocarbonaceous solids which comprises:

(a) passing a stream of particulate iron oxides comprising principally Fe_3O_4 and FeO and a stream of particulate carbonaceous solids concurrently and downwardly into the top of a reduction zone,

(b) subjecting said stream of particulate iron oxides to direct reactive contact with said stream of particulate carbonaceous solids in a downwardly moving bed in said reduction zone, there being no molecular oxygen-containing gases introduced into said moving bed in said reduction zone,

(c) maintaining the following conditions in said reduction zone: temperature, 1000 to 2600° F.; pressure, atmospheric or superatmospheric; residence time of solids, 15 seconds to 60 minutes; carbon depletion of said carbonaceous solids per pass through said reduction zone, 1 to 10 percent of the carbon in said carbonaceous solids; and a carbon content of said carbonaceous solids which is at least twenty percent by weight, whereby said iron oxides are reduced to a mixture comprising principally FeO and Fe,

(d) withdrawing the mixture of carbon-depleted carbonaceous solids and reduced iron oxides from said reduction zone and transferring said mixture to a separation zone,

(e) passing a fluidizing gas through said mixture of carbon-depleted carbonaceous solids and reduced iron oxides in said separation zone at such a velocity that a fluidized bed of said carbonaceous solids is established and maintained from which said iron

oxides and said carbonaceous solids may be separately withdrawn,

(f) withdrawing carbon-depleted carbonaceous solids from said fluidized separation zone and partially burning same outside said reduction zone to raise the temperature of said carbonaceous solids sufficiently high to supply adiabatically the heat required in said reduction zone,

(g) returning said partially-burned carbonaceous solids to said reduction zone,

(h) withdrawing iron oxides from said separation zone and reacting same with steam in the presence of hydrocarbonaceous solids in an oxidation zone,

(i) maintaining the following conditions in said oxidation zone: temperature, 1000 to 2000° F.; pressure, atmospheric or superatmospheric; and residence time of the solids, 30 seconds to 200 minutes, whereby hydrogen and methane are formed and a mixture of iron oxides comprising principally Fe_3O_4 and FeO is produced, and

(j) returning said mixture of iron oxides from said oxidation zone to said reduction zone.

6. The process according to claim 5 in which the reduction zone is maintained at a temperature between 1500 and 2100° F. and a pressure between 100 and 1500 p.s.i.; and the oxidation zone is maintained at a temperature between 1400 and 1800° F. and a pressure between 100 and 1500 p.s.i.

7. The process according to claim 5 in which the fluidizing gas used in the separation zone is an inert gas.

8. The process according to claim 5 in which the fluidizing gas used in the separation zone contains steam.

9. The process according to claim 5 in which the hydrocarbonaceous solids in the oxidation zone are maintained therein as a fluidized bed.

10. A process for the gasification of hydrocarbonaceous solids which comprises:

(a) passing a stream of particulate iron oxides comprising principally Fe_3O_4 and FeO and a stream of particulate carbonaceous solids concurrently and downwardly into the top of a reduction zone,

(b) subjecting said stream of particulate iron oxides to direct reactive contact with said stream of particulate carbonaceous solids in a downwardly moving bed in said reduction zone, there being no molecular oxygen-containing gas introduced into the moving bed in the reduction zone,

(c) maintaining the following conditions in said reduction zone: temperature, 1500 to 2100° F. and a pressure between 100 and 1500 p.s.i.; residence time of said solids, 15 seconds to 60 minutes; carbon depletion per pass, 1 to 10 percent of the carbon in said carbonaceous solids; and a carbon content of said carbonaceous solids which is at least twenty percent by weight, whereby the iron oxides are reduced to a mixture comprising principally FeO and Fe,

(d) passing a gas through the mixture of reduced iron oxides and carbon-depleted carbonaceous solids from said reduction zone in a separation zone at such a velocity that a fluidized bed of the carbonaceous solids is formed from which the reduced iron oxides may be readily withdrawn,

(e) partially burning the separated carbonaceous solids outside the reduction zone to raise the temperature of said carbonaceous solids sufficiently high to supply adiabatically the heat required in the reduction zone;

(f) returning said partially-burned carbonaceous solids to said reduction zone,

(g) establishing and maintaining a first fluidized bed of hydrocarbonaceous solids at a temperature between 1400 and 1800° F. and a pressure between 100 and 1500 p.s.i.,

(h) conducting reduced iron oxides from said separation zone to the bed established in step (g) and allowing said iron oxides to fall by gravity in countercurrent relationship with steam flowing upwardly in said bed, whereby hydrogen and methane are formed.

(i) establishing and maintaining a second fluidized bed of hydrocarbonaceous solids at a temperature between 1400 and 1800° F. and a pressure between 100 and 1500 p.s.i., said second fluidized bed being interconnected to the fluidized bed of step (g) so that the solids from the second fluidized bed flow into the fluidized bed of step (g) and the product gas from the fluidized bed of step (g) flows into the second fluidized bed, whereby a product gas enriched in methane is produced in the second fluidized bed, and

(j) returning iron oxides withdrawn from the fluidized bed of step (g) to the reduction zone to repeat the cycle.

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