REACTION OF COAL WITH STEAM-HYDROGEN MIXTURES AT HIGH TEMPERATURES AND PRESSURES

H. L. FELDKIRCHNER AND JACK HUEBLER

Institute of Gas Technology, Chicago 16, Ill.

The rate of hydrogasification of low-temperature bituminous coal char with steam, hydrogen, and steam-hydrogen mixtures was measured at conditions not previously studied in a novel, rapid-charge, semiflow reactor system. Rates were measured at 1000 p.s.i.g. and at temperatures from 1700° to 2100° F. under conditions of very rapid coal heatup and very short exit gas residence times. The primary variables studied were temperature, degree of carbon gasification, and feed gas steam-hydrogen ratio. Data were obtained for use in designing reactors for high-pressure, high-temperature steam-hydrogen gasification of low-temperature bituminous coal char.

THREE basic problems have been encountered in the development of processes for the conversion of coals to pipeline gas by destructive hydrogenation at high pressures:

At 1300° to 1500° F., the temperature range which permits the direct production of a gas of high heating value, the rate of coal conversion is relatively low.

An external source of hydrogen is required.

The high heat release of the hydrogenation reactions cannot be utilized to the fullest advantage; this creates a serious problem in the design of a reactor in which adequate temperature control and optimum process heat economy can be achieved.

The first limitation has been partially overcome by using countercurrent reactor operation with a steep temperature gradient. The use of this operating scheme has been found to be effective for producing a gas of high heating value in a single step by destructive hydrogenation at 2000 p.s.i.g. and 1300° to 1700° F. (*11*). Several combined factors cause this countercurrent scheme to be preferred. First, at high levels of gasification, the hydrogasification rates of coals increase rapidly with increases in temperature; but at low levels of gasification, in the temperature range of 1300° to 1700° F., these rates are nearly independent of temperature (*1, 2, 6, 15*). Second, at all gasification levels, gasification rates are roughly proportional to the hydrogen partial pressure. Third, the equilibrium methane content of the product gas decreases with increases in temperature. For example, at 1700° F. and 1500 p.s.i.a., the maximum product gas methane concentration that can be obtained in the reaction of carbon with hydrogen is 47 mole %, while at 2000° F., this value is only 28 mole %.

In countercurrent operation, as now contemplated, a large excess of hydrogen comes in contact with the relatively unreactive residue at the high-temperature end of the reactor. At the low-temperature end of the reactor, highly reactive feed char comes in contact with the product gas. Methane concentrations in excess of those predicted for the carbon-hydrogen reaction can be produced when the gas is in contact with slightly gasified coal char (*14*). Thus, the contacting of fresh char and product gas at low temperatures, and spent char and feed hydrogen at high temperatures minimizes equilibrium limitations. Since the rate of gasification is roughly proportional to the difference between the hydrogen partial pressure in the gas and in equilibrium with the char, counter-

current operation also provides a maximum average hydrogen partial pressure and thus a maximum average gasification rate.

Other variations of this basic countercurrent operating scheme might allow further increases in gas heating value or reductions in reactor size. For example, residence time of the residual char, and thus hydrogasifier size, might be reduced by using an even higher temperature in the high-temperature end of the reactor.

Increase of the reaction temperature also offers an opportunity for reducing external hydrogen requirements. At 1700° F. and above, it should be possible to supply part of the hydrogen requirements by steam decomposition reactions taking place simultaneously with the hydrogasification reactions. In addition to providing a source of "free" hydrogen, the endothermic steam-carbon decomposition reaction should provide a means for temperature control by offsetting the exothermic heats of the coal hydrogasification reactions.

On the basis of the above considerations, it appeared that pilot plant studies of the production of methane from solid fossil fuels should not be limited to the low-temperature range previously investigated, but should be extended into the temperature range above 1700° F., where very rapid gasification rates can be achieved. However, before prototype pilot plant equipment could be designed to investigate such high-temperature processes, it was necessary to obtain basic data on the gasification characteristics of the various solid fossil fuels under these extreme conditions. No data of this type were available because of the great difficulty of constructing high-temperature apparatus and devising experimental techniques capable of achieving the following three objectives:

Attainment of temperatures in excess of 2000° F., at pressures up to 3000 p.s.i.g.

Temperature control in spite of the considerable exothermicity or endothermicity of the reactions of interest.

Control and reliable measurement of reaction time.

In the course of the studies conducted by the Institute of Gas Technology in its Basic Research Program and other studies, techniques had been developed which appeared to give an acceptable solution to these problems on a laboratory scale (*5, 6*). These techniques minimized uncertainties resulting from the gasification of a batch fuel charge during heatup, as well as the uncertain solids residence times encountered in

entrained-solids systems where the actual rate of flow of the solid fuel through the heated zone cannot be measured directly.

A study of available equipment indicated that the above-listed techniques could be applied to a reactor capable of operating at the extreme conditions desired. A suitable reactor was designed and built, consisting of an external pressure vessel operating at low temperature, an electrical resistance heating system insulated from this outer shell, and a thin-walled, high-temperature, alloy steel reactor tube with means provided for balanced-pressure operation and fitted with a bellows to compensate for thermal expansion of the reactor tube.

Experimental

Apparatus. Figure 1 is a flow diagram of the system showing all major pieces of equipment and part of the control instrumentation.

Coal char was fed in single batches from a feed hopper, which was connected to the reactor by an air-operated, quick-opening ball valve. A pressure equilization line was used to keep the hopper pressure equal to the reactor pressure. A second hopper contained a rotating drum-type feeder for continuous coal char feeding.

Hydrogen was fed from a high-pressure gas storage system and was metered by an orifice meter. Hydrogen flow rates were controlled manually. Orifice differential pressures were sensed and converted to a 3- to 15-p.s.i.g. air signal by a differential-pressure transmitter. This air signal was then recorded, along with the orifice and reactor pressures, by conventional pneumatic recorders.

Controlled rates of steam feed were obtained by pumping water from a weigh tank through a steam generator by a positive-displacement, adjustable-stroke, metering pump. The steam generator consisted of a coil of stainless steel tubing, $3/8$ inch in outside diameter and $1/8$ inch in inside diameter, contained in an electric furnace. The temperature of the steam from the steam generator was controlled manually. Superheated steam and hydrogen were preheated to reaction temperature in passing through the upper heating zone of the reactor.

Exit gases from the bottom of the reactor were cooled by being passed through a water-cooled stainless steel coil. Condensed steam was collected in a high-pressure sight glass. To minimize loss of carbon dioxide or other dissolved gases in the condensed steam, the water was drained from the high-pressure sight glass into a low-pressure flash chamber which was vented into the low-pressure exit gas system, before water was drained from the unit.

Exit gases were metered continuously by a wet-test meter. A small portion of this stream was passed through a recording densitometer (to aid in selection of sampling times) and metered with a smaller wet-test meter. To avoid distortion of the reaction rate–time relationship because of backmixing and gas holdup, which would occur if gas samples were taken after gas metering, the gas-sampling manifold was installed in the exit gas line immediately after the pressure-reducing, back-pressure regulator, which was used to control the reactor pressure.

The reactor, shown in detail in Figure 2, was internally insulated and contained a stainless steel reactor tube which consisted of a length of $1\frac{1}{4}$-inch I.P.S., Schedule 40, Type 310 stainless steel pipe attached to two adapter fittings by pipe threads. This tube was heated electrically by a $2^3/_8$-inch inside-diameter heater, containing three 8-inch-long zones. The heater was fabricated from a single length of heating wire which was tapped for three-zone operation. A balanced pressure was maintained on the reactor tube by means of an on-off type pressure-balancing system. The design and operation of this reactor have been fully described (1). Design followed closely that of reactors described by Wasilewski (13) and Hodge and others (9).

Satisfactory operation was achieved at pressures up to 1000 p.s.i.g. and reaction zone temperatures up to 2100° F. Higher
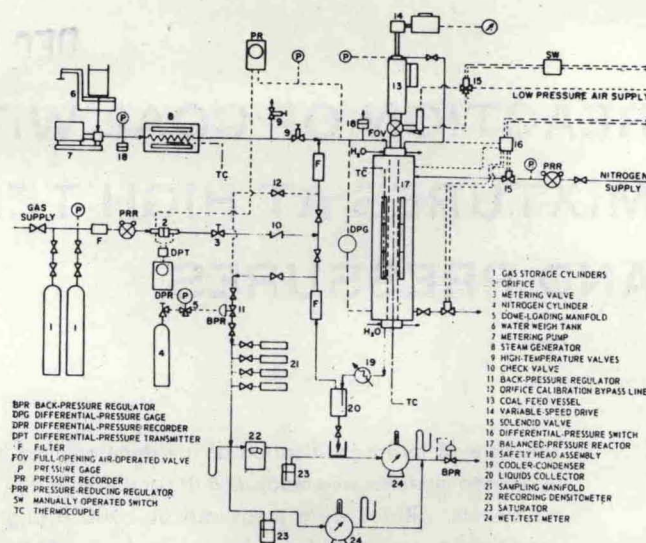

Figure 1. Semiflow reactor system

BPR BACK-PRESSURE REGULATOR
DPG DIFFERENTIAL-PRESSURE GAGE
DPR DIFFERENTIAL-PRESSURE RECORDER
DPT DIFFERENTIAL-PRESSURE TRANSMITTER
F FILTER
FOV FULL-OPENING AIR-OPERATED VALVE
P PRESSURE GAGE
PR PRESSURE RECORDER
PRR PRESSURE-REDUCING REGULATOR
SW MANUALLY OPERATED SWITCH
TC THERMOCOUPLE

1 GAS STORAGE CYLINDERS
2 ORIFICE
3 METERING VALVE
4 NITROGEN CYLINDER
5 DOME-LOADING MANIFOLD
6 WATER WEIGH TANK
7 METERING PUMP
8 STEAM GENERATOR
9 HIGH-TEMPERATURE VALVES
10 CHECK VALVE
11 BACK-PRESSURE REGULATOR
12 ORIFICE CALIBRATION BYPASS LINE
13 COAL FEED VESSEL
14 VARIABLE-SPEED DRIVE
15 SOLENOID VALVE
16 DIFFERENTIAL-PRESSURE SWITCH
17 BALANCED-PRESSURE REACTOR
18 SAFETY HEAD ASSEMBLY
19 COOLER-CONDENSER
20 LIQUIDS COLLECTOR
21 SAMPLING MANIFOLD
22 RECORDING DENSITOMETER
23 SATURATOR
24 WET-TEST METER

temperature operation should be possible by use of higher temperature heaters, such as silicon carbide and refractory metal reactor tubes. Insulation having a higher operating temperature limit than that of the insulation used here would also be required in the vicinity of the electric heater.

An insert, fabricated from a length of 1-inch I.P.S., Schedule 40, Type 310 stainless steel pipe, was installed within the reactor tube to provide for containment and complete recovery of the coal char charge. An integral thermowell, fabricated from $1/8$-inch I.P.S., Schedule 40, Type 310 stainless steel pipe, was located axially within the insert and contained three Chromel-Alumel, magnesium oxide–insulated, 0.062-inch outside-diameter, Inconel-sheathed thermocouples. The temperatures sensed by these thermocouples were recorded at approximately 1-second intervals by a high-speed potentiometric-type temperature recorder.

Reactor temperatures were controlled by three on-off. indicating temperature controllers and three thermocouples located within the centers of the heating elements. Satisfactory operation was obtained with this type of thermocouple mounted in the electric heaters as well as in the insert at reactor temperatures up to 2100° F. Electric heater temperatures were kept below 2300° F. to ensure as long a heater life as possible.

Table I. Analysis of Coal Char

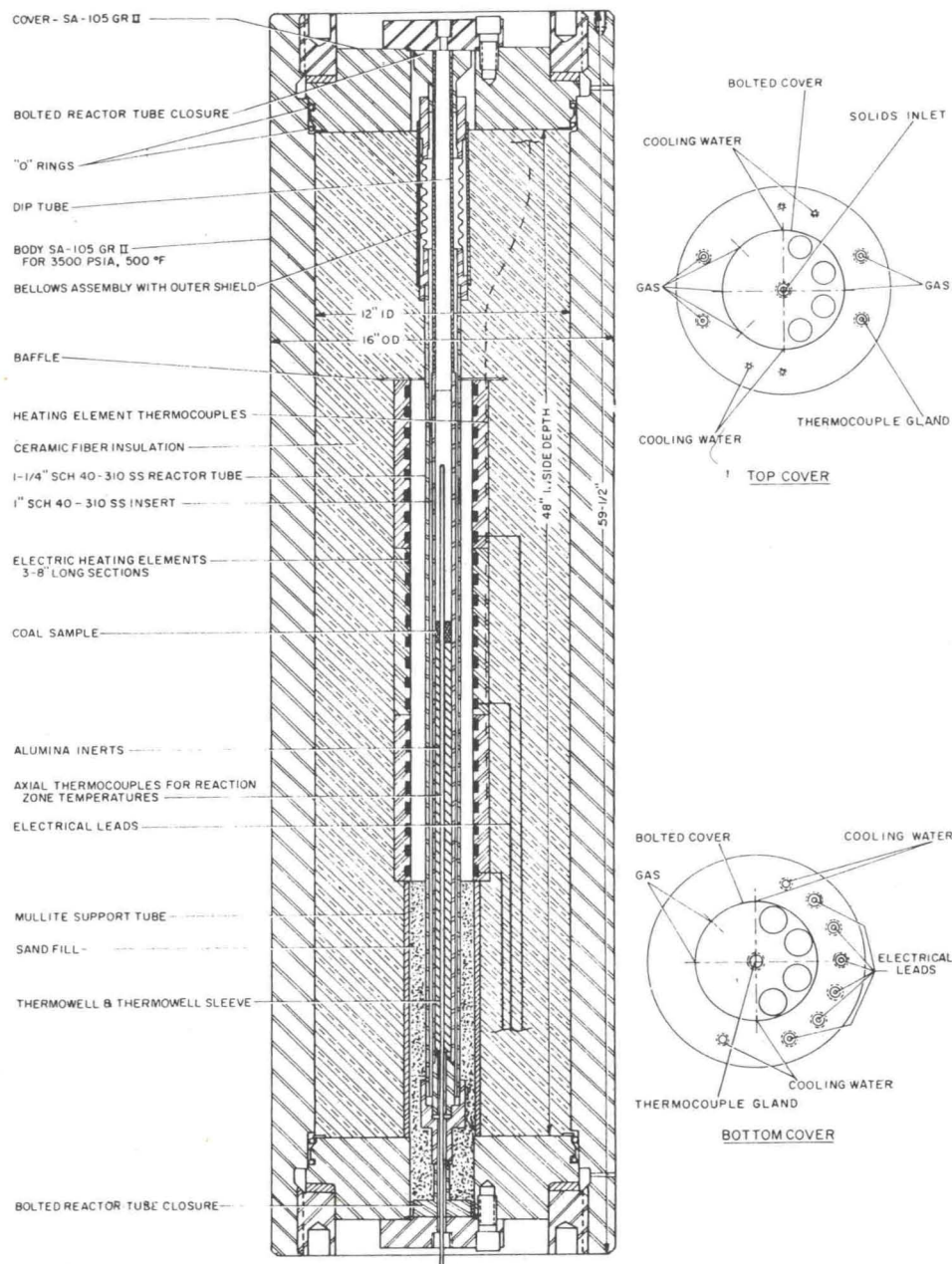|	
Sample designation	5851
Type	Low-temperature, bituminous coal char
Source	Consolidation Coal Co.
Particle size, U.S.S. sieve size	−16. +20
Ultimate analysis, wt. % (dry basis)	
Carbon	76.6
Hydrogen	3.25
Nitrogen	1.76
Oxygen	10.07
Sulfur	0.86
Ash	7.46
Total	100.00
Proximate analysis, wt. %	
Moisture	0.9
Volatile matter	18.1
Fixed carbon	73.6
Ash	7.4
Total	±100.0

Figure 2. Balanced pressure reactor

Materials. In tests with hydrogen feed gas and steam-hydrogen feed gas mixtures, the hydrogen contained a small, accurately measured amount of helium or argon (usually about 1 mole %) as a tracer for exit gas flow rate measurement. The hydrogen–inert gas mixtures were mixed during compression and stored in a central gas storage system at pressures up to 3600 p.s.i.g. Commercially available grades of hydrogen (99.987% pure), helium (99.99% pure), and argon (99.998% pure) were used.

The coal char was separated by screening from the char used in pilot plant tests to ensure that the results obtained in these tests would be applicable to work to be done in the larger, pilot plant reactor system. This coal char was prepared by the Consolidation Coal Co. from Pittsburgh Seam bituminous coal from the Montour No. 10 mine by a low-temperature fluidized-bed pretreatment process. The analysis of the feed char is shown in Table I.

Procedure. In all the tests, a semiflow technique employing a flowing gas and a single, static coal char charge was used. It was essentially the same as that used in recent studies on the hydrogasification of solid fossil fuels (5, 6). Test periods averaged about 1000 seconds.

Because heat losses by free convection from internally insulated reactors increase greatly when operating at high pressures, it was expedient to bring the reactor to operating temperature before pressurizing it to avoid long heatup times. When the reactor had reached the run temperature, the reactor pressure was brought to the desired level by increasing pressure inside the reactor tube. As pressure was increased, the pressure-balancing system maintained a balanced pressure on the reactor tube by admitting pressurized nitrogen to the insulated area surrounding the reactor tube. About 15 minutes was required to bring the pressure to 1000 p.s.i.g.

After the desired pressure was attained, the flow of reactant gas through the reactor tube was initiated. In tests with steam feeds, the reactor tube was first pressurized with nitrogen and then, when the steam generator pressure had been increased to slightly more than the reactor pressure, the steam was admitted to the reactor and the nitrogen was shut off.

This procedure was necessary to avoid introduction of large quantities of steam condensate into the instrument lines. In addition, since noncondensable exit gas flow rates were very small when pure steam feed gases were used, the exit gas system was purged at a controlled flow rate of 25 SCF per hour

Table II. Typical Results on Hydrogen–Coal Char Reaction

(Coal char sample weight, 2.5008 grams)

Time of sampling, sec.	0	20	30	40	60	100	180	360	480	600	1000	1500
Temp. at bottom of charge, ° F.	1800	1490	1510	1550	1662	1786	1800	1800	1800	1796	1800	1800
Unit pressure, p.s.i.g.	1010	1010	1010	1010	1010	1010	1010	1010	1010	1010	1011	1011
Feed hydrogen rate, SCF/hr.	39.3	39.4	39.3	39.1	39.3	39.8	39.8	39.8	40.8	40.8	40.8	40.8
Exit gas rate, SCF/hr.	39.3	40.0	39.5	39.0	38.1	38.6	39.0	39.7	41.0	41.0	41.0	41.4
Exit gas composition, mole %												
N_2	0.48	1.59	0.73	0.56	1.13	0.75	0.82	0.68	0.59	0.73	1.26	1.26
CO	...	...	...	0.40	0.50	0.20	...	...	...	...	...	...
H_2	99.47	98.36	99.21	97.44	92.19	94.19	97.09	98.62	98.96	98.93	98.54	98.59
CH_4	0.05	0.05	0.06	1.60	6.18	4.86	2.09	0.70	0.45	0.34	0.20	0.15
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
Rate of formation of gaseous carbon, lb./lb. C fed-hr.												
As hydrocarbons	...	0.1	0.2	4.6	17.5	14.0	6.1	2.1	1.4	1.0	0.6	0.5
Total carbon	...	0.1	0.2	5.8	18.9	14.6	6.1	2.1	1.4	1.0	0.6	0.5
Conversion of carbon fed, %	...	...	0.0	0.3	10.4	29.4	51.6	70.0	75.5	79.5	88.2	95.6

with helium to avoid any distortion of the rate-time relationship because of backmixing or holdup in the exit gas system.

When feed gas flow rates, temperatures, and pressures had become completely stabilized, the feed gas was sampled. One minute later, the tests were initiated by opening the quick-opening ball valve between the hopper and the reactor. Single charges of either 2.5 or 5 grams of coal char were fed and reactant gas flow rates of 50 SCF per hour were employed in all tests. The coal charge was supported on a stainless steel screen on top of approximately 19 inches of high-purity alumina inerts in the form of cylinders, $1/8$ inch long by $1/8$ inch in diameter. Temperatures of the bottom of the coal char charge and of the centers of the top and bottom heating zones were recorded. Exit gas samples were taken in the early stages of a test at frequent intervals (as small as 10 seconds) and later as required to delineate the entire course of the reaction.

The first reaction products appeared in the exit gas sampling system in about 15 to 35 seconds. This holdup time depended on the feed gas used, holdup times being shortest in tests with pure hydrogen feeds and longest in tests with pure steam feeds. In tests with steam-containing feed gases, a constant liquid level was maintained in the sight glass, so that gas holdup times in the exit system would not vary. This was necessary because a sizable variation in gas holdup times could distort the gasification rate–time relationship. When the reaction rate had reached a value too small to be measured accurately, the run was stopped. The feed gas flow was stopped, the reactor heaters were turned off, and the unit was depressurized to minimize further reaction of the coal charge after the run.

The feed gas and helium-purge gas orifices were calibrated before each run with the exit gas wet-test meter. Exit gas flow measurements were made also during each run by a wet-test meter to provide a check on the flow rates calculated with the helium or argon tracers. Gas analyses were performed by mass spectrometer at high sensitivity. Carbon monoxide was determined by infrared spectrophotometer, since it was not possible to measure the relative amounts of carbon monoxide and nitrogen with sufficient accuracy in the presence of methane with the mass spectrometer.

Results

Hydrogen–Coal Char Reaction. Initial testing was done at 1000 p.s.i.g. and 1700° to 2100° F., with hydrogen feed gas, 5-gram coal char samples, and feed gas flow rates of 50 SCF per hour. At temperatures of 1800° F. and above, no consistent effect of temperature on rate of gasification could be observed. In addition, during the tests at 1800° F. and above, stainless steel screens which had been used to support the coal char charges were found to have melted, which indicated that very large temperature rises had occurred during these tests. Heat balance calculations made using finite difference techniques and assuming a heat of reaction equal to that for hydrogenation of beta-graphite to methane showed that, at the high rates of reaction obtained with this highly reactive feedstock, sample temperatures could easily rise to over 2500° F. from a starting temperature of 2000° F., even with the high gas flow rates and small sample sizes used. Further tests were conducted with 2.5-gram samples at 1700° to 2100° F. A 2.5-gram sample size was deemed the smallest that would give sufficient methane in the product gas for accurate measurement. However, even with such small samples, sample temperatures increased greatly. For example, when pieces of −16, +20 U.S.S. sieve size temperature-indicating pellets having fusion temperatures of 1700°, 1900°, 2100°, 2250°, and 2500° F. were mixed with the feed char in one check run made at 1700° F., both the 1700° and 1900° F. pellets melted.

Therefore, three more tests were conducted with 2.5 grams of coal char mixed with 30 grams of alumina inerts to act as a heat sink. The results of these tests at 1800° and 2000° F. (which approached isothermal conditions) are shown graphically in Figure 3 along with results of tests conducted without inerts at 1800° and 2000° F. (which approached adiabatic conditions). Typical tabulated data are presented in Table II. This dilution technique was used in all further tests with hydrogen feed gas, and all further results presented for hydrogen feed gas were obtained by this method. In tests where char and inerts were fed, the indicated bed temperature at first
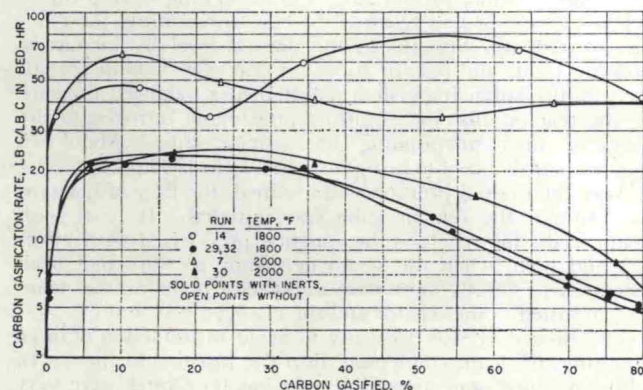

Figure 3. Comparison of results under conditions approaching adiabatic and approaching isothermal
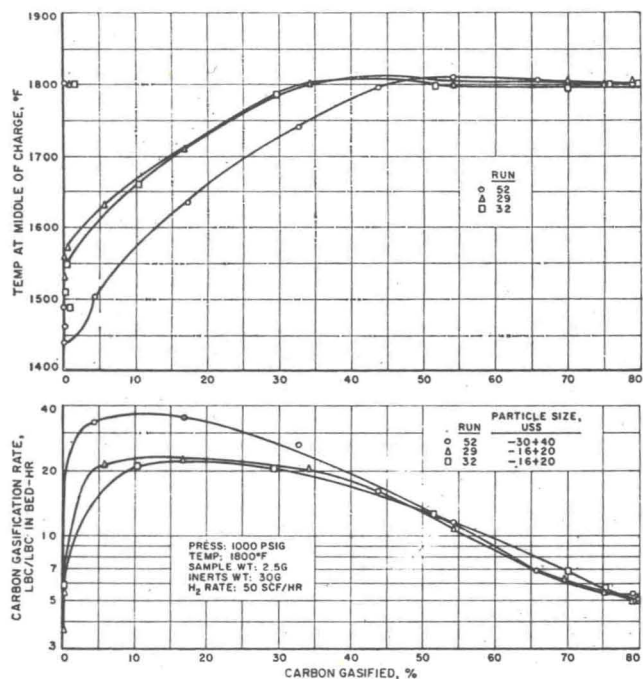
Figure 4. Effect of particle size on rate of hydrogasification of bituminous coal char at 1800° F.

Figure 5. Effect of hydrogen feed rate on rate of hydrogasification of bituminous coal char at 1800° F.

dropped rapidly several hundred degrees, but by the time about 40% of the carbon was gasified, the indicated bed temperature had returned to the nominal run temperature. There is a gradual decrease in gasification rate with increasing carbon gasification, which indicates a decrease in char reactivity. The degree of reproducibility of these tests can be seen by the close agreement of the two tests conducted at 1800° F. The finding that initial rates of gasification observed in these tests were almost as high as those in tests conducted without inerts is further evidence that initial rates are essentially independent of temperature above 1300° F. (6).

Other investigators—for example, Hunt and others (10) and von Fredersdorff (12)—found diffusional limitations present with the carbon-steam reaction. Therefore, several tests were conducted at 1800° F. with hydrogen feed gas to show whether diffusional effects may have been present in the char-hydrogen system. The results of the tests using char samples having different particle sizes are shown in Figure 4. At carbon gasifications above about 50%, there are no differences in the rates of gasification of −16, +20 and −30, +40 U.S.S. sieve size particles. Because of the temperature upsets which occurred when inerts were fed with the char, no reliable information can be obtained on this system for low carbon gasification levels. The results of tests conducted at different feed hydrogen flow rates are shown in Figure 5. Again, at carbon gasifications above about 50%, hydrogen flow rate apparently has no effect on gasification rate.

Steam–Hydrogen–Coal Char Reaction. The next set of tests was conducted with equimolar steam-hydrogen mixtures, at 1700° to 2100° F., with 50-SCF-per-hour feed gas flow rates, and with 2.5-gram coal char samples. The results of these tests are shown graphically in Figure 6. Typical tabulated data are presented in Table III. Temperature-indicating pellets, mixed with the coal char in these tests, did not indicate the presence of large heat effects which were found in tests with hydrogen feed gas. Heat-balance calculations indicated that temperature changes during these tests would be less than
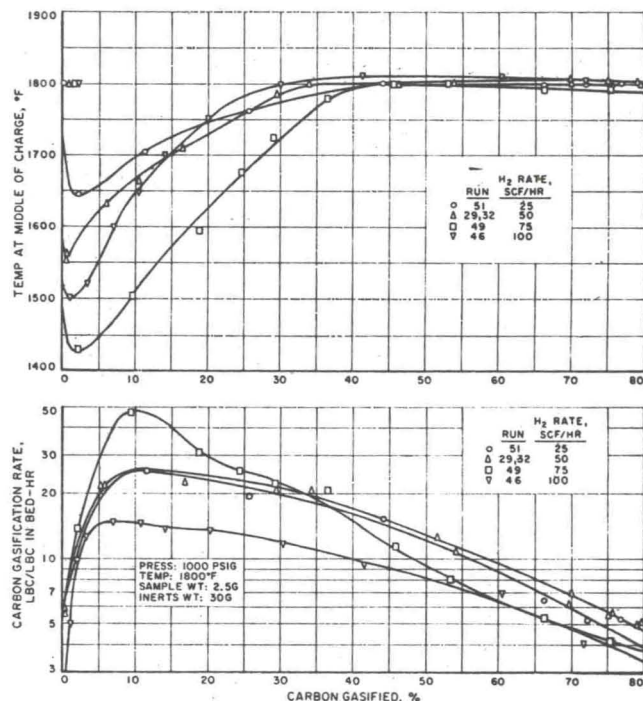
100° F. In general, the rate of gasification increased with increases in temperature. These results also indicate that greater structural changes, resulting in lost reactivity, may occur after prolonged exposures of the char to steam-hydrogen mixtures at 2100° F. than at lower temperatures, or in gasification with pure hydrogen.

The effect of temperature on the relative rates of formation of carbon oxides and methane, shown graphically in Figure 7, is more pronounced than the effect of temperature on the total gasification rate. Since some carbon oxides are evolved during the early stages of gasification with hydrogen, these data are also included for comparison. At higher temperatures, the char is apparently more reactive toward steam than toward hydrogen. However, it was not possible to measure the rates of the steam-char and char-hydrogen reactions quantitatively here, since some of the methane formed by the char-hydrogen reaction may undergo reforming to carbon monoxide and hydrogen in the gas phase or by secondary reaction catalyzed by the coal surface. Further work using isotopes- or radio-active-tracer techniques to distinguish between these two primary reactions is desirable.

Several conclusions can be drawn. First, since the rate of carbon oxides formation is greater than that of methane formation above 1900° F. and less below 1900° F., temperature control should not be a severe problem in steam-hydrogen coal gasifiers. For example, if bed temperatures began to increase, carbon oxide–forming reactions, which are endothermic, should eventually predominate and impose an upper limit on the bed temperature. If, on the other hand, the temperature began to decrease, exothermic methane-forming reactions should eventually predominate and impose a lower limit on the bed temperature. Second, the reactivity of the char for the carbon oxide–forming and for methane-forming reactions depends strongly on the carbon gasification level. Thus, selection of operating conditions for process design will also depend on the carbon gasification level in the reactor.

The equilibrium relationships for the steam-hydrogen-

Table III. Typical Results on Steam-Hydrogen—Coal Char Reaction
(Coal char sample weight, 2.1735 grams)

|												
Time of sampling, sec.	0	25	35	45	55	65	75	100	200	300	500	1003
Temp. at bottom of charge, ° F.	1800	1795	1795	1795	1795	1795	1795	1800	1802	1795	1792	1815
Unit pressure, p.s.i.g.	1000	1000	1000	1000	1000	999	1000	998	1001	1001	998	1000
Feed hydrogen rate, SCF/hr.	26.4	26.5	26.5	26.1	26.4	26.1	24.3	26.1	26.4	26.3	26.5	26.9
Feed steam rate, SCF/hr.	28.3	28.3	28.3	28.3	28.3	28.3	28.3	28.3	28.3	28.3	28.3	28.3
Exit gas rate, SCF/hr.	26.4	26.3	27.1	27.8	27.5	27.1	25.3	26.9	26.7	26.6	26.5	26.9
Exit gas composition, mole %												
N_2	0.84	0.09	0.45	0.43	0.18	0.54	0.48	0.30	0.58	0.25	0.24	0.84
CO	...	...	0.50	2.00	1.90	1.30	1.10	0.70	0.40	0.20	0.10	...
CO_2	0.01	0.01	0.31	0.99	0.84	0.70	0.61	0.45	0.27	0.19	0.12	0.12
H_2	99.15	99.90	97.05	92.46	93.68	94.70	95.51	97.10	97.77	98.67	99.14	98.85
CH_4	...	...	1.69	4.12	3.40	2.76	2.30	1.45	0.98	0.69	0.40	0.19
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
Rate of formation of gaseous carbon, lb./lb. C fed-hr.												
As hydrocarbons	...	...	3.9	9.8	8.0	6.4	5.0	3.3	2.2	1.6	0.9	0.4
Total carbon	...	...	5.8	16.9	14.5	11.1	8.7	6.0	3.8	2.5	1.4	0.7
Conversion of carbon fed, %	...	...	0.7	3.8	8.5	12.0	14.7	19.6	32.9	41.4	51.6	64.7
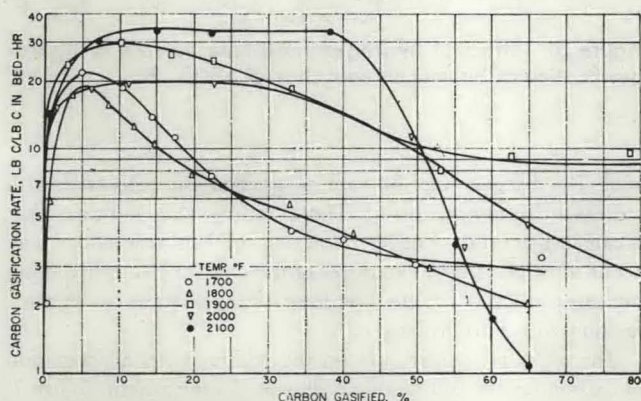
Figure 6. Effect of temperature and carbon gasification on gasification rate with equimolar steam-hydrogen mixtures
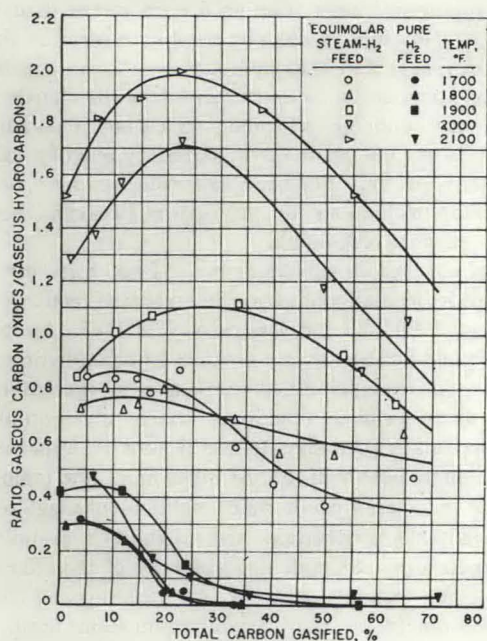

Figure 7. Effect of temperature and conversion on relative rates of formation of carbon oxides and hydrocarbons with equimolar steam-hydrogen mixtures

carbon system also indicate that temperature control should not be a severe problem in steam-hydrogen coal gasifiers. Figure 8 shows the effects of temperature for three pressure levels on the equilibrium gas composition for steam-hydrogen gasification of carbon. In calculating these equilibrium compositions, ideal gas behavior and a unit activity for carbon were assumed. As temperature increases, the yield of methane and carbon dioxide decreases and the yield of carbon monoxide increases. Thus chemical equilibrium limitations will exert a temperature-moderating influence on the reactions.

Since the concentration of reaction products in the exit gas was very small in all tests, the relative rates of the various gasification reactions would probably be somewhat different under actual operating conditions from those shown in Figure 7. However, the approximate trends shown should still be valid.

Calculations were also performed to show the degree of approach to the carbon monoxide shift reaction equilibrium in these tests. Although the concentration of reaction products in the exit gas was too small at high carbon gasification levels for making these calculations accurately, it was possible to make calculations for carbon gasifications below about 50%. At 2000° and 2100° F., the equilibrium was approached closely, but below 2000° F. the approach to equilibrium became progressively less with decreases in temperature. At 1700° F. the experimentally determined value for the ratio $(CO_2)(H_2)/(CO)(H_2O)$ averaged approximately 0.55 times the equilibrium value calculated from thermodynamic data.

Steam–Coal Char Reaction. The final set of tests was conducted with pure steam feeds, at 1700° to 2050° F., with 50-SCF-per-hour steam rates (Figure 9 and Table IV). Because of the generally lower gasification rates measured with steam feed gas, it was necessary to use larger—5-gram—coal char samples so that the concentration of gaseous products in the exit gas would be large enough for measurement by existing techniques. The concentration of products could also have been increased by using a lower helium sweep gas flow rate, but this would have resulted in longer holdup times in the exit gas system, which could cause distortion of the rate-time relationship by backmixing. Proportionately greater losses of dissolved carbon dioxide in the condensed steam with smaller

Table IV. Typical Results on Steam–Coal Char Reaction

(Coal char sample weight, 3.4280 grams)

| Time of sampling, sec.	0	25	50	75	100	125	150	200	300	500	1000	1567
Temp. at bottom of charge, °F.	2067	1937	1946	1958	1981	1998	2008	2030	2050	2055	2059	2049
Unit pressure, p.s.i.g.	999	998	1000	1000	998	996	995	995	994	994	995	995
Feed steam rate, SCF/hr.	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
Helium sweep gas rate, SCF/hr.	24.7	24.4	24.6	24.7	24.9	25.2	25.4	25.4	25.9	26.0	25.6	25.4
Exit gas rate, SCF/hr.	24.7	38.9	37.5	35.9	34.3	31.8	30.4	27.8	26.6	26.5	25.8	25.7
Exit gas composition, mole %												
N_2	0.53	1.42	0.75	0.78	0.48	...	0.07	0.56	0.46	0.06	0.07	0.88
CO	...	3.80	3.60	2.40	1.70	1.32	1.00	0.10	...	...	...	...
CO_2	0.01	8.88	7.69	7.37	6.65	5.32	4.18	1.78	0.66	0.91	0.13	0.14
H_2	0.93	23.19	22.30	20.64	18.51	14.33	11.40	5.92	1.36	0.91	0.81	0.31
He	98.53	62.71	65.66	68.81	72.66	79.03	83.35	91.64	97.52	98.12	98.99	98.67
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
Rate of formation of gaseous carbon, lb./lb. C fed-hr.	...	26.8	23.0	19.1	15.6	11.5	8.6	2.8	1.0	1.3	0.2	0.2
Conversion of carbon fed, %	...	10.0	26.9	41.7	53.5	62.8	69.2	76.3	80.4	86.0	91.9	94.9
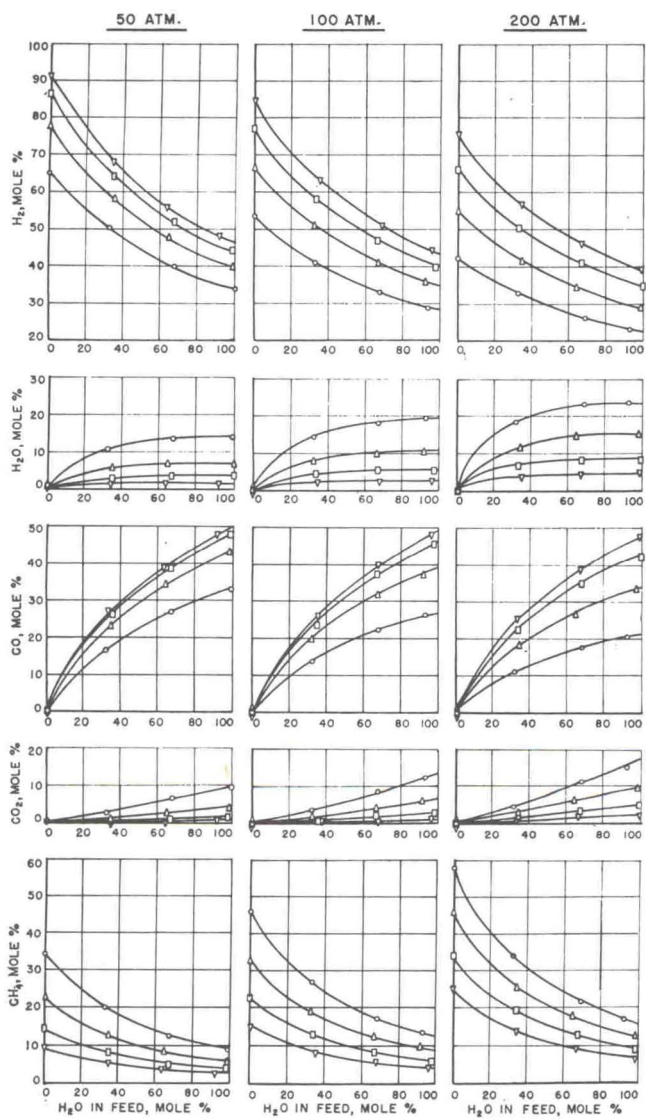
Figure 8. Ideal gas equilibrium compositions for steam-hydrogen gasification of carbon at high temperatures and pressures

Temp., °F.
O   1700
△   1900
□   2100
▽   2300

sample sizes would be a further reason for using larger coal char sample sizes.

The relationship between gasification rate and the degree of gasification is somewhat different from that with steam-hydrogen mixtures or hydrogen. Here, the rate of gasification is strongly influenced by temperature at all levels of carbon gasification, and the char reactivity decreases with increases in carbon gasification. The reactivity begins to drop very rapidly for all temperatures after about 100 to 150 seconds from the start of the run. A similar, but less pronounced, behavior was observed in a test at 2100° F. with steam-hydrogen feed gas. These results indicate that at higher temperatures the reactivity of the char may be affected by its previous gas environment. This loss in reactivity with steam-containing feed gases may apparently be counteracted by operation at higher temperatures, however, so that this should not be a serious limitation.

The combined results of tests conducted with −16, +20 U.S.S. sieve size char and at a 50-SCF-per-hour feed gas flow rate are presented in Figures 10 and 11. At lower temperatures,
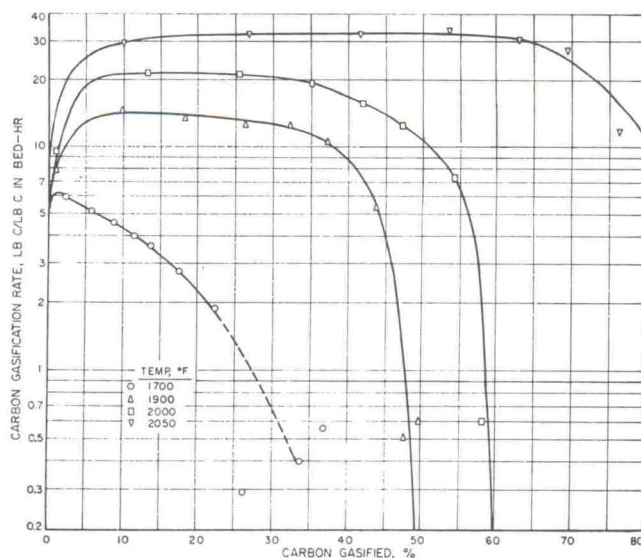

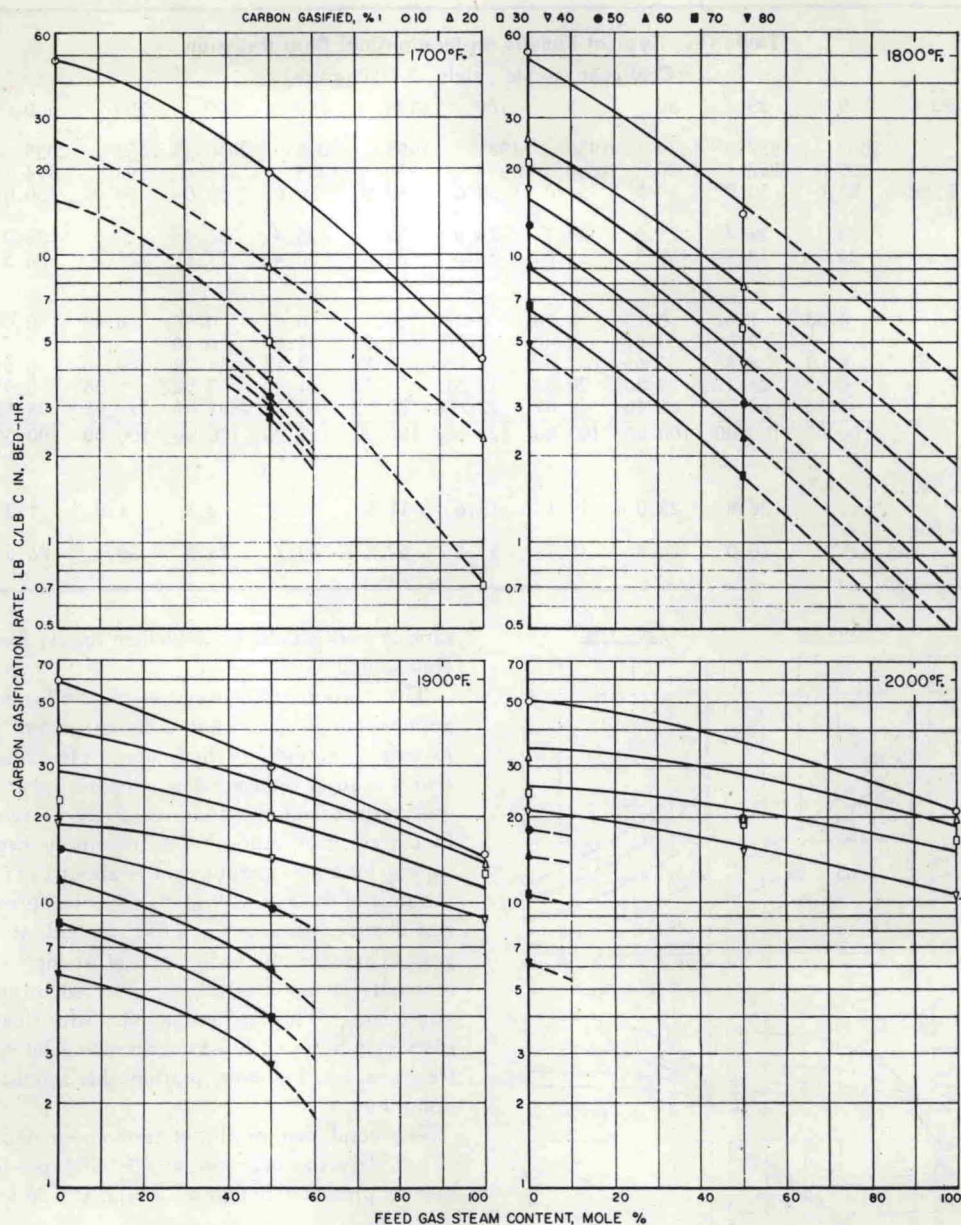Figure 9. Effect of carbon gasification and temperature on gasification rate with steam

Figure 10. Effect of feed gas steam content and conversion on gasification rate at 1000 p.s.i.g.

the rate of gasification with hydrogen is many times that with steam, but as temperature is increased, the rate of steam gasification approaches that for hydrogen.

The results of these tests differ from those conducted at lower temperatures and pressures with less reactive feedstocks. Previous investigators have found that, at hydrogen partial pressures below 30 atm. and at 1300° to 1700° F., the addition of steam increased the methane formation rate (3, 7, 8, 16), but no such "activating" effect was found here. This result is in agreement with previous work conducted at the institute (6). From Figure 11, it can be seen that the methane content of the product gas varies almost inversely with the feed gas steam content at higher carbon gasification levels. This decrease in methane yield with increases in feed gas steam content may, of course, be partially due to increased steam reforming of product methane with increases in steam partial pressure, discussed earlier. In addition, the high yields of carbon oxides at low carbon gasification levels and at low feed gas steam concentrations are partly due to devolatilization reactions which occur during the early phases of gasification. The relatively high oxygen content of this coal char (10.07 weight

%), along with the fact that these carbon oxide–forming reactions occur very rapidly and in the very early stages of gasification (6), would cause the effects of these reactions to be accentuated.

Other investigators have observed an inhibition of the steam char reactions by hydrogen when working with highly devolatilized chars (3, 8, 16). In recent work with low-temperature bituminous coal chars at 1700° F., this inhibiting effect was also observed during initial stages of gasification (6). The results shown in Figures 10 and 11 were studied, therefore, to see whether there was evidence of hydrogen inhibition of the steam char reactions. If a first-order rate relationship for the formation of carbon oxides by steam is assumed—i.e., the rate of formation of carbon oxides proportional to the steam partial pressure—the carbon oxide–formation rates per unit steam partial pressure were apparently no less in the tests with steam-hydrogen mixtures than with pure steam. This result may be due to somewhat different experimental conditions (6). In the previous work with coal char the residence times of the exit gas in the heated portion of the reactor were only about one quarter as large as those in
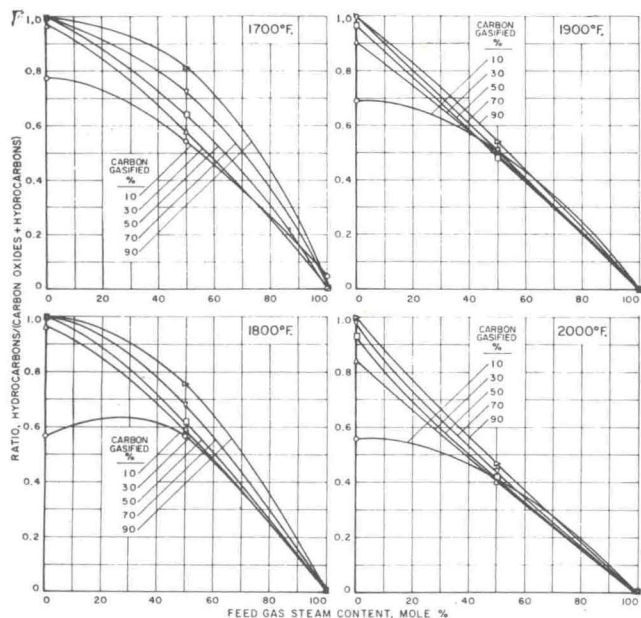
Figure 11. Effect of feed gas steam content and conversion on ratio of methane formation to carbon oxides formation at 1000 p.s.i.g.

this work. Therefore, since there may have been more steam reforming of exit methane in these tests, inhibition by hydrogen may have been obscured.

Acknowledgment

Literature Cited

(1) Birch, T. J., Hall, K. R., Urie, R. W., *J. Inst. Fuel* **33**, 422–35 (1960).
(2) Blackwood, J. D., *Australian J. Chem.* **12**, 14–28 (1959).
(3) Blackwood, J. D., McGrory, F., *Ibid.*, **11**, 16–33 (1958).
(4) Feldkirchner, H. L., Lee, A. L., Johnson, J. L., Eakin, B. E., 52nd National Meeting, American Institute of Chemical Engineers, Memphis, Tenn., Feb. 3–5, 1964.
(5) Feldkirchner, H. L., Linden, H. R., Division of Fuel Chemistry, 143rd Meeting, ACS, Cincinnati, Ohio, Jan. 13–18, 1963.
(6) Feldkirchner, H. L., Linden, H. R., IND. ENG. CHEM. PROC. DESIGN DEVELOP. **2**, 153–62 (1963).
(7) Goring, G. E., Curran, G. P., Tarbox, R. P., Gorin, E., *Ind. Eng. Chem.* **44**, 1051–65 (1952).
(8) Goring, G. E., Curran, G. P., Zielke, C. W., Gorin, E., *Ibid.*, **45**, 2586–91 (1953).
(9) Hodge, E. S., Boyer, C. B., Orcutt, F. D., *Ibid.*, **54**, 31–5 (1962).
(10) Hunt, E. B., Mori, S., Katz, S., Peck, R. E., *Ibid.*, **45**, 677–80 (1953).
(11) Linden, H. R., 48th National Meeting, American Institute of Chemical Engineers, Denver, Colo., Aug. 26–29, 1962; Preprint No. **14**, 17–52.
(12) von Fredersdorff, C. G., *Inst. Gas Technol. Res. Bull.* **19** (May 1955).
(13) Wasilewski, J. C., *Ind. Eng. Chem.* **52**, No. 6. 61A–64A (1960).
(14) Wen, C. Y., Huebler, J., 56th National Meeting, American Institute of Chemical Engineers, Houston, Tex., Dec. 1–5, 1963.
(15) Zielke, C. W., Gorin, E., *Ind. Eng. Chem.* **47**, 820–25 (1955).
(16) *Ibid.*, **49**, 396–403 (1957).