

Figure 4. Effect of particle size 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

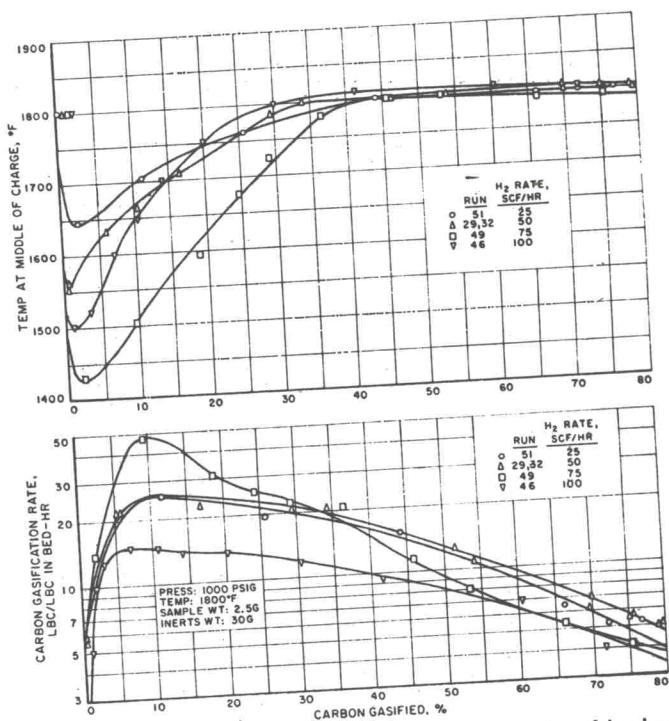


Figure 5. Effect of hydrogen feed rate on rate of hydrogasification of bituminous coal char at 1800° F.

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 radioactive-tracer techniques to distinguish between these two primary reactions is desirable.

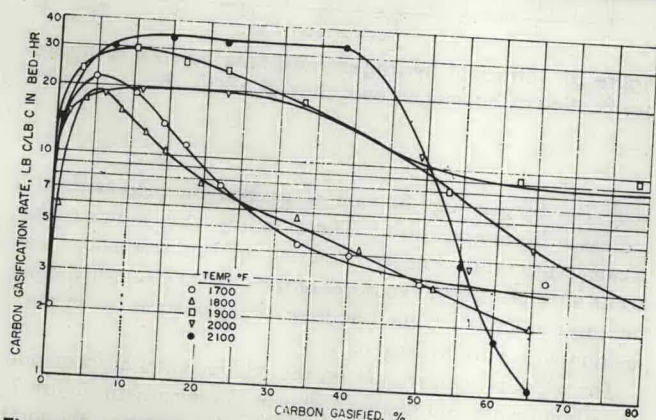
Several conclusions can be drawn. First, since the rate of carbon oxides formation is greater than that of methane formation above 1900° F. and less below 1900° F., temperature control should not be a severe problem in steam-hydrogen coal gasifiers. For example, if bed temperatures began to increase, 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-

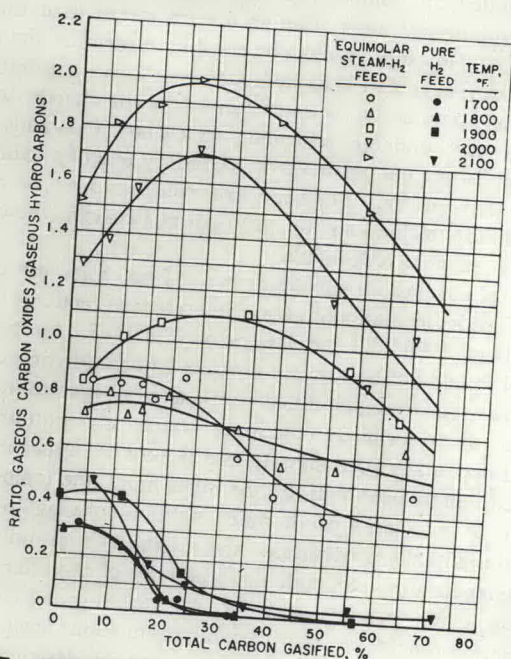


**Table III. Typical Results on Steam-Hydrogen-Coal Char Reaction**  
(Coal char sample weight, 2.1735 grams)

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 <sub>2</sub>	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 <sub>2</sub>	0.01	0.01	0.31	0.99	0.84	0.70	0.61	0.45	0.27	0.19	0.12	...
H <sub>2</sub>	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 <sub>4</sub>	...	...	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.	...	...	3.9	9.8	8.0	6.4	5.0	3.3	2.2	1.6	0.9	0.4
As hydrocarbons	...	...	5.8	16.9	14.5	11.1	8.7	6.0	3.8	2.5	1.4	0.7
Total carbon	...	...	0.7	3.8	8.5	12.0	14.7	19.6	32.9	41.4	51.6	64.7
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