

A better picture of the sequence of coal-hydrogen reactions under coal hydrogasification conditions can be obtained from the changes in hydrogen distribution with conversion of various feeds. The upper set of plots in Figure 10 shows the ratio of total hydrogen in the exit gas to the total hydrogen in the feed gas for a series of tests conducted at 1700° F. and 1500 p.s.i.g. The lower set shows the changes in gaseous feed hydrogen consumption with conversion, for the same series of tests.

The initial high-rate period is characterized by donation of hydrogen from the coals and char, as well as by large consumption of feed hydrogen, indicating the occurrence of both pyrolysis and hydrogenolysis reactions. The maximum feed hydrogen consumption tends to occur at higher carbon gasifications than the maximum hydrogen evolution, in accordance with the sequential nature of the pyrolysis and hydrogenolysis reactions. The rate of feed hydrogen consumption is an excellent indication of feed reactivity, except that, with the low-temperature bituminous coal char, a second period of high consumption occurs as a result of uncontrollable temperature increases.

Lignite, because of its high oxygen content, donated relatively little hydrogen and consumed a disproportionately large amount of gaseous feed hydrogen. This is due to the large amount of water formation, which can be readily measured in flow reactors, but could not be determined quantitatively in the present work. At the high hydrogen partial pressures used in this study, the only other major path for oxygen rejection is as carbon monoxide, since carbon dioxide formation is practically suppressed.

Steam-Hydrogen Coal Gasification. Much kinetic information on the reaction of steam-hydrogen mixtures and char exists for temperatures of 1500° to 1700° F. at hydrogen partial pressures below 30 atm. (3, 5, 6, 16). The addition of

steam substantially increased the rate of methane formation at these low hydrogen partial pressures. Extrapolation to hydrogen partial pressures sufficiently high to give rates of methane formation which are of practical interest indicates that the effect of steam becomes less significant.

In the present study, the rates of the steam-char and hydrogen-char reactions with an equimolar steam-hydrogen mixture were measured at 1700° F. and 1500 p.s.i.g. The rates of these two reactions (measured by the rates of evolution of gaseous carbon oxides and gaseous hydrocarbons) are shown in Figure 11 as functions of total carbon gasification. The results of the two tests conducted with 5- and 10-gram sample weights are in good agreement, and the second high-rate period, characteristic of the char-hydrogen tests at 1700° F., is absent. This is probably due to smaller temperature changes, with both exothermic hydrogenation reactions and endothermic steam-carbon reactions occurring simultaneously.

Unlike much of the earlier work at relatively low hydrogen partial pressure, the char-hydrogen reaction proceeded much more rapidly than the char-steam reaction, especially at the higher conversions. However, from comparison with Figures 7 and 8, the rate of char conversion to gaseous hydrocarbons was below the level expected for a feed gas hydrogen partial pressure of 750 p.s.i. Thus, the relatively high rates of carbon oxide formation at low conversion levels may have been largely due to steam reforming, catalyzed by the reactor walls, of a portion of the gaseous hydrocarbons produced. However, even if the total gasification rate is considered in a comparison with char-hydrogen results, there is no indication of the acceleration of methane formation by steam addition which has been observed at lower hydrogen partial pressures.

The rate of the steam-char reaction with an equimolar steam-helium mixture at 1700° F. and 1500 p.s.i.g., shown in Figure 12, was much higher than in the previous test with a

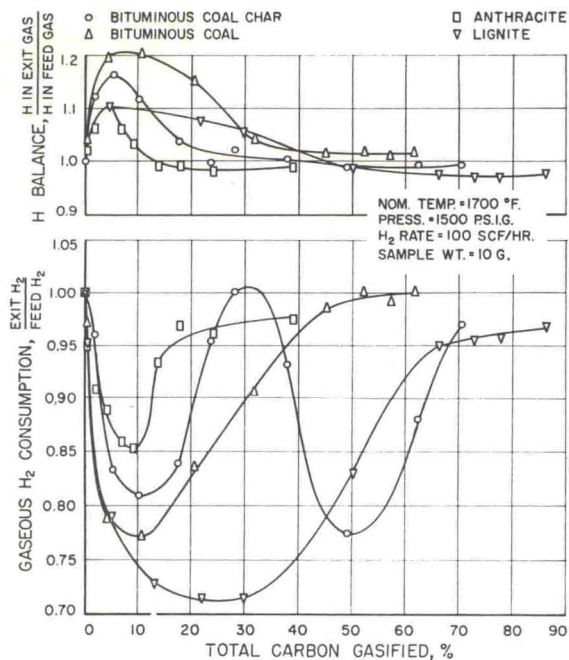


Figure 10. Gaseous hydrogen balance as a function of conversion of various feeds

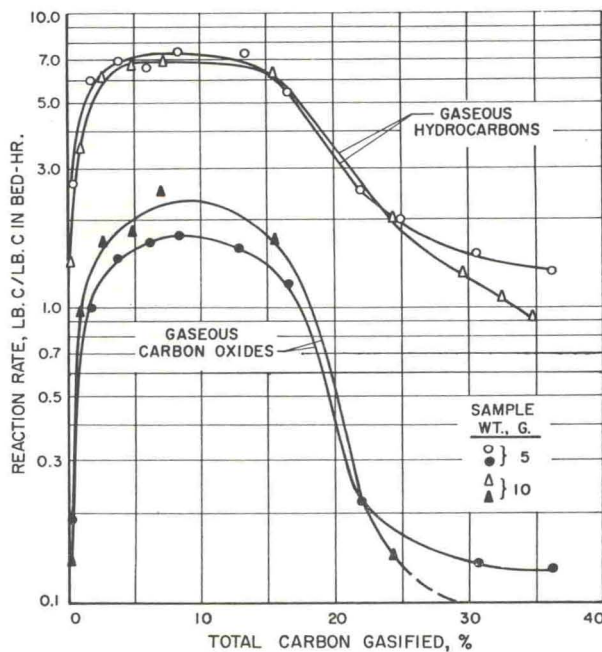


Figure 11. Effect of conversion on rate of gasification of coal char at 1700° F. and 1500 p.s.i.g. with an equimolar steam-hydrogen mixture

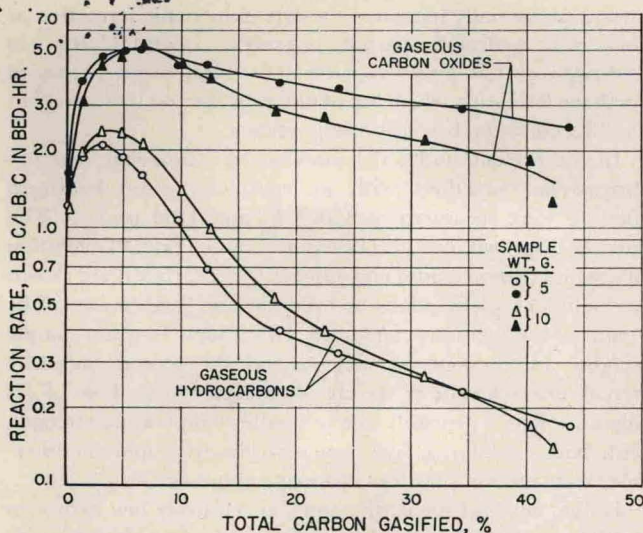


Figure 12. Effect of conversion on rate of gasification of coal char at 1700° F. and 1500 p.s.i.g. with an equimolar steam-helium mixture

steam-hydrogen feed at equal steam partial pressure. This is the result of the well-established inhibition of the steam-carbon reactions by hydrogen (6). Substantial quantities of gaseous hydrocarbons were also formed initially, probably largely by pyrolysis rather than by reaction of char with hydrogen formed in steam decomposition, or direct reaction of steam and char. This is supported by the fact that more hydrogen was produced than could be accounted for by carbon oxide-forming reactions.

Conclusions

Gasification of various coals with hydrogen and added steam at high temperatures and pressure, under conditions of very rapid coal heatup and product gas residence time of only a few seconds, has confirmed the generally accepted model derived from data without as detailed a definition of the critical initial stages of conversion. During this initial period, gasification rates are very rapid and the course of the methane-forming reactions is similar to that in hydrogenolysis of hydrocarbons. However, the reactivity of the pyrolysis intermediates formed during the high-rate period appears to be much greater than that of typical petroleum hydrocarbons, since no measurable liquid products were obtained at temperatures as low as 1300° F., and methane was the predominant product. Materials as different as lignite, bituminous coal, anthracite, and low-temperature bituminous coal char behaved similarly, except that initial conversion rates increased roughly in proportion to their volatile matter content, and hydrogen consumption and carbon oxide formation were affected by oxygen content. However, the conversion rates of the relatively unreactive residues were approximately the same. At the high hydrogen partial pressures employed in this study, steam

addition did not accelerate methane formation, as observed in previous studies at relatively low hydrogen partial pressures. The inhibiting effect of hydrogen on reactions with steam which form carbon oxides was observed for the initial high-rate period, as well as during the conversion of the residual char.

Acknowledgment

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Correction

HOLDUP STUDIES IN A PULSED SIEVE-PLATE SOLVENT EXTRACTION COLUMN

In this article by G. A. Schmel and A. L. Babb [*IND. ENG. CHEM. PROCESS DESIGN DEVELOP.* **2**, 38 (1963)], there are two typographical errors in Equation 1, page 42. The equation should read:

$$f_H = 40 (0.3 + 9 \times 10^{-8} \mu a \gamma \Delta \rho - \ln a)$$