

Figure 5. Reaction rate constants for various feeds at 1700° F. and 1500 p.s.i.g.

effects. The data for coconut char are based on the carbon initially present in the bed, but this is not significant in view of the low conversions.

Figure 5 further demonstrates the similarity in hydrogasification rate constants of the residual portion of coals and chars with greatly different initial properties. The rate constants during the high-rate period are roughly proportional to the volatile matter content of the feed, but at high conversion levels they approach one another. The results obtained with 5-gram samples of lignite and anthracite could not be closely duplicated with 10-gram samples, whereas with bituminous coal good agreement was obtained. The apparent rate constants with the larger samples were much higher for lignite and considerably lower for anthracite. This is not believed to be primarily due to lack of reproducibility.

The combined effect of changes in total and in hydrogen partial pressure at 1500° and 1700° F. is shown in Figures 6 and 7. The separate effect, at 1700° F., of a decrease in hydrogen partial pressure from 1500 to 1000 p.s.i. by the addition of nitrogen, is shown in Figure 8. These results indicate that, during the initial high-rate period, both pyrolysis

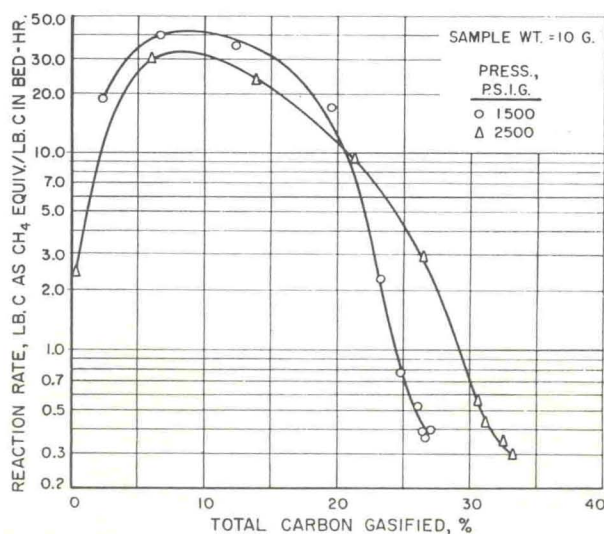


Figure 6. Effect of pressure on rate of char hydrogasification at 1500° F.

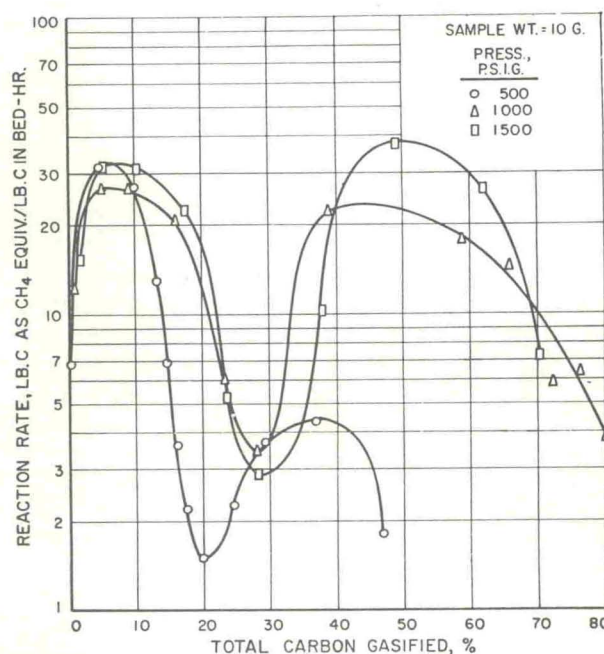


Figure 7. Effect of pressure on rate of char hydrogasification at 1700° F.

Table III. Rate Constants of Various Investigators

Investigator	Blackwood (2, 3) <sup>a</sup>	Birch (7) <sup>b</sup>	Zielke and <sup>b</sup> Gorin (15)	This study <sup>b</sup>
Coal	High-temperature coconut char	Brown coal	Disco bit. coal char	Low-temp. bit. coal char
Conversion	<10% char conversion	>40% carbon conversion	0-30% carbon gasification	25-30% carbon gasification
Temp., ° F.	<i>k</i> , Rate Constant			
1300	$1 \times 10^{-4}$	$6 \times 10^{-4}$	..	$2 \times 10^{-3}$
1500	$9 \times 10^{-4}$	$4 \times 10^{-3}$	$6.2 \times 10^{-3}$	$4 \times 10^{-3}$
1700	$6 \times 10^{-3}$	$2 \times 10^{-2}$	$1 \times 10^{-2}$	$3 \times 10^{-2}$

<sup>a</sup>  $k = \text{lb. C as CH}_4 \text{ equiv./lb. C fed-hr.-atm. H}_2 \text{ partial pressure.}$  <sup>b</sup>  $k = \text{lb. C as CH}_4 \text{ equiv./lb. C fed-hr.-atm. H}_2 \text{ partial pressure.}$

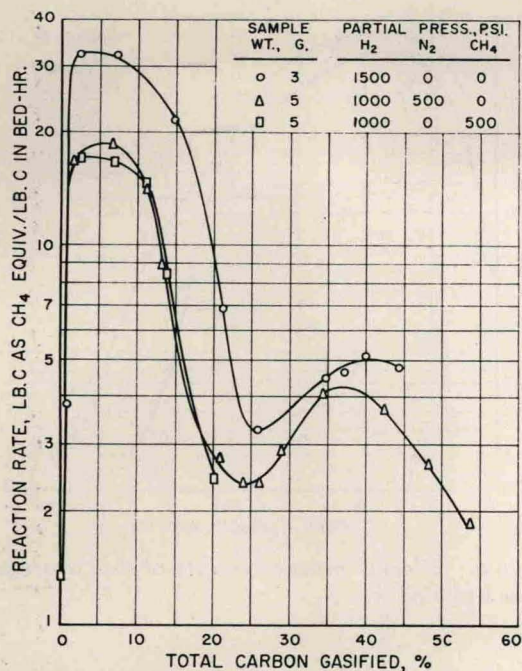


Figure 8. Effect of hydrogen and methane partial pressure on rate of char hydrogasification at 1700° F. and a total pressure of 1500 p.s.i.g.

and hydrogenolysis occur. Increases in hydrogen partial pressure would increase the rate of hydrogenolysis, and increases in total pressure would decrease the rate of pyrolysis. Thus, an increase in total pressure tended to broaden the range of the initial high-rate period. An increase in hydrogen partial pressure at constant total pressure both broadened the rate curve and increased its peak, during the initial high-rate period.

The true effect of hydrogen partial pressure during the highly exothermic residual char hydrogenolysis period was obscured at 1700° F. by the large temperature increases, depending on sample weight. However, it can still be observed qualitatively that increases in total pressure as well as in hydrogen partial pressure gave the expected increases in rate.

With devolatilized Disco bituminous coal char, Zielke and Gorin showed that the effect of methane partial pressure on hydrogasification rate is simple equilibrium hindrance (15). However, the results obtained with a partial pressure of 500 p.s.i. of nitrogen and 500 p.s.i. of methane were not significantly different during the initial high-rate period (Figure 8). This indicates no substantial equilibrium hindrance effect during this period, in spite of the large reduction in driving force for the reaction  $C + 2H_2 \rightarrow CH_4$ , if a carbon activity of 1 is assumed. On that basis, the equilibrium methane partial pressure at 1700° F. and 1500 p.s.i. is only about 700 p.s.i. The absence of a hindrance effect at low conversions is further evidence of the much higher initial carbon activity. The effect of 500-p.s.i. methane partial pressure in the feed gas during the low-rate period could not be determined because the measurement of product gas methane concentration was not accurate enough to obtain meaningful data.

**Course of Coal-Hydrogen Reactions.** The description of Birch, Hall, and Urie (7) of the sequence of coal-hydrogen reactions, at conditions where methane is the major hydrocarbon product, is in agreement with the experimental results of this

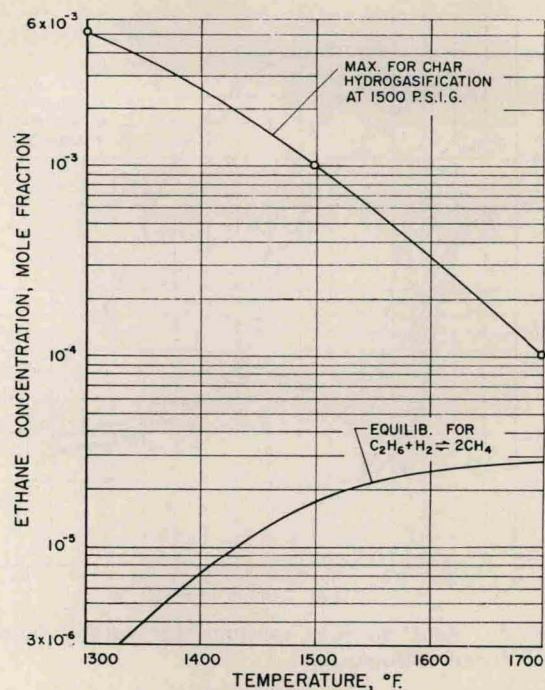


Figure 9. Approach of ethane concentrations to equilibrium values as a function of temperature

study. In somewhat modified form, this sequence is:

1. A high-rate period comprising pyrolysis of the more reactive structural units such as aliphatic hydrocarbon side chains and oxygenated functional groups, and hydrogenation and hydrogenolysis of the intermediate pyrolysis products.
2. A low-rate period of direct attack of hydrogen on the residual aromatic carbon structure.

Evidence for the two steps during the high-rate period can be found in the increase in formation of organic liquid products with decreases in product gas residence time observed by Hiteshuc, Anderson, and Friedman (7) at relatively low reaction temperatures encountered during heatup. Absence of substantial organic liquid product yields would correspond to the completion of the vapor-phase hydrogenolysis reactions, which are the chemical rate-controlling steps in methane formation during the initial high-rate period (14). Since, in this study, there was no major effect on the high-rate period from temperature changes in the 1300° to 1700° F. range at a pressure of 1500 p.s.i.g., a physical process may have been controlling under these conditions of extremely rapid hydrogenolysis.

Although no measurable liquid hydrocarbon formation occurred, even at 1300° F., as a result of rapid heatup of the coal charge, the presence of small amounts of C<sub>2</sub>- to C<sub>4</sub>-aliphatic hydrocarbons during the high-rate period indicates the initial formation of higher molecular weight intermediates which have been converted to methane by hydrogenolysis (12, 13, 14). In this case, ethane would have to be present in quantities exceeding the methane-ethane-hydrogen equilibrium values. In tests with bituminous coal char, ethane concentrations actually did exceed equilibrium values at the peak of the high-rate period (Figure 9). The formation of small amounts of benzene during the high-rate period is further evidence of the similarity with hydrocarbon hydrogenolysis.