# REACTIVITY OF COALS IN HIGH-PRESSURE GASIFICATION WITH HYDROGEN AND STEAM

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The rates of reaction of various coals and chars with hydrogen, steam, and hydrogen-steam mixtures were measured at pressures up to 2500 p.s.i.g. and temperatures up to 1700° F. A rapid-charge, semiflow reactor system was used in which very short coal heatup and product gas residence times were obtained. The primary variables studied were temperature, carbon conversion, total pressure, and feed gas composition. By means of the novel experimental technique employed, it was possible to follow directly the course of the coal-hydrogen-steam reactions during the initial high-rate period. The information obtained is of value in the design of reactors for conversion of coal to methane.

One of the major obstacles to the design of a reactor for direct conversion of coal to gas of high heating value by destructive hydrogenation at high pressure (hydrogasification) has been the lack of information on the rate and course of the reactions during the initial period of rapid conversion of the more reactive coal constituents. Kinetic studies have generally been made with highly devolatilized chars and carbons to avoid the problem of changes in feed composition during heatup. Where the rates of formation of low molecular weight hydrocarbons from reactive coals and low-temperature chars have been measured, experimental conditions did not permit both rapid heatup and short product gas residence times to minimize side and secondary reactions.

The primary variables affecting the rate of hydrogasification are coal reactivity, temperature, pressure, and feed gas composition. The coal reactivity, in turn, varies with the initial coal properties, the extent of conversion, the length of time at reaction conditions, and the severity of the reaction conditions. In previous studies, significant diffusional resistances have not been encountered (*15, 16*), although they might become important at higher temperatures, or with more reactive feedstocks.

#### Previous Work

In work at the institute, the major objective has been the determination of the conditions for the direct production of a gas of high heating value in a practical continuous reactor system. The feasibility of this approach had been indicated in batch reactor tests (*4*), and has recently been confirmed in a countercurrent moving-bed continuous reactor. Earlier results obtained with low-temperature bituminous coal char in a fluid-bed reactor at 1400° to 1500° F. and 500 to 2000 p.s.i.g. (*10*) did not fully attain the desired objective of 30 to 50% char conversion to a gas of 900 B.t.u. per SCF (standard cubic foot at 60° F., 30 inches of mercury, and saturated with water vapor). To obtain high conversions of hydrogen and coal to a high-methane-content gas, long coal and hydrogen residence times and low hydrogen-to-coal feed ratios were used. These conditions make it difficult to interpret the rate data, since the effects of equilibrium hindrance cannot be accurately defined because of lack of thermodynamic activity data for coal and char at various levels of conversion.

The U. S. Bureau of Mines (*7, 8, 9*) employed a reactor tube, $^5/_{16}$ inch in inside diameter, which was heated by passing an electric current through it. Pressures up to 6000 p.s.i.g. and a nominal operating temperature of 800° C. (1472° F.) were investigated. During the 2-minute heatup period, and afterward, hydrogen was passed through the tube at a sufficiently high rate to give gas residence times of only a few seconds. Substantial yields of liquids were obtained during the relatively long heatup period, so that the rates of gasification observed at 800° C. were for the less reactive, residual material. The liquid yields decreased with decreases in hydrogen rate as a result of the increase in residence time. For example, an increase in gas residence time from 6 to 30 seconds resulted in a decrease in liquid hydrocarbons from 26 to 4.5 weight % (moisture-, ash-free basis) of a high-volatile bituminous coal.

In contrast, negligible quantities of liquid hydrocarbons were formed in the fluid-bed tests at the institute (*10*). In these tests, low-temperature bituminous coal char or lignite (−60, +325 sieve size, U. S. Standard) was fed cocurrently with hydrogen to the hot fluidized bed, resulting in rapid heatup. However, product gas residence times were on the order of 1 minute, so the absence of liquid products could have been the result of secondary vapor-phase reactions.

In the work described herein, tests were conducted in which both coal heatup and product gas residence times were of the order of a few seconds. No measurable amounts of liquid products were formed and methane was the major gaseous hydrocarbon produced, only trace quantities of higher paraffins, olefins, and aromatics being formed. Some carbon oxides and nitrogen were also evolved during the initial phases of the reaction.

#### Apparatus

A flow diagram of the reaction system is shown in Figure 1. The −16, +20 sieve size (U. S. Standard) coal charges were fed in single batches (usually 5 or 10 grams) from a hopper mounted on top of the reactor. At zero time, a full-opening, air-operated ball valve, connecting the reactor and feed hopper, was opened and the coal charge was dropped into the reactor. A Syntron vibrator was mounted on the hopper to aid in feeding solids. A pressure-equalization line connecting the top of the hopper and the reactor inlet kept both vessels at the same pressure.

The gas flow in all tests was downward. Feed gases were preheated to the desired operating temperature as they passed through the upper part of the reactor. Exit gases passed through a water-cooled coil, a liquids knockout pot, a high-pressure filter, and a pressure-reducing back-pressure regulator, before sampling, metering, and monitoring.

Gas inlet flow rates were controlled manually and were measured by an orifice meter. Steam was generated at the desired operating pressure in an electrically heated stainless steel coil by feeding water from a weigh tank with a metering pump.

The reactor barrel was constructed of N-155 superalloy and was designed for operation at a maximum pressure of 1500 p.s.i.g. at a maximum temperature of 1700° F. A complete description of the reactor has been given (*11*), along with design details concerning the use of externally heated reactors at high temperatures and pressures. The reactor was 2 inches in inside diameter, 4 inches in outside diameter, and 60 inches in inside length. An Inconel X thermowell, $^3/_8$ inch in outside diameter, was mounted in the center of the bottom closure and extended 58 inches into the reactor. A removable, stainless steel insert, $1^5/_8$ inches in inside diameter and containing a $^1/_2$-inch outside diameter thermowell sleeve, was installed in the reactor to contain the coal charge and provide for complete recovery of the coal charge after each test. The bottom of the insert was filled with sufficient Alundum pellets to position the coal charge in the center of the third heating zone from the top.

Reactor temperatures were maintained by four individually controlled electrical resistance heating elements, each 12 inches long. Reactor pressures were controlled at the desired values by means of a back-pressure regulator and were continuously recorded along with orifice pressures.

The double-ended reactor contained an Autoclave Engineers self-sealing (modified Bridgman) closure at each end. The closures were rated for 1400° F. operation at 1500 p.s.i.g. This high-temperature service was facilitated by use of either 16-25-6 or Inconel alloy seal rings. A boundary lubricant of molybdenum disulfide, applied in aerosol form to produce a thin boundary layer coating, was used on all closure threads and on the seal rings.

#### Procedure

Feed gas mixtures, prepared by mixing during compression, were stored at pressures up to 3000 p.s.i.g. Commercially available grades of electrolytic hydrogen (99.8% pure), nitrogen (99.6% pure), helium (99.99% pure), and technical grade methane (95.0% pure) were used. All feed gases, except steam, contained approximately 2 mole % helium tracer for measurement of exit gas flow rate.

The feed gas orifice was calibrated before each run with a wet-test meter and the exit gases were also metered with this meter as a check on the helium tracer method for measurement of exit gas flow rate. In tests with pure steam feed, helium sweep gas was used to purge, from the exit gas system, the small volumes of permanent gases formed. The exit gas specific gravity was monitored continuously with a recording gravitometer as an aid in selecting times for exit gas sampling. A sampling manifold was installed in the exit gas line, upstream of the metering and monitoring system, to allow rapid sampling at small time intervals. Gas analyses were performed by mass spectrometer. The combined nitrogen and carbon monoxide content of the exit gas, determined by mass spectrometer, less nitrogen introduced in the feed gas was assumed to be carbon monoxide, except in selected tests where carbon monoxide was determined by infrared spectrophotometer.

The four coals investigated were a medium volatility anthracite, a North Dakota lignite, a Pittsburgh Seam bituminous coal, and a low-temperature bituminous coal char. The char was prepared from bituminous coal from the Montour No. 10 mine by a fluidized-bed pretreatment process of the Consolidation Coal Co. Analyses of these feeds are shown in Table I.

Most runs were conducted for a total time of 15 minutes

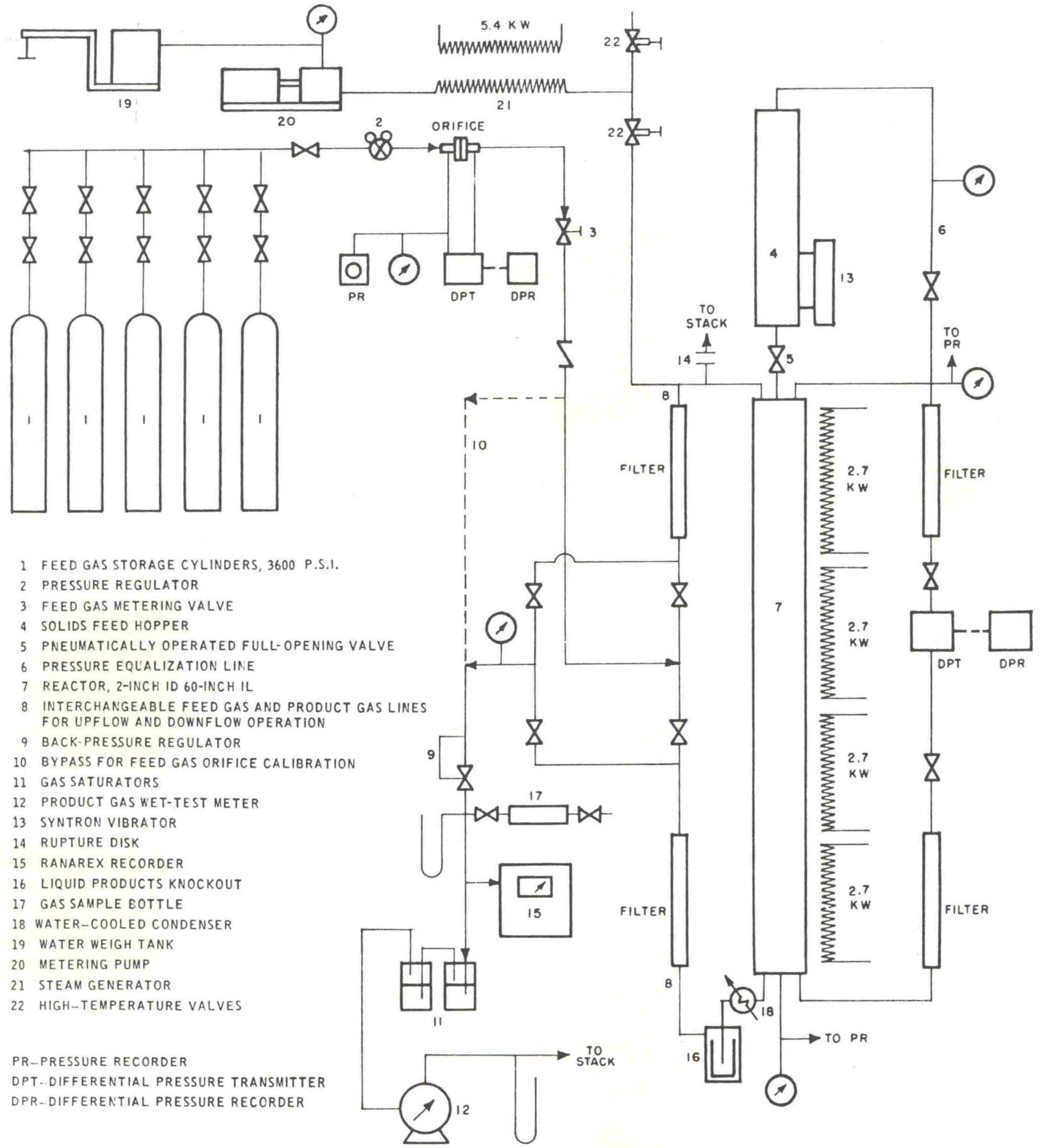


**Figure 1. Semiflow reactor system for study of rates of hydrogasification of solid fossil fuels at temperatures to 1700° F. and pressures to 3000 p.s.i.g.**

or less. The reactor was first heated up to the desired operating temperature. Then gas flow, at the desired rate, was started through the reactor. The heat input to the reactor was then adjusted so that all temperatures within the reactor remained constant. When the system was stabilized completely, the run was initiated by opening the valve between the feed hopper and the reactor.

At typical conditions of 1500 p.s.i.g., 1700° F., and a hydrogen flow rate of 100 SCF per hour, the first hydrogasification products appeared in the exit gas at the sampling manifold in approximately 10 seconds. During the initial period of high conversion rate, samples were taken at time intervals as short as 5 seconds to delineate the exact course of the reaction. Temperatures at the center of the coal charge, at a point 6 inches above the charge, and at the bottom of the insert were recorded continuously by means of a high-speed temperature recorder, which recorded each temperature at approximately 3-second intervals.

When the reaction rate had reached a value too small to be measured accurately at the high gas rates employed (usually after about 600 seconds), the run was stopped. The electric heaters were turned off and the reactant gases were purged from the reactor with nitrogen. The reactor was kept filled with nitrogen until the temperature was low enough to allow retrieval of the coal residue.

### Results

**Exploratory Tests.** Before the test program was initiated, several exploratory tests were conducted at the base condi-

**Table I. Coal Analyses**

| | | | |
|---|---|---|---|
| Coal | Bituminous coal char | | Anthracite |
| Type | Low temperature | | Medium volatility |
| Source | Consolidation Coal Co. (Montour No. 10 mine) | | Anthracite Experiment Station, U. S. Bur. Mines |
| Particle size, U. S. standard sieve | −16, +20 | −40, +50 | −16, +20 |
| Ultimate analysis, wt. % (dry basis) | | | |
| Carbon | 78.3 | 79.5 | 83.3 |
| Hydrogen | 3.46 | 3.46 | 2.47 |
| Nitrogen and oxygen (by difference) | 10.03 | 10.12 | 2.90 |
| Sulfur | 1.01 | 0.91 | 0.88 |
| Ash | 7.20 | 6.01 | 10.45 |
| Total | 100.00 | 100.00 | 100.00 |
| Proximate analysis, wt. % | | | |
| Moisture | 1.7 | 2.3 | 0.7 |
| Volatile matter | 17.3 | 17.9 | 5.7 |
| Fixed carbon | 73.9 | 73.9 | 83.2 |
| Ash | 7.1 | 5.9 | 10.4 |
| Total | 100.0 | 100.0 | 100.0 |

| | | |
|---|---|---|
| Coal | Bituminous coal | Lignite |
| Type | Pittsburgh Seam | North Dakota |
| Source | Consolidation Coal Co. (Montour No. 4 mine) | Truax-Traer Co. (Velva mine) |
| Particle size, U. S. standard sieve | −16, +20 | −16, +20 |
| Ultimate analysis, wt. % (dry basis) | | |
| Carbon | 75.9 | 65.4 |
| Hydrogen | 5.01 | 4.49 |
| Nitrogen and oxygen (by difference) | 8.99 | 23.21 |
| Sulfur | 1.54 | 0.45 |
| Ash | 8.56 | 6.45 |
| Total | 100.00 | 100.00 |
| Proximate analysis, wt. % | | |
| Moisture | 1.1 | 6.8 |
| Volatile matter | 33.5 | 41.2 |
| Fixed carbon | 56.9 | 46.0 |
| Ash | 8.5 | 6.0 |
| | 100.0 | 100.0 |

tions of 1000 or 1500 p.s.i.g. and 1700° F., with a hydrogen flow rate of 100 SCF per hour. It was necessary to select sample weights which gave small temperature changes and low concentrations of methane in the exit gas, without impairing analytical accuracy.

With 50- and 20-gram samples of low-temperature bituminous coal char (−8, +16 sieve size), the maximum exit gas methane content was too high and the temperature changes during the run were too great to allow the assumption of differential reaction conditions. In tests with 10- and 5-gram samples of −16, +20 sieve size low-temperature bituminous coal char, the exit gas methane contents approached the desired levels, and reaction rates (expressed as pounds of carbon converted to gaseous hydrocarbons per pound of carbon remaining in bed per hour) were similar. With bituminous coal char, temperature changes were not completely eliminated even with the 3-gram sample (Figure 2). However, further reductions in sample weight would have reduced methane concentrations in the exit gas to values too low for accurate measurement of reaction rates.

With low-temperature bituminous coal char at nominal run temperatures of 1700° F., two periods of high rate were observed (Figure 2). The second, occurring after approximately 30% carbon gasification, was a result of increases in the temperature of the char sample due to the inability of the char sample to dissipate the high heat of reaction to the surroundings. This was substantiated by conducting a further test with a 3-gram sample weight. Here rate increased only slightly at carbon conversions above 30%. In tests with unpretreated coals, and with bituminous coal char at 1300° and 1500° F., no second period of high rate was observed.

It was also necessary to select a coal particle size for the remainder of the test program. An effect of particle size on the rate of reaction could indicate the presence of significant diffusional resistances. Tests conducted with 10-gram samples of −16, +20 and −40, +50 sieve size material (Figure 3) indicate negligible effects of particle size on the reaction rate. The displacement of the rate curve for the −40, +50 sieve size material was probably due to the slower feeding rate of the more finely divided material, or to an initial holdup in the coal feed hopper. On the basis of duplicate tests to check reproducibility, it was believed that these small differences were within the limits of experimental and analytical accuracy.

From the results of these exploratory tests, the following base conditions were selected for the remainder of the tests, unless otherwise noted:

| | |
|---|---|
| Temperature | 1700° F. |
| Pressure | 1500 p.s.i.g. |
| Sample weight | 5 and 10 grams |
| Coal particle size | −16, +20 sieve size |
| Feed gas flow rate | 100 SCF per hour |

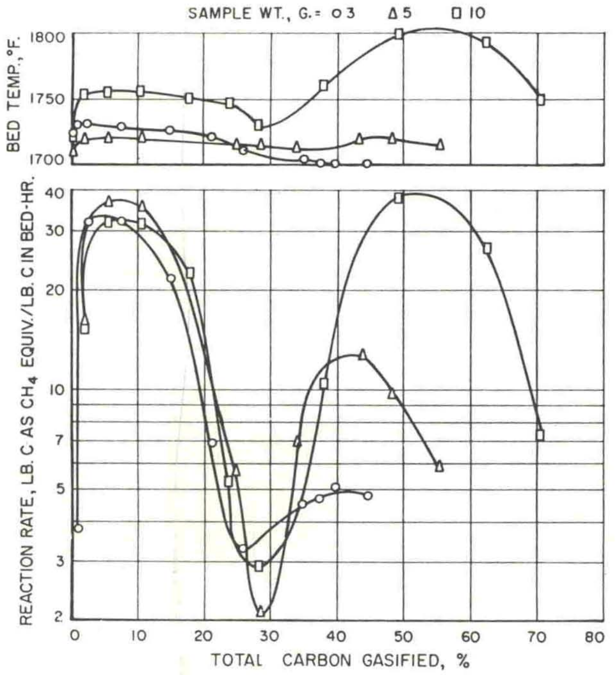


**Figure 2. Apparent effect of sample weight on rate of char hydrogasification at 1700° F. and 1500 p.s.i.g.**

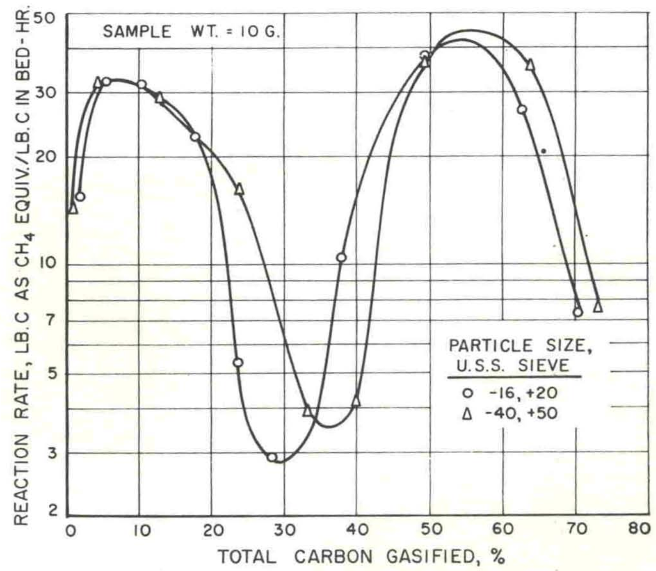


**Figure 3. Effect of char particle size on rate of hydrogasification at 1700° F. and 1500 p.s.i.g.**

Typical results for the four feeds used in this study are given in Table II.

**Effect of Variables.** The effects of temperature and extent of conversion on the rate of reaction of low-temperature bituminous coal char and hydrogen were measured in a series of tests conducted at 1500 p.s.i.g. and at 1300°, 1500°, and 1700° F. (Figure 4). During the initial phases, the reaction rate was not significantly affected by temperature in the range studied. Only after approximately 20% carbon gasification did the effects of temperature become apparent. The rate constants for the residual char would be expected to follow the pseudo-first-order relationship:

$$r = kp$$

where $r$ = rate of reaction in pounds of carbon in gaseous hydrocarbons per hour per pound of carbon in bed
$k$ = rate constant
$p$ = hydrogen partial pressure in atmospheres

This expression has been shown by Blackwood (*2*) to be applicable in the temperature range of 650° to 870° C. (1202° to 1598° F.) for the reaction of coconut char with excess hydrogen at pressures up to 40 atm. Birch, Hall, and Urie (*1*) have also applied it successfully to correlate data on the hydrogenation of the residual (aromatic) carbon portion of Australian brown coal with excess hydrogen in a fluid-bed reactor for the temperature range from 750° to 950° C. (1382° to 1742° F.). Zielke and Gorin (*15*) showed that, from 1500° to 1700° F. and at 1 to 30 atm. with devolatilized Disco bituminous coal char, the apparent reaction order is 2 at low pressures and approaches 1 at high pressures.

In Table III, pseudo-first-order hydrogasification rate constants for these chars are compared with the values for low-temperature bituminous coal char after 25 to 30% carbon conversion (Figure 4). Agreement is good, except for the acid-

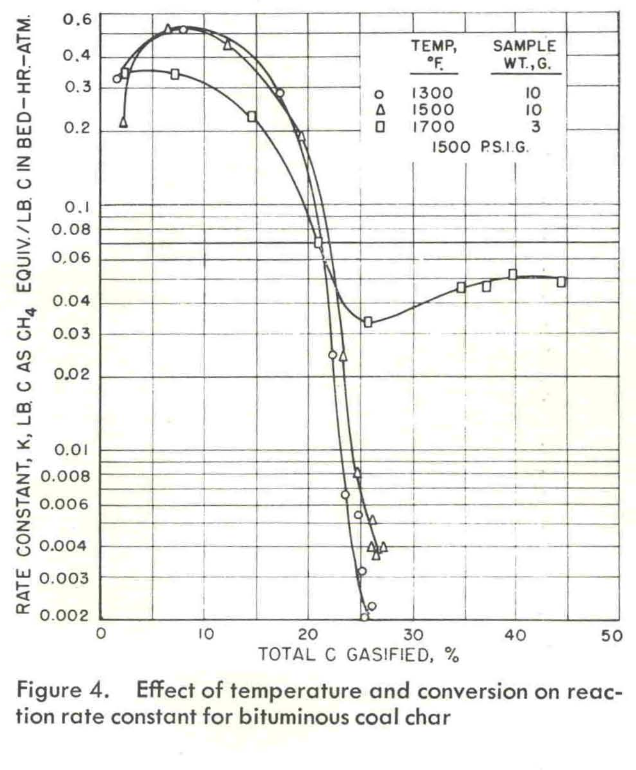


**Figure 4. Effect of temperature and conversion on reaction rate constant for bituminous coal char**

extracted, high-temperature coconut char. The rates for this specially prepared low-reactivity material are up to one order of magnitude lower, as would be expected.

All of the above results were obtained in differential-bed reactors of various types, except for the data for Australian brown coal, which were obtained in an integral fluid-bed reactor. However, methane concentrations in the product gases were low enough to minimize equilibrium hindrance

## Table II. Typical Test Results at 1700° F. and 1500 P.S.I.G.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Feed | 5 grams of bituminous coal, −16, +20 U. S. S. sieve size | | | | | | | | | | |
| Time of sampling, sec. | 10 | 20 | 25 | 30 | 35 | 40 | 60 | 80 | 120 | 240 | 480 |
| Temperature, ° F. | 1740 | 1740 | 1742 | 1742 | 1740 | 1735 | 1734 | 1732 | 1730 | 1732 | 1725 |
| Feed hydrogen rate, SCF/hr. | 104.4 | 104.3 | 104.3 | 104.3 | 104.3 | 104.3 | 104.3 | 104.3 | 104.2 | 104.1 | 103.6 |
| Exit gas rate, SCF/hr. | 103.7 | 102.2 | 101.5 | 101.5 | 100.8 | 100.8 | 101.5 | 100.1 | 101.4 | 102.7 | 100.8 |
| Exit gas composition, mole % | | | | | | | | | | | |
| $N_2$ + CO | 0.05 | 0.05 | 0.51 | 0.89 | 0.61 | 0.49 | 0.12 | 0.04 | 0.03 | 0.04 | 0.01 |
| $CO_2$ | ... | ... | 0.03 | 0.02 | 0.01 | 0.01 | ... | ... | ... | ... | ... |
| $H_2$ | 99.94 | 99.94 | 94.28 | 87.48 | 89.36 | 90.14 | 96.25 | 98.22 | 99.19 | 98.96 | 99.58 |
| $CH_4$ | 0.01 | 0.01 | 5.13 | 11.49 | 9.88 | 9.28 | 3.55 | 1.72 | 0.77 | 0.99 | 0.41 |
| $C_2H_6$ | ... | ... | 0.04 | 0.02 | 0.02 | 0.01 | ... | ... | ... | ... | ... |
| Benzene | ... | ... | 0.01 | 0.10 | 0.12 | 0.07 | 0.08 | 0.02 | 0.01 | 0.01 | ... |
| Total | 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 hydrocarbon carbon, lb./lb. carbon fed-hr. | ... | ... | 20.2 | 46.4 | 40.4 | 36.9 | 15.4 | 6.9 | 3.2 | 4.1 | 1.6 |
| Total conversion of carbon in feed, % | ... | ... | 0.4 | 7.0 | 13.5 | 17.5 | 32.6 | 38.4 | 43.4 | 56.6 | 77.0 |
| Total carbon recovery, % | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 87.9 |
| Feed | 5 grams of lignite, −16, +20 U. S. S. sieve size | | | | | | | | | | |
| Time of sampling, sec. | 10 | 20 | 25 | 30 | 40 | 50 | 80 | 120 | 240 | 480 | 600 |
| Temperature, ° F. | 1712 | 1722 | 1723 | 1725 | 1728 | 1726 | 1721 | 1717 | 1714 | 1713 | 1714 |
| Feed hydrogen rate, SCF/hr. | 98.6 | 98.9 | 99.0 | 98.7 | 99.4 | 102.1 | 98.1 | 98.6 | 98.9 | 97.6 | 95.9 |
| Exit gas rate, SCF/hr. | 98.7 | 98.4 | 100.1 | 97.6 | 95.2 | 98.3 | 97.1 | 97.0 | 97.8 | 96.6 | 94.4 |
| Exit gas composition, mole % | | | | | | | | | | | |
| $N_2$ + CO | 0.06 | 0.04 | 0.56 | 1.82 | 1.91 | 1.02 | 0.08 | 0.05 | 0.04 | 0.06 | 0.04 |
| $CO_2$ | ... | ... | 0.01 | 0.05 | 0.05 | 0.03 | ... | ... | ... | ... | ... |
| $H_2$ | 99.93 | 99.94 | 96.99 | 89.68 | 88.84 | 93.57 | 98.77 | 99.38 | 99.58 | 99.69 | 99.75 |
| $CH_4$ | 0.01 | 0.02 | 2.43 | 8.38 | 9.15 | 5.37 | 1.15 | 0.57 | 0.38 | 0.25 | 0.21 |
| $C_2H_6$ | ... | ... | ... | 0.01 | ... | ... | ... | ... | ... | ... | ... |
| Benzene | ... | ... | 0.01 | 0.06 | 0.05 | 0.01 | ... | ... | ... | ... | ... |
| Total | 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 hydrocarbon carbon, lb./lb. carbon fed-hr. | ... | 0.1 | 11.6 | 39.7 | 41.7 | 24.8 | 5.2 | 2.6 | 1.7 | 1.1 | 0.9 |
| Total conversion of carbon in feed, % | ... | ... | 0.8 | 5.9 | 20.0 | 32.2 | 42.1 | 46.0 | 53.3 | 62.9 | 66.3 |
| Total carbon recovery, % | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 82.3 |
| Feed | 5 grams of medium volatility anthracite, −16, +20 U. S. S. sieve size | | | | | | | | | | |
| Time of sampling, sec. | 10 | 20 | 25 | 30 | 35 | 40 | 60 | 120 | 240 | 360 | 600 |
| Temperature, ° F. | 1696 | 1694 | 1693 | 1695 | 1698 | 1702 | 1702 | 1702 | 1700 | 1700 | 1698 |
| Feed hydrogen rate, SCF/hr. | 97.4 | 97.3 | 97.3 | 97.3 | 97.3 | 97.3 | 97.3 | 97.2 | 97.0 | 96.9 | 97.4 |
| Exit gas rate, SCF/hr. | 96.9 | 95.8 | 95.3 | 95.7 | 93.6 | 93.1 | 94.3 | 95.4 | 94.5 | 95.4 | 96.1 |
| Exit gas composition, mole % | | | | | | | | | | | |
| $N_2$ + CO | 0.04 | 0.10 | 0.29 | 0.24 | 0.20 | 0.17 | 0.07 | 0.04 | 0.03 | 0.03 | 0.03 |
| $CO_2$ | 0.01 | 0.01 | 0.03 | 0.01 | ... | ... | ... | ... | ... | ... | ... |
| $H_2$ | 99.95 | 99.67 | 96.65 | 94.27 | 93.97 | 94.58 | 97.51 | 98.90 | 99.11 | 99.15 | 99.52 |
| $CH_4$ | ... | 0.22 | 3.01 | 5.47 | 5.83 | 5.25 | 2.41 | 1.04 | 0.86 | 0.82 | 0.45 |
| $C_2H_6$ | ... | ... | 0.01 | ... | ... | ... | ... | ... | ... | ... | ... |
| $C_5H_{12}$ | ... | ... | ... | ... | ... | ... | ... | 0.01 | ... | ... | ... |
| Mono-olefins | ... | ... | ... | ... | ... | ... | 0.01 | 0.01 | ... | ... | ... |
| Benzene | ... | ... | 0.01 | 0.01 | ... | ... | ... | ... | ... | ... | ... |
| Total | 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 hydrocarbon carbon, lb./lb. carbon fed-hr. | ... | 0.7 | 10.1 | 18.1 | 18.7 | 16.7 | 7.9 | 3.7 | 2.8 | 2.7 | 1.5 |
| Total conversion of carbon in feed, % | ... | 0.1 | 0.7 | 2.9 | 5.6 | 8.1 | 14.6 | 24.0 | 34.8 | 43.9 | 57.8 |
| Total carbon recovery, % | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 94.8 |
| Feed | 5 grams of low-temperature bituminous coal char, −16, +20 U. S. S. sieve size | | | | | | | | | | |
| Time of sampling, sec. | 10 | 20 | 25 | 30 | 60 | 120 | 240 | 290 | 320 | 400 | |
| Temperature, ° F. | 1708 | 1718 | 1720 | 1720 | 1717 | 1714 | 1712 | 1720 | 1720 | 1715 | |
| Feed hydrogen rate, SCF/hr. | 98.2 | 98.2 | 98.2 | 98.2 | 98.2 | 98.2 | 98.2 | 98.2 | 98.2 | 98.2 | |
| Exit gas rate, SCF/hr. | 96.4 | 94.9 | 95.3 | 93.9 | 95.7 | 96.0 | 96.7 | 94.9 | 97.8 | 96.0 | |
| Exit gas composition, mole % | | | | | | | | | | | |
| $N_2$ + CO | 0.08 | ... | 0.98 | 0.95 | 0.08 | 0.05 | 0.07 | 0.04 | 0.06 | 0.05 | |
| $CO_2$ | ... | 0.03 | 0.01 | ... | ... | ... | ... | ... | ... | ... | |
| $H_2$ | 99.90 | 95.63 | 89.22 | 90.08 | 98.72 | 99.52 | 98.70 | 97.99 | 98.56 | 99.26 | |
| $CH_4$ | 0.01 | 4.30 | 9.77 | 8.95 | 1.20 | 0.43 | 1.22 | 1.96 | 1.38 | 0.68 | |
| $C_2H_6$ | ... | 0.01 | 0.01 | ... | ... | ... | ... | ... | ... | ... | |
| $n$-$C_4H_{10}$ | ... | 0.01 | ... | ... | ... | ... | ... | ... | ... | ... | |
| $C_6H_{10}$ | 0.01 | 0.01 | ... | ... | ... | ... | ... | ... | ... | 0.01 | |
| $C_7H_{14}$ | ... | ... | ... | ... | ... | ... | 0.01 | 0.01 | ... | ... | |
| Benzene | ... | 0.01 | 0.01 | 0.02 | ... | ... | ... | ... | ... | ... | |
| Total | 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 hydrocarbon carbon, lb./lb. carbon fed-hr. | 0.2 | 15.5 | 34.5 | 31.3 | 4.2 | 1.5 | 4.6 | 7.1 | 5.0 | 2.6 | |
| Total conversion of carbon in feed, % | ... | 1.9 | 5.4 | 10.5 | 24.8 | 28.5 | 33.8 | 43.2 | 48.2 | 55.5 | |
| Total carbon recovery, % | ... | ... | ... | ... | ... | ... | ... | ... | ... | 86.4 | |

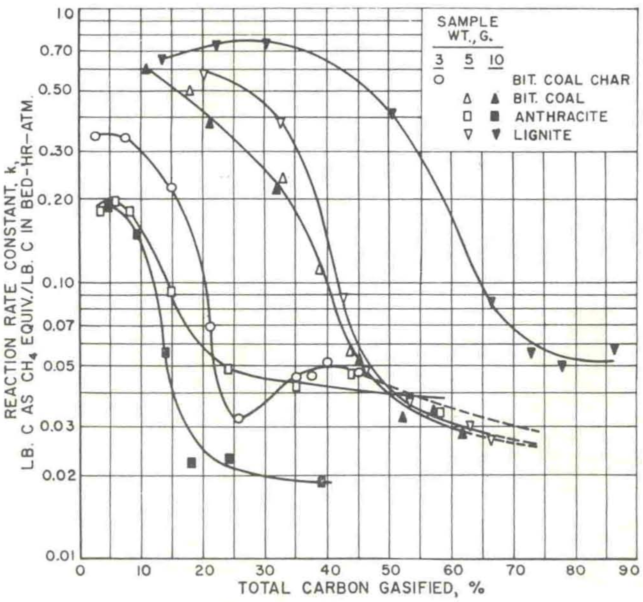


Figure 5. Reaction rate constants for various feeds at 1700° F. and 1500 p.s.i.g.

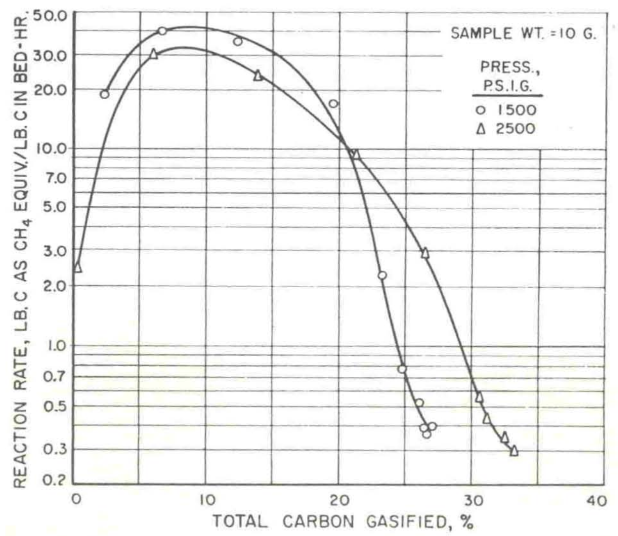


Figure 6. Effect of pressure on rate of char hydrogasification at 1500° F.

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

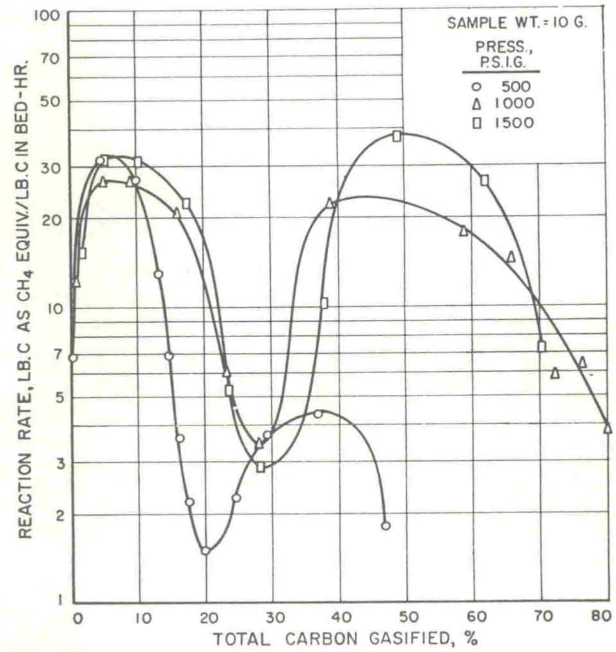


Figure 7. Effect of pressure on rate of char hydrogasification at 1700° F.

**Table III. Rate Constants of Various Investigators**

| Investigator | Blackwood (2, 3)[a] | Birch (7)[b] | Zielke and[b] Gorin (15) | This study[b] |
|---|---|---|---|---|
| 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.* | *k, Rate Constant* | | | |
| 1300 | $1 \times 10^{-4}$ | $6 \times 10^{-4}$ | . . . | $2 \times 10^{-3}$ |
| 1500 | $9 \times 10^{-4}$ | $4 \times 10^{-3}$ | $6\text{-}2 \times 10^{-3}$ | $4 \times 10^{-3}$ |
| 1700 | $6 \times 10^{-3}$ | $2 \times 10^{-2}$ | $1 \times 10^{-2}$ | $3 \times 10^{-2}$ |

[a] *k = lb. C as $CH_4$ equiv./lb. C fed-hr.-atm. $H_2$ partial pressure.* [b] *k = lb. C as $CH_4$ equiv./lb. C fed-hr.-atm. $H_2$ partial pressure.*

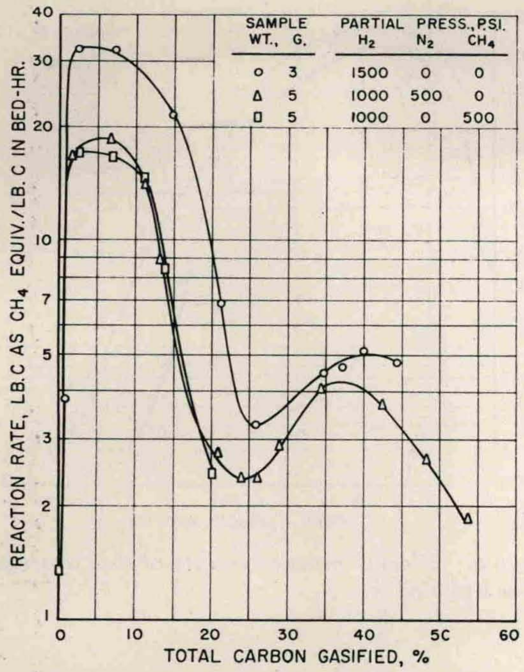


**Figure 8. Effect of hydrogen and methane partial pressure on rate of char hydrogasification at 1700° F. and a total pressure of 1500 p.s.i.g.**

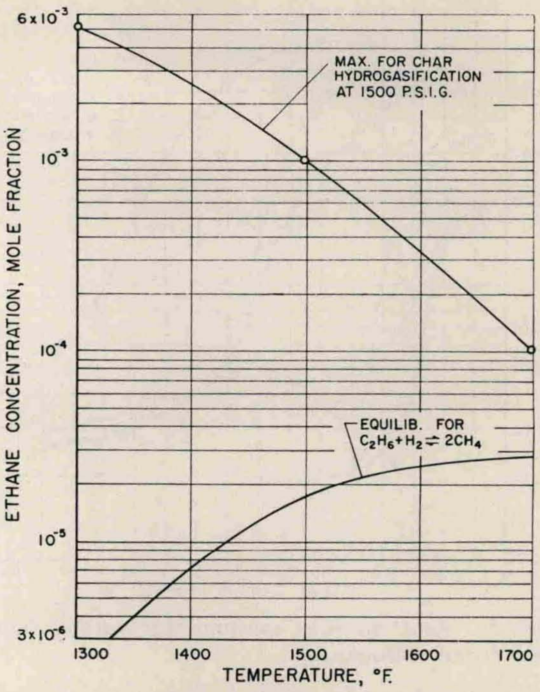


**Figure 9. Approach of ethane concentrations to equilibrium values as a function of temperature**

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 (*1*) 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 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 Hiteshue, 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 $C_2$- to $C_4$-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.

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

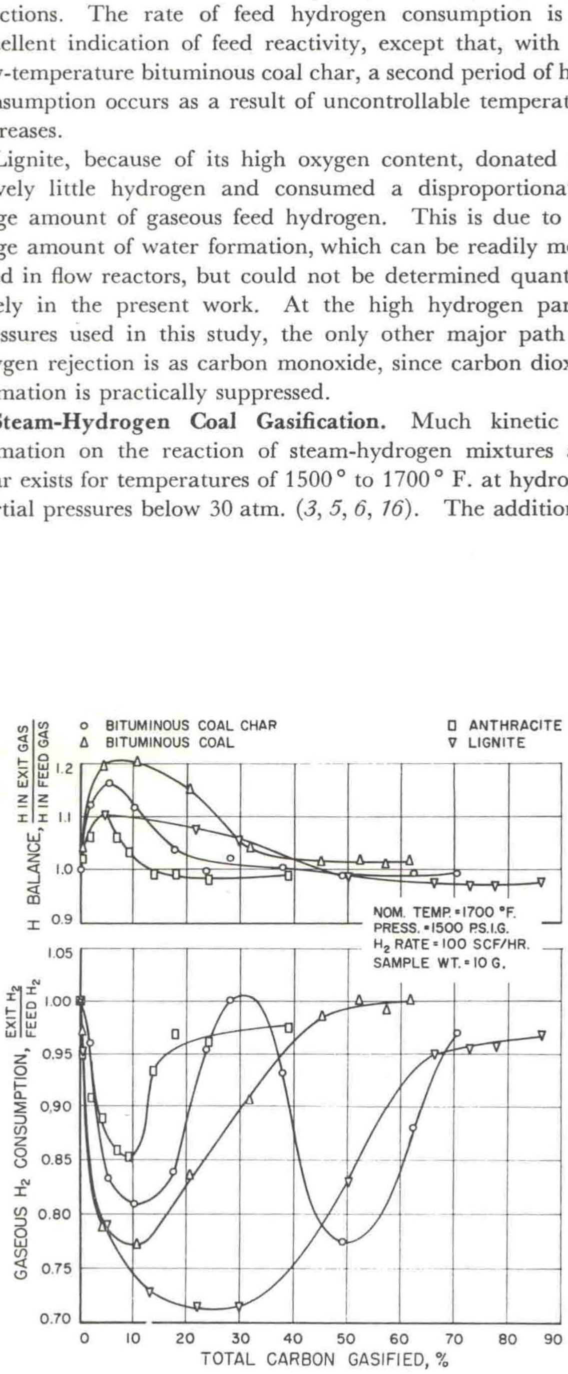


Figure 10. Gaseous hydrogen balance as a function of conversion of various feeds

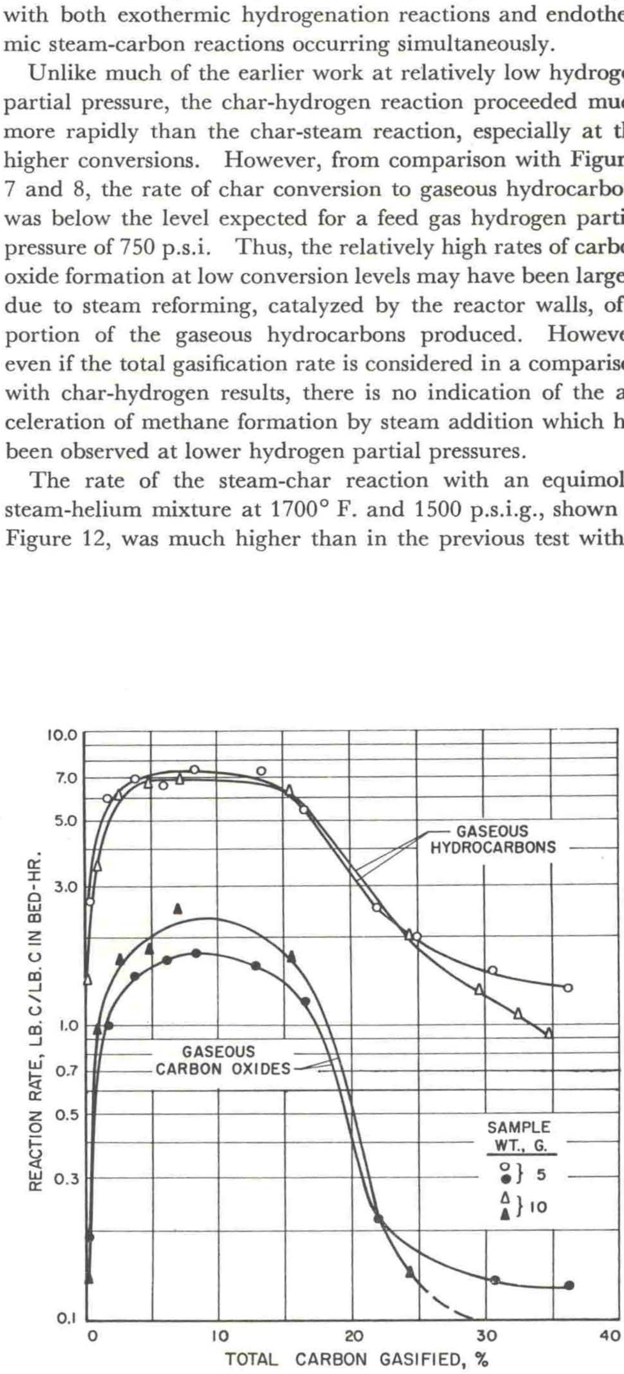


Figure 11. Effect of conversion on rate of gasification of coal char at 1700° F. and 1500 p.s.i.g. with an equimolar steam-hydrogen mixture

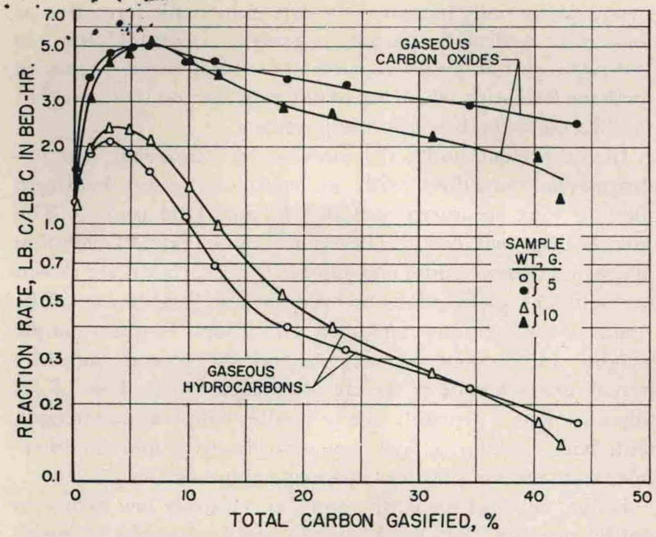


**Figure 12. Effect of conversion on rate of gasification of coal char at 1700° F. and 1500 p.s.i.g. with an equimolar steam-helium mixture**

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

This work was conducted under the sponsorship of the Research Department of the Consolidated Natural Gas System (now Con-Gas Service Corp.) under the guidance of F. E. Vandaveer and H. E. Benson. Thanks are due to E. B. Shultz, Jr., who designed most of the apparatus and helped develop the experimental procedure. A. E. Richter and R. F. Johnson assisted in data collection and D. M. Mason and J. E. Neuzil supervised the analytical work.


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### Correction

## HOLDUP STUDIES IN A PULSED SIEVE-PLATE SOLVENT EXTRACTION COLUMN

In this article by G. A. Sehmel 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:

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