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