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REACTION OF COAL WITH STEAM-HYDROGEN MIXTURES AT HIGH TEMPERATURES AND PRESSURES

H. L. FELDKIRCHNER AND JACK HUEBLER

Institute of Gas Technology, Chicago 16, Ill.

The rate of hydrogasification of low-temperature bituminous coal char with steam, hydrogen, and steam-hydrogen mixtures was measured at conditions not previously studied in a novel, rapid-charge, semiflow reactor system. Rates were measured at 1000 p.s.i.g. and at temperatures from 1700° to 2100° F. under conditions of very rapid coal heatup and very short exit gas residence times. The primary variables studied were temperature, degree of carbon gasification, and feed gas steam-hydrogen ratio. Data were obtained for use in designing reactors for high-pressure, high-temperature steam-hydrogen gasification of low-temperature bituminous coal char.

THREE basic problems have been encountered in the development of processes for the conversion of coals to pipeline gas by destructive hydrogenation at high pressures:

At 1300° to 1500° F., the temperature range which permits the direct production of a gas of high heating value, the rate of coal conversion is relatively low.

An external source of hydrogen is required.

The high heat release of the hydrogenation reactions cannot be utilized to the fullest advantage; this creates a serious problem in the design of a reactor in which adequate temperature control and optimum process heat economy can be achieved.

The first limitation has been partially overcome by using countercurrent reactor operation with a steep temperature gradient. The use of this operating scheme has been found to be effective for producing a gas of high heating value in a single step by destructive hydrogenation at 2000 p.s.i.g. and 1300° to 1700° F. (17). Several combined factors cause this countercurrent scheme to be preferred. First, at high levels of gasification, the hydrogasification rates of coals increase rapidly with increases in temperature; but at low levels of gasification, in the temperature range of 1300° to 1700° F., these rates are nearly independent of temperature (1, 2, 6, 15). Second, at all gasification levels, gasification rates are roughly proportional to the hydrogen partial pressure. Third, the equilibrium methane content of the product gas decreases with increases in temperature. For example, at 1700° F. and 1500 p.s.i.a., the maximum product gas methane concentration that can be obtained in the reaction of carbon with hydrogen is 47 mole %, while at 2000° F., this value is only 28 mole %.

In countercurrent operation, as now contemplated, a large excess of hydrogen comes in contact with the relatively unreactive residue at the high-temperature end of the reactor. At the low-temperature end of the reactor, highly reactive feed char comes in contact with the product gas. Methane concentrations in excess of those predicted for the carbon-hydrogen reaction can be produced when the gas is in contact with slightly gasified coal char (14). Thus, the contacting of fresh char and product gas at low temperatures, and spent char and feed hydrogen at high temperatures minimizes equilibrium limitations. Since the rate of gasification is roughly proportional to the difference between the hydrogen partial pressure in the gas and in equilibrium with the char, counter-

current operation also provides a maximum average hydrogen partial pressure and thus a maximum average gasification rate.

Other variations of this basic countercurrent operating scheme might allow further increases in gas heating value or reductions in reactor size. For example, residence time of the residual char, and thus hydrogasifier size, might be reduced by using an even higher temperature in the high-temperature end of the reactor.

Increase of the reaction temperature also offers an opportunity for reducing external hydrogen requirements. At 1700° F. and above, it should be possible to supply part of the hydrogen requirements by steam decomposition reactions taking place simultaneously with the hydrogasification reactions. In addition to providing a source of "free" hydrogen, the endothermic steam-carbon decomposition reaction should provide a means for temperature control by offsetting the exothermic heats of the coal hydrogasification reactions.

On the basis of the above considerations, it appeared that pilot plant studies of the production of methane from solid fossil fuels should not be limited to the low-temperature range previously investigated, but should be extended into the temperature range above 1700° F., where very rapid gasification rates can be achieved. However, before prototype pilot plant equipment could be designed to investigate such high-temperature processes, it was necessary to obtain basic data on the gasification characteristics of the various solid fossil fuels under these extreme conditions. No data of this type were available because of the great difficulty of constructing high-temperature apparatus and devising experimental techniques capable of achieving the following three objectives:

Attainment of temperatures in excess of 2000° F., at pressures up to 3000 p.s.i.g.

Temperature control in spite of the considerable exothermicity or endothermicity of the reactions of interest.

Control and reliable measurement of reaction time.

In the course of the studies conducted by the Institute of Gas Technology in its Basic Research Program and other studies, techniques had been developed which appeared to give an acceptable solution to these problems on a laboratory scale (5, 6). These techniques minimized uncertainties resulting from the gasification of a batch fuel charge during heatup, as well as the uncertain solids residence times encountered in

entrained-solids systems where the actual rate of flow of the solid fuel through the heated zone cannot be measured directly.

A study of available equipment indicated that the above-listed techniques could be applied to a reactor capable of operating at the extreme conditions desired. A suitable reactor was designed and built, consisting of an external pressure vessel operating at low temperature, an electrical resistance heating system insulated from this outer shell, and a thin-walled, high-temperature, alloy steel reactor tube with means provided for balanced-pressure operation and fitted with a bellows to compensate for thermal expansion of the reactor tube.

Experimental

Apparatus. Figure 1 is a flow diagram of the system showing all major pieces of equipment and part of the control instrumentation.

Coal char was fed in single batches from a feed hopper, which was connected to the reactor by an air-operated, quick-opening ball valve. A pressure equilization line was used to keep the hopper pressure equal to the reactor pressure. A second hopper contained a rotating drum-type feeder for continuous coal char feeding.

Hydrogen was fed from a high-pressure gas storage system and was metered by an orifice meter. Hydrogen flow rates were controlled manually. Orifice differential pressures were sensed and converted to a 3- to 15-p.s.i.g. air signal by a differential-pressure transmitter. This air signal was then recorded, along with the orifice and reactor pressures, by conventional pneumatic recorders.

Controlled rates of steam feed were obtained by pumping water from a weigh tank through a steam generator by a positive-displacement, adjustable-stroke, metering pump. The steam generator consisted of a coil of stainless steel tubing, $\frac{3}{8}$ inch in outside diameter and $\frac{1}{8}$ inch in inside diameter, contained in an electric furnace. The temperature of the steam from the steam generator was controlled manually. Superheated steam and hydrogen were preheated to reaction temperature in passing through the upper heating zone of the reactor.

Exit gases from the bottom of the reactor were cooled by being passed through a water-cooled stainless steel coil. Condensed steam was collected in a high-pressure sight glass. To minimize loss of carbon dioxide or other dissolved gases in the condensed steam, the water was drained from the high-pressure sight glass into a low-pressure flash chamber which was vented into the low-pressure exit gas system, before water was drained from the unit.

Exit gases were metered continuously by a wet-test meter. A small portion of this stream was passed through a recording densitometer (to aid in selection of sampling times) and metered with a smaller wet-test meter. To avoid distortion of the reaction rate-time relationship because of backmixing and gas holdup, which would occur if gas samples were taken after gas metering, the gas-sampling manifold was installed in the exit gas line immediately after the pressure-reducing, back-pressure regulator, which was used to control the reactor pressure.

The reactor, shown in detail in Figure 2, was internally insulated and contained a stainless steel reactor tube which consisted of a length of $1\frac{1}{4}$ -inch I.P.S., Schedule 40, Type 310 stainless steel pipe attached to two adapter fittings by pipe threads. This tube was heated electrically by a $2\frac{3}{8}$ -inch inside-diameter heater, containing three 8-inch-long zones. The heater was fabricated from a single length of heating wire which was tapped for three-zone operation. A balanced pressure was maintained on the reactor tube by means of an on-off type pressure-balancing system. The design and operation of this reactor have been fully described (1). Design followed closely that of reactors described by Wasilewski (13) and Hodge and others (9).

Satisfactory operation was achieved at pressures up to 1000 p.s.i.g. and reaction zone temperatures up to 2100° F. Higher

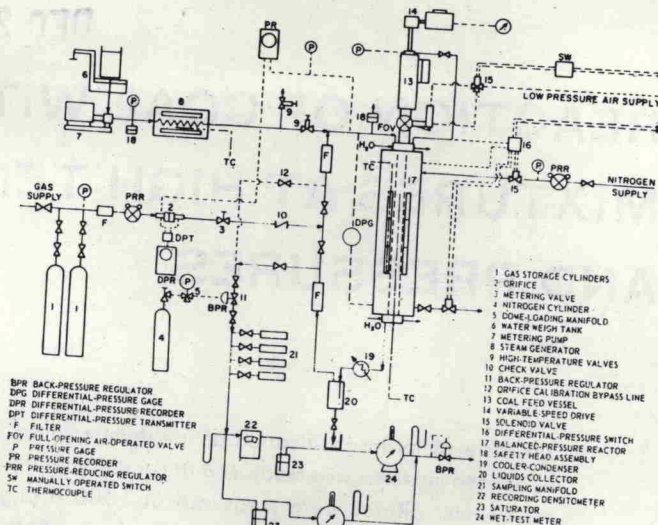


Figure 1. Semiflow reactor system

temperature operation should be possible by use of higher temperature heaters, such as silicon carbide and refractory metal reactor tubes. Insulation having a higher operating temperature limit than that of the insulation used here would also be required in the vicinity of the electric heater.

An insert, fabricated from a length of 1-inch I.P.S., Schedule 40, Type 310 stainless steel pipe, was installed within the reactor tube to provide for containment and complete recovery of the coal char charge. An integral thermowell, fabricated from $\frac{1}{8}$ -inch I.P.S., Schedule 40, Type 310 stainless steel pipe, was located axially within the insert and contained three Chromel-Alumel, magnesium oxide-insulated, 0.062-inch outside-diameter, Inconel-sheathed thermocouples. The temperatures sensed by these thermocouples were recorded at approximately 1-second intervals by a high-speed potentiometric-type temperature recorder.

Reactor temperatures were controlled by three on-off, indicating temperature controllers and three thermocouples located within the centers of the heating elements. Satisfactory operation was obtained with this type of thermocouple mounted in the electric heaters as well as in the insert at reactor temperatures up to 2100° F. Electric heater temperatures were kept below 2300° F. to ensure as long a heater life as possible.

Table I. Analysis of Coal Char

Sample designation	5851
Type	Low-temperature, bituminous coal char
Source	Consolidation Coal Co.
Particle size, U.S.S. sieve size	-16. +20
Ultimate analysis, wt. % (dry basis)	
Carbon	76.6
Hydrogen	3.25
Nitrogen	1.76
Oxygen	10.07
Sulfur	0.86
Ash	7.46
Total	100.00
Proximate analysis, wt. %	
Moisture	0.9
Volatile matter	18.1
Fixed carbon	73.6
Ash	7.4
Total	±100.0