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# Hydrocarbonization Research: Completion Report

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HYDROCARBONIZATION RESEARCH: COMPLETION REPORT

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## ABSTRACT

Hydrocarbonization is a relatively simple process used for producing oil, substitute natural gas, and char by heating coal under a hydrogen-rich atmosphere. This report describes studies that were performed in a bench-scale hydrocarbonization system at Oak Ridge National Laboratory (ORNL) during the period 1975 to 1978. The results of mock-up studies, coal metering valve and flowmeter development, and supporting work in an atmospheric hydrocarbonization system are also described.

Oil, gas, and char yields were determined by hydrocarbonization of coal in a 0.1-m-diam fluidized-bed reactor operated at a pressure of 2170 kPa and at temperatures ranging from 694 to 854 K. The nominal coal feed rate was 4.5 kg/h. Wyodak subbituminous coal was used for most of the experiments. A maximum oil yield of ~21% based on moisture- and ash-free (maf) coal was achieved in the temperature range of 810 to 840 K. Recirculating fluidized-bed, uniformly fluidized-bed, and rapid hydrolysis reactors were used. A series of operability tests was made with Illinois No. 6 coal to determine whether caking coal could be processed in the recirculating fluidized-bed reactor. These tests were generally unsuccessful because of agglomeration and caking problems; however, these problems were eliminated by the use of chemically pretreated coal. Hydrocarbonization experiments were carried out with Illinois No. 6 coal that had been pretreated with CaO-NaOH, Na<sub>2</sub>CO<sub>3</sub>, and CaO-Na<sub>2</sub>CO<sub>3</sub>. Oil yields of 14, 24, and 21%, respectively, were obtained from the runs with treated coal. Gas and char yield data and the composition of the oil, gas, and char products are presented.

## 1. INTRODUCTION

Hydrocarbonization is an important type of coal liquefaction process that combines low-temperature, high-pressure, and fluidized-bed operation, using hydrogen-rich gas for fluidization. The hydrocarbonization process can produce liquid fuels and substitute natural gas and char with a reduced sulfur content, and the relative yields of these products

can be controlled. In addition to the valuable liquid and gas products obtained, the char is also useful for gasification or as a fuel.

This project was sponsored by the Division of Fossil Fuel Processing for supporting research and development in coal hydrocarbonization. The program was composed of three tasks. The first was a review and evaluation of existing process technology. This was completed and a summary report<sup>1</sup> published in August 1975. Task 2 consisted of testing models of hydrocarbonization system components and measuring yields from atmospheric-pressure carbonization and hydrocarbonization. The results of these experiments are given in Appendices A, B, and C of this report. Task 3 consisted of the design and operation of a bench-scale hydrocarbonization system. The main purpose of this report is to summarize the results obtained from operation of the bench-scale system. Results of this work have also been reported in monthly and quarterly ORNL Coal Technology Program progress reports that were published from 1975 through 1978.

The objectives of the bench-scale hydrocarbonization project were as follows: (1) establish the optimum conditions for operation of fluidized-bed hydrocarbonization reactors, (2) operate a fluidized-bed reactor capable of continuously processing 4.5 kg of coal per hour at conditions up to and including 922 K and 2170 kPa, and (3) establish hydrocarbonization conditions favoring operability, low char yield, and economics.

In the course of the program, a bench-scale hydrocarbonization reactor using a 0.1-m-diam fluidized-bed reactor was constructed, and 28 experiments were conducted using Wyodak subbituminous coal and Illinois No. 6 coal. Both a description of the process and equipment and the results of the experiments are presented in this report.

## 2. SUMMARY

The bench-scale hydrocarbonization studies were carried out in a fluidized-bed reactor constructed of 0.1-m (4-in.) sched 80 pipe. In most experiments, a 0.017-m-ID x 0.74-m-long draft tube was installed in the reactor to produce a recirculating fluidized bed. For comparison,

experiments were also performed in a uniformly fluidized reactor (no draft tube) and in a rapid hydrolysis reactor in which the draft tube was connected directly to a cyclone to give rapid disengagement of the gas and solids. Coal (-45 +170 mesh) was processed at a nominal rate of 4.5 kg/h. Hydrogen gas was used for fluidization and to provide a hydrogen atmosphere in the reactor. The normal operating pressure for the reactor was 2170 kPa; however, two experiments were performed at 1136 kPa to study the effect of pressure on product yield. A total of 28 experiments were performed. Initially, product yields were determined as a function of temperature for Wyodak subbituminous coal. A series of operability tests were then made with Illinois No. 6 coal to determine whether caking coal could be processed in the recirculating fluidized-bed reactor. These tests were generally unsuccessful because of agglomeration and caking in the reactor; however, these problems were eliminated by chemical pretreatment of the coal. Hydrocarbonization experiments were carried out with Illinois No. 6 coal that had been pretreated with CaO-NaOH, Na<sub>2</sub>CO<sub>3</sub>, and CaO-Na<sub>2</sub>CO<sub>3</sub>. The composition and properties of the products from typical runs were then determined.

Product yields were determined as a function of temperature in the range of 694 to 854 K for Wyodak subbituminous coal from the Roland-Smith seam. Wyodak is a noncaking coal having a low sulfur content (0.5 wt %). Maximum oil yields of 21% (based on maf coal) were obtained in the temperature range of 810 to 840 K using coal that had been dried and sized under an inert atmosphere. Coal that was freely exposed to air during preparation gave a considerably lower oil yield of only ~11% in the same temperature range. The typical oil product from Wyodak coal had a relatively low viscosity (0.018 Pa·s at 311 K). On a dry basis, the oil contained 86% carbon, 8% hydrogen, 1% nitrogen, 0.4% sulfur, and 4.6% oxygen (by difference). The gas yield from hydrocarbonization of Wyodak coal increased as a function of temperature from 15 to 19% (based on maf coal) over the temperature range of 700 to 850 K. Coal exposed to air during preparation gave a somewhat higher gas yield (17% to 28%). Under the operating conditions used, there was very little production or utilization of hydrogen. The composition of the gas

product was highly dependent on operating temperature. The concentrations of  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ , and  $\text{C}_3\text{H}_6 + \text{C}_3\text{H}_8$  increased as a function of operating temperature while the concentration of  $\text{CO}_2$  decreased. The typical composition (vol % on a  $\text{H}_2$ - and  $\text{N}_2$ -free basis) of the gas produced at 840 K was 53%  $\text{CH}_4$ , 22%  $\text{CO}$ , 8%  $\text{CO}_2$ , 13%  $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ , and 4%  $\text{C}_3\text{H}_6 + \text{C}_3\text{H}_8$ . The  $\text{H}_2\text{S}$  concentration was near the lower limit of detection (<1%). Char yields (on a maf basis) decreased as a function of temperature from ~60% at 700 K to 46% at 850 K. Typical char product from runs made with Wyodak coal at 840 K (on a dry basis) contained 0.3 wt % sulfur, 80 wt % carbon, 13 wt % ash, and had a heating value of 31 MJ/kg. Experiments performed with Wyodak coal in the uniformly fluidized-bed reactor and the rapid hydrolysis reactor at 830 and 854 K gave essentially the same product yields as those achieved in the recirculating-bed reactor. Experiments done at a reduced operating pressure (1136 kPa) gave slightly lower oil yields as predicted based on correlations developed in the Phase 1 study.<sup>1</sup> The general equipment performance with Wyodak coal was good. Pressure surges that caused operational difficulties during the earlier runs were eliminated by installing a filter upstream of the pressure control valve.

Although noncaking coal is easily processed in fluidized-bed reactors, most of the coal found in the eastern United States agglomerates when heated above ~672 K and requires special methods of processing. Two methods that have been used to reduce the problems of agglomeration are char dilution and dilute phase flow.<sup>2,3</sup> These two methods are provided by the recirculating-bed reactor. Eight operability tests were made with Illinois No. 6 bituminous coal to study the behavior of caking coal in the reactor. The studies were carried out in the temperature range of 714 to 872 K with the coal feed diluted with char at ratios up to 6/1. The system was successfully operated at 714 K using a char-to-coal ratio of 6/1; however, very little devolatilization took place at that temperature. Bed caking occurred at the top of the draft tube at higher temperatures, indicating that the coal had not been sufficiently devolatilized during the short residence time (~0.3 s) in the draft tube to prevent agglomeration in the mildly fluidized annular

region of the reactor. The length of the draft tube was increased from 0.74 m to 2.26 m in order to increase the coal residence time to  $\sim 0.8$  s. Because of time limitations, only one experiment was performed at 872 K with the longer draft tube. Caking occurred early in the experiment; however, the amount of testing done was not sufficient to definitely determine whether agglomeration problems can be eliminated by longer residence times in the draft tube.

The agglomeration problems of Illinois No. 6 coal were eliminated by three chemical pretreatment methods using CaO-NaOH,  $\text{Na}_2\text{CO}_3$ , and CaO- $\text{Na}_2\text{CO}_3$ . The pretreatment methods are similar to those used by Battelle Memorial Institute for sulfur removal from coal.<sup>4,5</sup> The CaO-NaOH and  $\text{Na}_2\text{CO}_3$  pretreatments were done by heating a slurry of coal, water, and reagents in an autoclave for 1 to 2 h at temperatures in the range of 473 to 573 K. The CaO- $\text{Na}_2\text{CO}_3$  pretreatment was performed by heating the coal slurry at 353 K for 16 h and is based on scouting tests done at ORNL to develop a pretreatment method that could be conducted at atmospheric pressure. Hydrocarbonization runs using the pretreated coal were conducted at  $\sim 844$  K and at 2170 kPa. Oil yields (based on maf coal) of 14, 24, and 21% were obtained from the CaO-NaOH-,  $\text{Na}_2\text{CO}_3$ -, and CaO- $\text{Na}_2\text{CO}_3$ -treated coal, respectively. The 24% oil yield obtained from the  $\text{Na}_2\text{CO}_3$ -treated Illinois No. 6 coal is higher than the maximum yield of 21% obtained from Wyodak coal under the same operating conditions. Sufficient data are not available to determine whether the improved oil yield is a result of the chemical pretreatment method or is due to the type of coal used. The oil product from the  $\text{Na}_2\text{CO}_3$ -pretreated coal has a somewhat higher viscosity (0.120 Pa·s at 311 K) than the oil produced from Wyodak coal. The sulfur content of the oil was  $\sim 1.5\%$ , as compared to 4% sulfur in the coal. Although not studied extensively in this program, the use of chemical pretreatments may also offer advantages in improved oil and gas quality and yields and increased char reactivity for gasification.

Work done in support of the bench-scale hydrocarbonization studies included atmospheric-pressure carbonization and hydrocarbonization studies in a 0.1-m-diam reactor. Eleven experimental runs were made in

the temperature range of 802 to 922 K using Wyodak subbituminous coal. Ambient mock-up studies were performed to study fluidization and bed recirculation. Work was also done to develop a coal feeder valve and coal flowmeter for use in the bench-scale system.

### 3. EXPERIMENTAL EQUIPMENT

The bench-scale hydrocarbonization equipment is designed to process coal at a nominal rate of 4.5 kg/h at temperatures of up to 922 K and pressures of up to 2170 kPa. The equipment is sized to handle a coal charge of ~45 kg per run. The focus of the system is the hydrocarbonization reactor in which a fluidized bed is used to convert coal into liquid, gas, and char by heating under a hydrogen atmosphere. Minimal facilities, as necessary for the experimental objectives, were provided for feed preparation, gas handling, and product recovery.

A simplified flowsheet of the system is presented in Fig. 3.1. Pulverized coal (nominally -45 +170 mesh) was fed from the feed hopper through a metering valve into a pneumatic transfer line. A portion of the hydrogen feed was used to transport the coal to the reactor. In later runs, a preheater was used to heat the coal stream to ~477 K before it entered the reactor. In the reactor, the coal was pyrolyzed under a hydrogen atmosphere to produce liquid, gas, and residual solid char. The liquids, as vapors and fine aerosols, were carried with the gas stream through an internal cyclone for solids removal and then out the top of the reactor. The solids overflowed from the reactor to the char receiver, where they were collected. The product stream from the reactor passed through a heated line to a scrubber in which vapors were condensed and the aerosol removed. The cooled product stream then passed through a cold trap to condense any remaining vapors. System pressure was controlled by a throttling valve located downstream of the cold trap. After pressure letdown, the gases passed through an absolute filter and charcoal trap to remove entrained solids and light hydrocarbon vapors. The gas effluent rate and composition were measured by a flow orifice and gas chromatograph located downstream of the charcoal trap. The gas effluent was vented through a 4.5-m stack that

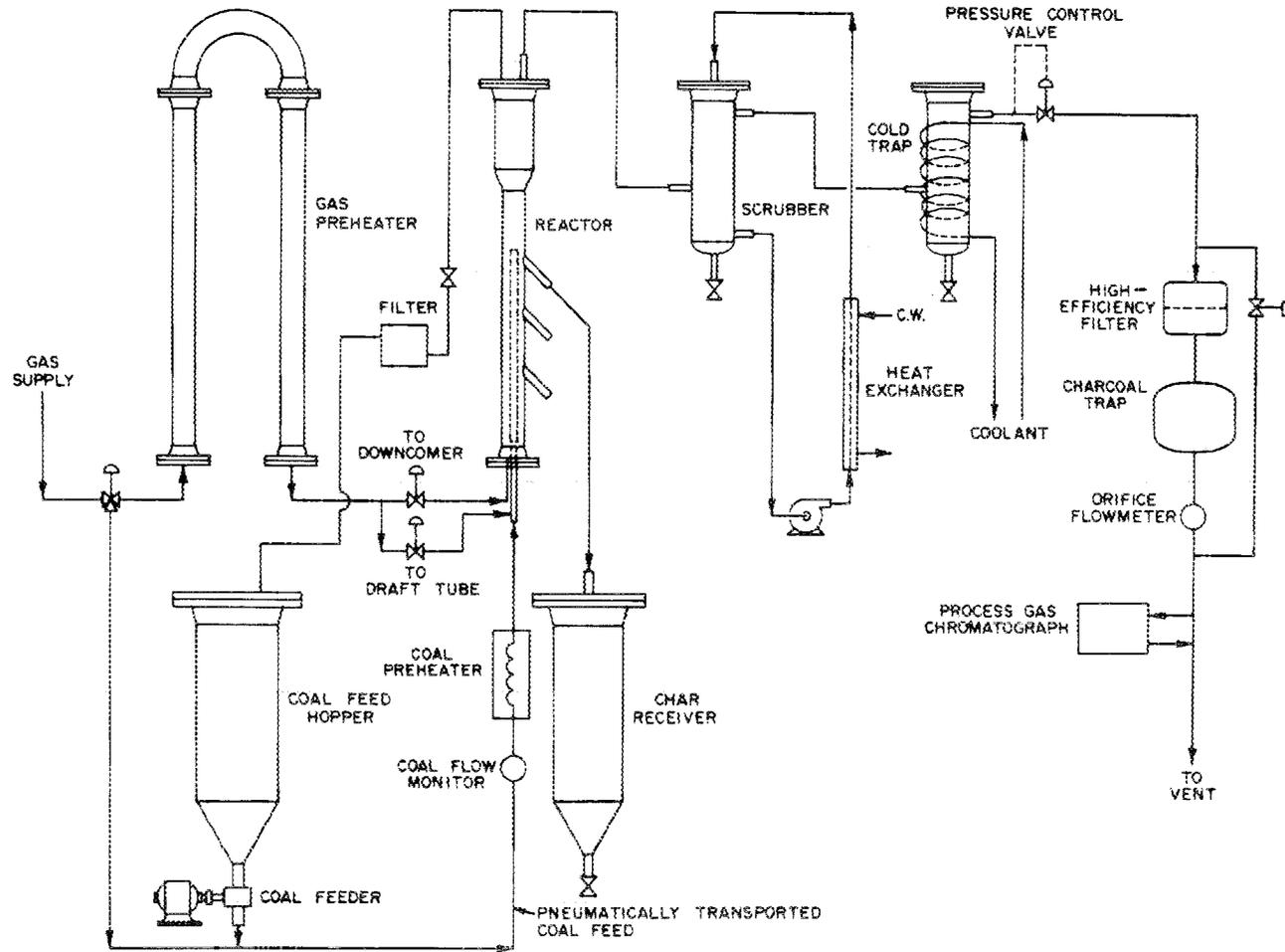


Fig. 3.1. Bench-scale hydrocarbonization flowsheet.

extends above the building. A photograph of the equipment is shown in Fig. 3.2.

The facility was located in Building 2528. Three blowout panels measuring 4.5 m wide and 6 m high were located immediately behind the equipment. A block wall separated the experimental area from the control room. The ventilation system provided an airflow of 105 std m<sup>3</sup>/min at all times through the experimental area to prevent hydrogen accumulation. The hydrogen supply to the system was automatically shut off if the ventilation airflow was low or if the hydrogen flow rate into the building became excessive. A description of the reactor is given below. Other equipment used in the bench-scale hydrocarbonization system is described in Appendix D.

The reactor vessel consisted of a 0.1-m (4-in.)-diam sched 80 pipe fluidized-bed section and a 0.15-m (6-in.)-diam sched 80 pipe expanded section for solids disengagement from the gas stream, as shown in Fig. 3.3. A char overflow line was located on the side of the vessel as shown. The gas distributor plate at the bottom of the reactor was 0.0064 m thick and had a diameter of 0.097 m with seventy-three 0.001-m-diam holes on 0.012-m centers (staggered). The length of the 0.1-m-diam bed sections of the reactor was 1.02 m for the first 26 experiments (HC-1 through HC-26). The 0.1-m-diam section was lengthened to 2.54 m for the last two experiments (HC-27 and HC-28) to provide increased coal residence time in the draft tube. The reactor was heated by tubular electric heaters fastened to the outside surface. The original reactor had five 4.7-kW heating zones, while the longer reactor used five 5-kW heating elements on the fluidized-bed section and two 4.7-kW heaters on the upper disengaging section. Chromel-Alumel thermocouples were attached to the outer surface of the reactor and inserted into the vessel for temperature measurement and control. A 0.057-m-ID cyclone was located in the expanded section of the reactor to remove particulates from the gas stream.

The reactor was operated as a uniformly fluidized bed (no draft tube) for seven experiments (HC-1 through HC-6 and HC-21), with coal

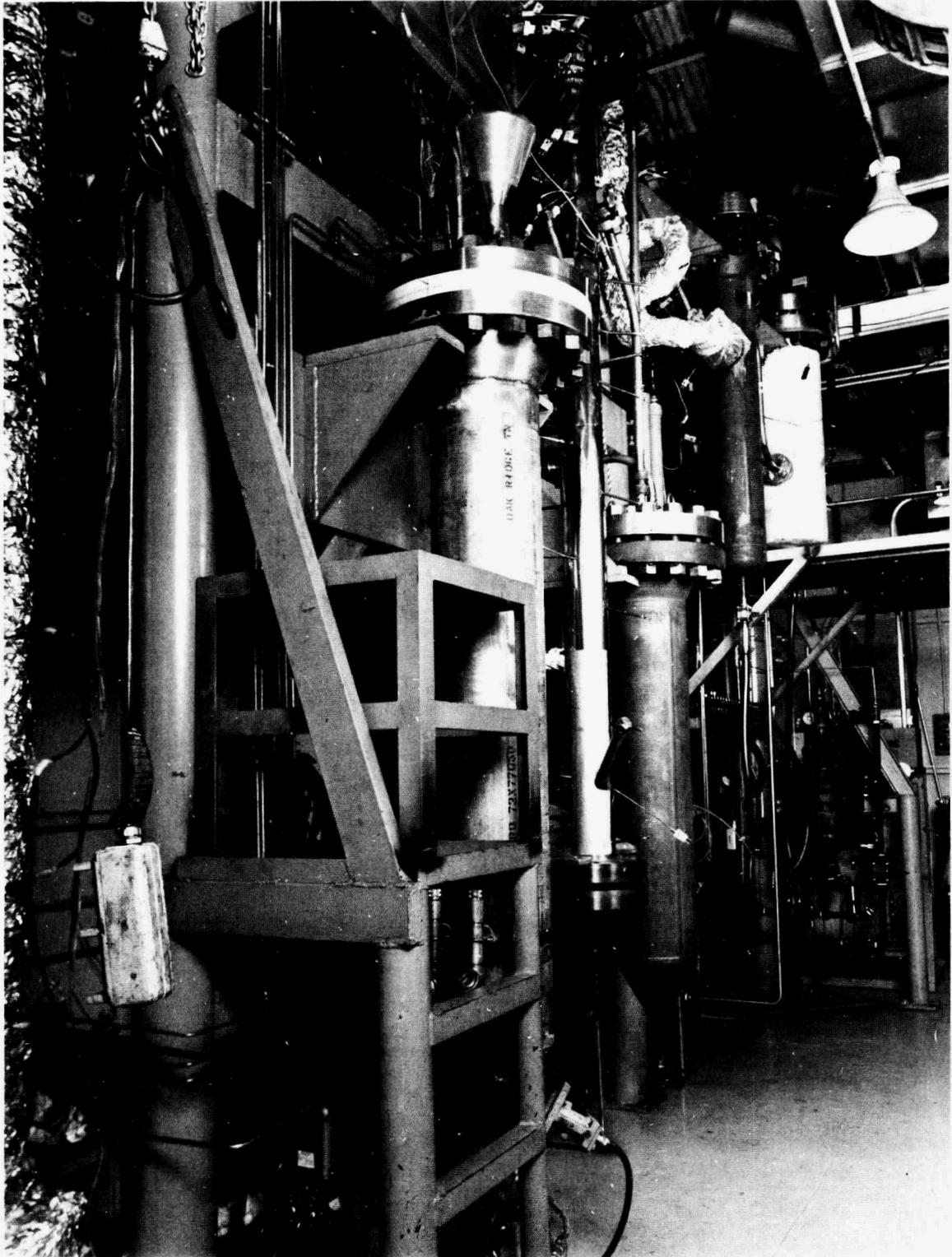


Fig. 3.2. Bench-scale hydrocarbonization system.

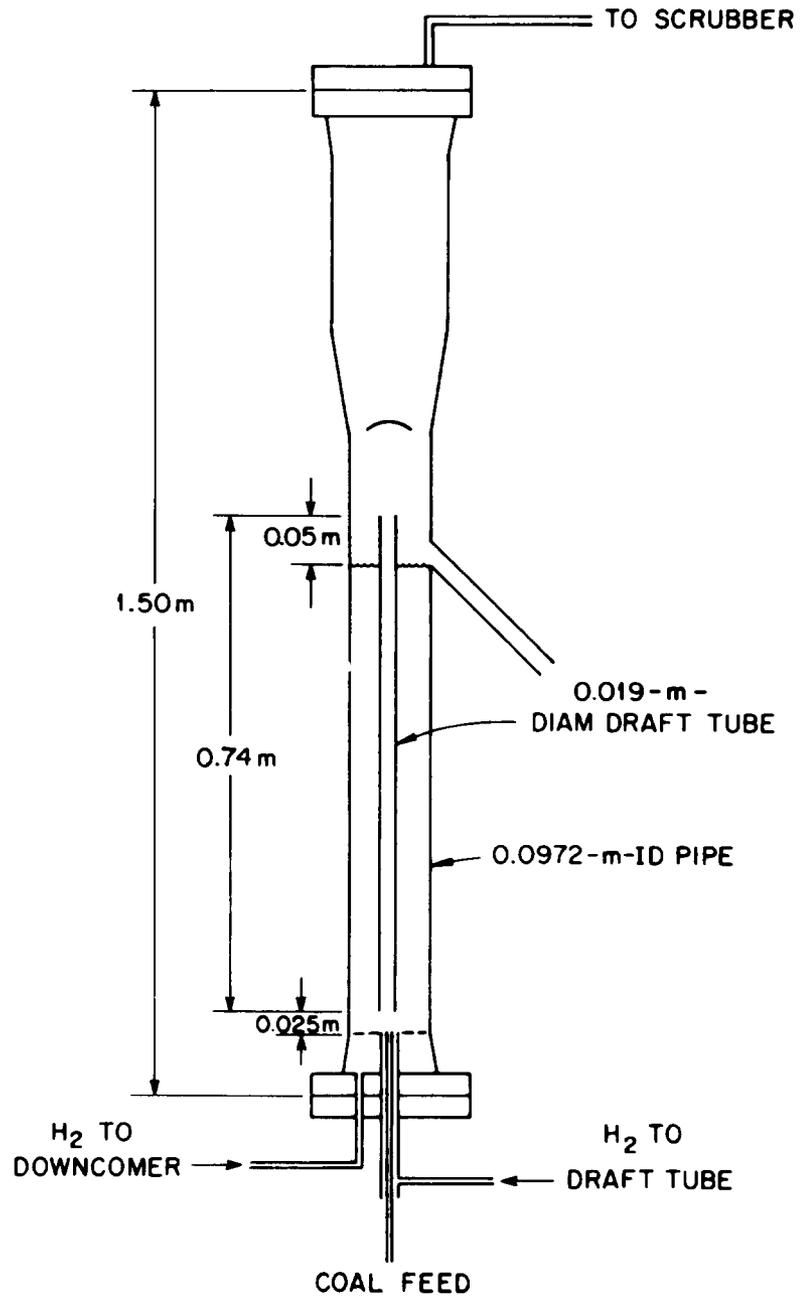


Fig. 3.3. Recirculating fluidized-bed reactor.

injected pneumatically near the bottom of the bed. Prior to run HC-7, a 0.017-m-ID x 0.74-m-long draft tube was installed in the reactor to provide recirculation of the fluidized bed. The draft tube was centered in the reactor 0.025 m above the distributor plate. A cup-shaped deflector was mounted 0.25 m above the top of the draft tube. Coal feed was pneumatically fed to the draft tube through 0.0035-m-ID tubing. Hot hydrogen was fed to draft tube and annular region (downcomer) to provide fluidization and circulation of the char. The 0.017-m-ID draft tube was used during runs HC-7 through HC-15; prior to run HC-16, the inside diameter of the draft tube was changed to 0.022 m. The length of the draft tube was increased to 2.26 m for run HC-27, as shown in Fig. 3.4.

For run HC-28, the internal circulation pattern was modified to give rapid disengagement of the char by attaching the draft tube directly to a cyclone, as shown in Fig. 3.5. The draft tube was 2.67 m long and was constructed to 0.022-m-ID stainless steel tubing. Coal feed was introduced through a 0.0048-m-OD line that entered the bottom of the draft tube through 0.0077-m-ID tubing. The annular space between the two lines was used to introduce additional gas to the draft tube. Char from the fluidized bed entered the bottom of the draft tube through a side arm having a 0.016-m-ID opening. The upper end of the draft tube was attached to an open cyclone (0.048-m ID) in which the char was disengaged from the gas stream and returned to the fluidized bed for recirculation. The gas stream passed through a second cyclone (0.024-m ID) before leaving the reactor.

The reactor and other major vessels in the bench-scale hydrocarbonization system were constructed of 316 stainless steel and were designed for pressures up to 2515 kPa. Each vessel was protected by a 2515-kPa rupture disc.

#### 4. EXPERIMENTAL PROCEDURE

With minor variations, all of the bench-scale hydrocarbonization experiments were carried out using the same general operating procedure.

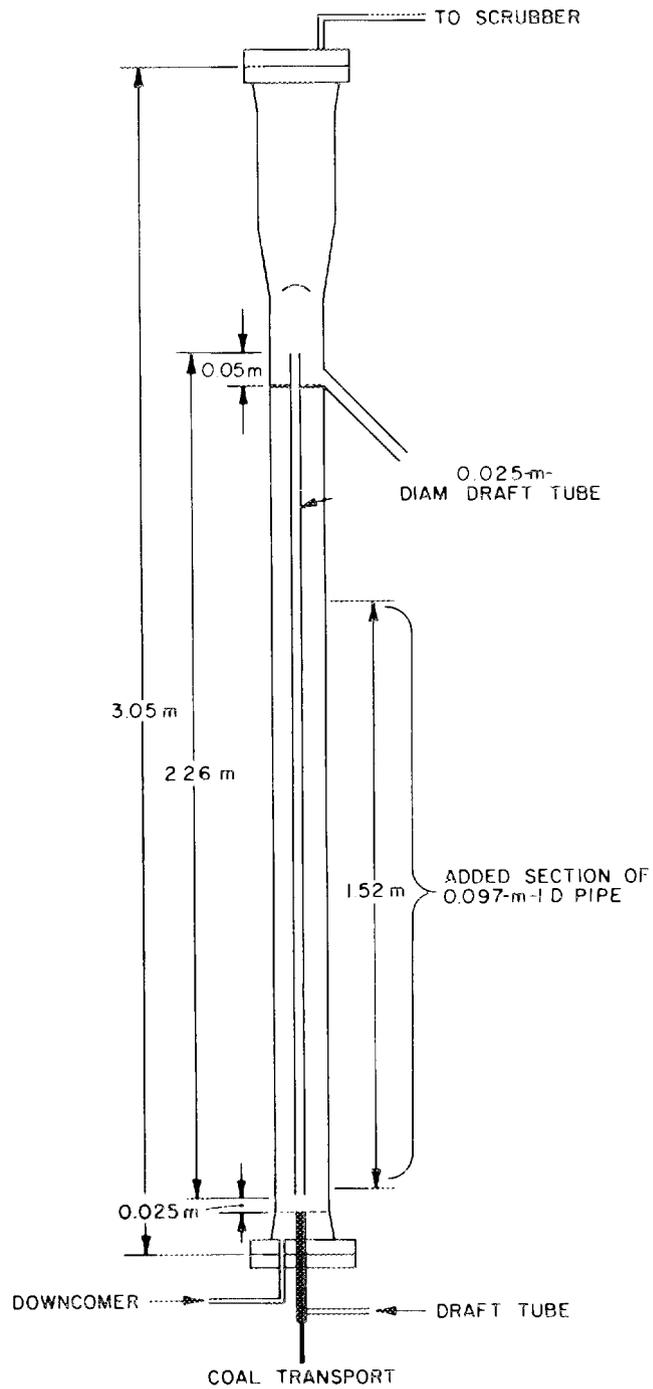


Fig. 3.4. Revised reactor with longer fluidized-bed section.

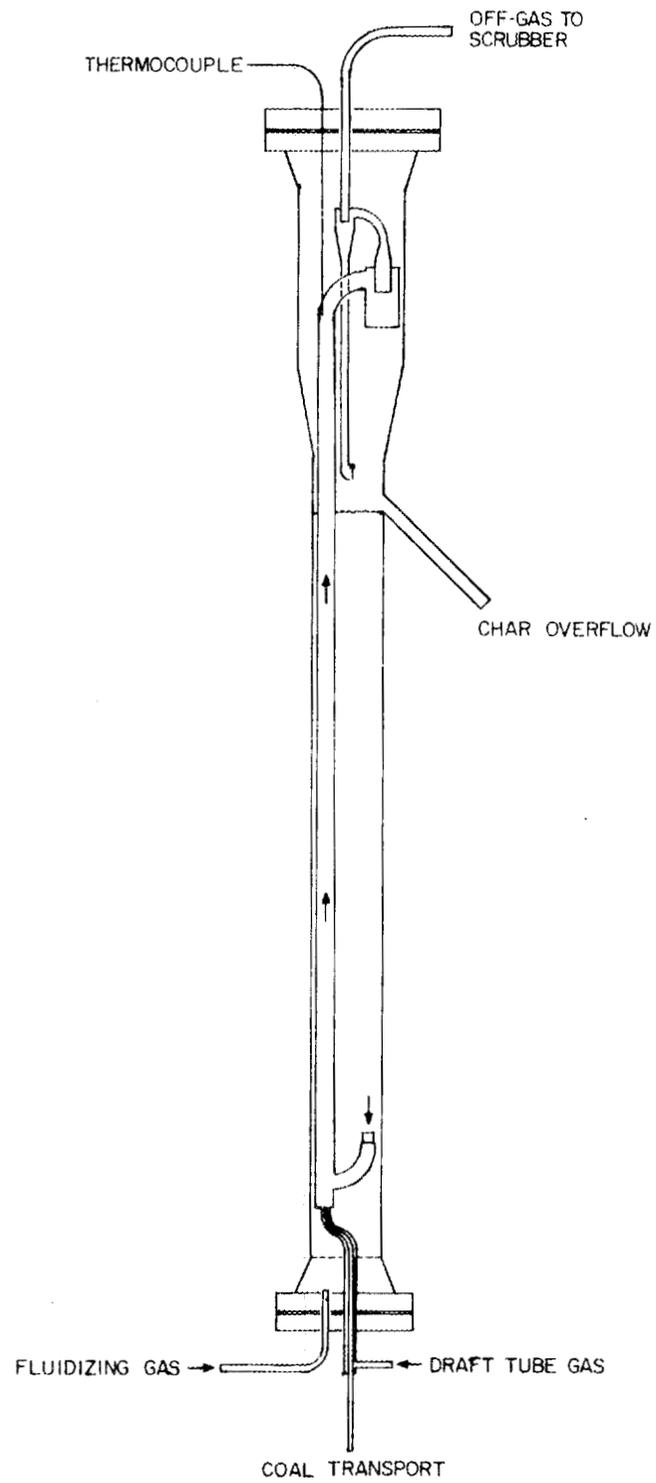


Fig. 3.5. Rapid hydrolysis reactor.

Approximately 45 kg of coal was processed in each experiment. The actual run time for an experiment was on the order of 10 h; however, the run time varied in some experiments because of operational difficulties. The general procedures used for the experiments are given below.

#### 4.1 Prerun Preparation

The major operations that were required to prepare for a hydrocarbonization experiment are coal feed preparation, charging material to the system, leak testing, instrument calibration, and check of safety equipment.

Coal preparation was necessary in order to obtain a particle size distribution that could be fluidized in the reactor. Feed for the first seven experiments was prepared at Morgantown Energy Research Center, with unrestricted exposure of the coal to air during preparation. Feed for the remaining runs was prepared at ORNL, with care being taken to minimize exposure of the coal to air during preparation. Coal (-1½ +0 mesh) that had been covered with water and placed in sealed drums was received from the mine. The water was removed from the coal in a vacuum dryer at a temperature of 323 K. After drying, the coal was pulverized in a large-capacity hammer mill and Mikro-Pulverizer hammer mill to a nominal particle size range of -45 to +170 mesh. All particles larger than 45 mesh are removed in a Sweco separator. Excess undersize material was removed by screening through Sonic Sifters. The equipment was purged with argon to prevent exposure of the coal to air during the grinding and sieving operations.

Prior to each run, a weighed quantity of distilled water (18 to 22 kg) was added to the scrubber. The charcoal trap was loaded with ~3 kg of coconut charcoal that had previously been heated to 423 K to remove moisture, and a new high-efficiency filter was installed in the off-gas line. After the above material had been charged, the system was pressurized to 1480 kPa with nitrogen and checked for leaks with soap bubbles and a sonic leak detector. The gas chromatograph, oxygen analyzer, and combustible gas monitors are calibrated before each experiment using

standard-calibration gas mixtures. Operability of the automatic shutdown system was also checked prior to each experiment.

#### 4.2 Run Procedure

In making a run, coal (or char for the starting bed) was loaded into the feed hopper, and the system was purged with nitrogen to remove air. This was done by a series of pressurizations to 1480 kPa followed by venting. While the system was being purged, the reactor, preheater, and lines were heated to near operating temperature. A hot pressure test was performed with nitrogen at operating pressure to ensure that the system was leak tight. In runs using caking coal (Illinois No. 6), a starting bed of char was charged to the reactor after the system had been purged. When noncaking coal (Wyodak) was used, it was fed to the hot reactor to provide char for the bed. Hydrogen flows were then started at the desired rate. Coal feed to the reactor was started after operating conditions had been reached. In most experiments, the pressure, flow rates, and temperature were maintained at near-constant values throughout the run. Generally, the run was continued until the entire coal charge was fed from the feed hopper. Upon completion of the experiment, the system was again purged with nitrogen by alternately pressurizing and venting to remove hydrogen.

#### 4.3 Sampling and Material Balance Determination

The system was drained and the material removed was weighed and sampled to determine yields and the material balances upon completion of an experiment. The scrubber and coal trap were washed with perchloroethylene to remove residual oil and tar that had not drained freely. The oil and water phases from the scrubber and cold trap were separated by decantation. The oil phase contained both water and char that had been entrained in the reactor effluent gas. Samples of the material were analyzed for water, ash, and carbon so that the oil content could be determined. The char content was determined from the ash analysis, assuming that all ash was present as char. Soxhlet extraction with benzene was also used in some experiments to separate the oil and char

for analytical determination. The oil content of the perchlorethylene wash was determined by evaporating the perchlorethylene and analyzing the residue for ash and carbon content. The quantity of oil collected on the charcoal trap was determined by the weight gain of the charcoal and from samples collected by desorption of the charcoal at 700 K. The organic carbon content of the aqueous phase of the scrubber was also included in determining the oil yield. The char yield was determined by summing the weight of char removed from the reactor and char receiver with that in the oil phases from the scrubber and cold trap. Samples of char were analyzed for ash, carbon, and sulfur content for material balance calculations. The gas yield and quantities of  $H_2$ , CO,  $CO_2$ ,  $CH_4$ ,  $C_2H_4 + C_2H_6$ ,  $C_3H_6 + C_3H_8$ ,  $N_2$ , and  $H_2S$  in the gas effluent were determined from flow and gas chromatograph data by summing the quantities of each component evolved over 8-min intervals during the run.

## 5. DESCRIPTION OF EXPERIMENTS

A total of 28 experimental runs was conducted. The primary variables studied were fluidized-bed temperature, type of coal, coal pretreatment, and fluidized-bed configuration. Operating variables for the experiments are summarized in Table 5.1. A detail description of the runs is given in Appendix E. The range of operating temperature studies was from 694 to 854 K for runs using Wyodak coal and 714 to 872 K for runs using Illinois No. 6 coal. Twenty-six of the experiments were carried out at a hydrogen pressure of 2170 kPa, and the remaining two (HC-6 and HC-25) were done at 1136 kPa. The two types of coal that were used were Wyodak subbituminous coal from the Roland-Smith seam at Gillette, Wyoming, and Illinois No. 6 bituminous coal from River King Pit No. 3 surface mine, New Athens, Illinois. Wyodak is a noncaking coal with a low sulfur content. Illinois No. 6 is a caking coal (Free-Swelling Index of  $\sim 3$ ) having a high sulfur content. The compositions of these two types of coal are given in Tables 5.2 and 5.3. Wyodak coal for the first seven experiments (HC-1 through HC-7) was freely exposed to air during preparation. Air exposure was found to significantly

Table 5.1. Description of hydrocarbonization runs

Run No.	Temperature (K)	Pressure (kPa)	Type of fluidized bed	Type of coal	Coal feed rate (kg/h)	H <sub>2</sub> rate (std m <sup>3</sup> /min)	Char residence time in reactor (min)
HC-7	711	2170	Recirculated	Air-exposed Wyodak	6.7	0.22	38
HC-3 <sup>a</sup>	761	2170	Uniform	Air-exposed Wyodak	6.0	0.14	45
HC-5	791	2170	Uniform	Air-exposed Wyodak	7.0	0.14	41
HC-4	811	2170	Uniform	Air-exposed Wyodak	6.4	0.16	46
HC-2	827	2170	Uniform	Air-exposed Wyodak	3.8	0.16	80
HC-1	852	2170	Uniform	Air-exposed Wyodak	0.6	0.20	540
HC-8	694	2170	Recirculated	Wyodak	6.2	0.31	40
HC-13	758 <sup>b</sup>	2170	Recirculated	Wyodak	5.0	0.32	54
HC-9 <sup>a</sup>	786	2170	Recirculated	Wyodak	3.1	0.32	92
HC-12	825	2170	Recirculated	Wyodak	4.6	0.32	66
HC-11	830	2170	Recirculated	Wyodak	4.0	0.33	
HC-21	830	2170 <sup>d</sup>	Uniform	Wyodak	4.6	0.37	70
HC-10	839	2170	Recirculated	Wyodak	2.0	0.33	155
HC-14	850 <sup>c</sup>	2170	Recirculated	Wyodak	4.2	0.32	89
HC-28	854	2170	Rapid pyrolysis	Wyodak	6.2	0.65	150
HC-6	827	1136	Uniform	Air-exposed Wyodak	7.4	0.07	41
HC-25	844	1136	Recirculated	Wyodak	5.0	0.31	60
HC-23	844	2170 <sup>e</sup>	Recirculated	Treated Ill. No. 6	2.1	0.57	71
HC-24	844	2170	Recirculated	Treated Ill. No. 6	4.3	0.57	46
HC-26	841	2170	Recirculated	Treated Ill. No. 6	3.9	0.54	35
HC-16 <sup>f</sup>	714	2170	Recirculated				
HC-17 <sup>f</sup>	714	2170	Recirculated				
HC-19 <sup>f</sup>	769	2170	Recirculated				
HC-18 <sup>f</sup>	797	2170	Recirculated				
HC-20 <sup>f</sup>	839	2170	Recirculated				
HC-22 <sup>f</sup>	852	2170	Recirculated				
HC-15 <sup>f</sup>	866	2170	Recirculated				
HC-27 <sup>f</sup>	872	2170	Long reactor				

<sup>a</sup>Oil yields from runs HC-3 and HC-9 are questionable.

<sup>b</sup>Time-average temperature. Operated at 783 K for 4.6 h; lost bed during shutdown; restarted at 783 K for 1.8 h, dropped to 755 K for 0.8 h; then 705 K for 3.1 h.

<sup>c</sup>Time-average temperature. Operated at 866 K for 3.3 h; dropped to 847 K for 1.1 h; then 816 K for 1.5 h.

<sup>d</sup>Reactor was at 2170 kPa for first 5.9 h and 1894 kPa during the remaining 6.3 h.

<sup>e</sup>Reactor pressure was 2170 kPa for first 4 h and 2032 kPa for the remaining 9.3 h.

<sup>f</sup>Illinois No. 6 - Caking occurred before useful data could be obtained.

Table 5.2. Properties of Wyodak subbituminous coal

Shipment No.	1 <sup>a</sup>	2
<u>Proximate analysis, wt %:</u>		
Volatile matter	40.4	40.5
Fixed carbon	43.6	46.9
Moisture	10.0	6.2 <sup>b</sup>
Ash	6.0	6.4
<u>Ultimate analysis, wt % maf:</u>		
Carbon	71.8	72.5
Hydrogen	5.5	5.5
Nitrogen	1.1	1.0
Sulfur	0.4	0.5
Oxygen (by difference)	21.2	20.5
Heating value, MJ/kg dry	26.5	27.2

<sup>a</sup>Shipment 1 was dried and pulverized at the Morgantown Energy Research Center, Morgantown, W. Va., and was used for runs 1 through 7.

<sup>b</sup>Moisture content varied from 5 to 15%, depending on the degree of drying.

Table 5.3. Properties of Illinois No. 6 coal

<u>Proximate analysis, wt %:</u>	
Volatile matter	38.8
Fixed carbon	48.4
Moisture	0.6
Ash	12.2
<u>Ultimate analysis, wt %</u>	
Carbon	77.7
Hydrogen	5.8
Nitrogen	1.4
Sulfur	4.5
Oxygen (by difference)	10.6
Heating value, MJ/kg dry	29.1

reduce the liquid yield in comparison to that obtained using coal prepared under an inert atmosphere, as will be discussed later.

Eight experiments (HC-15 through HC-20, HC-22, and HC-27) were attempted using untreated Illinois No. 6 coal; however, agglomeration and caking occurred in the fluidized bed before useful data could be obtained. The agglomerating tendency of the coal was successfully eliminated by chemical pretreatment, and three experiments were performed with Illinois No. 6 coal that had been pretreated with CaO-NaOH in run HC-23, Na<sub>2</sub>CO<sub>3</sub> in HC-24, and CaO-Na<sub>2</sub>CO<sub>3</sub> in run HC-26. The pretreatment procedure is described in Appendix E.

The configuration of the fluidized bed in the reactor was modified in order to study the effects of increased bed circulation and rapid disengagement of the gas phase. Experiments HC-1 through HC-6 and HC-21 were performed with a uniformly fluidized-bed reactor with no draft tube present. After run HC-6, a 0.017-m-ID x 0.74-m-long draft tube was installed to provide rapid recirculation of the reactor bed. Char circulated downward through the annular (downcomer) region as a mildly fluidized or moving packed bed. It then flowed rapidly upward through the draft tube in dilute phase flow. Coal feed was introduced at the bottom of the draft tube where it mixed and was rapidly heated by the circulating char. An additional function of the draft tube was to reduce the gas residence time in the fluidized bed in order to minimize cracking and coking. Char dilution and the rapid dilute phase flow in the draft tube are methods that have been used to reduce problems of agglomeration that are associated with caking coal.<sup>2,3</sup> Before run HC-16, the inside diameter of the draft tube was increased to 0.022 m in an attempt to improve the handling of caking coals. In run HC-27, the length of the draft tube was increased from 0.74 m to 2.26 m so that the residence time of the coal in the draft tube could be increased. One hydrolysis run (HC-28) was made in which the draft tube was connected directly to a cyclone to permit disengagement and quenching of the volatile products.

Some variations occurred in other parameters such as hydrogen rate, coal feed rate, and coal particle size during the program, but these

were not considered to be of major significance in these experiments. Coal feed was prepared by the same method in each experiment. Material with a mean particle diameter in the range of 135 to 190  $\mu\text{m}$  was thus produced. Table 5.4 gives a typical particle size distribution for the feed material. As shown in Table 5.1, typical feed rates ranged from 4 to 7 kg/h. Operational difficulties sometimes caused slower feed rates. The average char residence time in the reactor exceeded 30 min for all experiments. The hydrogen flow rate to the reactor was determined by the rate required to obtain good fluidization and circulation of the reactor bed. As shown in Table 5.1, the flow rates were changed for different bed configurations and operating conditions. In all runs, the flow rate was sufficient to maintain a high hydrogen concentration (81 to 98%) in the gas effluent stream. Typical operating conditions for the three reactor configurations are given in Table 5.5.

Operational difficulties resulted in changes being made in operating conditions during some runs. These changes are noted in Table 5.1 and are included in the description of the experiments given in Appendix E.

Table 5.4. Typical size distribution of coal feed used in hydrocarbonization experiments

Mesh size	Wt %
+45	1.1
-45 +60	28.7
-60 +80	26.4
-80 +120	23.6
-120 +140	5.7
-140 +170	6.1
-170	8.4
Mean diameter	157 $\mu\text{m}$

Table 5.5. Typical operating conditions  
for hydrocarbonization reactors

Conditions	Recirculating bed	Uniformly fluidized bed	Rapid hydrolysis
Coal feed rate, kg/h	5.0	4.6	6.2
Hydrogen feed rate, m <sup>3</sup> /h	17.0	22.0	39.0
Bed temperature, K	850	830	854
Draft tube temperature, K	830		847
Pressure, kPa	2170	2170	2170
Superficial gas velocity, m/s <sup>a</sup>			
Draft tube	2.5		2.9
Reactor	0.01	0.11	0.05
Char residence time, s			
Draft tube <sup>b</sup>	0.3		0.9
Reactor	3600	4200	9000
Bed level, m	0.7	0.7	2.2

<sup>a</sup>The split of gas flow between the draft tube and downcomer is based on mock-up studies.

<sup>b</sup>Based on gas superficial velocity assuming no slip.

## 6. EXPERIMENTAL RESULTS

Operating conditions, yields, steady-state gas analyses, and hydrogen consumption for runs using Wyodak coal are summarized in Table 6.1. Results for runs with pretreated Illinois No. 6 coal are given in Table 6.2. A more detailed discussion of the results is given below. Where applicable, the experimental data are compared with correlations of previous data developed during the first phase of the program at ORNL.<sup>1</sup>

### 6.1 Liquid Hydrocarbon Yields and Composition

#### 6.1.1 Liquid hydrocarbon yields

During the experimental program, emphasis was placed on determining conditions under which high liquid yields could be obtained. Liquid yields from hydrocarbonization are strongly dependent on operating temperature. The maximum yields were obtained in the temperature range of 810 to 840 K. Gross exposure of the coal to air before processing significantly reduced the liquid yield. The type of chemical pretreatment used in the runs with Illinois No. 6 coal also had an effect. In addition, reduction of the operating pressure from 2170 kPa to 1136 kPa and changes in the bed configuration resulted in minor yield changes.

Liquid yields from Wyodak runs at 2170 kPa (as a percentage of maf) are shown as a function of temperature in Fig. 6.1. Curves are shown for runs using air-exposed coal and for runs using coal prepared under an inert atmosphere. Runs with major operational difficulties are not included. As shown in Fig. 6.1, a maximum yield of ~21% (based on maf coal) was obtained in the range of 810 to 840 K using coal prepared under an inert atmosphere. The maximum liquid yield under similar operating conditions from air-exposed coal was only ~11%. Yields for coal prepared under an inert atmosphere are somewhat higher than those predicted by data correlations based on data from other bench-scale studies,<sup>1</sup> as shown in Fig. 6.2. The liquid yield curve shown in Fig. 6.1 for Wyodak coal prepared under an inert atmosphere is used in the following section as the basis for comparison of yield from pretreated Illinois No. 6 coal and for Wyodak coal processed under other operating conditions.

Table 6.1. Summary of hydrocarbonization experiments with Kyodak subbituminous coal

Hydrocarbonization Run No.	HC-1 <sup>a</sup>	HC-2 <sup>a</sup>	HC-3 <sup>a</sup>	HC-4 <sup>a</sup>	HC-5 <sup>a</sup>	HC-6 <sup>a</sup>	HC-7 <sup>a</sup>	HC-8	HC-9	HC-10	HC-11	HC-12	HC-13	HC-14	HC-21	HC-25	HC-28
Uniform, recirculating fluidized-bed, or rapid hydrolysis reactor (UFB, RFB, or RHP)	UFB	UFB	UFB	UFB	UFB	UFB	RFB	RFB	RFB	RFB	RFB	RFB	RFB	RFB	UFB	RFB	RHP
Bed temperature, K	852	827	761	811	791	827	711	594	786	839	830	825	758 <sup>b</sup>	850 <sup>c</sup>	830	844	854
Reactor pressure, kPa	2170	2170	2170	2170	2170	1136	2170	2170	2170	2170	2170	2170	2170	2170	2170 <sup>d</sup>	1136	2170
Coal feed																	
Rate (as-received), kg/h	0.6	3.8	6.0	6.4	7.0	7.4	6.7	6.2	3.1	2.0	4.8	4.5	5.0	4.2	4.5	5.0	5.2
Elapsed time, h	9.6	13.2	8.1	7.3	7.7	5.1	6.9	5.2	4.8	10.6	2.3	10.5	10.3	6.0	12.2	10.0	6.9
Hydrogen feed rate, std m <sup>3</sup> /min	0.20	0.16	0.14	0.16	0.14	0.07	0.22	0.31	0.32	0.33	0.33	0.32	0.32	0.32	0.37	0.31	0.65
Hydrogen consumption, <sup>e</sup> kg H <sub>2</sub> /kg maf coal fed	f	0.079	0.012	0.003	0.013	0.001	-0.025	-0.011	-0.009	-0.017	g	0.025	-0.026	-0.053	0.001	0.01	0.53
Yields, wt % of maf coal fed																	
Oil	8.7	11.2	11.2 <sup>h</sup>	10.3	6.7	8.0	5.4	6.1	2.9 <sup>h</sup>	15.8	g	18.1	15.4	21.0	21.3	18.1	19.2
Gas	28.0	25.4	18.1	26.3	24.2	25.4	19.3	16.0	17.4	17.0	g	16.5	15.6	20.6	18.9	15.2	21.7
Char (maf)	40.0	40.1	57.6	51.7	50.6	53.3	57.5	59.4	51.0	48.7	g	48.4	55.3	45.8	48.8	52.9	44.5
Steady-state gas analyses (H <sub>2</sub> and N <sub>2</sub> free)																	
% CH <sub>4</sub>	64.0	49.7	34.7	44.2	43.9	40.8	20.4	40.2	51.0	55.4	g	50.4	44.8	54.5	49.8	46.3	57.7
% C <sub>2</sub>	14.0	11.4	12.0	13.4	14.0	12.5	12.8	5.8	8.0	14.1	g	13.3	10.6	14.7	11.8	9.1	12.9
% C <sub>3</sub>	7.0	7.7	8.9	7.9	7.1	5.6	9.3	2.1	2.0	2.3	g	4.1	5.0	4.1	4.4	3.9	2.7
% CO	14.0	19.3	14.8	19.1	16.6	16.1	17.3	11.7	15.0	23.1	g	22.6	15.8	22.0	22.9	28.4	22.9
% CO <sub>2</sub>	0	11.2	28.4	14.9	18.0	24.2	39.2	37.0	23.0	3.4	g	9.0	23.2	4.5	10.5	11.6	3.8

<sup>a</sup>Coal used in runs HC-1 through HC-7 was exposed to air during grinding and sizing. For subsequent runs, coal has been prepared in an inert atmosphere.

<sup>b</sup>Time-average temperature. Operated at 783 K for 4.6 h; lost bed during shutdown; restarted at 783 K for 1.8 h; dropped to 755 K for 0.8 h; then 705 K for 3.1 h.

<sup>c</sup>Time-average temperature. Operated at 866 K for 3.3 h; dropped to 847 K for 1.1 h; then 815 K for 1.5 h.

<sup>d</sup>Pressure was 2170 kPa for the first 5.9 h and 1894 kPa for the remaining 6.3 h.

<sup>e</sup>Average error in measurement  $\pm 0.021$  kg H<sub>2</sub>/kg maf coal fed.

<sup>f</sup>Effluent gas flow rate was not directly measured; instrument out of range.

<sup>g</sup>Steady-state period was too short to produce yield data.

<sup>h</sup>Oil yields in HC-3 and HC-9 are questionable because of operational, sampling, and analysis problems.

Table 6.2. Summary of hydrocarbonization experiments with pretreated Illinois No. 6 coal

Hydrocarbonization Run No.	HC-23	HC-24	HC-26
Type of fluidized bed <sup>a</sup>	RFB	RFB	RFB
Bed temperature, K	844	844	841
Reactor pressure, kPa	2170/2032 <sup>b</sup>	2170	2170
Coal feed			
Rate, kg/h	2.1	4.3	3.9
Elapsed time, h	13.3	7.7	12.8
Hydrogen feed rate, std m <sup>3</sup> /min	0.57	0.57	0.54
Hydrogen consumption, kg H <sub>2</sub> /kg maf coal	0.03	0.01	-0.01
Yields, wt % of maf coal			
Oil	14.0	24.0	20.8
Gas	18.2	13.7	15.3
Char	67.4	50.4	56.0
Steady-state gas analysis (H <sub>2</sub> and N <sub>2</sub> free)			
% CH <sub>4</sub>	53.9	60.3	60.2
% C <sub>2</sub>	16.6	15.0	13.6
% C <sub>3</sub>	2.1	3.1	2.5
% CO	24.9	14.7	20.2
% CO <sub>2</sub>	2.1	3.1	3.0
% H <sub>2</sub> S	0.5	4.1	0.5

<sup>a</sup>—Recirculating fluidized-bed reactor.

<sup>b</sup>—Reactor pressure was 2170 kPa for first 4.0 h and 2032 kPa for the remaining 9.3 h.

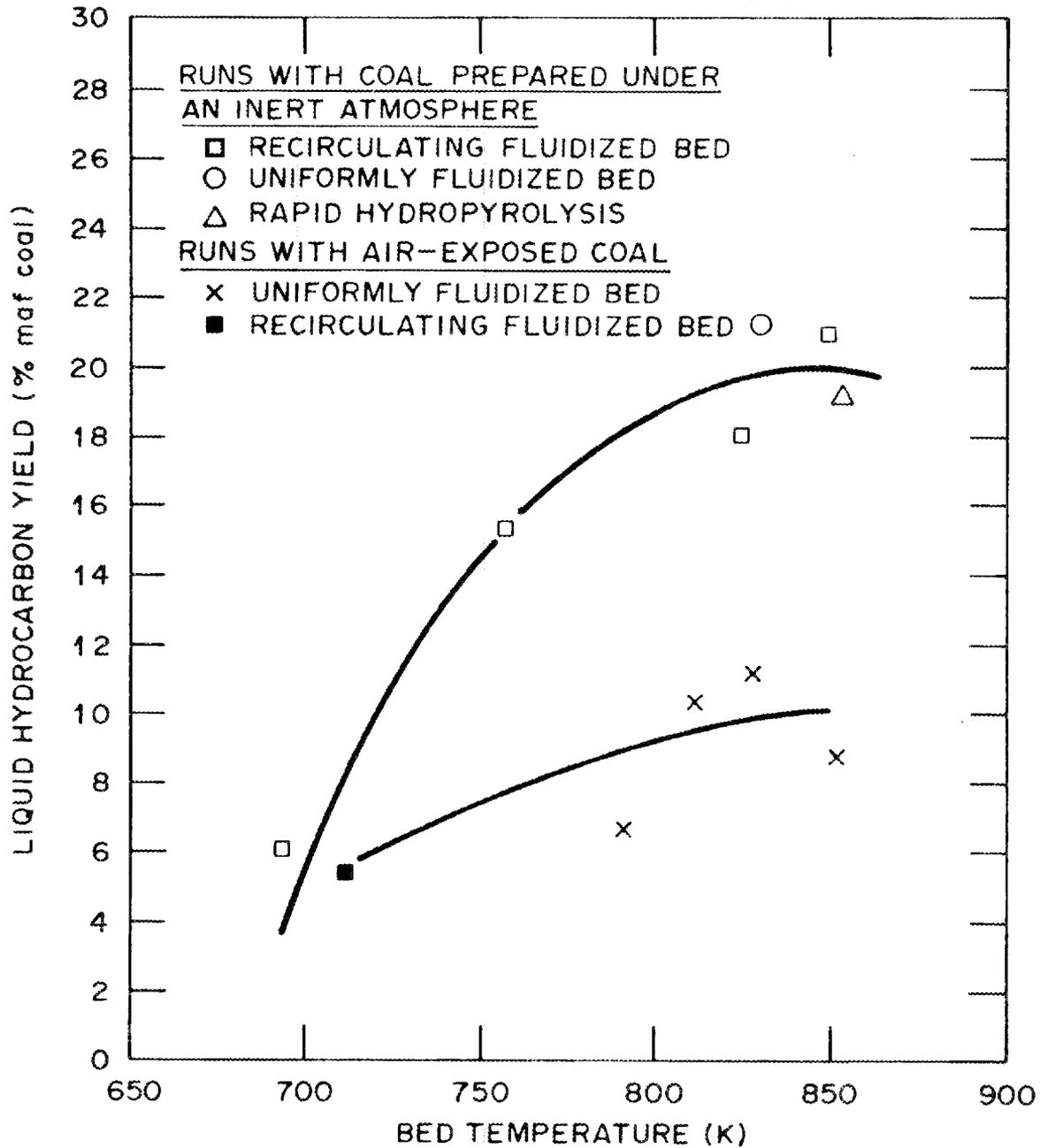


Fig. 6.1. Oil yield for hydrocarbonization runs with Wyodak coal.

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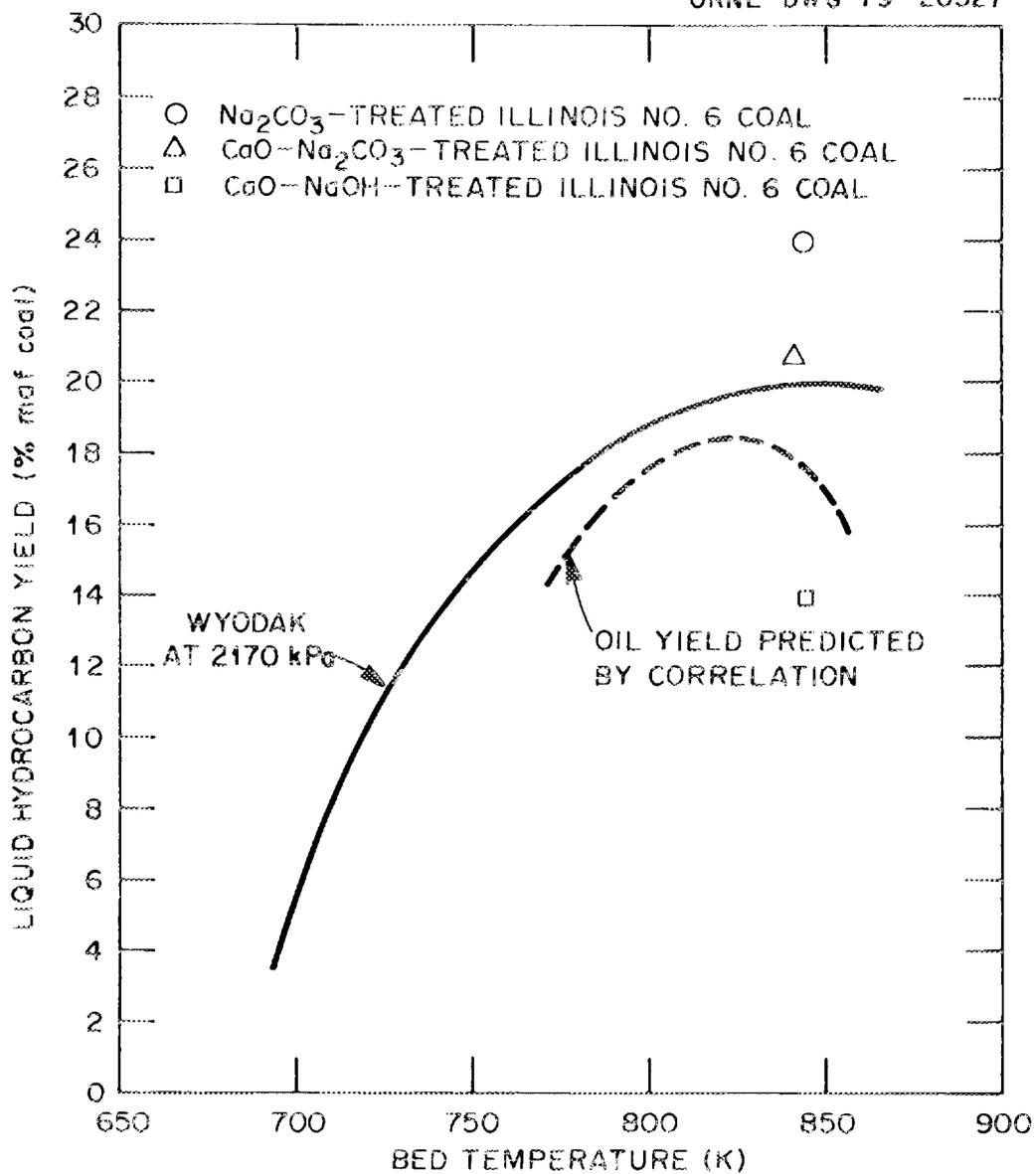


Fig. 6.2. Oil yield for hydrocarbonization runs with treated Illinois No. 6 coal.

As shown in Fig. 6.2, the liquid yields from the three experiments using pretreated Illinois No. 6 coal varied from 14% for the CaO-NaOH pretreatment to 24% for the Na<sub>2</sub>CO<sub>3</sub> pretreatment. The 24% yield exceeded that obtained from Wyodak runs under similar operation conditions and was the highest yield obtained during the program. A liquid yield of 20.8% was obtained using the Na<sub>2</sub>CO<sub>3</sub>-CaO pretreated coal.

The pressure effect may be inferred from data for runs HC-6 and HC-25, which were made using Wyodak coal at a pressure of 1136 kPa. The oil yields from HC-6 (air-exposed coal) and HC-25 were 8 and 18%, respectively. Both yields are 2 or 3% (based on maf coal) lower than the average yields obtained from runs at approximately the same temperature but at a pressure of 2170 kPa. Although the results fall within the scatter of the data for the 2170-kPa runs, they are consistent with earlier data correlations which predict a reduction in liquid yield of ~2% (based on maf coal) with a reduction in hydrogen pressure from 2170 kPa to 1136 kPa.

Yields from three different types of fluidized-bed configurations are also shown in Fig. 6.1. Runs HC-1 through HC-6 and run HC-21 used uniformly fluidized-bed reactors, and run HC-28 used the rapid hydro-pyrolysis reactor. All other runs shown in Fig. 6.1 used a recirculating fluidized bed. Changes in bed configuration did not appear to result in appreciable changes in liquid yield for the small number of experiments and operating conditions studied.

### 6.1.2 Composition of liquid hydrocarbons

Liquid hydrocarbon products from selected runs were characterized by determining ultimate and proximate analysis, specific gravity, viscosity, and simulated boiling point. The scrubber material was used for product characterization since a major portion of the oil produced is collected in this material. Samples were either filtered or centrifuged to remove solids (char) and water before analyses were made. Properties and analyses of the product obtained from experiments with both Wyodak and pretreated Illinois No. 6 coal are given in Table 6.3. Typical

Table 6.3. Properties and composition of oil from hydrocarbonization experiments

	Illinois No. 6		Wyodak		
	run HC-26 (Na <sub>2</sub> CO <sub>3</sub> -CaO-treated)	run HC-24 (Na <sub>2</sub> CO <sub>3</sub> -treated)	run HC-25	run HC-21	run HC-12
Specific gravity	1.07	1.1	1.02	1.04	1.07
Viscosity, Pa·s					
at 311 K	0.05	0.120	0.036	0.018	0.018
at 373 K	0.004			0.003	0.003
Composition, %					
Moisture	0.9	6.8	5.7	1.7	0.7
Ash	0.06	0.7	0.3	<0.05	<0.01
Carbon (maf)	87.1	85.8	84.9	86.9	85.4
Hydrogen (maf)	7.6	7.2	8.3	8.4	7.4
Nitrogen (maf)	1.3	1.2	1.0	0.9	1.0
Sulfur (maf)	1.2	1.5	0.4	0.6	0.3
Oxygen (by difference)	2.8	4.3	5.4	3.2	5.9

simulated\* boiling point curves for the temperature range of 311 to 811 K are shown in Fig. 6.3. The elemental compositions of the products obtained from all runs are quite similar with the exception of the Illinois No. 6 product, which generally contains more sulfur and less oxygen than the Wyodak product, as does the original coal. The viscosity of the Illinois No. 6 product was also generally higher than that of the Wyodak product. The average heating value for the liquid product from Wyodak runs HC-21 and HC-25 was 38.6 MJ/kg (dry basis).

Fractionation of oil from runs HC-21, HC-24, and HC-26 was done by Gel Partition Chromatography, which is a method that was developed at Oak Ridge National Laboratory for the separation of organic mixtures into chemical compound classes using Sephadex LH-20 gel.<sup>6</sup> The results are shown in Table 6.4. Run HC-21 was conducted using Wyodak subbituminous coal, whereas runs HC-24 and HC-26 were conducted using Illinois No. 6 bituminous coal that had been pretreated. Coal for run HC-24 was pretreated with  $\text{Na}_2\text{CO}_3$  in an autoclave, and coal for run HC-26 was pretreated with  $\text{Na}_2\text{CO}_3$  and CaO at atmospheric pressure. The results indicate that the oil products obtained from the two runs made with Illinois No. 6 coal have a similar composition which is considerably different from the composition obtained for Wyodak coal in run HC-21.

In addition, the oil product from run HC-12 was analyzed by gas chromatography-mass spectroscopy for polynuclear aromatic hydrocarbons (PNA), such as benzo(a)pyrene, that are potential biological hazards. The HC-12 oil contained 1.8 mg/g benzo(a)pyrene. Other compounds that were tentatively identified are listed in Table 6.5.

Prior to run HC-21, an activated charcoal trap was installed in the off-gas line downstream of the cold trap to collect volatile components that had not been collected by the scrubber and cold trap. The trap contained three layers of coconut charcoal, with each layer containing ~1 kg of charcoal. The material collected, based on the weight gain

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\*Determined by standard method of test for boiling range distribution of petroleum fractions by gas chromatography. ASTM designation: D2887-73. For material with a final boiling point below 538°C and a vapor pressure sufficiently low to permit sampling at ambient temperature.

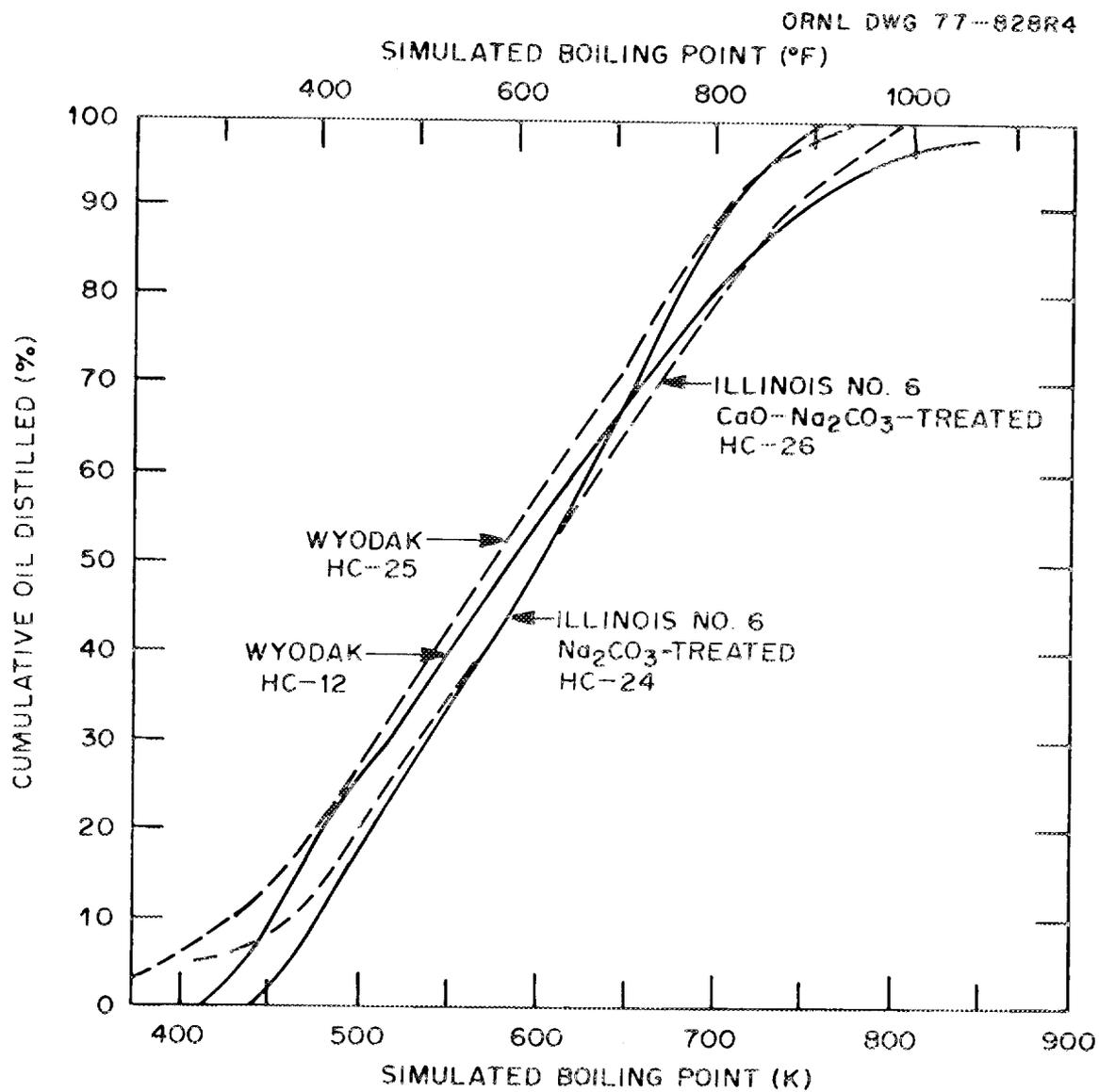


Fig. 6.3. Simulated boiling point curves for oil product from selected hydrocarbonization runs.

Table 6.4. Fractionation of oil from runs HC-21, HC-24, and HC-26 by Gel Partition Chromatography

Fraction <sup>a</sup>	HC-21 (wt %)	HC-24 (wt %)	HC-26 (wt %)
Hexane insolubles	35.0	64.4	66.5
Hydrophilic (polar)	18.5	11.7	8.8
Polymeric (>5000 mol. wt)	10.9	0.4	0.1
Hydrogen bonding	b	2.2	6.6
Aliphatic	10.2	6.7	6.9
Monoaromatic	15.8	2.3	1.4
Di- and triaromatic	12.8	6.1	3.3
Polyaromatic	13.3	4.2	2.1
Residue	c	2.5	0.6

<sup>a</sup>Dry and volatile-free basis. The sum of the fractions total to >100% due to the incomplete removal of the eluting solvents.

<sup>b</sup>None found.

<sup>c</sup>Not determined.

of the charcoal trap, was equivalent to 2 to 3% of the coal (maf) fed. The composition of the material collected was determined by desorption of the charcoal at 700 K and collection of the product in a dry-ice cold trap. The recovered product consisted of an organic phase (~90%) and an aqueous phase (10%). Typical composition and initial and final boiling points for the organic phase collected during runs HC-23 through HC-28 are shown in Table 6.6.

## 6.2 Gas Yields and Composition

Gas effluent composition was continuously analyzed by an on-line gas chromatograph. Periods of steady-state operation were used to determine gas composition. The gas yield was determined from the total off-gas minus the hydrogen content. The water content of the gas effluent was not analyzed because meaningful yields could not be obtained after the water scrubbing and cold trapping process steps. Gas yields and composition were dependent on operating temperature, as described below.

Table 6.5. Direct gas liquid chromatography analysis  
of polynuclear aromatic hydrocarbons  
in oil from run HC-12

Polynuclear aromatic hydrocarbon (tentative identification)	Estimated concentration (mg/g)
Naphthalene	23.6
2-Methyl Naphthalene	15.7
1-Methyl Naphthalene	9.4
Biphenyl	4.2
2,6-Dimethyl Naphthalene	3.4
1,3- and/or 1,6-Dimethyl Naphthalene	3.4
1,5- and/or 2,3-Dimethyl Naphthalene	1.8
1,2-Dimethyl Naphthalene and/or Acenaphthalene	1.5
Acenaphthene	3.1
Fluorene	8.2
9-Methyl Fluorene	1.4
1-Methyl Fluorene	4.8
Phenanthrene	11.4
Anthracene	6.1
2-Methyl Anthracene	2.3
1-Methyl Phenanthrene	1.8
9-Methyl Anthracene	4.6
Fluoranthene	6.1
Pyrene	6.6
Benzo(a)fluorene	4.1
Benzo(b)fluorene	4.6
Benzo(c)phenanthrene	~1.3
Benzo(ghi)fluoranthene	~0.9
Benz(a)anthracene	4.0
Chrysene/Triphenylene	3.0
Benz(b)anthracene	~0.2
Benzo(b and/or j and/or k)fluoranthene	~4.6
Benzo(a + e)pyrenes (incomp. resolved)	3.8
Perylene	0.7
3-Methyl Cholanthrene	1.4
o-Phenylene pyrene and/or Dibenz(a,c and/or a,h)-anthracene	1.9
Picene	0.8
Benzo(ghi)perylene	1.5
Anthanthrene	0.7
Coronene	~1.3
Dibenzo(a,i)pyrene	~0.5
TOTAL.	154.7 mg/g

Table 6.6. Composition<sup>a</sup> of material collected on charcoal trap

Run	Total weight <sup>b</sup> of material collected (g/kg maf coal)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulfur (%)	Initial boiling point (K)	Final boiling point (K)
HC-23	30.2	70.0	7.7	0.06	0.50	388	504
HC-24	30.8	53.0	5.1	0.06	0.19	335	440
HC-25	26.5	82.4	10.1	0.08	0.29	340	431
HC-26	19.6	81.2	9.9	0.10	0.56	317	467
HC-28	22.4	84.5	8.7	0.06	0.57		

<sup>a</sup>Composition of organic phase obtained by desorption of charcoal at 700 K.

<sup>b</sup>Includes some absorbed water.

### 6.2.1 Gas yields

The overall gas yield as a percentage of the maf coal weight is shown as a function of operating temperature in Fig. 6.4. The results show an increase in the gas yield from 15% to 19% (for Wyodak coal prepared in an inert atmosphere) as the operating temperature increased from 700 K to 850 K. The gas yield from Wyodak coal exposed to air before processing was somewhat higher (from 17% to 28%). The use of pretreated Illinois No. 6 coal, the reduction in operating pressure from 2170 kPa to 1136 kPa, and changes in bed configuration did not result in major changes in overall gas yields, as shown in Figs. 6.4 and 6.5, although the effect of these variables can not be fully determined from the limited number of runs performed. The gas yields obtained in these studies are somewhat higher than the value of ~14% predicted by previous correlations.<sup>1</sup>

### 6.2.2 Gas composition

The composition of the gas effluent stream (downstream of the cold trap and charcoal filter) during steady-state operation is given for each experiment in Table 6.7. The composition is given on a carrier-free basis in Tables 6.1 and 6.2. The hydrogen content of the gas is due almost entirely to the hydrogen that is supplied for fluidization and overpressure since very little hydrogen is produced or consumed under the process conditions used in the experiments, as will be discussed in a later section. Also, the nitrogen content of the gas is largely due to the use of nitrogen purge gas. The gas effluent compositions on a H<sub>2</sub>- and N<sub>2</sub>-free basis for Wyodak coal prepared under an inert atmosphere and for pretreated Illinois No. 6 coal are shown as a function of temperature in Figs. 6.6 through 6.9. As shown, the gas contains a high fraction of methane, thus making it valuable as a substitute natural gas. The concentrations of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> + C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub> + C<sub>3</sub>H<sub>8</sub>, and CO increase with temperature over the temperature range of 700 to 850 K, whereas the CO<sub>2</sub> content decreases. Although not shown, the composition of the gas from runs made with air-exposed Wyodak coal exhibits a similar trend. The higher heating value (HHV) of the H<sub>2</sub>- and

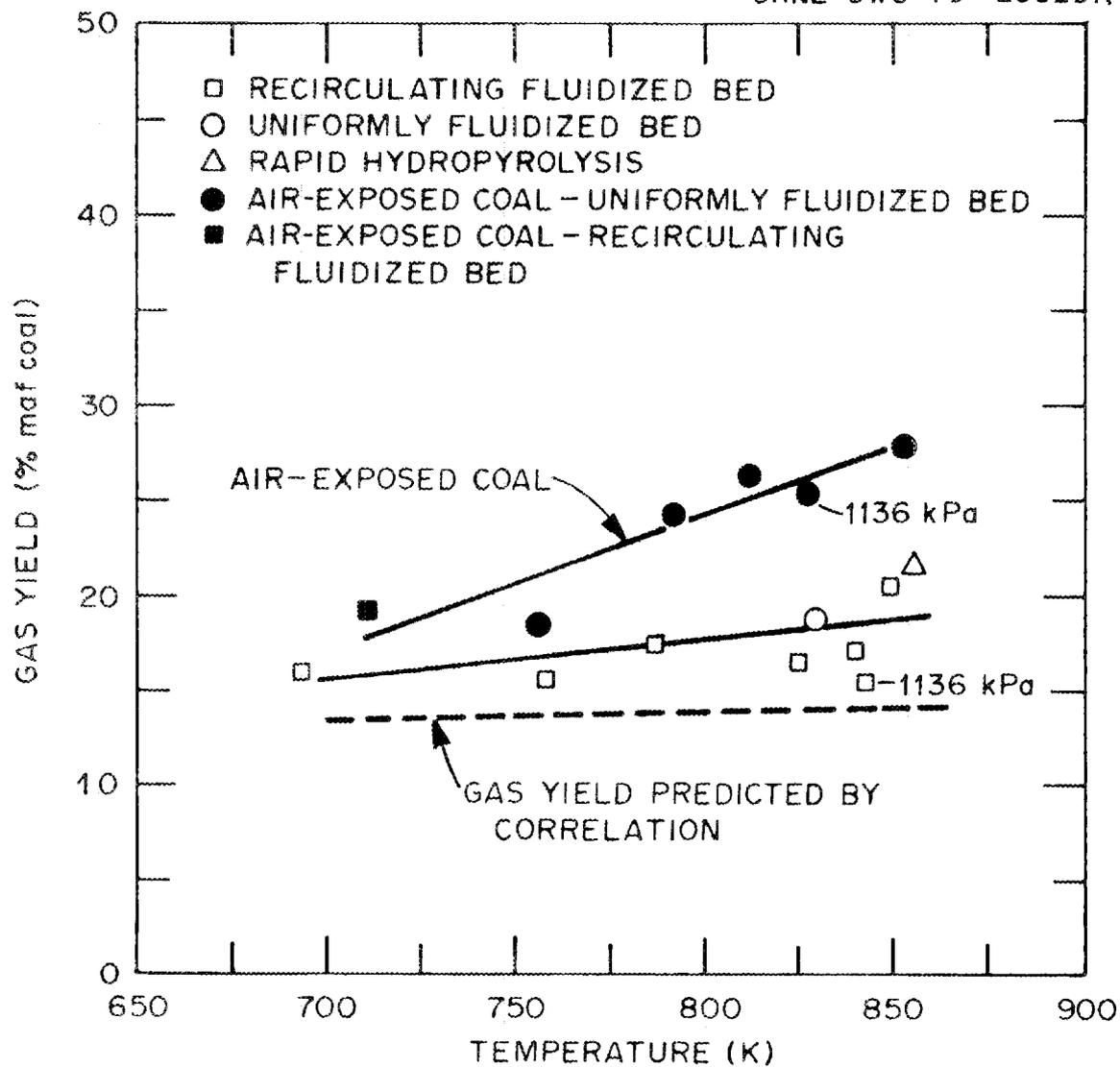


Fig. 6.4. Gas yield for hydrocarbonization runs with Wyodak coal.

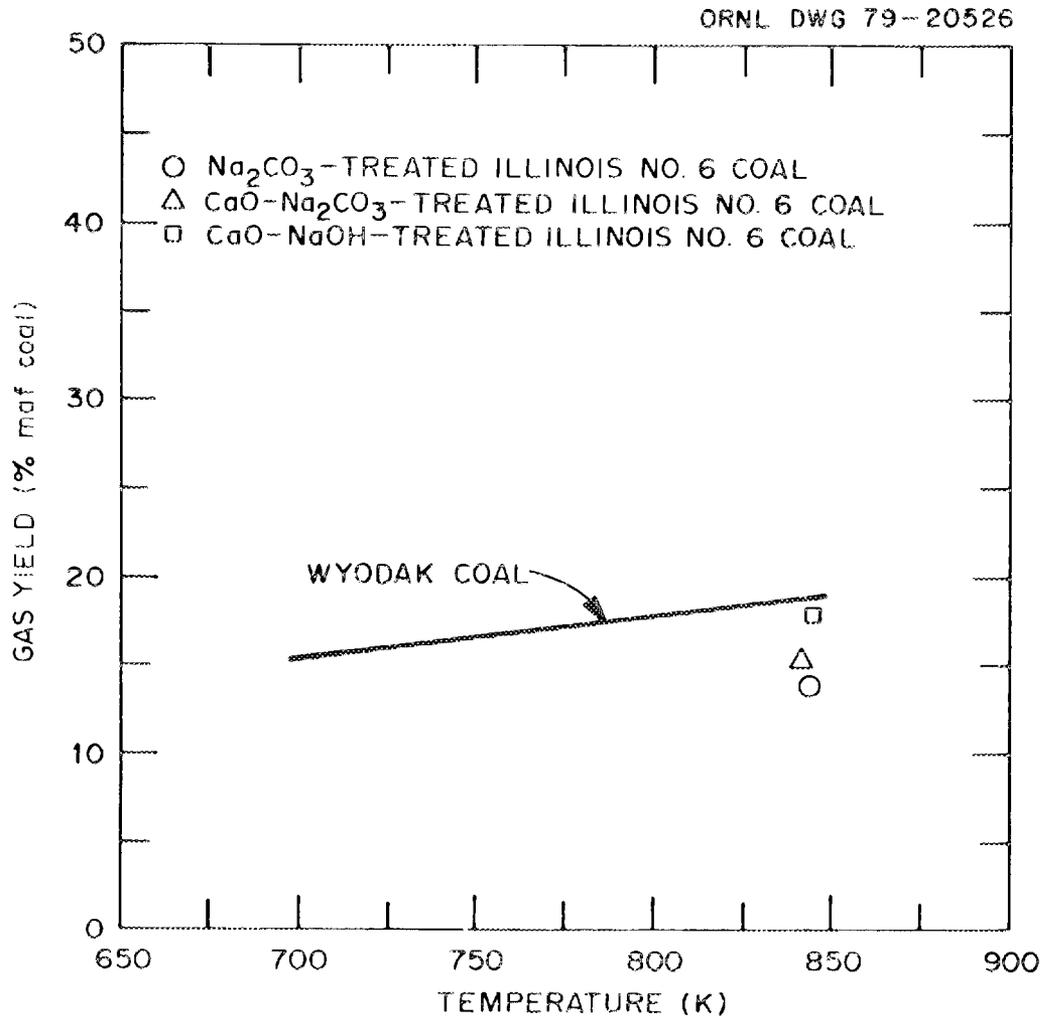


Fig. 6.5. Gas yield from hydrocarbonization runs with treated Illinois No. 6 coal.

Table 6.7. Gas effluent concentration (%) at steady state during hydrocarbonization experiments

Run No.	CH <sub>4</sub>	C <sub>2</sub> <sup>a</sup>	C <sub>3</sub> <sup>b</sup>	CO	CO <sub>2</sub>	H <sub>2</sub> S <sup>c</sup>	H <sub>2</sub>	N <sub>2</sub>
HC-1	0.92	0.20	0.10	0.20	0.00	0.10	93.0	5.57
HC-2	4.47	1.03	0.70	1.74	1.01	0.05	88.0	3.04
HC-3	3.19	1.10	0.82	1.36	2.61	0.10	90.3	0.50
HC-4	5.73	1.74	1.02	2.48	1.93	0.07	86.9	0.10
HC-5	6.33	2.02	1.02	2.40	2.60	0.05	85.6	0.0
HC-6	7.34	2.24	1.01	2.89	4.36	0.14	81.0	1.01
HC-7	1.06	0.67	0.49	0.91	2.05	0.05	94.1	0.66
HC-8	1.24	0.21	0.07	0.36	1.14	0.07	96.8	0.15
HC-9	1.11	0.17	0.04	0.33	0.50	0.02	97.6	0.21
HC-10	0.79	0.20	0.03	0.32	0.05	0.01	96.52	2.09
HC-12	1.74	0.46	0.14	0.78	0.31	0.02	94.79	1.77
HC-13	1.49	0.35	0.17	0.53	0.78	0.02	96.20	0.47
HC-14	2.25	0.61	0.17	0.91	0.19	0.01	95.66	0.22
HC-21	1.57	0.37	0.14	0.72	0.33	0.02	96.60	0.26
HC-23	0.52	0.16	0.02	0.24	0.02	0.005	95.49	3.54
HC-24	0.89	0.22	0.05	0.22	0.045	0.060	98.37	0.16
HC-25	1.52	0.30	0.13	0.93	0.38	0.03	96.55	0.16
HC-26	0.92	0.21	0.04	0.31	0.05	0.007	93.6	4.89
HC-28	1.88	0.42	0.09	0.75	0.13	<u>d</u>	96.51	0.23

<sup>a</sup>Total concentration of C<sub>2</sub>H<sub>4</sub> + C<sub>2</sub>H<sub>6</sub>.

<sup>b</sup>Total concentration of C<sub>3</sub>H<sub>6</sub> + C<sub>3</sub>H<sub>8</sub>.

<sup>c</sup>Near lower limit of sensitivity; accuracy questionable.

<sup>d</sup>Calibration was not satisfactory.

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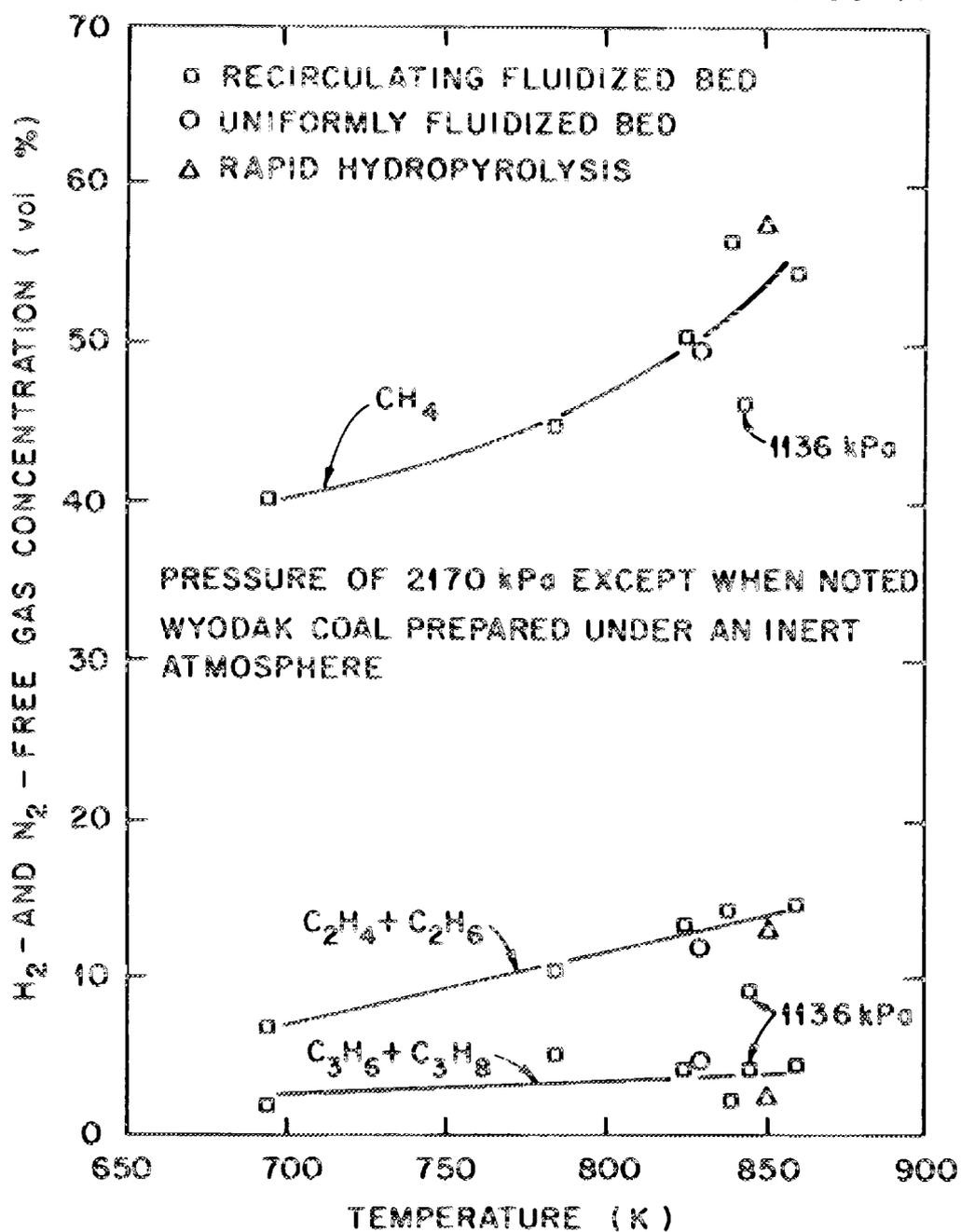


Fig. 6.6. Concentration of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>+C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>6</sub>+C<sub>3</sub>H<sub>8</sub> in the gas product from hydrocarbonization runs with Wyodak coal.

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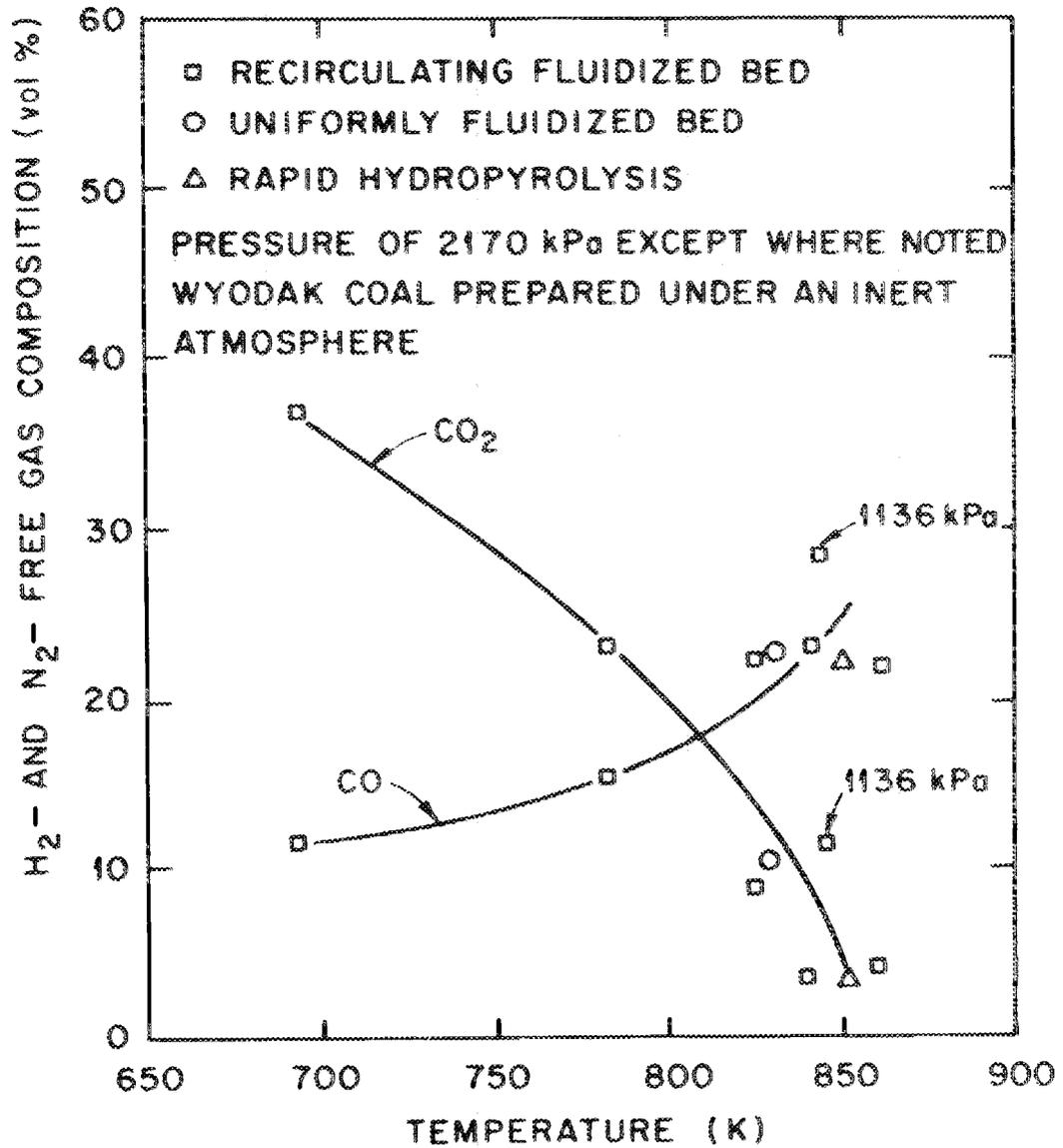


Fig. 6.7. Concentration of CO and CO<sub>2</sub> in gas product from hydrocarbonization runs with Wyodak coal.

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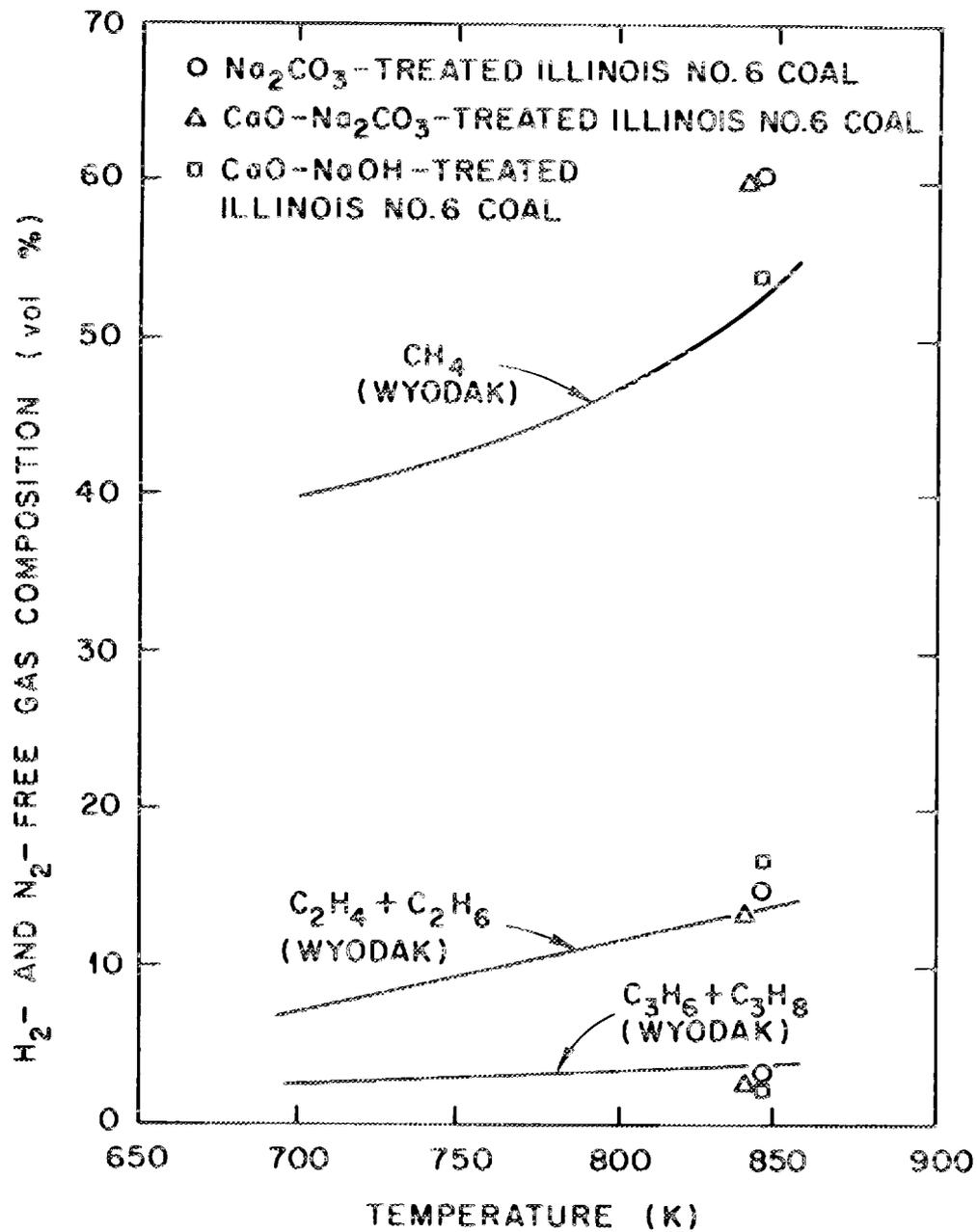


Fig. 6.8. Concentration of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ , and  $\text{C}_3\text{H}_6 + \text{C}_3\text{H}_8$  in the gas product from hydrocarbonization runs with treated Illinois No. 6 runs.

ORNL-DWG 80-94R

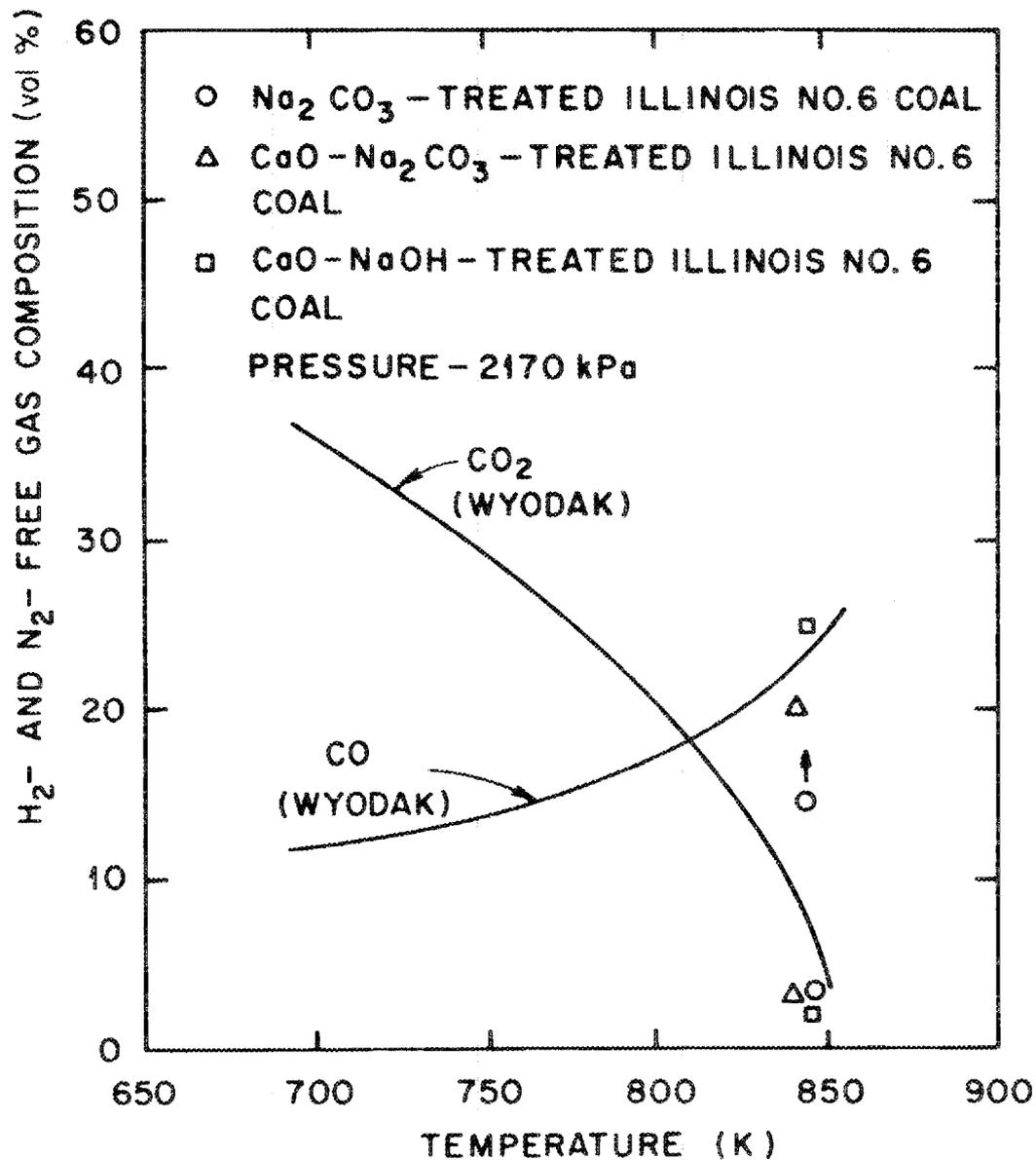


Fig. 6.9. Concentration of CO and CO<sub>2</sub> in gas product from hydrocarbonization runs with treated Illinois No. 6 coal.

$N_2$ -free gas increased with operating temperature, as shown in Fig. 6.10, primarily as a result of the decrease in  $CO_2$  concentration. On a  $H_2$ -,  $N_2$ -, and  $CO_2$ -free basis, the heating value of the gas remained relatively constant at  $\sim 40 \text{ MJ/m}^3$ . No major changes in gas effluent composition resulted from the use of pretreated Illinois No. 6 coal, the reduced pressure, or the bed configuration. The consistent trend in the data as a function of temperature suggests that the components may be at equilibrium; however, calculations indicate that although the trend is toward equilibrium, it has not been reached in these experiments.

### 6.3 Char Yield and Composition

Although char is suitable for gasification or for use as fuel, it is desirable to minimize its production in favor of increased liquid production. The char yield decreases with increased operating temperatures, as shown in Fig. 6.11. In the temperature range of 811 to 850 K, the char yield (maf) from runs with Wyodak coal (prepared under an inert atmosphere) at 2170 kPa made up 45 to 50% of the total maf coal. The char yield for the run with Wyodak coal at 1136 kPa is also shown in Fig. 6.11.

A summary of the char data obtained from the hydrocarbonization experiments is given in Table 6.8. In general, the char contains a lower moisture content (<1%) and a higher ash content than the original coal. For Wyodak experiments at  $\sim 850 \text{ K}$ , the ash content of the char (moisture-free basis) was  $\sim 13$ , as compared to  $\sim 7\%$  for the original coal. On a maf basis, the carbon content and heating value of the char increases with increased operating temperature, whereas the volatile matter content decreases, as shown in Fig. 6.12. Wyodak char produced at a temperature of 850 K has a heating value of  $\sim 31 \text{ MJ/kg}$  (dry basis) as compared to  $27 \text{ MJ/kg}$  for the coal, and the char contains  $\sim 10\%$  volatile matter (maf) as compared to  $47\%$  volatile matter (maf) in the original coal. The sulfur content of the char from the Wyodak runs averaged  $\sim 0.35\%$  (maf) and did not appear to be temperature dependent under the conditions studied, as shown in Fig. 6.12.

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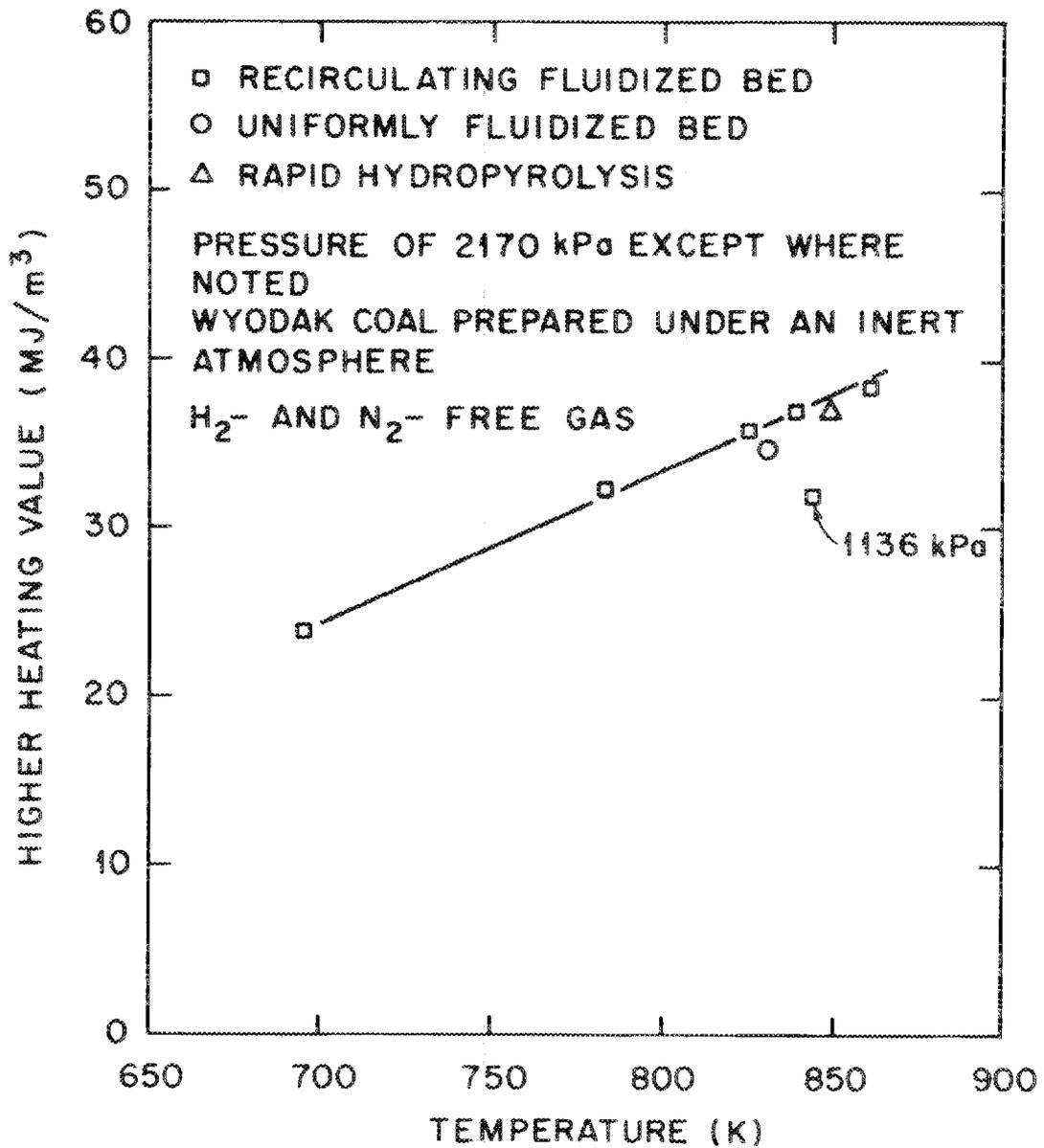


Fig. 6.10. Heating value of gas product from hydrocarbonization runs with Wyodak coal.

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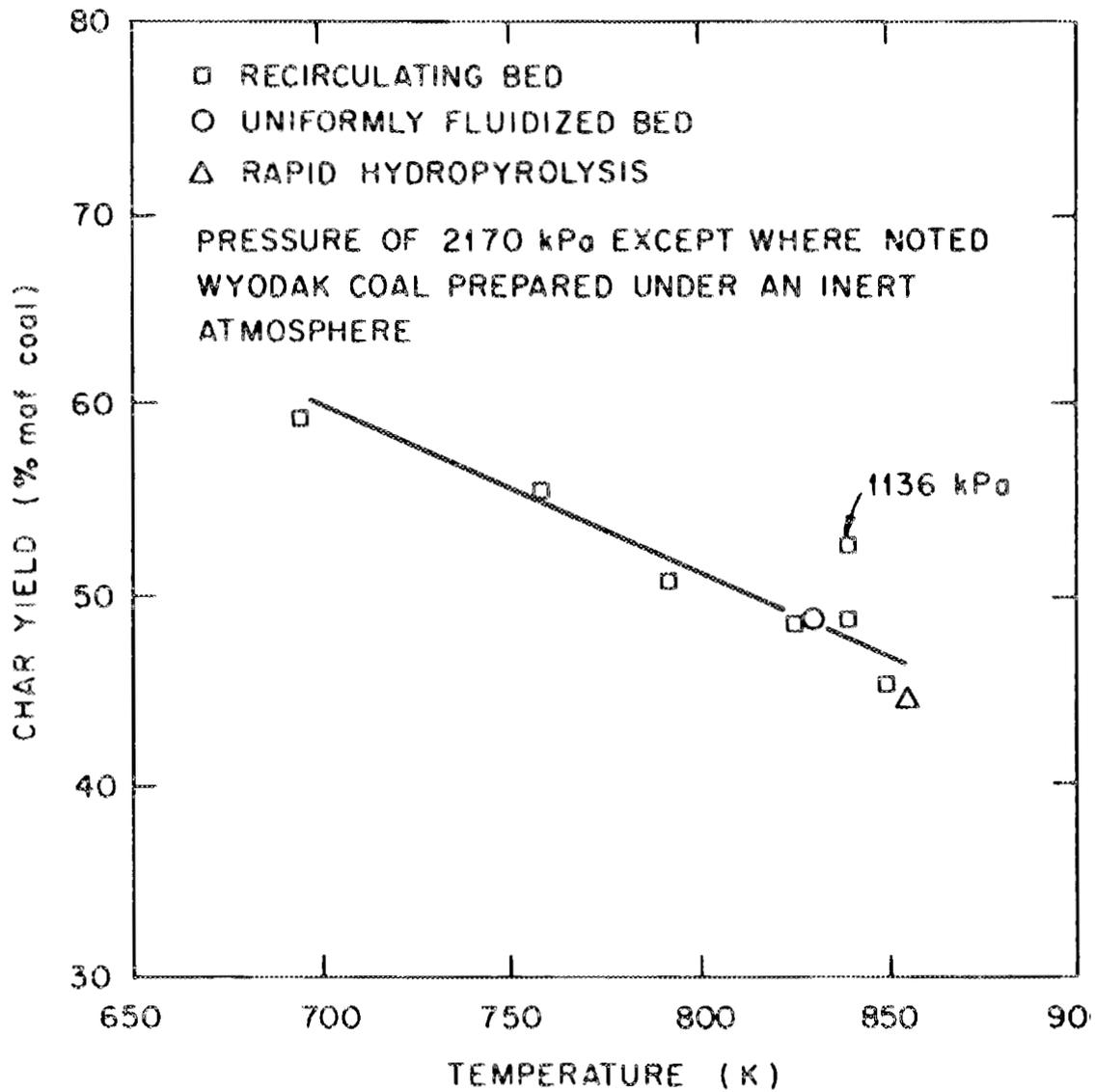


Fig. 6.11. Char yield from hydrocarbonization runs with Wyodak coal.

Table 6.8. Summary of char data

Run no.	Temperature (K)	Ash, dry basis (%)	Volatile matter, maf (%)	Carbon, maf (%)	Sulfur, maf (%)	Heating value (MJ/kg)
<u>Wyodak coal,<sup>a</sup> 2170 kPa</u>						
HC-8	694	11.4	17.4	86.7	0.45	30.3
HC-13	758	10.5	15.8	89.0	0.33	30.9
HC-9	786	11.4	11.2	91.9	0.36	31.1
HC-12	825	11.8	10.2	92.3	0.26	31.4
HC-21	830	12.2	12.8	92.8	0.20	31.0
HC-10	839	13.6	9.28	92.3	0.47	30.6
HC-14	850	12.4	9.94	91.9	0.33	31.0
HC-28	854	13.6	8.1	93.7	0.59	31.0
<u>Wyodak coal (air-exposed), 2170 kPa</u>						
HC-7	711	9.7	18.3	87.5	0.33	31.0
HC-3	761	10.1	19.1	87.3	0.29	30.3
HC-5	791	10.6	14.4	89.6	0.27	30.7
HC-4	811	12.4	13.2	91.1	0.30	30.9
HC-2	827	12.2	14.9	91.6	0.23	30.6
HC-1	852	14.7	13.2	92.6	0.60	30.1
<u>Wyodak coal, 1136 kPa</u>						
HC-6	827	10.4	14.6	89.8	0.31	31.0
HC-25	844	11.4	12.5	91.3	0.34	31.6
<u>Treated Illinois No. 6 coal, 2170 kPa</u>						
HC-26	841	28.9	12.5	98.6 <sup>b</sup>	3.90	26.8
HC-23	844	29.0	18.6	95.0	2.18	25.3
HC-24	844	27.7	12.3	98.8 <sup>b</sup>	3.11	27.9

<sup>a</sup>Prepared under an inert atmosphere.

<sup>b</sup>The apparent high carbon content may be due to interference of  $\text{Na}_2\text{CO}_3$  pretreatment with the carbon analysis.

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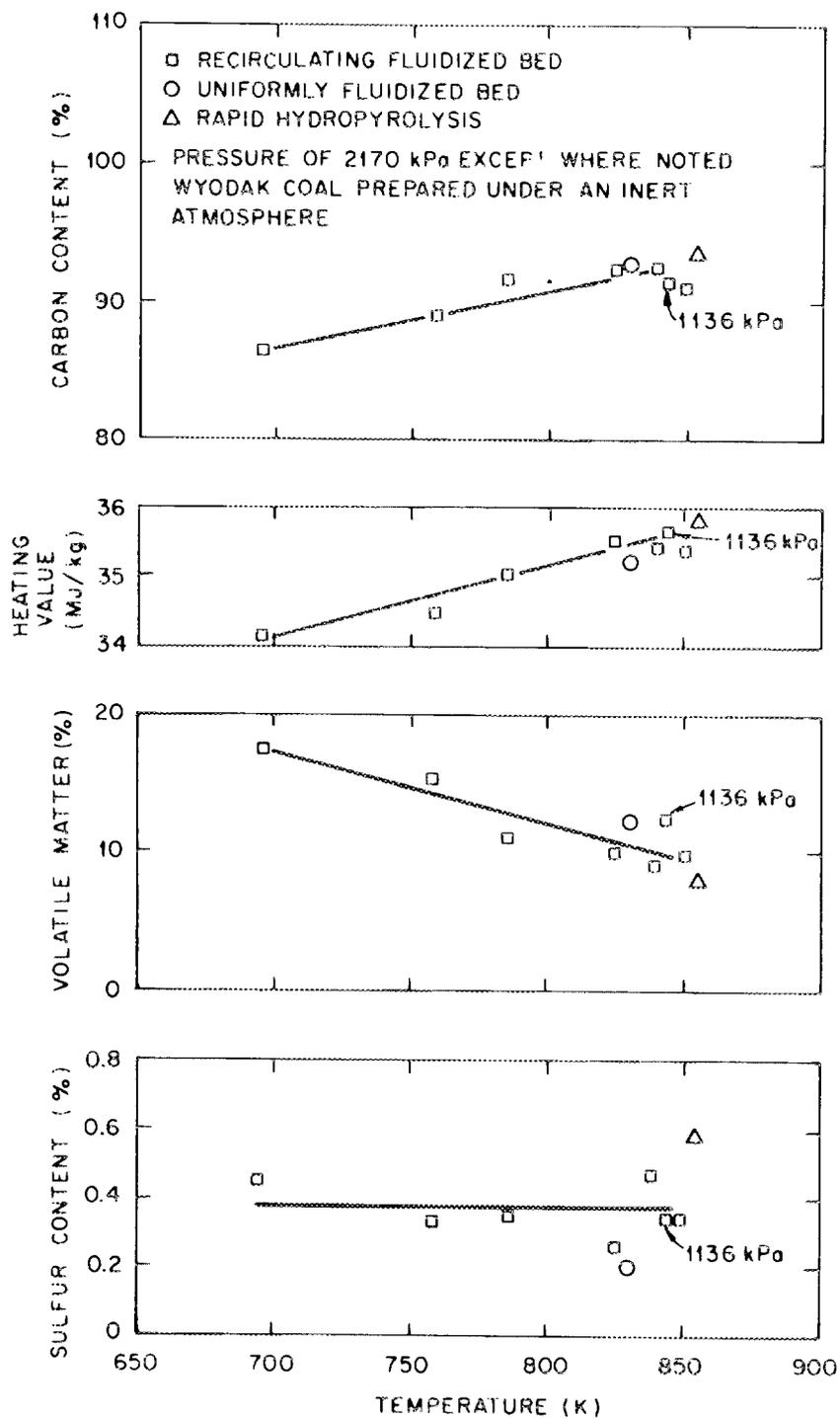


Fig. 6.12. Char composition (maf basis) for experiments with Wyodak coal.

## 6.4 Composition of Aqueous Scrubber Solution

In each of the hydrocarbonization experiments, ~20  $\mu$  of demineralized water was used for scrubbing the off-gas stream from the hydrocarbonization reactor. This water, plus water collected from the process, was continuously recycled during the run, resulting in the accumulation of a variety of organic compounds in the aqueous phase. Detailed analyses of the aqueous scrubber solutions produced in typical runs with Wyodak subbituminous coal are presented in Tables 6.9 to 6.11. (These analyses were obtained from another development program at ORNL.) Table 6.9 gives the concentrations of carbon, phenols, thiocyanate, ammonia, nitrate, and phosphate for runs HC-3 through HC-14. Table 6.10 lists organic compounds that were identified in the scrubber water from run HC-6. Analyses were performed by gas and liquid chromatography. Table 6.11 presents detailed characteristics of scrubber water from run HC-4, including the acidity, amount of suspended solids, concentration of phenolic compounds, and a detailed trace element analysis.

Table 6.9. Analyses of scrubber water from the hydrocarbonization of Wyodak coal

Run	Concentration ( $\mu\text{g}/\text{cm}^3$ )						
	Total carbon	Total organic carbon	Total phenols	Thio-cyanate	Ammonia	Nitrate	Phos-phate
HC-3	9,100	8,100	9,150	427	2,580	7,180	6
HC-4	9,100	8,100	11,225	212	5,600	6,470	7
HC-5	10,200	8,300	9,850	200	5,800	11,600	2.4
HC-6	20,000	18,000	10,000	350	6,900	6,475	4
HC-8	10,000	8,200	6,000	330	6,600	10,500	5
HC-9	3,820	3,200	2,460	400	970	3,750	11
HC-10	6,780	5,680	6,550	620	2,900	5,240	5
HC-11	4,500	3,800	3,420	330	1,200	3,970	3.6
HC-12	11,370	10,200	9,725	435	3,040	5,670	2.9
HC-13	8,800	7,500	8,270	424	5,600	10,080	6.5
HC-14	7,700	6,200	8,820	820	3,050	6,575	4.8

Table 6.10. Identified soluble organic compounds  
in scrubber water from run HC-6

Compound	Concentration ( $\mu\text{g}/\text{cm}^3$ )	
	By gas chromatography	By high-pressure liquid chromatography
Dimethyl- or ethyl-substituted hydroxypyridine	20	
Methyl carbazole	4	
Hydroxypyridine	10	
Methylhydroxypyridine	10	
Catechol		~1700
Hydroquinone	4	7
Resorcinol	29	30
Methylresorcinol		~2000
Orcinol		~2000
Methylcatechol	11	30
C <sub>2</sub> -substituted dihydroxybenzene	<1	
C <sub>3</sub> -substituted dihydroxybenzene	<1	
C <sub>4</sub> -substituted dihydroxybenzene	<1	

### 6.5 Trace Element Distribution

The trace element distribution was determined for run HC-12 by spark source mass spectrometry. Table 6.12 shows the trace element content in the coal, char, scrubber water, and oil. Coal and char were ashed at both low and high temperature with virtually no difference in the results. After ashing, they were mixed with high-purity silver powder containing 15 separated stable isotopes as internal standards. National Bureau of Standards standard reference materials 1632 (coal) and 1633 (fly ash) were used to determine relative sensitivity factors. Normal isotopic europium was also present and was used to measure the remaining elements. A total of 53 elements were reported, ranging in concentration from 50,000 down to <1  $\mu\text{g}$  per gram. Oil and aqueous samples were wet ashed with

Table 6.11. Characteristics of scrubber water from run HC-4

Acidity	pH = 8.82
Suspended solids, $\mu\text{g}/\text{cm}^3$	64
Phenolic compounds, $\mu\text{g}/\text{cm}^3$	
Phenol	10,600
o-cresol	730
m- and p-cresol	2,560
Catechol	290
Trace elements, $\mu\text{g}/\text{cm}^3$	
Ag	<0.5
Al	1.0
As	ND <sup>a</sup>
B	0.3
Ba	0.1
Be	0.01
Ca	5
Cd	<0.5
Co	<0.2
Cr	0.5
Cu	0.1
Fe	1
Hg	<sup>b</sup>
K	<sup>3</sup>
Li	<0.2
Mg	<sup>3</sup>
Mn	ND <sup>a</sup>
Mo	0.3
Na	10
Nb	0.3
Ni	3
P	3
Pb	ND <sup>a</sup>
S	20
Sb	ND <sup>a</sup>
Se	ND <sup>a</sup>
Si	20
Sn	ND <sup>a</sup>
Sr	ND <sup>a</sup>
Ta	ND <sup>a</sup>
Te	ND <sup>a</sup>
Ti	2
U	ND <sup>a</sup>
V	ND <sup>a</sup>
Zn	0.5

<sup>a</sup>ND = not detected.

<sup>b</sup>Not measured.

Table 6.12. Trace element measurements for Wyodak coal and hydrolysis products by mass spectroscopy

Trace element concentration (µg/g)							Trace element concentration (µg/g)							
Element	oil						Analytical precision (%)	Element	oil					
	Coal	Char	Scrubber water <sup>a</sup>	Including char carry-over	Char-free basis <sup>b</sup>				Coal	Char	Scrubber water <sup>a</sup>	Including char carry-over	Char-free basis <sup>b</sup>	Analytical precision (%)
Al	20,000	60,000	1	160	--	+50	Nb	3	6	0.01	1	0.8	+50	
As	3	8	0.004	0.2	--	+50	Ni	5	10	1	7	7	+20	
An	<1	<1	<0.01	<0.1	<0.1	+50	Os	<1	<1	<0.01	<0.1	<0.1	+50	
B	880	2,000	0.5	0.2	--	+50	P	200	500	0.2	6	--	+50	
Ba	510	1,570	0.4	10	--	+20	Pb	3	7	0.003	0.2	--	+50	
Br	6	16	0.02	0.1	--	+50	Pd	<1	<1	<0.01	<0.1	<0.1	+50	
Ce	8	16	0.001	0.1	--	+50	Pt	<1	<1	<0.01	<0.1	<0.1	+50	
Cd	0.2	0.9	<1	0.1	0.07	+20	Rb	<1	<1	<0.01	<0.1	<0.1	+50	
Co	1	3	0.03	0.2	0.1	+50	Re	<1	<1	<0.01	<0.1	<0.1	+50	
Cr	7	18	0.1	3	2.5	+20	Rh	<1	<1	<0.01	<0.1	<0.1	+50	
Cs	<1	<1	<0.01	<0.1	<0.1	+50	Ru	1	3	<0.01	<0.1	<0.1	+50	
Cu	9	17	0.06	2.5	2.0	+20	Sb	5	14	0.001	0.02	--	+50	
Fe	1,700	3,800	1	95	--	+20	S	1,000	800	6	100	80	+50	
Ga	9	25	0.008	0.1	--	+50	Si	5,000	>10,000	0.5	400	<80 <sup>c</sup>	+50	
Ge	1	3	<0.01	<0.1	<0.1	+50	Sn	3	5	0.01	0.4	0.25	+50	
Hf	<1	<1	<0.01	<0.1	<0.1	+50	Sr	320	490	0.1	4	--	+20	
Hg	<1	<1	<0.01	<0.1	<0.1	+50	Te	1	3	<0.01	0.2	0.1	+50	
In	0.2	0.7	<1	0.1	0.08	+20	Th	<1	<1	<0.1	<0.1	<0.1	+50	
Ir	1	3	<1	<1	<1	+50	Ti	260	630	0.1	30	10	+50	
K	40	70	0.1	0.3	--	+50	Tl	0.3	0.4	0.02	0.1	0.1	+20	
La	16	31	<0.001	0.04	--	+50	U	<1	<1	<0.01	<0.1	<0.1	+50	
Mg	5,000	15,000	7	200	--	+50	V	20	36	0.02	0.07	--	+50	
Mn	10	30	0.01	1	--	+50	Y	3	10	<0.001	0.1	--	+50	
Mo	0.2	1.1	0.01	0.1	0.07	+20	Zn	6	14	0.06	1.5	1.1	+20	
Na	120	360	0.2	6	--	+50	Zr	10	21	0.3	7	7	+50	

<sup>a</sup>Includes suspended solids.

<sup>b</sup>Computed from ash balance, assuming all 0.39% ash in oil is derived from char (12.2% ash). Dashes are entered for concentrations calculated to be negative, which apparently are very low.

<sup>c</sup>Probably zero, since silicon, like aluminum, would remain in the char as a refractory oxide.

$\text{HNO}_3/\text{H}_2\text{O}_2$  and then spiked with a multielement-separated isotope mixture. The samples were then ashed to completely remove organics, redissolved in  $\text{HNO}_3$ , and dried on graphite electrodes. Detection limits were lower because of sample concentration (2 ml of oil and 10 ml of aqueous), and elements concentrations as low as 0.1  $\mu\text{g/g}$  were reported for the oil and 0.01  $\mu\text{g/g}$  for the aqueous sample. Europium was again used to report those elements not available for isotope dilution. Precision for isotope dilution measurements was estimated to be  $\pm 20\%$ ; precision using europium was estimated to  $\pm 50\%$ .

### 6.6 Hydrogen Utilization

In the phase I report,<sup>1</sup> the available results for hydrogen utilization in hydrocarbonization processes were found to be a function of pressure, temperature, and residence time of the char in the reactor and could be described by the following equation:

$$\underline{H} = 3.1089 \times 10^{-5} \underline{TP} - 0.02066 \underline{P} + 0.39356 \underline{P}^{1/2} + 0.04492\underline{\theta} - 5.4816 ,$$

where

- $\underline{H}$  = lb  $\text{H}_2$ /lb maf coal x 100;
- $\underline{T}$  = temperature,  $^\circ\text{C}$ ;
- $\underline{P}$  = partial  $\text{H}_2$  pressure, psia;
- $\underline{\theta}$  = residence time, min.

The data correlation is shown in graphical form in Fig. 6.13. As shown, there is a net production of hydrogen by hydrocarbonization at low pressures, with increased hydrogen utilization at increased pressure.

In the bench-scale hydrocarbonization studies described in this report, operating conditions of 2170 kPa and 700 to 850 K were in the range at which hydrogen utilization was near zero. Hydrogen utilization, which is shown as a function of temperature in Fig. 6.14, was determined by measuring the difference between the hydrogen input and output throughout the experiment. This method is sensitive to small errors in flow, and hydrogen concentration measurements and high accuracies are difficult to achieve. The results are, however, in reasonable agreement with the data correlation.

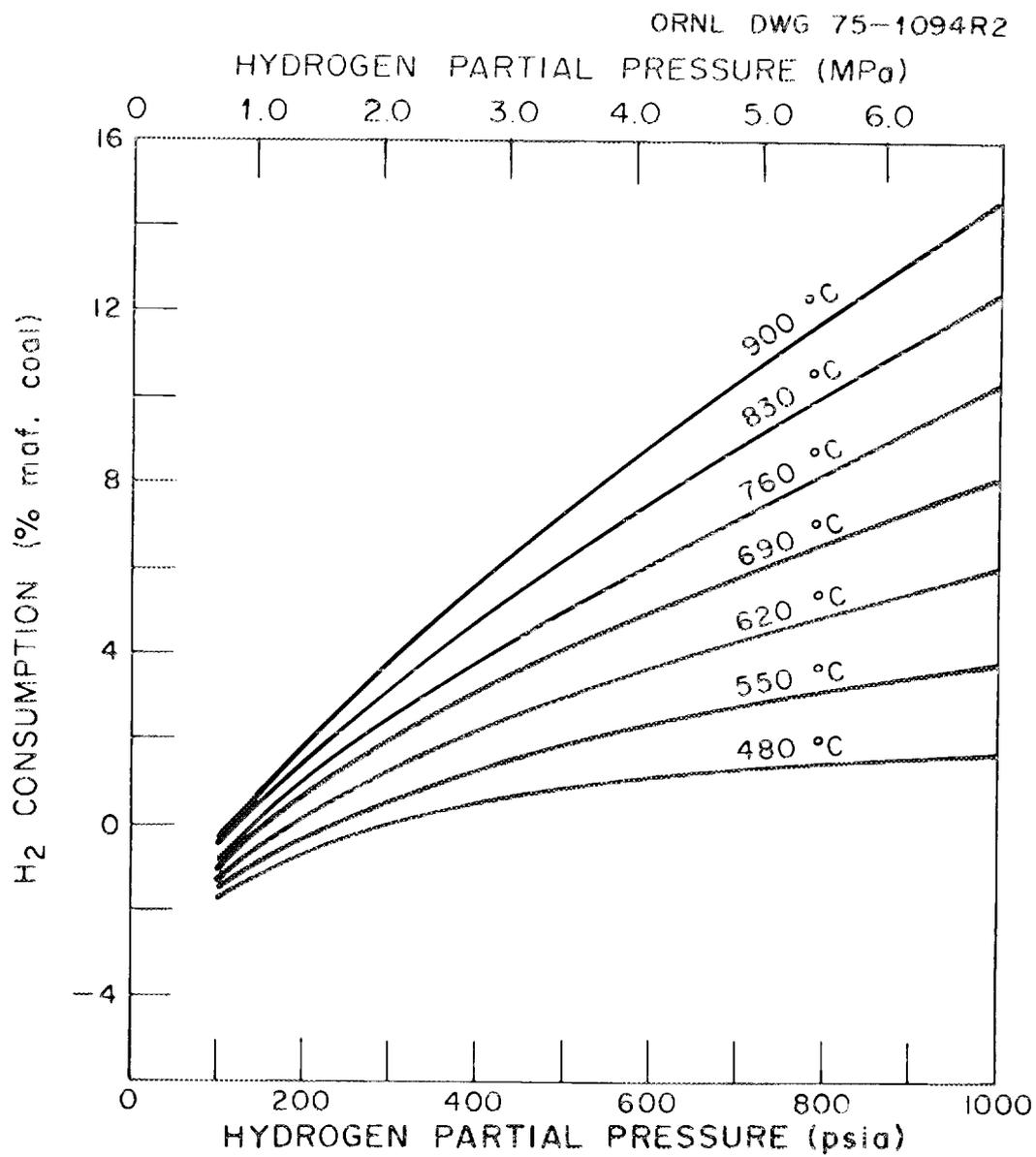


Fig. 6.13. Hydrogen consumption from 10-min residence time in a fluidized-bed reactor.

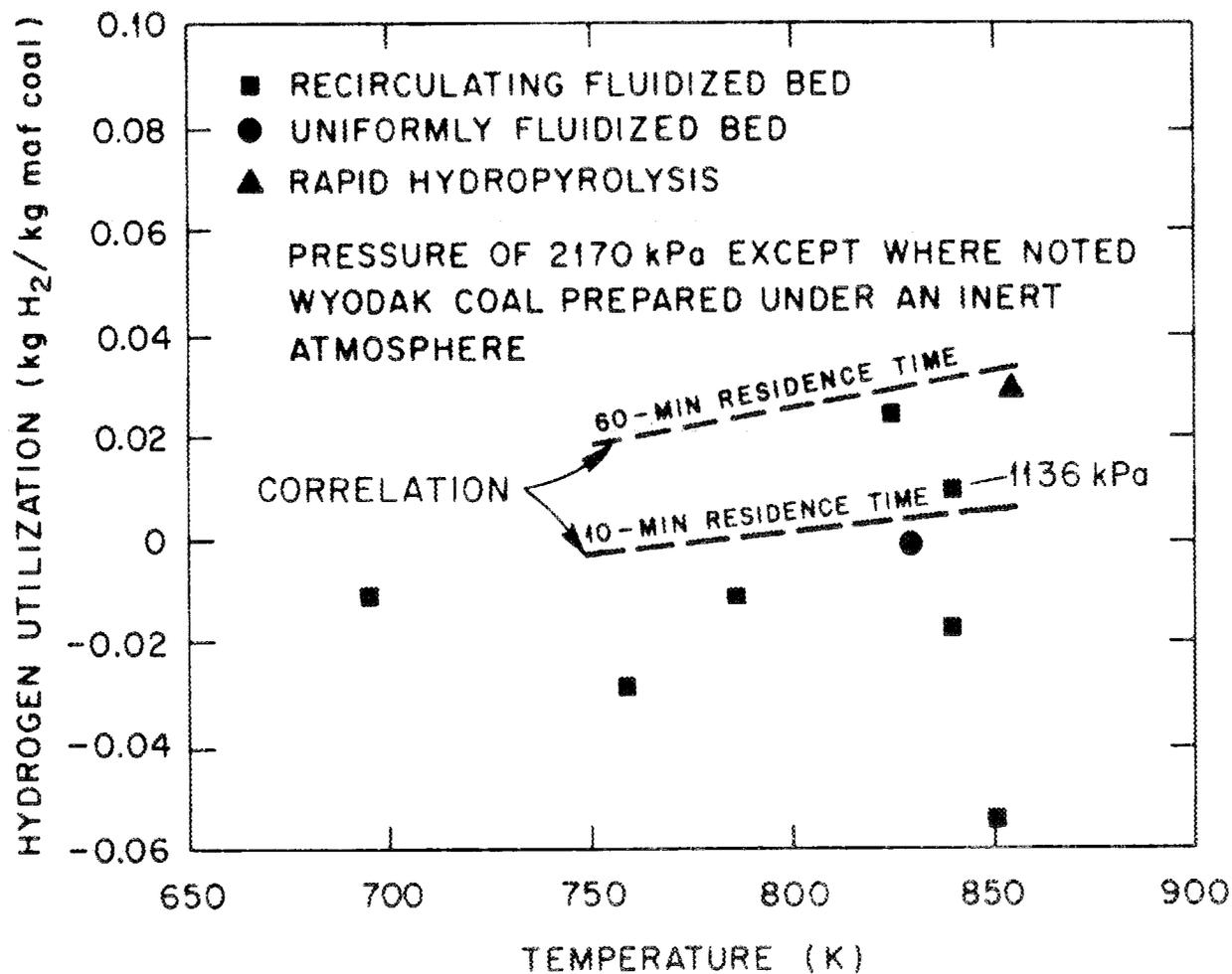


Fig. 6.14. Hydrogen utilization for runs with Wyodak coal.

## 6.7 Material Balances

Components for which material balances were routinely prepared are carbon, ash, sulfur, and an overall mass balance for material in and out of the system. The results of these balances are summarized in Table 6.13. Consistent closure of material balance is difficult to achieve. In general, more emphasis was placed on the measurement of oil and gas yields than on complete material balance closure. Data from runs with unaccountably poor material balances were not used. The overall material balance for most runs was in the range of  $100 \pm 5\%$ . Runs HC-9 and HC-14 had material balances well above 100% due to inleakage of water through the scrubber pump seal. Errors in the overall material balance were due primarily to errors in scrubber water makeup due to pump seal leakage. Failure of rupture discs in some of the runs resulted in the loss of char from the system. Errors due to scrubber water should not significantly affect other balances or yields. Carbon and ash balances were consistently low; carbon balances averaged  $\sim 95\%$  and ash balances averaged  $\sim 90\%$  for the experiments. The reason for these consistently low balances was not determined.

Closure of the sulfur material balance was not made because of difficulties in measuring the quantity in the gas stream, since part of the sulfur-containing gases was removed by the scrubber and the amount remaining in the off-gas was near the lower limit of detection of the gas chromatograph. Sulfur recovery as a percentage of the sulfur fed was determined for char and oil (Table 6.13), and the remaining sulfur was assumed to be in the gas phase.

Direct measurement of the water produced in the process was not made because of the use of the water scrubber and difficulties in separating water from the products and washes used for cleanup. Within the errors of the material balances, water can be obtained from the difference in the weight of the coal and the char, oil, and gas products. A typical distribution of the major elements in the process has been calculated as shown in Fig. 6.15 by using average values for yields and composition of products from experiments conducted with Wyodak coal at  $\sim 839$  K. Only 74% of the nitrogen and 66% of the sulfur are accounted for in the

Table 6.13 Summary of material balances for hydrocarbonization experiments

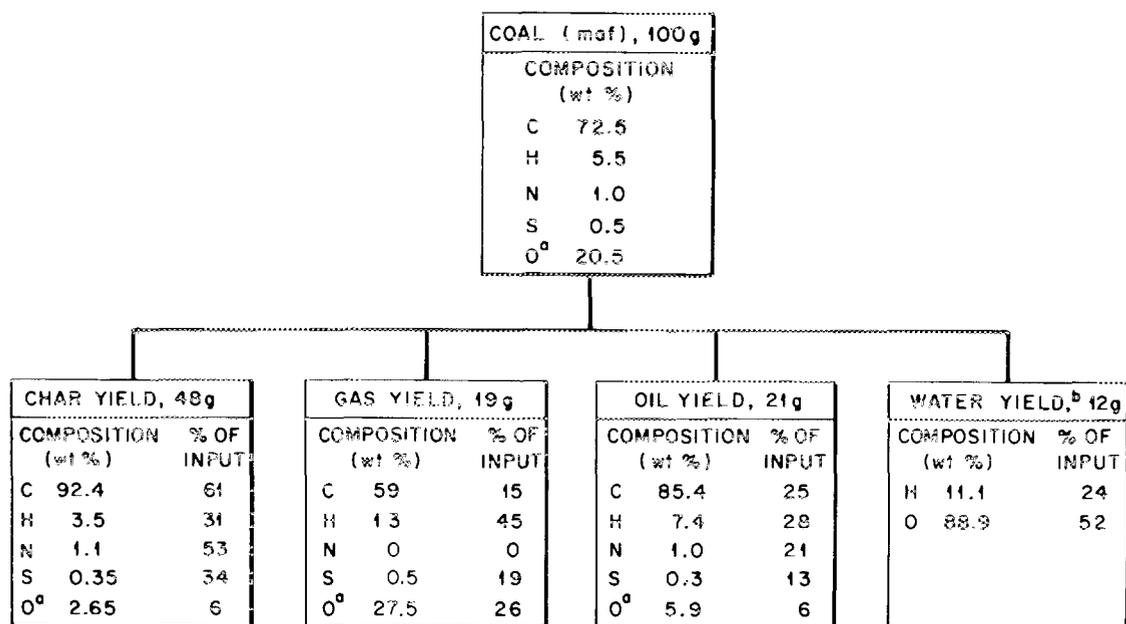
Run number HC-	1	2	3	4	5	6	7	8	9	10	11 <sup>a</sup>	12	13	14	21	23	24	25	26	28
Carbon recovery, % of carbon fed																				
in char	51.5	51.3	70.3	66.5	63.2	66.2	73.3	71.4	64.2	62.2	--	61.3	70.3	58.4	59.2	83.0	60.1	66.0	62.7	57.4
in oil	11.7	14.3	14.7	13.0	8.4	10.1	6.7	7.0	3.1	15.4	--	17.8	13.4	18.5	23.8	11.0	25.0	28.8	21.7	22.5
in gas	<u>29.0</u>	<u>22.8</u>	<u>13.5</u>	<u>22.4</u>	<u>20.3</u>	<u>19.7</u>	<u>13.0</u>	<u>9.8</u>	<u>12.9</u>	<u>17.3</u>	--	<u>14.3</u>	<u>11.7</u>	<u>18.4</u>	<u>13.9</u>	<u>15.1</u>	<u>10.4</u>	<u>11.3</u>	<u>12.2</u>	<u>18.8</u>
Overall carbon recovery	92.2	88.4	98.5	101.9	91.9	96.0	93.0	88.2	80.2	94.9	--	93.4	95.4	96.3	96.9	109.1	95.5	98.1	96.6	98.7
Sulfur recovery, % of sulfur fed																				
in char	52.0	20.9	41.0	38.0	44.0	42.0	50.0	45.0	37.5	44.0	--	27.0	40.5	32.7	21.2	87	42.0	35.6	54.0	62.0
in oil	7.1	5.7	7.4	4.9	3.4	4.4	3.2	4.7	4.6	2.5	--	10.5	7.3	10.1	16.1	13 <sup>b</sup>	11.0	13.0	5.9	12.7
in gas <sup>b</sup>	41	74	52	57	53	54	47	50	58	53	--	62	52	57	63		47	51	40	25
Ash recovery, % of ash fed	90.1	71.9	92.4	97.3	79.1	88.6	93.8	91.3	86.9	94.4	--	92.0	89.7	91.5	91.5	87.0	98.0	93.4	79.7	101.4
Overall, % of mass charged	--	87.7	--	--	100.8	95.9	94.9	101.2	147.6 <sup>c</sup>	104.4	--	93.4	98.2		103.0	98.0	98.0	102	99.9	94.6 <sup>d</sup>

<sup>a</sup>Steady-state period too short to produce yield data.

<sup>b</sup>By difference.

<sup>c</sup>Includes influx of water from scrubber pump seal.

<sup>d</sup>Approximately 4 % of scrubber water was lost due to seal leakage.



<sup>a</sup> OXYGEN DETERMINED BY DIFFERENCE.

<sup>b</sup> WATER YIELD DETERMINED BY DIFFERENCE.

#### MATERIAL BALANCE

COMPONENT	% OF INPUT
CARBON	101
HYDROGEN	128 (equivalent to a hydrogen utilization of 0.015 kg H <sub>2</sub> /kg maf coal)
NITROGEN	74
SULFUR	66 (the remaining 34% is assumed to be in the scrubber water)
OXYGEN	90
OVERALL MASS	100 (obtained by determining water weight by difference)

Fig. 6.15. Distribution and material balance for elements in a typical hydrocarbonization experiment with Wyodak coal at 839 K.

products in the example. A large portion of the missing fraction could be contained in the scrubber water.

## 7. CONCLUSIONS AND RECOMMENDATIONS

The bench-scale hydrocarbonization studies demonstrated that hydrocarbonization is an effective method for producing oil, gas, and char products from coal. The oil product has a relatively low viscosity and appears suitable for upgrading so that it can be used as a fuel or as a chemical feedstock; however, further characterization and evaluation of the oil product is needed to determine its potential uses. The gas product has a high methane content which can be used as a substitute natural gas. The char has a reduced sulfur content and a heating value approximately equal to that of coal and may be used as a fuel or for gasification. At operating conditions of 840 K and 2170 kPa,  $\sim 1$  barrel of oil is produced per ton ( $1.75 \times 10^{-4} \text{ m}^3/\text{kg}$ ) of coal processed. The process appears to be particularly suitable for use in conjunction with a gasification or power plant where valuable oil and gas products could be removed from the coal prior to gasification or combustion of the char.

Because of the large reserves of caking coals located in the eastern United States, it is desirable that additional work be done to investigate reactor designs and operating conditions that will permit the direct processing of caking coals. Although problems of agglomeration of caking coals were not eliminated under the limited range of operating variables studied, the recirculating fluidized-bed reactor appears to offer potential for direct processing of caking coal. Further study of the recirculating fluidized-bed reactor with longer residence times in the draft tube, larger bed diameter, and with improved methods of introducing coal into the reactor is recommended. Additional study on the effect of bed configuration and residence time on product yields and composition is also desirable.

The use of chemical pretreatment was shown to be effective in eliminating the agglomerating tendencies of Illinois No. 6 coal. The higher oil yield of 24% from hydrocarbonization of  $\text{Na}_2\text{CO}_3$ -treated coal indicates

that chemical pretreatment may result in improved oil yields, although no data are available for direct comparison of the yield with untreated Illinois No. 6 coal. Other potential benefits of chemical pretreatments that appear worthy of further investigation are improved oil product quality (reduced asphaltene content), improved gas product yields, sulfur removal, and increased reactivity of the char for gasification or combustion. Investigation of methods for recovering and recycling chemicals used in pretreatment is needed so that inexpensive pretreatment methods can be developed. Additional information is also needed on the combustibility of char in conventional coal burners.

## 8. ACKNOWLEDGMENTS

This project was initiated under the sponsorship of the Office of Coal Research, during which time Zeke Clark assisted in establishing the objectives, scope, and approach of the work. Under the Energy Research and Development Administration, John Morris served as project manager. Subsequently, Charlie Miller assumed this guiding role under Jim Batchelor's supervision, carrying the project into the Department of Energy. Their assistance is gratefully acknowledged.

During the course of this project, numerous engineers and technicians participated and performed all of the engineering and operational tasks with a fine spirit of teamwork. In alphabetical order, the engineers performing substantial roles were Fred Endelman, Jim Gibson, and Grady Yoder. Jere Nichols, Gene McNeese, Bob Hightower, Jack Watson, and Chuck Scott provided guidance and encouragement. Technicians assisting greatly in operations were, in alphabetical order, Ron Andrews, Jack Beams, Leonard Dickerson, Randy Gibson, Sherry Gibson, Dave McWhirter, Jack Rose, and Don Spangler. To all of these people we express our sincere appreciation, realizing that, were the list not so long, all should be included as coauthors to this report. Finally, we thank Debbie Brown, Wanda England, Janice Shannon, and Pam Valliant for secretarial assistance during the course of this project.

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10. APPENDICES

## APPENDIX A: ATMOSPHERIC CARBONIZATION AND HYDROCARBONIZATION STUDIES

As part of the experimental development program (Task 2) in support of the bench-scale hydrocarbonization system, a high-temperature fluidized-bed reactor system was constructed for operation at atmospheric pressure. Batches of Wyodak subbituminous coal were heated in ~60 min from ambient temperature to maximum temperatures of 802 to 922 K (985 to 1200°F) and maintained at temperature until carbonization or hydrocarbonization was complete. Analysis of product solids, liquids, and gases permitted the calculation of carbon balances and relative product yields. Eleven experiments (AHC-1 through AHC-11) were run, although three of the experiments were not completed because of operational difficulties. Nitrogen or argon was used as the fluidizing gas for five experiments, and hydrogen was used in six experiments. A uniformly fluidized-bed reactor was used in all but the final two experiments (AHC-10 and 11), in which a draft tube was used to provide a recirculating fluidized bed.

### A.1 Experiment Design and Procedure

A 0.1-m (4-in.)-diam reactor was used for all of the experiments. A flow diagram of the revised experimental equipment used in the runs beginning with AHC-5 is shown in Fig. A.1. The reactor was 1.32 m long and was constructed of 0.1-m (4-in.)-diam sched 40 347 stainless steel pipe, flanged on both ends. Chromel-Alumel thermocouples were welded to the exterior surface and positioned axially within the bed for temperature measurement and control. The reactor was heated with electrical clamshell heaters during the first two experiments; in the later experiments, the vessel was heated with tubular electric heaters mounted on the outside surface. A distribution plate having sixty-one 0.0012 m (3/64-in.)-diam holes on 0.012-m (15/32-in.) centers (staggered) was used for the uniformly fluidized-bed runs. Spiral-wound gaskets (304L stainless steel with asbestos) were used for sealing the distributor plate flanges. The recirculating fluidized bed for runs AHC-10 and 11 was constructed by positioning a 0.019-m (3/4-in.)-diam 304L stainless steel draft tube along the reactor axis; this tube was supported by

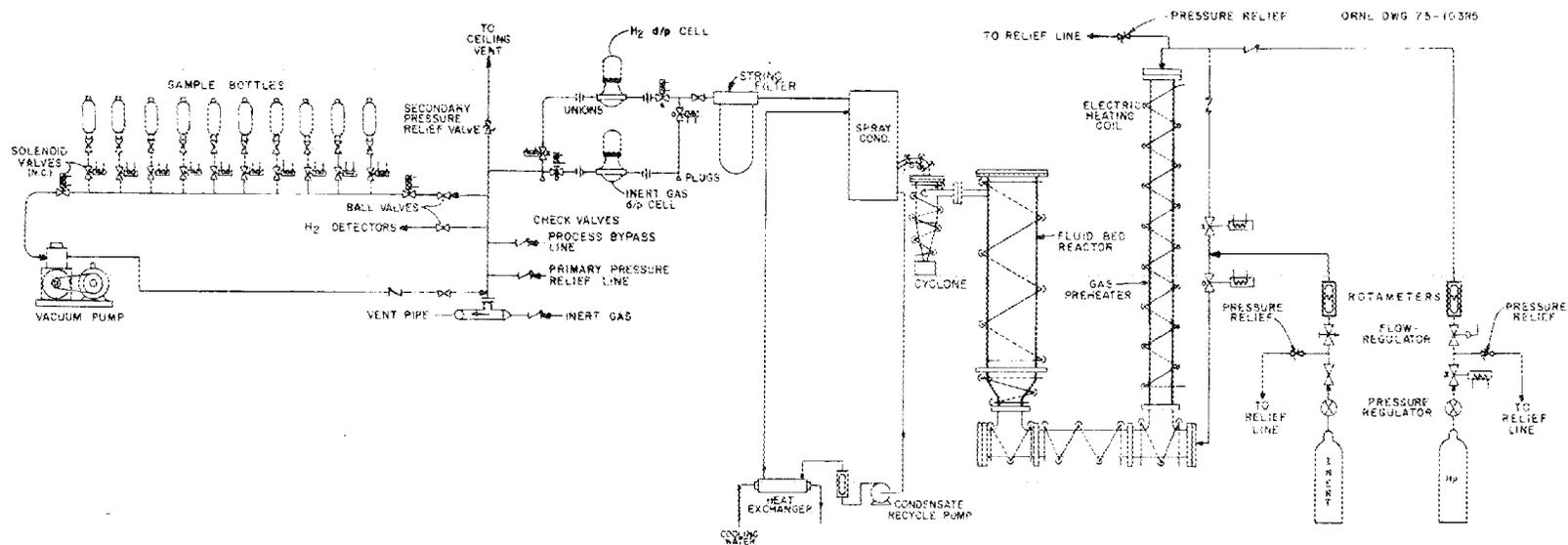


Fig. A.1. Flow diagram for atmospheric hydrocarbonization.

0.0032-m pressure tap tubes located 0.05 m above the jet nozzle of a special distributor plate (Fig. A.2). By selecting the proper gas flows from the plenum into the annular downcomer and from the nozzle into the draft tube, solids will flow downward through the downcomer and then flow rapidly upward through the draft tube. Coal is injected with the nozzle gas. Its rapid heating by hot recirculating char under hydrogen pressure with low vapor residence time should result in increased liquid yields and decreased agglomeration problems.

Reactor effluent passed through a heated cyclone, a cold-water spray condenser, and fiber filters. After run AHC-3, an electrically heated external cyclone was installed to reduce solids carry-over from the reactor exhaust. Separated solids were accumulated in a catch pot rather than being returned. Various condenser designs were used, each involving direct, countercurrent contact of a cold-water spray with the hot gas-vapor-aerosol effluent from the reactor. The final condenser design (first used with run AHC-5) contained  $\sim 10$   $\ell$  of water, which was filtered, water-cooled, and metered during recirculation. A mat of fine glass wool placed at the condenser exit filtered out entrained water and aerosol. After run AHC-5, a cartridge string filter was also used for further cleanup of the gas.

Gas flow rates were monitored using differential pressure (dp) cells with integral orifices (two sizes for two flow ranges). Gas compositions for orifice meter interpretation and for gas evolution measurements were determined from samples collected in ten pre-evacuated stainless steel cylinders. These gas samples were analyzed first by low-resolution mass spectrometry. In a separate step, gas chromatography was used to resolve nitrogen and CO. Analyses were corrected for air leakage into the samples primarily by measuring the oxygen content, and from these corrected analyses, gas evolution was determined either from total gas flow or from a known tie-component flow (nitrogen, argon, or helium).

Fluidizing gases were preheated upstream of the reactor. For experiments AHC-1 through AHC-9 (uniform fluidization), a single preheater was used. This preheater was constructed of 0.05-m (2-in.)-diam sched 40

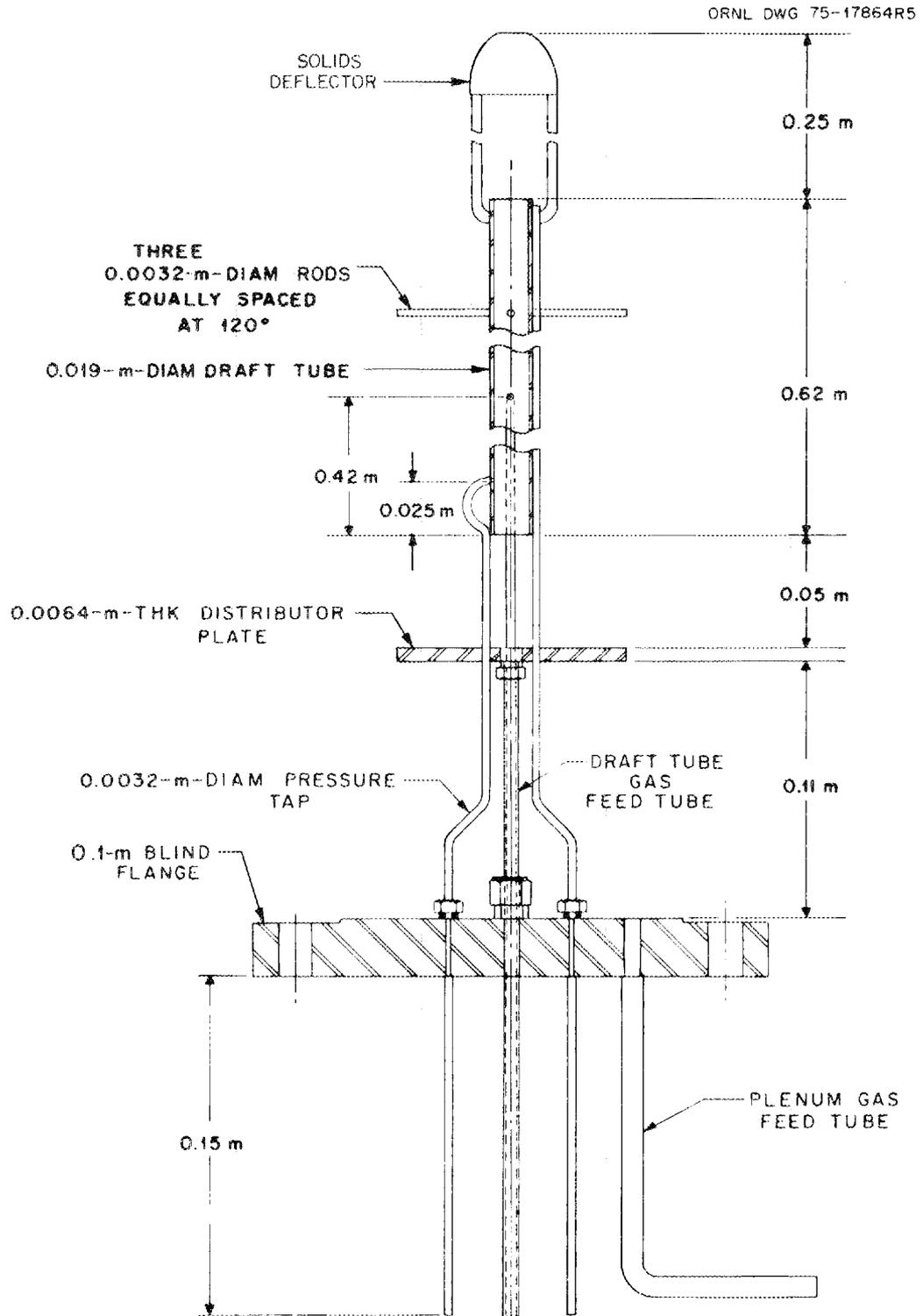


Fig. A.2. Draft tube assembly for atmospheric hydrocarbonization system.

flanged 347 stainless steel pipe measuring 1.52 m long with surface-mounted calrod heating elements. The preheater was filled with packing of 0.025-m segments of 0.0064-m (1/4-in.)-diam stainless steel tubing. For recirculating fluidized-bed experiments, draft tube gas was preheated in this unit, but gas for the plenum below the downcomer was heated by coiled copper tubing heated in a clamshell heater.

Unweathered subbituminous coal from the Roland and Smith seams was obtained from Wyodak Resources Development Corporation, Gillette, Wyoming. Proximate and ultimate analyses are presented in Table A.1. After size reduction in a jaw crusher and hammer mill, the coal was sized at -40 +200 mesh (Experiments 1 to 6) or -50 +140 mesh (Experiments 7 to 11) in a Ro-Tap sieve shaker. Each 1.8- to 2.0-kg reactor charge was dried in a vacuum oven maintained at near-ambient temperature to reduce the moisture content to between 7.5 to 27%.

Before each experiment, the system was checked for leaks at operating temperature by helium detectors and by pressure tests. Coal was then charged as a batch at ambient temperature, oxygen was purged from the system, and gas flow was discontinued while the preheaters and cyclone were heating. The reactor bed was fluidized and reactor heatup was started when the desired temperatures were achieved. A maximum temperature of 802 to 922 K was achieved in ~60 min, and this temperature was maintained until gas evolution became negligible. Gas sampling was timed in order to best define the gas evolution curve. The procedure for earlier experiments differed in that heatup began simultaneously for the entire unit; differences in the heating rates among various units made this procedure unsatisfactory.

After purging and cooldown, solid and liquid products were recovered, weighed, and sampled for analysis. Tar carbon and ash contents, as well as total carbon in the water, were measured to determine the carbon in product liquid. Carbon balances were determined from these and other analyses, and relative carbon yields in the solid, liquid, and gas were used as bases for comparison.

Table A.1. Analyses of Wyodak coal

---

Equilibrium moisture content: 30.87%<sup>a</sup>

Proximate analysis, moisture-free:

Ash	7.2% ( $s^b = 0.16$ , six samples)
Volatile matter	46.7% ( $s = 0.61$ , six samples)
Fixed carbon	46.0% ( $s = 0.71$ , six samples)

Ultimate analysis, maf:

Carbon	72.4% ( $s = 0.86$ , six samples)
Hydrogen	5.63% ( $s = 0.21$ , six samples)
Nitrogen	1.043% ( $s = 0.005$ , six samples)
Sulfur	0.85% ( $s = 0.34$ , five samples)
Oxygen	20.08% (by difference)

Calorific content: 29.1 MJ/kg ( $s = 68$ , five samples)

---

<sup>a</sup>Data obtained from Lawrence Livermore Laboratory. Analysis of Roland seam coal by CT&E Co., Denver, Colo., Division of Commercial Testing & Engineering Company.

<sup>b</sup> $s$  represents standard deviation.

## A.2 Experimental Results

Atmospheric hydrocarbonization experiments are summarized chronologically in Table A.2. Three experiments were aborted before completion when a reactor gasket failed (AHC-2), when the reactor-to-cyclone line plugged (AHC-7), and when the cyclone-to-condenser line plugged (AHC-10).

Satisfactory carbon balance closure ( $100 \pm 4\%$ ) was achieved in only three experiments (AHC-5, -8, and -11), but those three were the most important hydrocarbonization experiments. In addition, useful observations can still be made about other experiments despite incomplete recovery of products. Carbon balances on these other carbonization

Table A.2. Chronological summary of atmospheric hydrocarbonization (AHC) experiments

AHC experiment	Fluidizing gas	Maximum temperature (K)	Overall carbon balance (%)	Percent carbon as:			Moisture content of charged coal (%)	Overall ash balance (%)
				Liquid	Gas	Char		
1	N <sub>2</sub>	811	56.0	1.5	3.4	51.2	22.8	55
2	N <sub>2</sub>	Aborted	Aborted					
3	Ar	802	76.4	2.2	9.1	65.2	26.9	82
4	Ar	922	84.0	5.0	17.8	61.2	27.5	79
5 <sup>a</sup>	H <sub>2</sub>	866	102.7	6.9	19.1	76.7	11.26	99
6	H <sub>2</sub>	839	83.9	5.0	9.8	69.1	9.7	89
7	H <sub>2</sub>	Aborted	Aborted					
8 <sup>a</sup>	H <sub>2</sub>	839	100.0	12.2	13.2	74.6	25.4	91
9	H <sub>2</sub>	811	90.8	11.2	12.5	67.1	18.6	92
10	Ar <sup>b</sup>	Aborted	Aborted					
11 <sup>a</sup>	H <sub>2</sub> <sup>b</sup>	822	103.1	11.1	9.1	82.9	19.2	99

<sup>a</sup>Runs having a good overall carbon balance.

<sup>b</sup>Recirculating fluidized-bed operation.

experiments were unsatisfactory. Ash balances were also unsatisfactory when carbon balances were poor, which suggests that either an unrecovered blowover of unreacted coal (decreasing all yields) or blowover of char from the reactor (decreasing char yield only) accounted for most of the deviations.

Yields from coal carbonization and hydrocarbonization depend upon many variables, including heating rate, maximum coal temperature, hydrogen partial pressure, vapor residence time, the coal used, and coal pretreatment. Heating rate could not be varied widely because of the reactor's thermal inertia during the unsteady-state heatup. Maximum coal temperature was varied instead, while the heating rate was kept nearly constant and relatively low (reactor heatup time of ~60 min; an average of 9 K/min).

Experiments AHC-5 (866 K) and AHC-8 (839 K) gave carbon balances near 100%, while AHC-9 (811 K) also gave a reasonably good carbon balance (90.8%, error thought to be char loss). The carbon yields for the gas, liquid, and char for these runs are compared in Table A.3. In experiments AHC-9 and AHC-8, carried out at 811 and 839 K, the liquid product contained 11.2 and 12.5% of the carbon in the coal feed, respectively. In run AHC-5 at 866 K, only 6.9% of the carbon content of the coal was collected as liquid product, and an increased amount of the carbon was found in the gas. This suggests that the increased gas evolution at the higher temperatures (866 K) occurred at the expense of the liquid yield through thermal hydrocracking; hence, the maximum liquid yield is obtained at ~811 to 839 K.

Gas yields in the three experiments increase with temperature as expected. Char yields stay nearly constant if all carbon deficiency in AHC-9 is due to char loss.

A single recirculating fluidized-bed experiment (AHC-11) was accomplished with a satisfactory carbon balance. The apparent liquid yield was 11.1%, which was similar to the yields of uniformly fluidized-bed experiments at similar temperatures. As was observed in the bench-scale hydrocarbonization, residence times may not be changed enough at this scale to show a difference between the reactor designs.

Table A.3. Carbon yields in atmospheric hydrocarbonization studies

Experiment	AHC-9	AHC-8	AHC-5
Maximum temperature, K	811	839	866
Liquid yield, % <sup>a</sup>	11.2	12.2	6.9
Gas yield, % <sup>a</sup>	12.5	13.2	19.1
Char yield, % <sup>a</sup>	<u>67.1 (76.3<sup>b</sup>)</u>	<u>74.6</u>	<u>76.7</u>
Overall carbon balance, %	90.8 (100.0 <sup>b</sup> )	100.0	102.7

<sup>a</sup>Carbon in liquid, gas, and char as a percentage of the carbon contained in the coal feed.

<sup>b</sup>Attributing balance deficiency to poor char recovery or analysis (see text).

## APPENDIX B: AMBIENT MOCK-UP STUDIES

Studies were carried out in a Lucite mock-up to study fluidization and bed recirculation with regard to the design and operation of the bench-scale hydrocarbonization system. The initial studies of bed recirculation were done in a "two-dimensional" mock-up. Subsequent studies were done in a 0.1-m (4-in.)-ID mock-up having dimensions and geometry similar to the reactor used in the hydrocarbonization system.

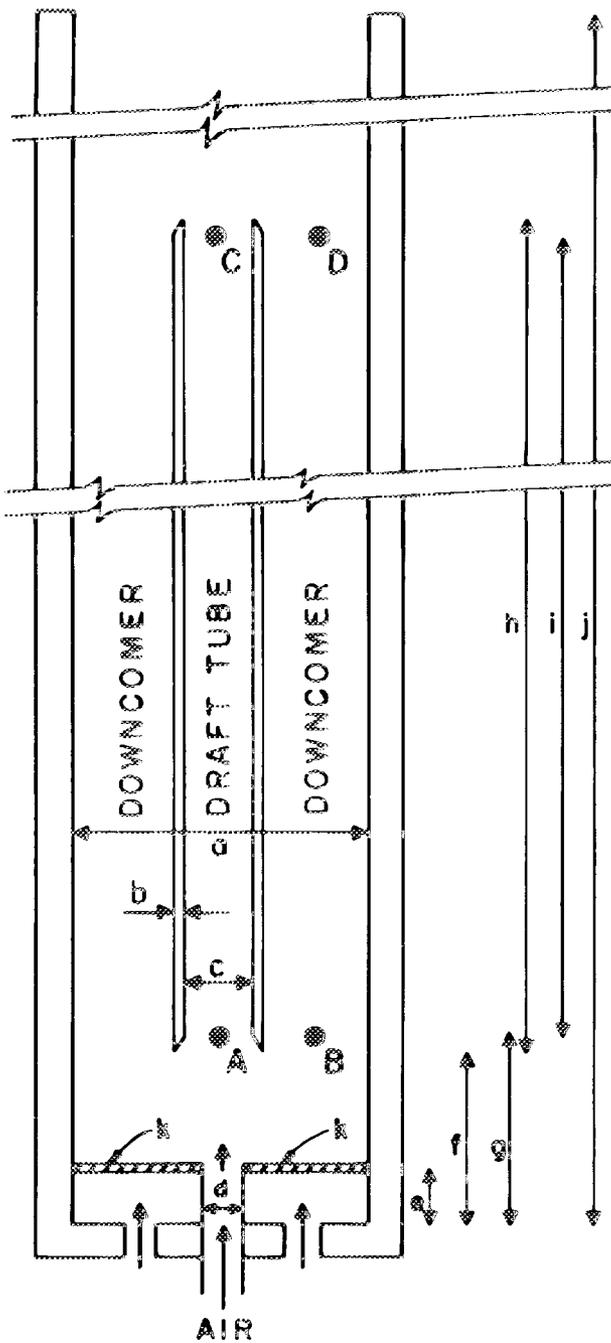
## B.1 Two-Dimensional Mock-Up

The two-dimensional mock-up of a recirculating fluidized-bed reactor shown in Fig. B.1 was built to provide insight and design data for recirculating fluidized beds. This mock-up contains a central draft tube in which the solids are lifted in dilute-phase transport and two downcomers in which the solids are recycled to the bottom of the column in dense-phase transport. This reactor concept has several advantages for the hydrocarbonization process:

1. Rapid heating of coal fed to the draft tube is provided by rapid mixing with recycled char.
2. Very short vapor product residence times can be achieved with the draft tube arrangement.
3. The dilute phase in the draft tube minimizes hot surface area in contact with the vapor product.
4. Problems of solid agglomeration can be minimized.

Sand and ion exchange resin were used as bed material in the initial studies. The bed recirculation rate was determined by observation of tracer particles. Manometers were used to measure the pressure differential across the draft tube and downcomer at locations shown in Fig. B.1. The distributor was a flat plate having 0.0016-m-diam holes spaced 0.0032 m apart. Humidified air was used as the fluidizing gas. The data from 65 experimental runs are summarized in Table B.1.

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DIMENSIONS

$$a = 0.108 \text{ m}$$

$$b = 0.0032 \text{ m}$$

$$c^* = 0.025 \text{ m}$$

$$d = 0.013 \text{ m}$$

$$e^* = 0.019 \text{ m}$$

$$f = 0.095 \text{ m}$$

$$g = 0.10 \text{ m}$$

$$h = 0.46 \text{ m}$$

$$i = 0.44 \text{ m}$$

$$j = 1.02 \text{ m}$$

k = PERFORATED  
0.0016-m HOLES ON  
0.0032-m SPACING

A, B, C & D = PRESSURE TAP

\* = ADJUSTABLE

DEPTH = 0.038 m

Fig. B.1. Two-dimensional mock-up of recirculating fluidized-bed reactor.

Table B.1. Bed recirculation rate data

Solid	Gas feed to draft tube (std m <sup>3</sup> /min x 10 <sup>3</sup> )	Gas feed to downcomers (std m <sup>3</sup> /min x 10 <sup>3</sup> )	Manometer readings (kPa)			Column pressure <sup>d</sup> (kPa)	Recirculation rate (m <sup>3</sup> /s x 10 <sup>5</sup> )
			1 <sup>a</sup>	2 <sup>b</sup>	3 <sup>c</sup>		
Resin	92.2	3.05	1.39	0.86	0.34	2.49	7.36
Resin	79.3	3.05	1.30	0.72	0.52	1.74	9.09
Resin	105.0	3.05	0.93	1.08	0.22	3.43	5.10
Resin	92.2	6.34	1.38	1.14	0.26	2.61	8.31
Resin	92.2	6.34	1.75	1.14	0.48	2.71	9.37
Resin	92.2	3.99	1.34	1.02	0.30	2.41	9.49
Resin	103.0	7.19	1.53	1.41	0.22	3.61	9.68
Resin	92.2	7.28	1.53	1.14	0.41	2.61	9.71
Resin	79.3	5.49	1.71	1.06	0.67	2.94	9.66
Resin	79.3	3.52	1.53	1.23	0.11	2.71	7.73
Resin	79.3	2.34	1.27	1.10	0.11	2.84	6.46
Resin	85.8	8.22	1.64	1.39	0.41	3.09	10.99
Resin	72.9	8.22	1.82	1.10	0.48	2.71	10.48
Resin	92.2	1.64	1.07	1.19	0.11	3.31	4.73
Resin	105.0	1.64	0.89	1.35	0.48	4.06	4.79
Sand	118.0	9.63	0.26	1.76	2.35	5.03	4.39
Sand	118.0	6.81	2.20	1.57	1.97	4.55	2.33
Sand	118.0	7.98	2.01	2.16	1.97	4.88	4.73
Sand	110.0	9.16	2.20	2.16	1.97	4.64	4.64
Sand	92.2	6.34	2.01	3.14	1.90	2.94	7.33
Sand	92.2	4.46	1.82	3.14	1.60	2.84	5.83
Sand	92.2	3.05	1.56	0.13	1.42	2.49	3.17
Sand	103.0	4.93	2.84	0.14	2.01	4.63	8.50
Sand	131.0	4.46	2.35	0.14	2.05	5.05	8.52
Sand	118.0	4.93	2.46	0.17	2.31	4.35	8.10
Sand	124.0	3.05	1.90	0.16	1.64	4.63	4.67
Sand	124.0	3.05	1.71	0.20	1.64	4.48	5.86
Sand	112.0	3.28	1.71	0.23	1.45	3.53	5.78
Sand	112.0		0.97	0.10	0.71	3.36	1.59
Sand	118.0	4.46	1.86	0.14	1.49	3.68	5.15
Sand	118.0	5.87	1.95	0.13	1.82	3.88	6.48
Sand	124.0	4.93	1.64	0.14	1.38	4.65	4.47
Sand	124.0	7.04	2.01	0.16	1.82	4.90	5.78
Sand	124.0	6.34	1.75	0.16	1.60	4.83	5.52
Sand	124.0	8.92	2.05	0.19	2.05	5.20	7.50
Sand	118.0	9.16	2.42	0.21	2.16	4.70	9.85
Sand	118.0	6.81	1.94	0.19	1.86	4.40	6.74
Sand	118.0	4.93	1.53	0.17	1.49	4.13	5.18
Sand	118.0	3.00	1.30	0.12	1.30	4.06	2.86
Sand	118.0	1.17	0.89	0.10	0.82	3.98	17.73
Sand	112.0	1.36	1.15	0.10	1.04	3.58	15.18
Sand	112.0	5.40	1.64	0.14	1.60	3.68	5.32
Sand	112.0	7.28	2.01	0.16	1.79	3.96	7.39
Sand	124.0	1.40	0.82	0.12	0.71	4.43	19.77
Sand	131.0	3.05	1.08	0.12	1.08	5.10	3.43
Sand	131.0	1.55	0.74	0.10	0.59	4.83	2.21
Resin	105.0	7.00	1.12	0.06	0.93	2.71	4.11
Resin	98.7		0.89	0.04	0.89	2.49	3.09
Resin	112.0	2.30	0.89	0.04	0.86	3.01	2.94
Resin	112.0	2.30	1.15	0.06	1.04	2.94	5.30
Resin	112.0	1.40	1.23	0.08	1.08	2.91	10.79
Resin	105.0		0.67	0.20	0.59	2.49	3.26
Resin	92.2	2.30	0.89	0.04	0.86	1.94	4.64
Resin	92.2		0.71	0.04	0.71	1.94	3.17
Resin	98.7	2.30	0.89	0.04	0.86	2.19	9.27
Resin	105.0	11.7	0.97	0.04	1.79		6.23
Resin	105.0	11.7	1.04	0.04	1.94	2.49	6.77
Resin	105.0		0.67	0.20	0.63	2.49	3.45
Resin	105.0	2.35	1.42	0.08	1.34	2.61	11.50
Resin	118.0		1.49	0.20	0.52	3.23	3.03
Resin	118.0		0.82	0.06	0.74	3.01	5.86
Resin	118.0	0.70	0.93	0.06	0.89	3.06	7.33
Resin	115.0	2.58	1.45	5.97	1.42	3.09	12.63
Resin	118.0	0.70	0.86	5.97	0.82	3.23	6.00
Resin	115.0	1.64	1.12	5.92	1.01	3.16	15.97

<sup>a</sup>Manometer No. 1 measured the pressure between points B and D in Fig. B.1.

<sup>b</sup>Manometer No. 2 measured the pressure between points A and B in Fig. B.1.

<sup>c</sup>Manometer No. 3 measured the pressure between points A and C in Fig. B.1.

<sup>d</sup>Pressure between point D (Fig. B.1) and atmosphere.

The recirculation rate data shown in Table B.1 were calculated from the average elapsed time for ten particles traced in each run. The 65 runs thus represent 650 observations. Figure B.2 is a plot of bed recirculation rate vs gas flow rate to the downcomers. The graph indicates a strong dependence on the gas flow rate to the downcomers and a weak dependence on the gas flow rate to the draft tube. Hence, recirculation rate is controlled by the rate of solids transport through the downcomers or on the amount of gas bypassing the downcomer into the draft tube. Operation in the other regime (the recirculation rate is controlled by the ability of the draft tube to pick up and transfer solids) results in slugging characterized by unstable operation and large pressure fluctuations.

## B.2 Alternative Distributor Plate Design

The two-dimensional mock-up was also used to study the performance of an alternate distributor plate shown in Fig. B.3. The purpose of the alternate design was to reduce bypassing of gas from the downcomer to the draft tube, thus ensuring good downcomer fluidization. The distributor plate was elevated above the draft tube entrance, leaving a gap for flow. A 0.016-m-wide draft tube was used in the studies. Gas from a separate plenum (denoted as 1) can be injected around the axial gas jet to supplement the draft-tube gas supply, while fluidizing the solids flowing through the draft tube distributor gap.

Char recirculation data with nitrogen fluidization are given in Table B.2 for char having an average particle diameter of 165  $\mu\text{m}$  and effective particle density of 1.05  $\text{g}/\text{cm}^3$ . For comparison, Table B.2 also contains three sets of data for a flat distributor plate. In Fig. B.4, the char recirculation rate for the alternate distributor plate in the two-dimensional mock-up is compared on a common basis with data obtained from the 0.1-m (4. in.)-ID three-dimensional mock-up having with a flat distributor plate (described in the following section).

The alternative distributor required more gas to achieve solid circulation rates equal to those obtained with the standard distributor;

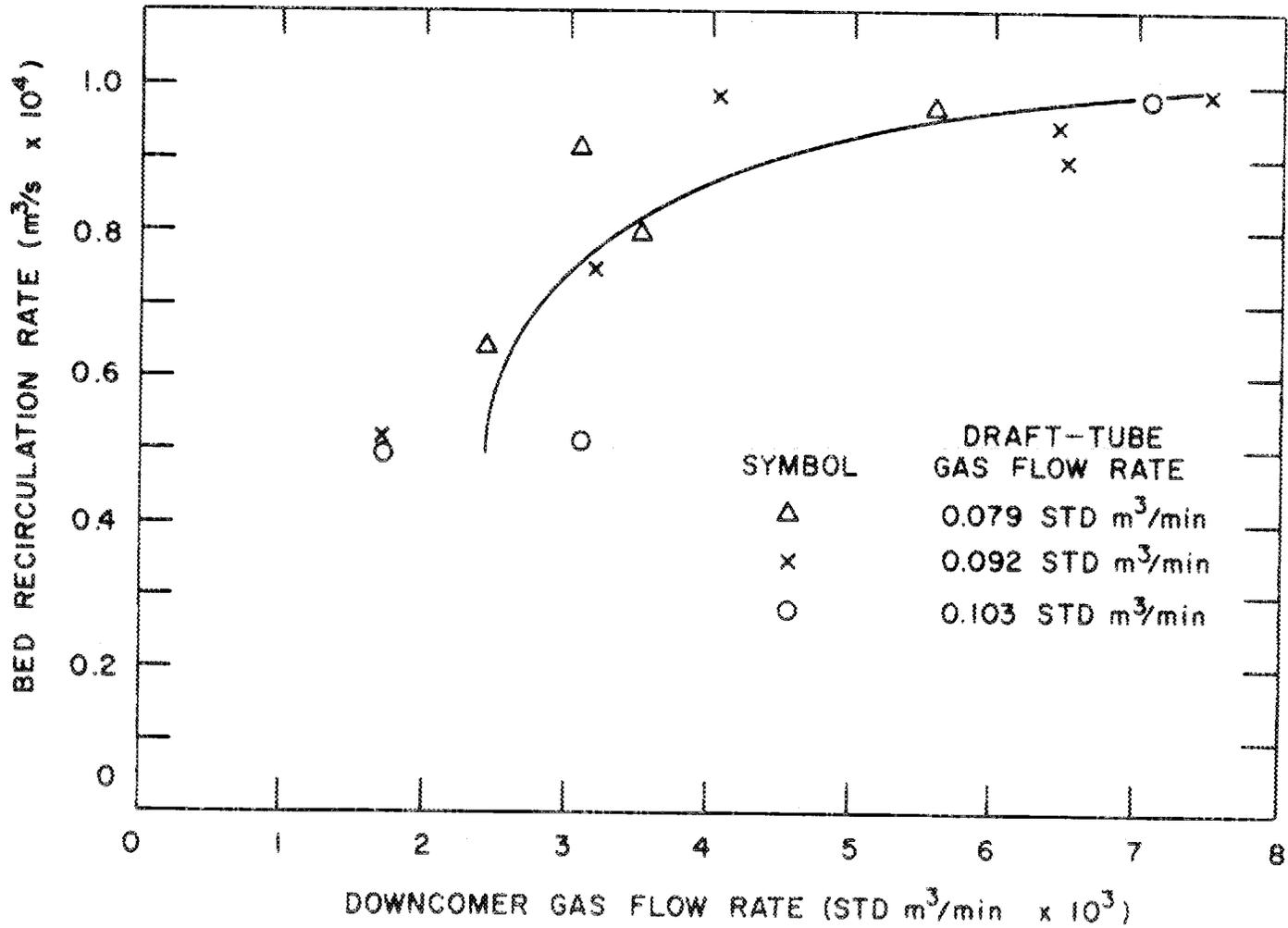


Fig. B.2. Bed recirculation rate in two-dimensional mock-up as a function of gas flow rate.

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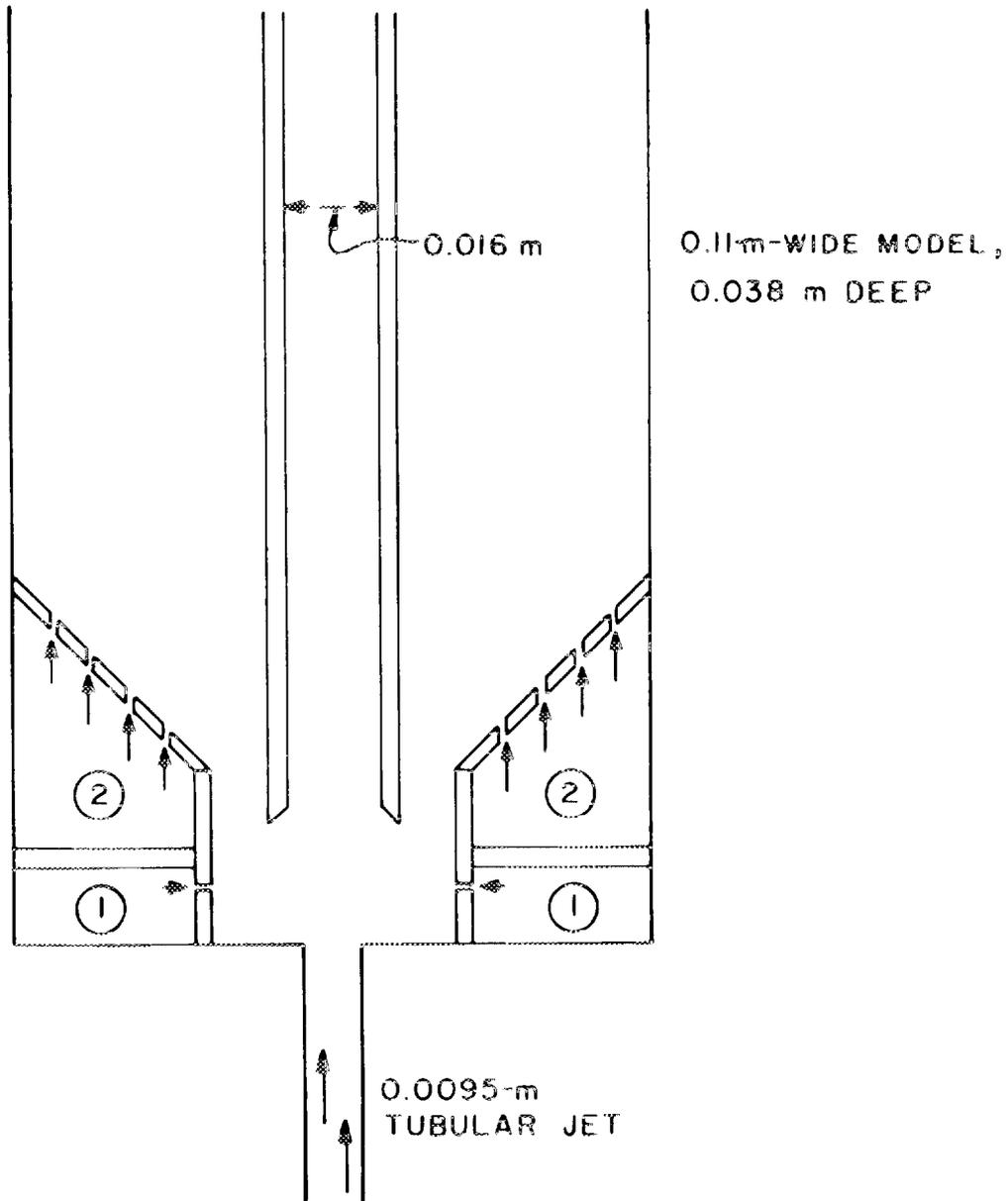


Fig. B.3. Two-dimensional model of alternative distributor design.

Table B.2. Circulation data for alternative distributor, two-dimensional model

Distributor plate	Nitrogen flow rates			Total cm <sup>3</sup> /s/cm <sup>2</sup> reactor	Char circulation rate g/s/cm <sup>2</sup> draft tube
	Jet (std m <sup>3</sup> /min x 10 <sup>3</sup> )	Plenum 1 (std m <sup>3</sup> /min x 10 <sup>3</sup> )	Plenum 2 (std m <sup>3</sup> /min x 10 <sup>3</sup> )		
Flat	11.6	0.0	13.0	10.0	0.9
Flat	11.6	11.6	13.0	14.7	2.4
Flat	11.6	23.2	13.0	19.4	0.9
Sloped	11.6	0.0	13.0	10.0	3.3
Sloped	11.6	5.8	13.0	12.3	10.7
Sloped	11.6	11.6	13.0	14.7	8.2
Sloped	11.6	17.4	13.0	17.0	11.0
Sloped	11.6	23.2	13.0	19.4	9.2
Sloped	11.6	29.0	13.0	21.7	10.1
Sloped	11.6	35.1	13.0	24.2	10.3
Sloped	11.6	11.6	0.0	12.0	9.2
Sloped	11.6	11.6	6.5	17.3	13.9
Sloped	11.6	11.6	19.5	19.9	6.1
Sloped	11.6	11.6	26.0	10.0	7.4
Sloped	0.0	11.6	13.0	17.0	14.0
Sloped	17.4	11.6	13.0	19.4	11.9
Sloped	23.2	11.6	13.0	9.4	3.8

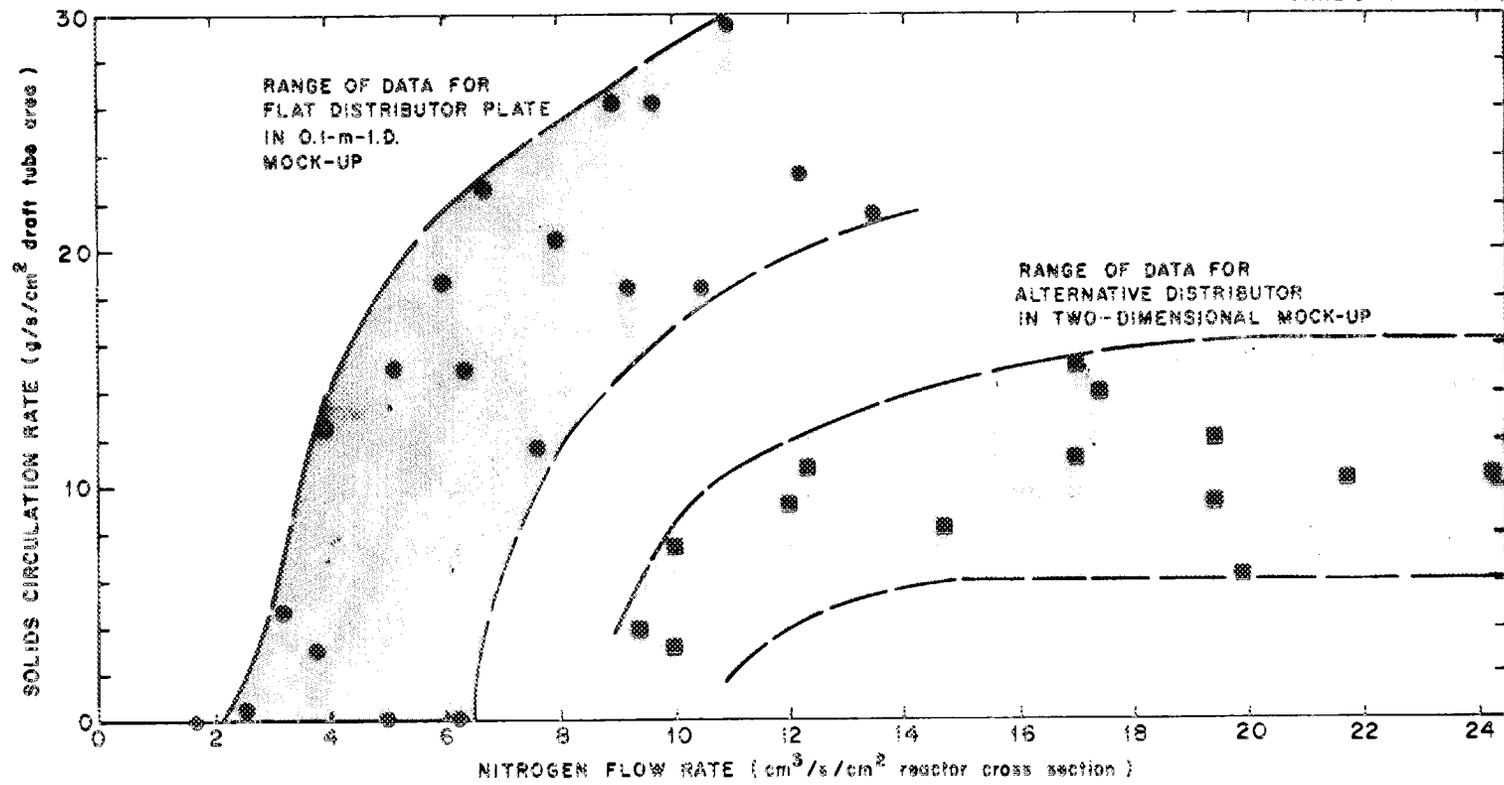


Fig. B.4. Solids circulation rate with flat distributor plate and alternative distributor plate design.

thus, it appears to be limited to circulation rates below those achievable with the standard distributor. However, the alternative design did permit downcomer fluidization to continue, regardless of whether the bed was circulating. Further development might decrease the gas requirements of this design.

### B.3 Three-dimensional Mock-up

Following the studies in the two-dimensional mock-up, a Lucite mock-up of approximately the same dimensions as the atmospheric and pressurized hydrocarbonizer (1.40 m long x 0.1 m diam) was constructed. The system shown in Fig. B.5 was used to investigate fluidization of coal and char mixtures. Figure B.6 gives the pressure drop vs velocity data for Wyodak coal particles (average particle size of 236  $\mu\text{m}$ ) determined in the mock-up. The results are in good agreement with results published in the open literature.

The 0.1-m-ID mock-up was used to establish operating conditions for recirculating fluidized beds in the atmospheric hydrocarbonization system and the bench-scale hydrocarbonization system. Prior to run AHC-11, in the atmospheric hydrocarbonization system, a 0.019-m-diam draft tube was installed in the mock-up, and char from Run AHC-9 (3.4 wt % less than 200 mesh) was used to determine conditions that would provide good bed circulation through the draft tube. The mock-up tests showed that with a 0.84-m-long draft tube, the coal plume above the draft tube exceeded 0.30 m throughout the optimal range of operation, resulting in substantial solids carry-over. Reduction of the draft tube length from 0.84 m to 0.62 m and addition of a solids deflector sharply decreased the carry-over. These modifications were duplicated on the atmospheric hydrocarbonizer for run AHC-11.

Coal prepared for Run AHC-11 was tested in the mock-up to establish gas flow settings for stable operations. A plot of downcomer gas feed rate vs draft-tube gas feed rate (Fig. B.7) indicated that stable recirculation occurred only within a range of flow settings. Outside of the range, there was either low solids circulation or an erratic circulation

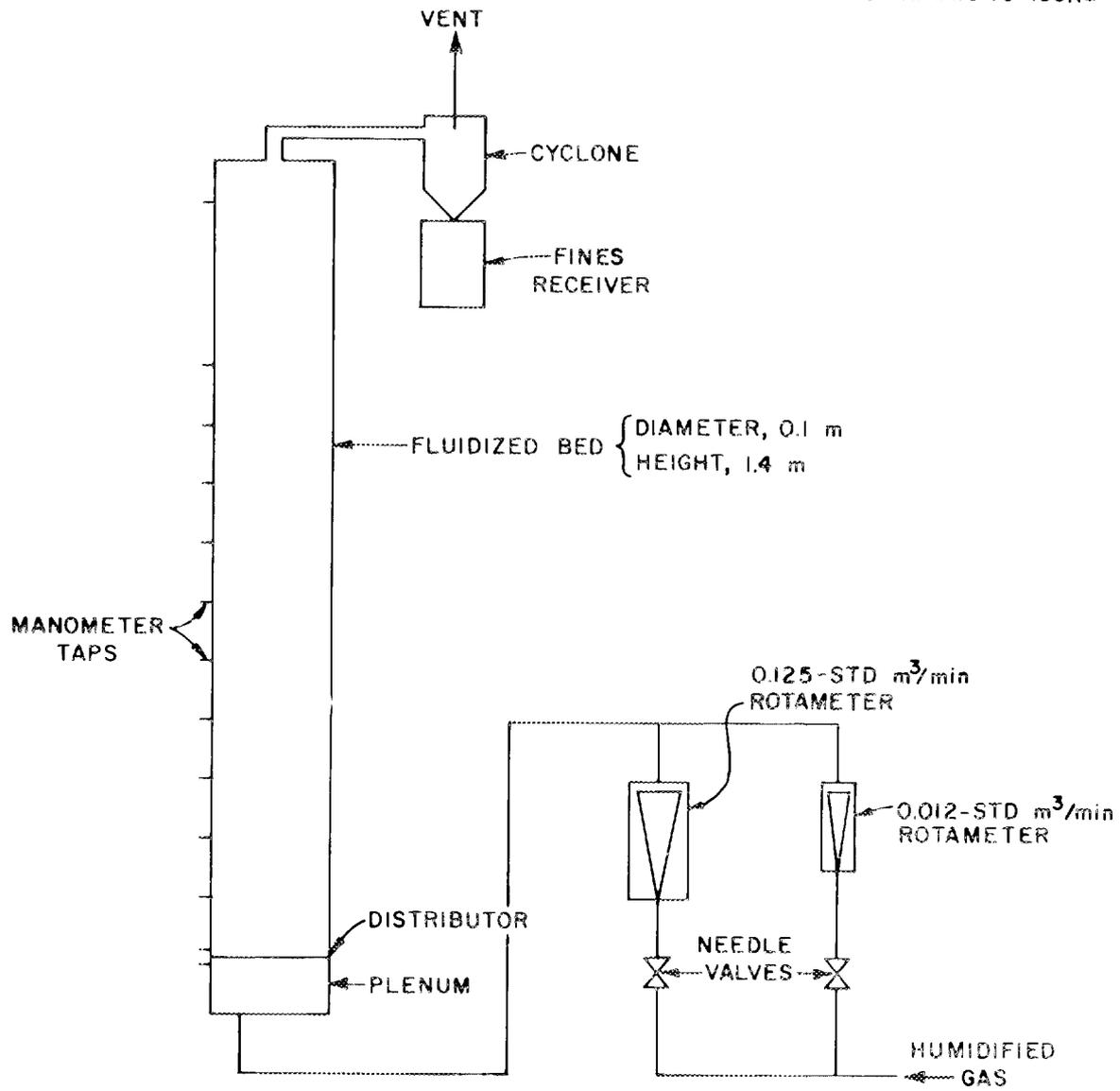


Fig. B.5. Schematic of three-dimensional mock-up.

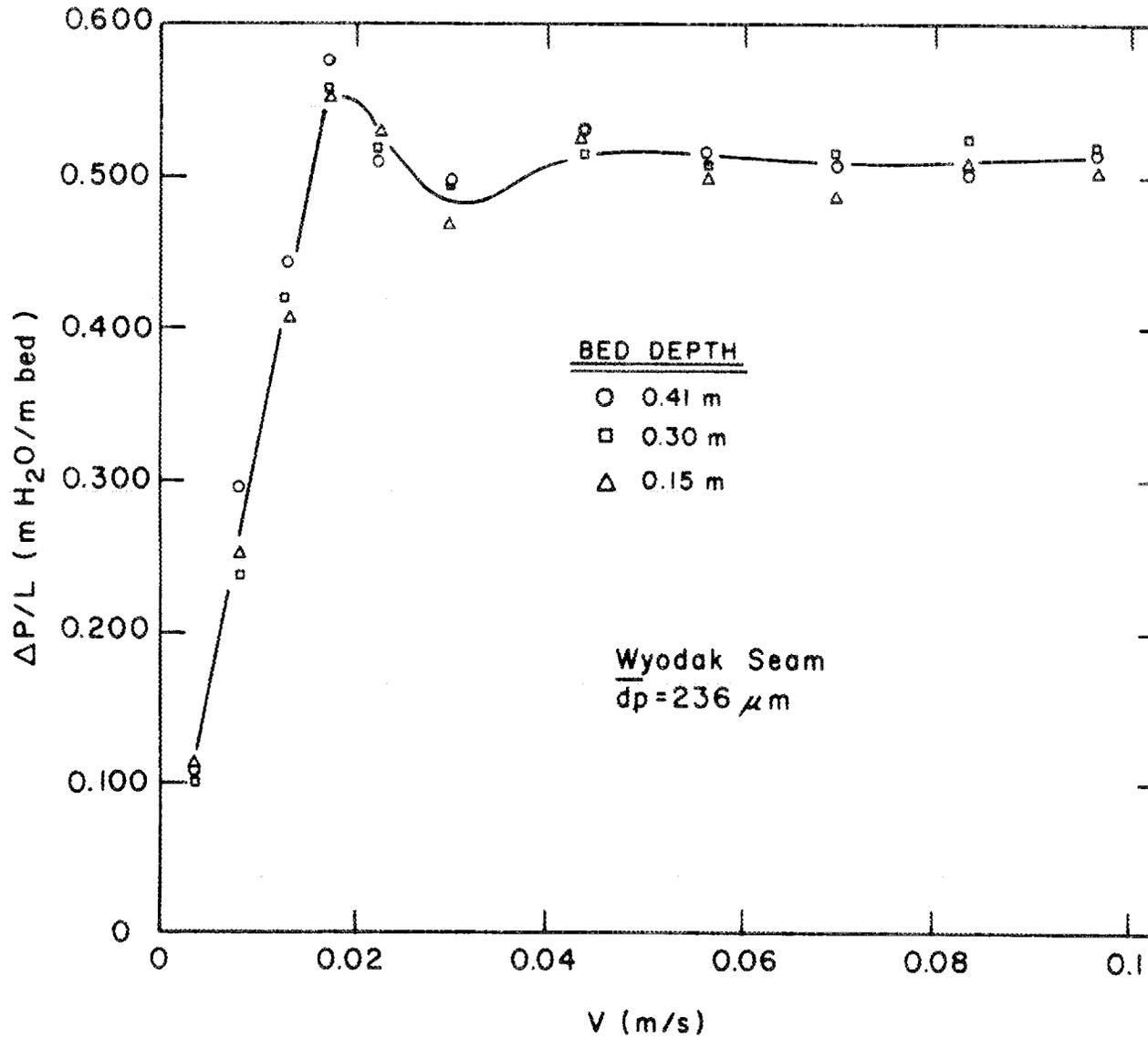
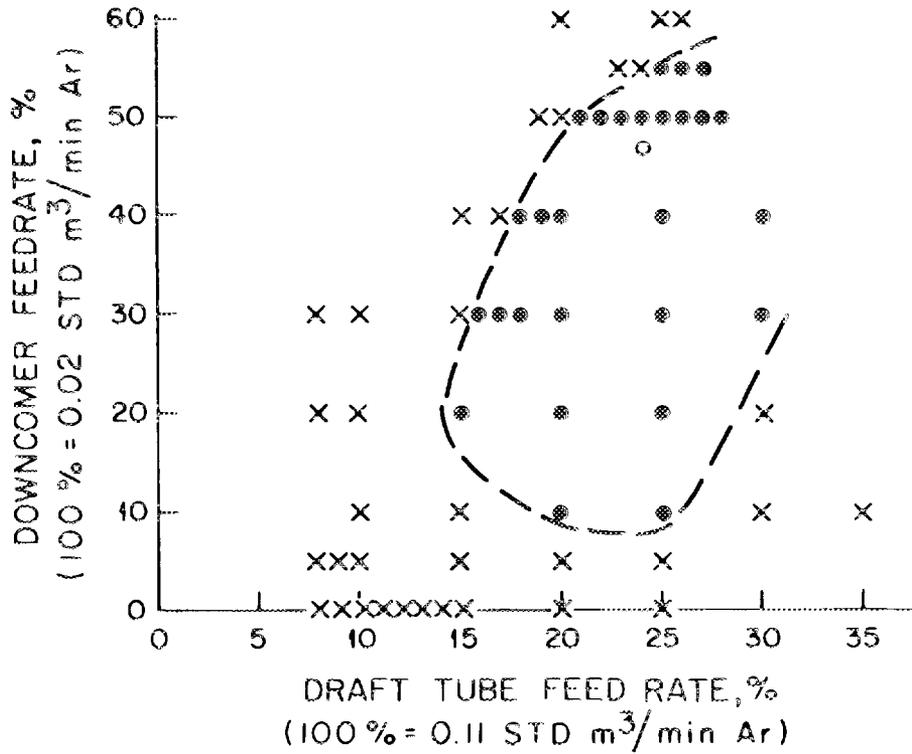


Fig. B.6. Pressure drop vs superficial velocity for coal in three-dimensional mock-up.

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- x ZERO OR UNSATISFACTORY CIRCULATION
- SATISFACTORY CIRCULATION
- o OPERATING POINT PREDICTED BY CORRELATION

Fig. B.7. Stable operating region for char circulation in three-dimensional mock-up.

with high voidage in the draft tube plume. Using the minimum fluidization flows calculated by the correlation of Wen and Yu,<sup>1</sup> and minimum entrained flow for the draft tube approximated by Kunii and Levenspiel,<sup>2</sup> feed rates were predicted which fit within the range of stable recirculation. Ambient mock-up tests of the coal prepared for Run AHC-11 confirmed that stable recirculation occurred at the predicted gas feed rates; so the correlations were used to set flows for temperature hydrogen operation of Run AHC-11. That run was successful, thus demonstrating the value of the reactor modifications and the flow correlations.

After the experiments described above were completed, the mock-up was modified to study bed circulation under conditions expected in the bench-scale hydrocarbonization reactor.

Initially, behavior of char in a uniformly fluidized bed (no draft tube) was tested. Tests used char from bench-scale experiment HC-12 (Wyodak coal hydrocarbonized at 825 K and 2170 kPa). The char had an average particle diameter of 165  $\mu\text{m}$  and effective particle density of 1.05  $\text{g}/\text{cm}^3$ , as determined by mercury pycnometry. From data on bed expansion and pressure drop at different gas flow rates, minimum fluidization velocities for helium, nitrogen, and argon were measured. These data agree satisfactorily with predictions from the correlation of Wen and Yu,<sup>1</sup> which has a standard deviation of 34% (Table B.3).

Three distributor plates were evaluated for their effects on recirculating fluidized-bed operation:

1. a 54-hole plate with 0.0012-m-diam holes,
2. a 42-hole plate with 0.0004-m-diam holes, and
3. a 42-hole plate with 0.00013-m-diam holes.

Only the plate with 0.0004-m-diam holes both distributed gas well into the recirculating fluidized bed and operated at the desired pressure drop of 2.9 to 4.4 kPa. Also, although the weeping of solids into the plenum was a recurring problem in the bench-scale hydrocarbonizer, decreasing the hole size to 0.0004 m or 0.0001 m reduced this weeping to acceptably low levels.

Table B.3. Minimum fluidization conditions for HC-12 char<sup>a</sup>

Gas	Minimum fluidization velocity (m/s x 10 <sup>2</sup> )		
	Experimental	Calculated <sup>b</sup>	Percent error
Helium	1.49	0.956	-36%
Nitrogen	1.22	0.876	-28%
Argon	0.73	0.765	+4.8%

<sup>a</sup>Fluidization test conditions: temperature, 293-308 K; pressure, 0.1 mPa (1.0 atm); bed cross-sectional area, 81.07 cm<sup>2</sup>; voidage at minimum fluidization, 0.53; bed pressure drop at minimum fluidization, 0.45 m H<sub>2</sub>O/m bed.

<sup>b</sup>Method of Wen and Yu (ref. 1).

By experimenting with the recirculating fluidized-bed mock-up, procedures and hardware were developed that led to improved start-up of the bench-scale hydrocarbonization reactor and increased the degree of mixing of feed with char. Mock-up tests confirmed that the bed of char could be lost from the hydrocarbonization reactor during start-up because solids showered directly from the draft tube into the char overflow pipe. A char bed must also be present during start-up to dilute fresh agglomerating coal with dry char. Char loss was significantly decreased by using reduced gas flow rates during start-up, by other procedure changes, and by installing a deflector above the entrance to the char overflow pipe.

In order to better extrapolate the results obtained from the mock-up at ambient conditions to the operation of the bench-scale hydrocarbonization system at operating conditions, an empirical correlation was tested. The same combination of dimensionless gas velocities (ratio of superficial velocity to minimum fluidization velocity,  $u/u_{mf}$ ) should produce the same bed behavior independently of gas or solid properties for a given reactor geometry and configuration. To test this hypothesis, char

from experiment HC-12 was fluidized first by helium and then by nitrogen in the 0.1-m-diam model of a recirculating fluidized bed. (Other reactor dimensions are summarized in Table B.4.)

Experimental data from the tests of this correlation are summarized in Table B.5. By plotting  $u/u_{mf}$  for the draft tube gas supply vs  $u/u_{mf}$  for the downcomer gas supply (the two manipulated variables), a matrix of test conditions was graphed. Such a graph shows reasonable agreement of pressure drop and solid circulation rate between the two different gases.

Figure B.8 shows the solid circulation rate data presented in this fashion. The effect of  $u/u_{mf}$  to the downcomer is pronounced. In contrast, increasing  $u/u_{mf}$  to the draft tube has a smaller effect on the circulation rate.

The dependence of solids circulation rate on downcomer gas supply rate alone is graphed in Fig. B.9. As was seen in the earlier mock-up studies, circulation rates were affected primarily by the downcomer supply. A 20-fold variation in draft-tube gas supply feed rate is represented by these data, but only slight deviations from the general trend result. From Fig. B.9, char circulation rate would appear to be limited to a maximum value. Restrictions of solids flow in some cross section of solids flow path—downcomer cross-sectional area, draft tube-distributor plate spacing, or draft tube area—probably cause this apparent maximum limitation. Maximum solid circulation rates might be increased by adjusting these geometric factors.

Nitrogen and helium recirculations at 305 K and 101.3 kPa (1 atm) correlated well with each other, but applying this correlation to hydrogen recirculation at 839 K and 2170 kPa required a significant extrapolation. Hydrogen supply rates for run HC-22 in the bench-scale hydrocarbonizer were set, based on the cold model data in Table B.6. Both good recirculation of the char starter bed and good downcomer fluidization were achieved based on temperature measurements in the draft tube and downcomer for run HC-22.

Table B.4. Dimensions and configuration of recirculating fluidized-bed reactor model

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Reactor	0.1016-m (4-in.) ID 1.334 m (52-1/2 in.) long
Draft tube	0.025-m (1-in.) ID 0.0032-m (1/8-in.) wall thickness 0.635 m (25 in.) long 0.025 m (1 in.) above distributor plate
Draft tube gas supply nozzle	8.76-mm <sup>2</sup> cross-sectional area (3/16-in. OD, 0.028-in.-wall tubing) Aligned with draft tube axis Flush with distributor plate
Distributor plate	42 holes spaced under the downcomer on a 0.012-m (15/32-in.) triangular pitch Holes, 398- $\mu$ m diam (1/64-in.)

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#### B.4 Reference for Appendix B

1. C. Y. Yen and H. H. Yu, *AIChE J.* 12, 610 (May 1966).
2. D. Kunii and O. Levenspiel, *Fluidization Engineering*, Wiley, N.Y., 1969.

Table 8.5. Data for evaluation of recirculating fluidized-bed flow rate correlation

Gas	Flow at bottom of downcomer		Flow from draft tube gas supply		Pressure drop ( $\times H_2O/m$ height)		Solids circulation rate	
	Volumetric (std m <sup>3</sup> /min $\times 10^3$ )	$u/u_{mf}$ (dimensionless)	Volumetric (std m <sup>3</sup> /min $\times 10^3$ )	$u/u_{mf}$ (dimensionless)	Downcomer bed	Draft tube	Downcomer particle velocity	Mass flux (g/s $\cdot$ cm <sup>2</sup> draft tube)
N <sub>2</sub>	0.0	0.0	2.35	380	0.158	0.040	0.00	0.0
	6.5	1.2	2.35	380	0.117	0.144	0.00	0.0
	13.2	2.4	2.38	380	0.438	0.356	0.55	4.6
	26.9	4.7	2.38	380	0.437	0.374	2.19	18.6
	41.1	7.0	2.38	370	0.438	0.373	3.11	25.2
	0.0	0.0	5.86	950	0.191	0.056	0.00	0.0
	6.6	1.2	5.89	950	0.231	0.206	0.06	0.5
	13.3	2.4	5.86	950	0.452	0.197	1.46	12.3
	26.8	4.7	5.89	940	0.443	0.361	2.65	22.5
	40.9	7.0	5.97	930	0.435	0.357	3.11	26.2
	0.0	0.0	11.75	1890	0.016	0.035	0.00	0.0
	6.5	1.2	11.81	1890	0.208	0.190	0.37	3.0
	13.2	2.4	11.86	1880	0.368	0.312	1.77	14.9
	26.9	4.7	11.95	1870	0.430	0.349	2.41	20.4
	41.3	6.9	12.01	1850	0.427	0.352	3.47	29.5
	0.0	0.0	17.6	2800	0.046	0.019	0.00	0.0
	6.5	1.2	17.7	2840	0.057	0.075	<0.03	<0.2
	13.2	2.4	17.8	2810	0.274	0.233	1.77	14.9
	26.9	4.7	17.9	2800	0.412	0.165	2.26	19.0
	41.4	6.9	18.0	2780	0.419	0.177	2.74	23.2
0.0	0.0	23.6	3780	0.032	0.019	0.00	0.0	
6.6	1.2	23.7	3750	0.020	0.016	<0.03	<0.2	
13.2	2.4	23.8	3730	0.214	0.166	1.37	11.6	
27.0	4.6	24.0	3700	0.399	0.291	2.16	18.3	
41.5	6.9	24.3	3670	0.409	0.317	2.56	21.6	
He	35.0	5.1	6.3	800	0.430	0.369	2.26	17.2
	70.0	10.3	6.3	800	0.411	0.382	2.35	17.9
	80.0	11.8	6.3	800	0.389	0.408	3.35	25.5
	17.0	2.6	15.8	2020	0.448	0.373	2.04	15.5
	35.0	5.1	15.8	2020	0.418	0.374	4.54	34.6
	70.0	10.3	15.8	2020	0.408	0.373	3.47	26.4
	17.0	2.6	31.6	4030	0.461	0.328	2.04	15.5
	35.0	5.1	31.6	4030	0.407	0.345	4.53	35.3
	70.0	10.3	31.6	4030	0.399	0.352	4.39	33.4
	17.0	2.6	47.5	6040	0.380	0.280	1.68	12.8
	15.0	5.1	47.5	6040	0.417	0.310	2.93	22.3
	70.0	0.3	47.5	6040	0.399	0.291	3.09	28.1
	17.0	2.6	63.3	8060	0.376	0.240	1.22	9.3
	35.0	5.1	63.3	8060	0.428	0.299	2.74	20.9
	70.0	10.3	63.3	8060	0.415	0.305	2.74	20.9

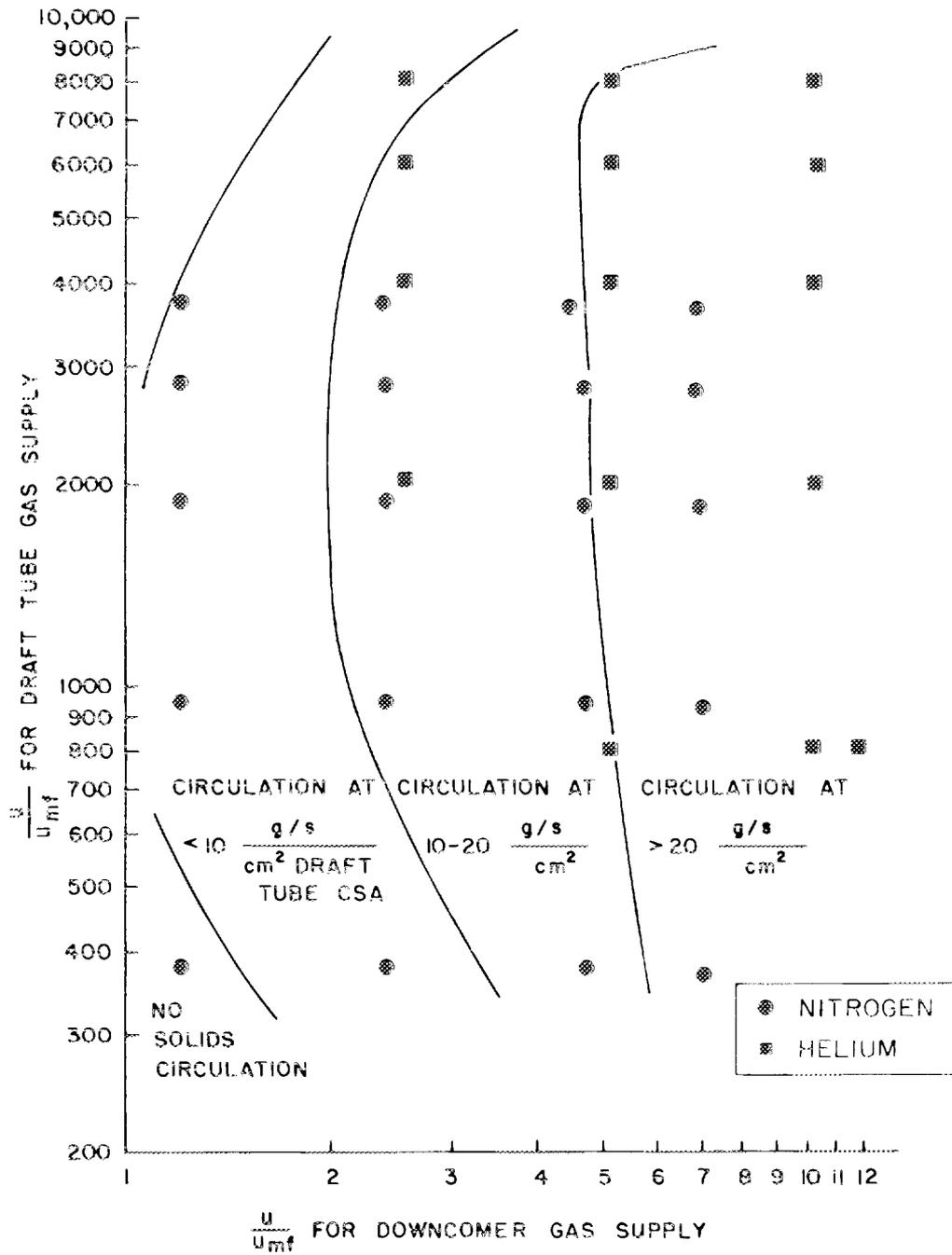


Fig. B.8. Solids circulation in a 0.1-m-diam recirculating fluidized-bed — interdependence of draft tube and downcomer gas supply rates.

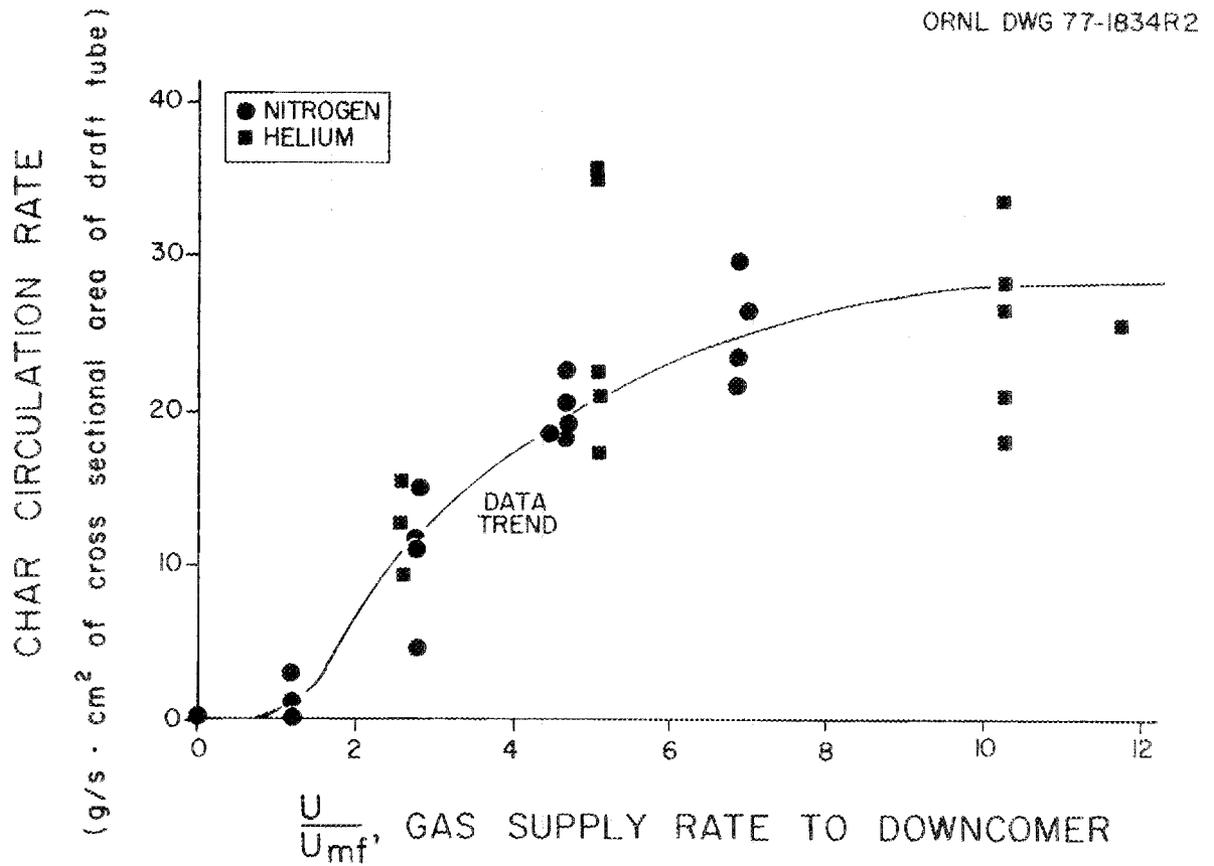


Fig. B.9. Solids circulation in a 0.1-m (4-in.)-diam recirculating fluidized bed — dependence on downcomer gas supply rate.

Table B.6. Comparison of data at fixed dimensionless velocity<sup>a</sup>

Gas	$\Delta P/L$ , downcomer (m H <sub>2</sub> O/m)	$\Delta P/L$ , draft tube (m H <sub>2</sub> O/m)	Particle velocity in downcomer (m/s x 10 <sup>2</sup> )
Helium	0.421	0.374	4
Nitrogen	0.409	0.342	3

<sup>a</sup>At the bottom of the annular downcomer,  $u/u_{mf} = 6$ ; for the draft tube supply jet,  $u/u_{mf} = 2300$ .

## APPENDIX C: COAL FEEDER VALVE AND FLOWMETER DEVELOPMENT

The bench-scale hydrocarbonization system requires that coal be fed to the reactor at a rate on the order of 4.5 kg/h. The work described below was conducted to develop a coal feeder valve and flowmeter for that purpose.

## C.1 Coal Feeder Valve Development

A modified ball valve, in which the bore of the ball was blocked to form two cups, was used for the first feeder valve tests. During each revolution of the ball, two cupfuls of coal were delivered from the feed hopper to the pneumatic transfer line below, as shown in Fig. C.1.

In the first experiments, an attempt was made to feed coal from the hopper at atmospheric pressure to the pressurized transport line. Stable operation was not obtained due to the blowback of gas into the hopper from the "empty" cup. The hopper was modified to allow pressure equilibration between the hopper and the transport line. Steady coal feeding could be obtained for short periods with this arrangement; however, coal flow would stop occasionally, possibly because of blowback or particle bridging in the hopper. In order to provide continuous coal feeding for longer periods, the hopper was pressurized to  $\sim 7$  kPa, relative to the transport line pressure. This configuration proved satisfactory, and coal could be fed smoothly and without interruption. The coal was deposited in a container mounted on a load cell. The strip-chart record from the load cell was graphically differentiated to obtain the coal flow rate. Figure C.2 is a plot of coal flow rate vs the shaft speed of the rotary ball valve feeder with pneumatic transport. The solid line represents data obtained by feeding into an open container (no pneumatic transport); the dashed line is the least-squares approximation of the data with pneumatic transport.

After  $\sim 50$  h of operation, the modified ball valve feeder developed a leak around the valve stem. The ball valve was subsequently

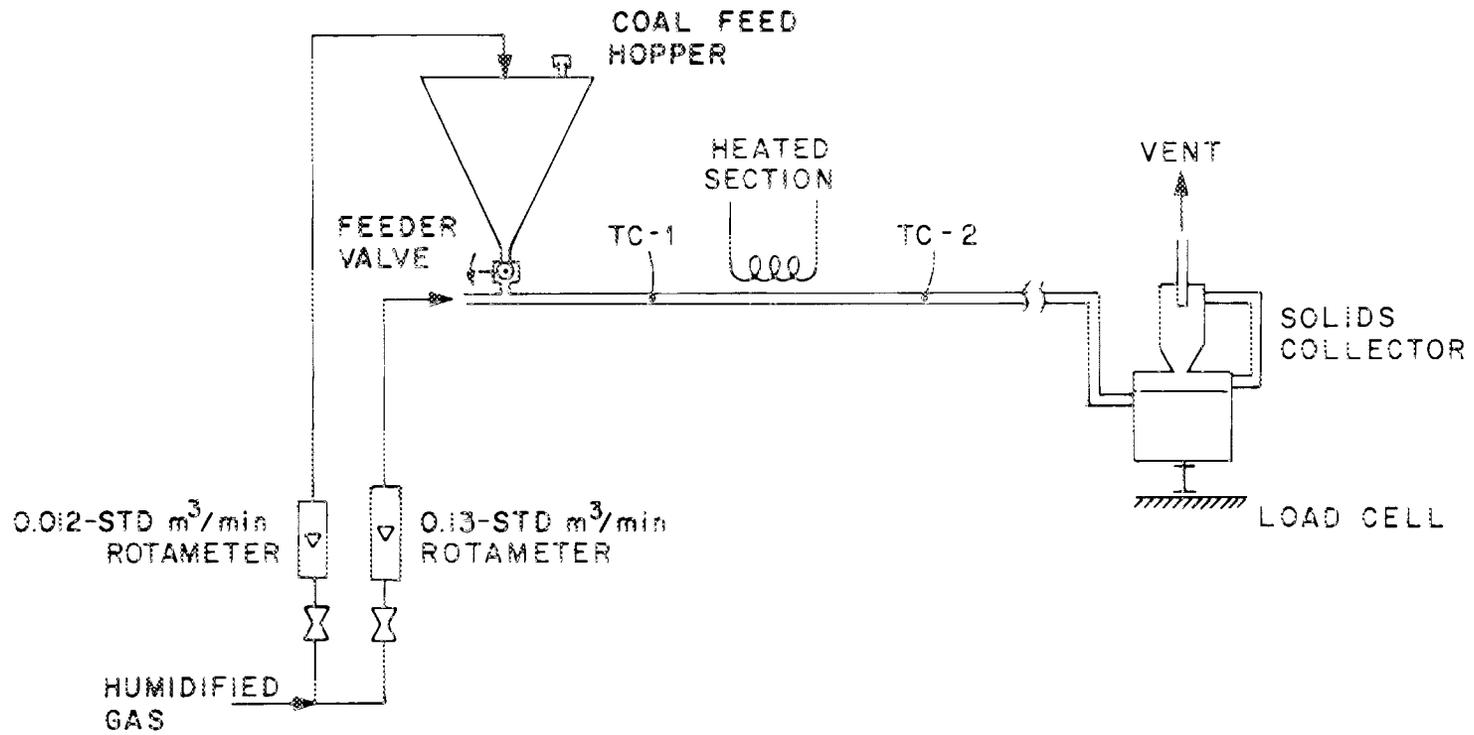


Fig. C.1. Coal feeder and flowmeter test system.

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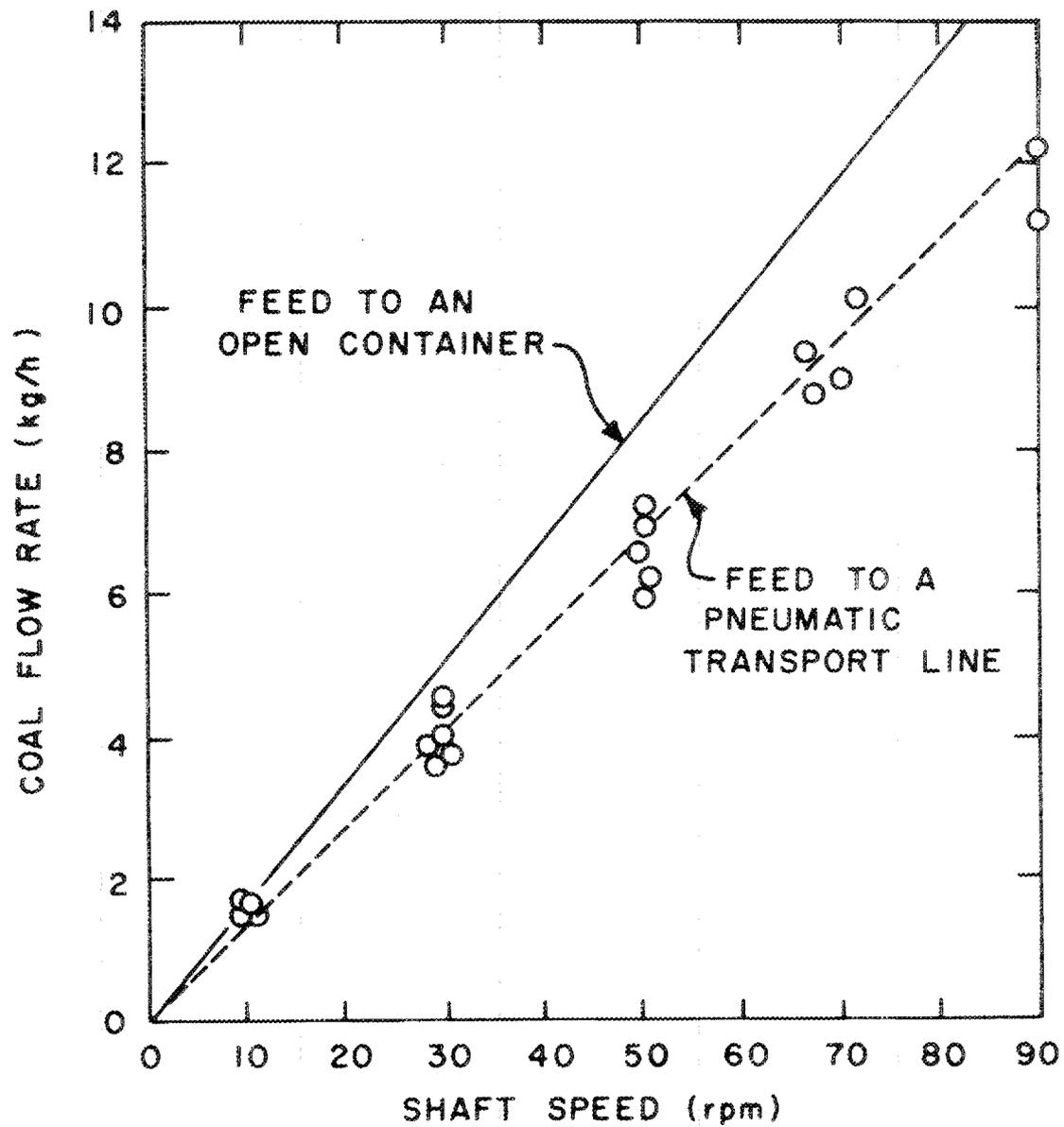


Fig. C.2. Coal flow rate for ball valve feeder as a function of shaft speed.

disassembled and inspected. The stem packing washer had worn out, allowing gas and coal to escape to the atmosphere. The Teflon valve seats were also permanently damaged, and all seats, washers, O-rings, and packing were replaced. The permanent parts of the valve showed little or no damage. The ball locked in position in subsequent tests using brass valve seats, thus causing the shaft to break.

As a result of the difficulties with the modified ball valve, the feeder valve shown in Fig. C.3 was developed. This valve used a rotating Teflon cylinder (0.028-m diam x 0.045 m long) containing six cups (0.016 m x 0.01 m wide x 0.006 m deep) to transfer the coal. The Teflon cylinder was rotated by a brass shaft that was driven by a variable-speed air motor, and the housing contained cooling-water channels for removing heat generated by friction. This feeder was used in the bench-scale hydrocarbonization system. The feed rate was found to be dependent on the bulk density and particle size of the coal feed. The feeder performed satisfactorily during the hydrocarbonization experiments, but inspection and maintenance were required after each run to ensure good performance.

## C.2 Coal Flowmeter Development

Development and testing of solids mass flowmeters were performed to provide a flow monitor for the coal feed stream to the bench-scale hydrocarbonization systems. The first unit tested consisted of a section of 0.013-m (1/2-in.)-diam 304 stainless steel sched 40 pipe with thermocouples attached upstream and downstream of a 0.3-m heated section. Since a coal-gas mixture has a higher heat capacity than gas alone, the temperature difference between upstream and downstream thermocouples will give an indication of the mass flow of coal in the gas stream.

The system shown schematically in Fig. C.1 was used to test the flowmeter. Measurements of the steady-state temperature rise have been made at several gas and coal flow rates, as shown in Fig. C.4.

Equation (1) is the least squares approximation of the coal flowmeter calibration data in the test unit:

$$\Delta T = 20.0 + 127.8 G - 1.47 C, \quad (1)$$

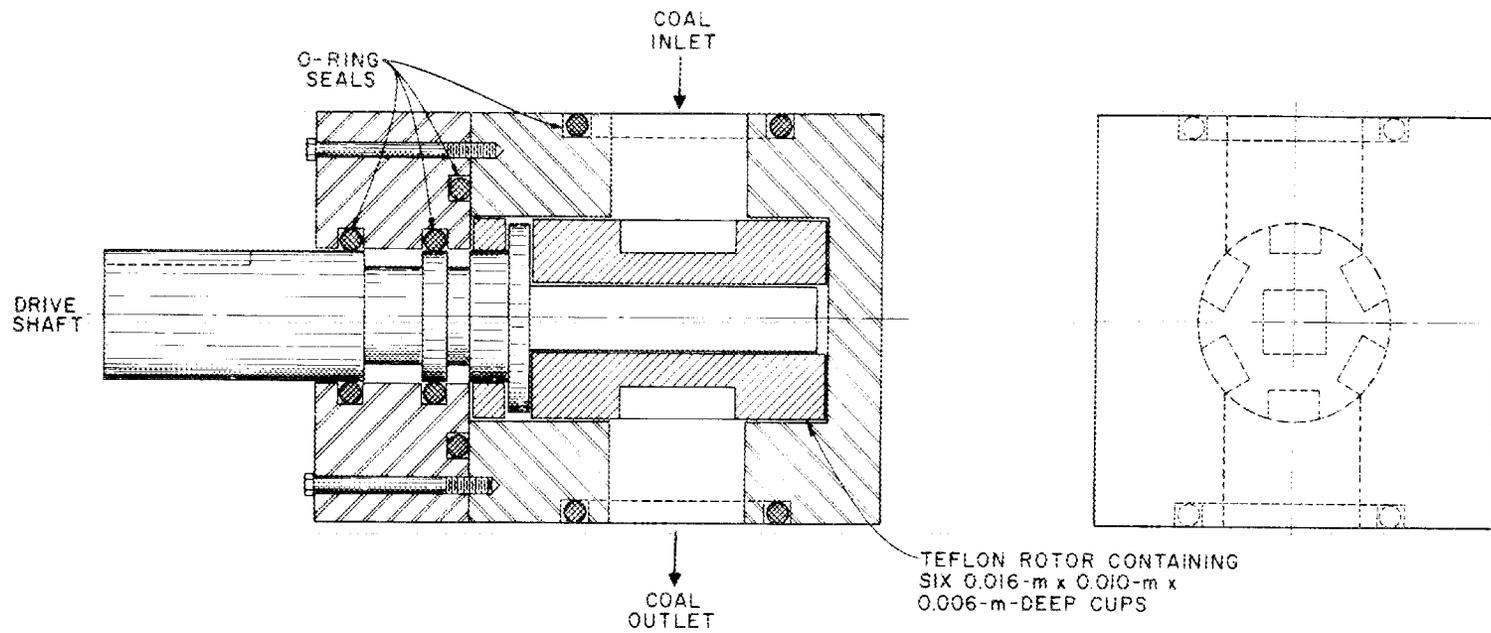


Fig. C.3. Coal feeder valve.

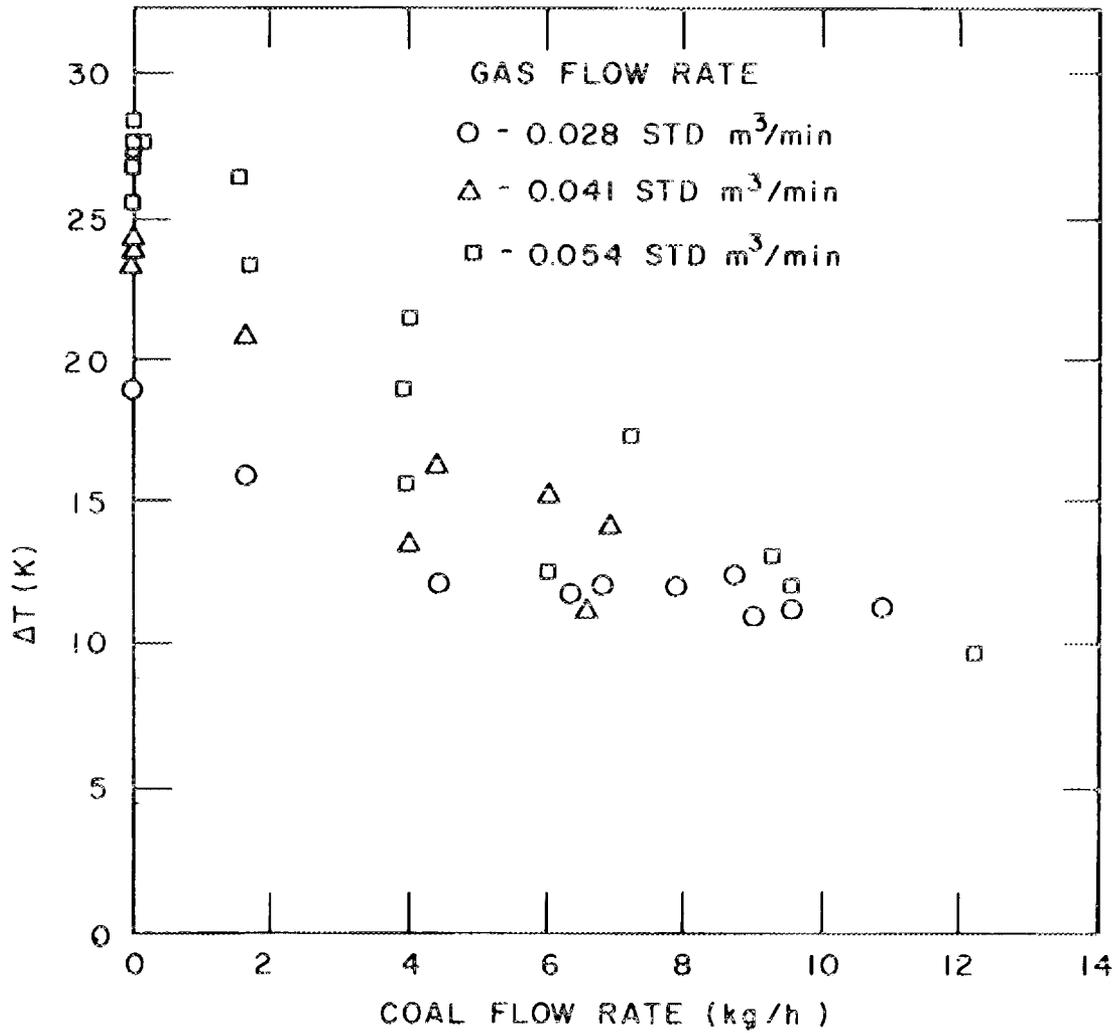


Fig. C.4. Coal flowmeter calibration data.

where

$\Delta T$  = temperature rise in the flowmeter, K;

$G$  = gas flow rate, std m<sup>3</sup>/min;

$C$  = coal flow rate, kg/h.

Figure C.5 is a plot of Eq. (1) vs the data. The correlation coefficient of 0.91 indicates that Eq. (2) is a good approximation of the data. Equation (1) is rearranged so that it can be used to calculate the coal feed rate,  $C$ , as a function of the known gas flow rate,  $G$ , and the measured temperature difference,  $\Delta T$ :

$$C = 13.6 + 86.9 G + 0.68 \Delta T . \quad (2)$$

The estimated standard error in the calculated value of  $C$  is  $\pm 50\%$ . Although this standard error is unsuitably large for quantitative measurements, the coal flowmeter appears to be of value for monitoring the coal flow, especially as an indicator of flow stoppage.

To reduce the sensitivity of the coal flow monitor to the gas transport rate, heating tapes were attached to the coal transport line upstream and downstream of the coal feeder valve, as shown in Fig. C.6. Heating tapes of equal resistance were used and were connected to a common power supply to ensure equal power input to each leg of the monitor. Both heated sections were thermally insulated to prevent heat loss. Thermocouples were attached at the inlet and exit ends of each heated section. The thermocouples were connected in opposition and connected to a millivolt recorder, as shown in Fig. C.6. With proper adjustment, the recorder receives a zero signal when gas alone is flowing and a positive signal when coal is flowing. The system was used for the bench-scale runs. A semiquantitative indication of coal flow can also be obtained with this system.

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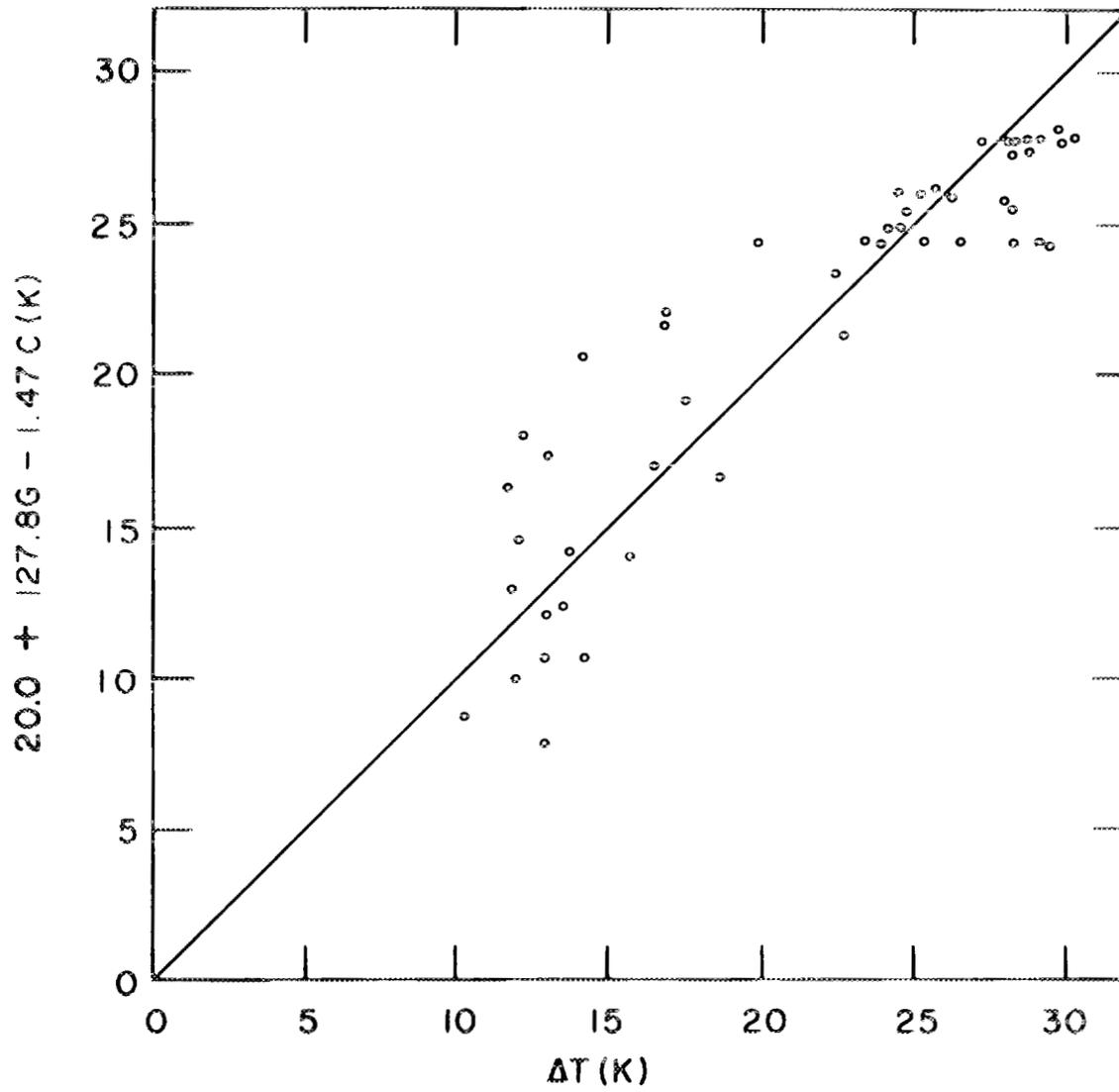


Fig. C.5. Data correlation for coal flowmeter.

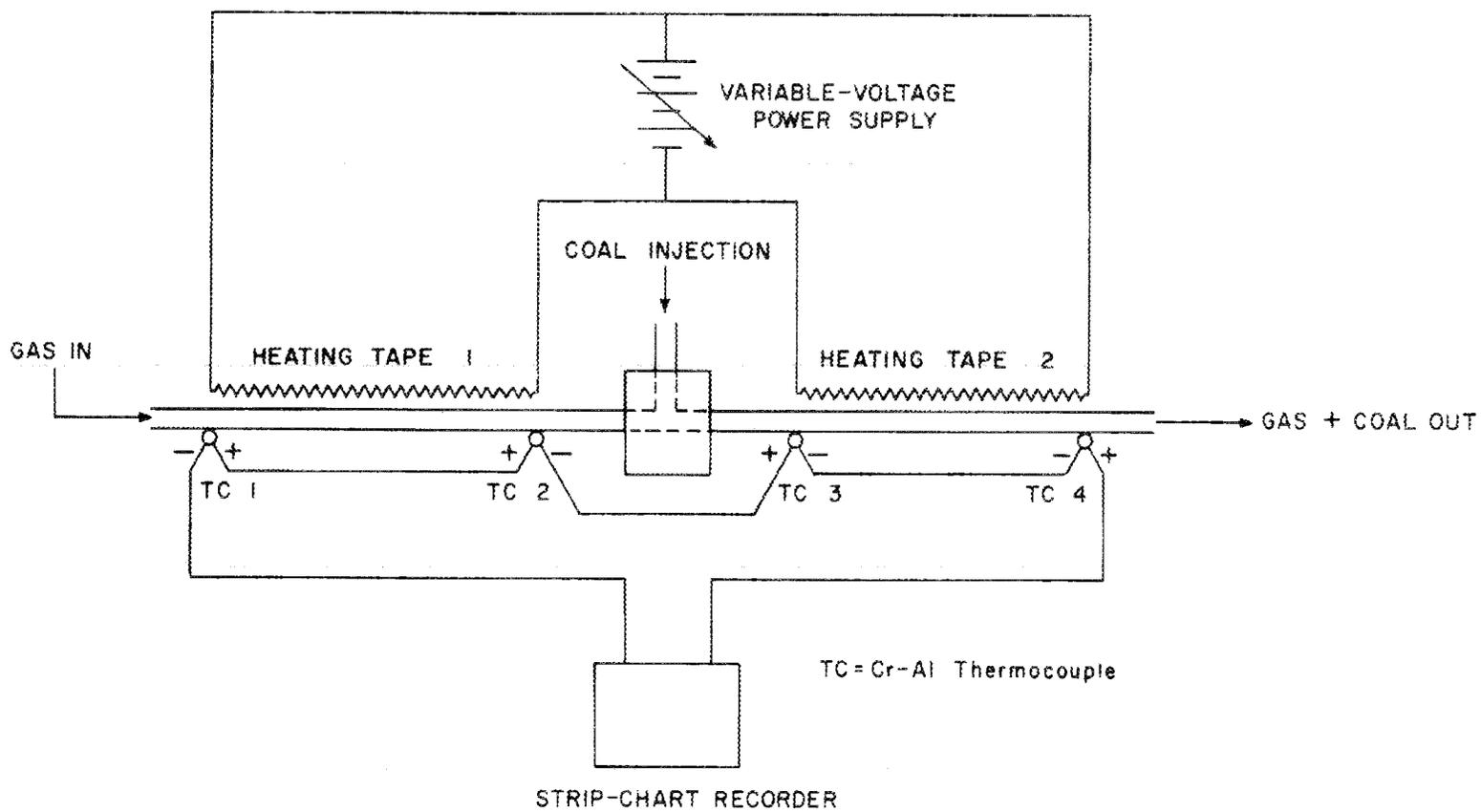


Fig. C.6. Schematic of coal flow monitor.

## APPENDIX D: DESCRIPTION OF EQUIPMENT

The reactor and the modifications that were made during the experimental program are described in Sect. 3. Major pieces of equipment, the instrumentation, and the gas supply system for the bench-scale hydrocarbonization system are described below. The main process vessels were constructed of 316 stainless steel.

## D.1 Gas Preheater

The preheater was an externally heated U-shaped vessel made of 0.076-m (3-in.) sched 80 pipe. It was designed to operate at temperatures of up to 1033 K and pressures up to 2515 kPa. Room-temperature gas enters via a 0.013-m (1/2-in.) sched 80 nozzle flanged to one leg of the U, and heated gas exits through a 0.025-m (1-in.) sched 80 nozzle located on the opposite leg. Heating was provided by surface-mounted electrical resistance heaters. Originally, the vertical legs of the preheater were filled with packing made from 0.0064-m-OD tubing measuring 0.025 m long. After run HC-9, the packing was replaced with a filler constructed of 0.064-m-OD tubing closed at each end. The filler rods were used to increase the gas velocity and to improve the heat transfer in the preheater.

## D.2 Feed Hopper

The feed hopper was a flanged vessel made of 0.25-m (10-in.) sched 40 pipe with a conical lower section rolled from 0.009-m plate. A 0.025-m (1-in.)-diam sched 40 nozzle was used for coal feed. A 0.05-m ball valve was located at the top of the vessel for coal charging. The vessel has a design rating of 2515 kPa at 533 K.

## D.3 Coal Feeder Valve

The coal feed valve, located at the bottom of the feed hopper, was used to meter coal into the transport line where it was pneumatically transported to the reactor (shown in Fig. C.3 in Appendix C). The valve

consisted of a rotating Teflon cylinder (0.028-m diam x 0.045 m long) containing six cups (0.016 m x 0.01 m x 0.006 m deep), which were used to transfer the coal. The feeder valve was rotated by a variable-speed air motor operated from the control room. Additional information on the feed valve is given in Appendix C.

#### D.4 Char Receiver

The char receiver was connected to the reactor through a 0.025-m (1-in.) sched 80 pipe and expansion joints. The body of the receiver was constructed of 0.25-m (10-in.) sched 80 pipe, and the lower conical section was rolled from 0.013-m plate. Char could be removed through a 0.025-m (1-in.) sched 80 nozzle located at the bottom of the vessel. Maximum operating conditions for the vessel were 866 K and 2515 kPa.

#### D.5 Scrubber System

The scrubber was fabricated from 0.2-m (8-in.) sched 80 pipe. Reactor products entered the scrubber through a 0.025-m (1-in.) sched 80 nozzle located on the lower side of the vessel. Noncondensable liquids and gases exited the scrubber through another 0.025-m (1-in.) sched 80 pipe welded to the upper side of the vessel. Water and condensed products in the scrubber were drawn from the nozzle located on the lower side and circulated by a centrifugal pump (R. S. Corcoran Model 4000 FHP) through two water-cooled heat exchangers, each having 0.78 m<sup>2</sup> of cooling area, to a spray nozzle (Spraying System Company No. 1H316SS10) at the top of the scrubber. Tar products collected in the scrubber were removed through a 0.025-m (1-in.) sched 80 pipe welded to the bottom of the vessel. The vessel is designed to operate at a temperature of up to 950 K and a pressure of 2515 kPa.

#### D.6 Cold Trap

The cold trap was used to collect any remaining condensable liquids that passed through the scrubber. It was constructed of 0.2-m (8-in.) sched 40 pipe and was designed to operate at pressures up

to 2515 kPa. The vessel was cooled to  $\sim 200$  K using coils wrapped around the outside surface through which refrigerated Dowtherm J coolant was circulated. Gas from the scrubber entered the lower portion of the vessel through a 0.025-m pipe and exited through 0.025-m line located at the upper side of the vessel. The cold trap was filled with wire mesh packing for runs HC-1 through HC-15. Fiberglass and cotton string packing were used in addition to the wire mesh for runs HC-16 through HC-28 to reduce the carry-over of oil and tar to the pressure control valve located downstream. Product liquid was removed through a 0.025-m (1-in.)-diam sched 80 pipe at the bottom of the vessel.

#### D.7 Coal Preheater

The coal preheater consisted of a heated Dowtherm G bath containing a 9.1-m coil of 0.0048-m-OD x 0.0007-m wall tubing through which the coal feed to the reactor passed. The preheater was installed in the system prior to run HC-22 and was designed to heat the coal feed stream to  $\sim 477$  K. The preheater vessel was constructed of 0.3-m (12-in.)-diam sched 40 carbon steel pipe. The Dowtherm was heated with a 7.9-kW electrical heater, which was submerged in the liquid.

#### D.8 Activated Charcoal Trap

Before run HC-21 was conducted, the activated charcoal trap was installed in the system downstream of the cold trap and high-efficiency filter to remove light hydrocarbons that were not condensed or otherwise captured in the scrubber, cold trap, or filter. The charcoal trap was constructed of 0.15-m (6-in.)-diam sched 40 carbon steel pipe with a flange at one end. The trap was 0.36 m long and held  $\sim 3$  kg of activated charcoal. The charcoal was divided into three layers by screen partitions in the vessel.

#### D.9 High Efficiency Filter

The high-efficiency filter was located downstream of the cold trap and pressure control valve to remove particulates from the gas effluent stream. A M.S.A. Ultra Air Cylindrical Filter was used for this purpose.

The filters were individually tested and certified to be at least 99.9% efficient in removing 0.3- $\mu$ m particles. The filter was contained in a housing constructed of 0.2-m (8-in.)-diam sched 40 carbon steel pipe.

#### D.10 Instrumentation

Instrumentation for the bench-scale hydrocarbonization system was designed to permit all operations to be performed from the control room once hydrogen was introduced. Flow rates of gases ( $H_2$  and  $N_2$ ) to the system and gas effluent from the system were measured by integral orifice differential pressure cells. Temperatures were measured with Chromel-Alumel thermocouples attached to multipoint recorders. These recorders were equipped with over-temperature alarms. Power to the electrical heaters on the reactor, gas preheater, and heated lines was controlled by solid-state temperature controllers. The heated equipment was protected from damage by electrical short circuits by a ground-fault interrupt system that automatically shuts off the power in the event of a short circuit. Pressure transmitters were used to measure system pressure and the pressure differential across the reactor. A coal flow monitor (described in Appendix C) was used to indicate the flow of coal from the feed hopper to the reactor.

On-line analysis of the gas effluent from the reactor was made using Bendix Model 7000 process gas chromatograph, which measured the concentration of  $H_2$ ,  $CH_4$ ,  $CO$ ,  $CO_2$ ,  $H_2S$ ,  $N_2$ ,  $C_2H_4$  and  $C_2H_6$ , and  $C_3H_6$  and  $C_3H_8$  on an 8-min cycle. The oxygen content of the gas effluent is measured with a General Monitors model 800 oxygen analyzer. The oxygen analyzer is used mainly to verify that oxygen has been removed from the system before hydrogen is introduced.

A General Monitors model 160 ten-channel combustible gas detector is used to monitor the equipment room and gas effluent stream (during start-up and shutdown) for hydrogen and hydrocarbon gases. Two Honeywell model 7012 flame detectors with ultraviolet sensors are used for detecting hydrogen flames in the equipment area. The equipment area also has a smoke detector connected to the plant fire-alarm system.

A major safety feature of the facility is an automatic shutdown system that puts the equipment in a safe standby condition in the event that a rapid shutdown is necessary. The shutdown system could be activated either manually by switches located in the control room and outside the building or automatically if unsafe operating conditions exist. Conditions that activate an automatic shutdown are inadequate ventilation, loss of instrument air, loss of electrical power, excessive flow of hydrogen into the system, or an abnormally low gas effluent rate (indicating a possible leak in the system). Actuation of the shutdown system turns off power to the heaters, vents the system to atmospheric pressure, stops the flow of hydrogen, and starts a nitrogen purge.

#### D.11 Gas Supply System

The major gas supplies for the bench-scale hydrocarbonization system were nitrogen and hydrogen. Piping was available for methane service, although it was not used. Nitrogen was used primarily for purging the system and for fluidization during start-up and shutdown. During hydrocarbonization, hydrogen was used for fluidization and for coal transport in order to maintain a hydrogen atmosphere in the reactor. Both hydrogen and nitrogen are supplied from 934-std m<sup>3</sup> tube trailers located near the facility. Pressure was reduced to 2651 kPa at the trailer station for delivery into the building. Individual gas cylinders containing standard gas mixtures are used for calibration of the gas chromatograph, oxygen monitor, and combustible gas monitors before each experiment.

## APPENDIX E: DETAIL DESCRIPTION OF EXPERIMENTS

## E.1 Description of Runs with Wyodak Coal

E.1.1 Uniformly fluidized-bed runs

Runs HC-1 through HC-5 were carried out in a uniformly fluidized bed (0.71 m deep) at a pressure of 2170 kPa. Wyodak coal that had been exposed to air during grinding and sieving was used as feed material. Experimental conditions for the runs are tabulated in Table E.1. In these runs, fluidized-bed temperatures ranging from 761 to 852 K were investigated. Run HC-21 was also made using a uniformly fluidized bed that was 0.71 m deep. However, run HC-21 used Wyodak coal prepared under an inert atmosphere. The fluidized-bed temperature during the run was 830 K. Although temperature control and operation of the system were generally good, the coal feed stopped several times. Each time, it was necessary to clear the transfer line with gas flow before operation could be resumed. The system was operated at a pressure of 2170 kPa during the first 5.9 h of feed, but this pressure was reduced to 1894 kPa during the last 6.3 h to allow a higher pressure drop across the transport line in order to overcome some minor feeding difficulties. These difficulties resulted from system pressure fluctuations caused by tar accumulating on the pressure control valve and by a partial restriction in the transport line resulting from a spacer that had been moved out of position during assembly.

Run HC-6 used a uniformly fluidized bed and Wyodak coal that had been exposed to air during its preparation; however, the run was made at a pressure of 1136 kPa as compared to ~2170 kPa, which had been used in the other uniformly fluidized-bed runs. The bed temperature for the run was 827 K.

E.1.2 Recirculating fluidized-bed runs

The recirculating fluidized-bed reactor shown in Fig. 3.3 was used for runs HC-7 through HC-14. A 0.017-m-ID draft tube measuring 0.74 m long was centered in the reactor 0.025 m above the distributor plate

Table E.1. Summary of experimental conditions for uniformly fluidized-bed runs with Wyodak coal<sup>a</sup>

Run No.	Bed temperature (K)	Reactor pressure (kPa)	Coal feed rate (kg/h)	Hydrogen rate (std m <sup>3</sup> /min)	Run time (h)
HC-1	852	2170	0.6	0.20	9.6
HC-2	827	2170	3.8	0.16	13.2
HC-3	761	2170	6.0	0.14	8.1
HC-4	811	2170	6.4	0.16	7.3
HC-5	791	2170	7.0	0.14	7.7
HC-6	827	1136	7.4	0.07	5.1
HC-21	830	2170/1894 <sup>b</sup>	4.6	0.37	12.2

<sup>a</sup>Coal for runs HC-1 through HC-6 was exposed to air during grinding and sizing.

<sup>b</sup>Reactor pressure was 2170 kPa for the first 5.9 h of coal feeding and 1894 kPa for the remaining 6.3 h.

to recirculate the bed. Coal was pneumatically transferred to the bottom of the draft tube through a 0.0035-m-ID line that ended flush with the distributor plate. A more detailed description of the reactor is given in Sect. 3. Lines were included for introducing additional gas into the draft tube and distributor plate in order to provide proper fluidization and bed circulation. Conditions that gave satisfactory fluidization and bed circulation were determined in mock-up studies described in Appendix B. The operating conditions used for the recirculating fluidized-bed runs with Wyodak coal are summarized in Table E.2. Runs HC-7 through HC-14 were made at a reactor pressure of nearly 2170 kPa; run HC-25 was made at an operating pressure of 1136 kPa. Wyodak coal that had been exposed to air during preparation was used for run HC-7. Runs HC-8 through HC-14 and HC-25 used Wyodak coal prepared under an inert atmosphere. Fluidized-bed temperatures ranging from 694 to 850 K were investigated.

Table E.2. Summary of experimental conditions used for recirculating fluidized-bed runs with Wyodak coal

Run No.	Bed temperature (K)	Reactor pressure (kPa)	Coal feed rate (kg/h)	Hydrogen rate (std m <sup>3</sup> /min)	Run time (h)
HC-7 <sup>a</sup>	711	2170	6.7	0.22	6.9
HC-8	694	2170	6.2	0.31	6.2
HC-9	786	2170	3.1	0.32	4.8
HC-10	839	2170	2.0	0.33	10.6
HC-11	830	2170	4.0	0.33	2.3 <sup>b</sup>
HC-12	825	2170	4.6	0.32	10.5
HC-13	758 <sup>c</sup>	2170	5.0	0.32	10.3
HC-14	850 <sup>d</sup>	2170	4.2	0.32	6.0
HC-25	844	1136	5.0	0.31	10.0

<sup>a</sup>Coal for run HC-7 was exposed to air during grinding and sizing.

<sup>b</sup>Steady-state operating period was too short to determine yields.

<sup>c</sup>Time-average temperature. Operated at 783 K for 4.6 h; lost bed during shutdown; restarted at 783 K for 1.8 h; dropped to 755 K for 0.8 h; then 705 K for 3.1 h.

<sup>d</sup>Time-average temperature. Operated at 866 K for 3.3 h; dropped to 847 K for 1.1 h; then 816 K for 1.5 h.

Operation of the equipment was generally satisfactory; however, some difficulties were encountered. In run HC-7, minor difficulties with the electrical heaters and controllers limited operation to below-design temperature. Equipment failure hindered two attempts at the beginning of HC-8. The liquid yield from HC-9 is questionable because of erratic system flows during the run. A lower-than-average coal feed rate in run HC-10 resulted from periodic bridging in the feed hopper. An excessive amount of fines in the feed (36% < 150 mesh) was thought to have caused the bridging. Run HC-11 was unsuccessful despite smooth operation for 2 h. The run was terminated because of difficulty in maintaining an adequate gas supply pressure, which resulted from icing

of the regulator on the supply trailer. Only 9 kg of coal was fed; hence, no material balance was attempted.

Operation during run HC-12 was quite satisfactory. Run HC-13 produced useful data, but it was interrupted after 4.6 h of smooth operation at a temperature of 783 K by a loss of feed. Apparently, the coal feed line became plugged during system pressure fluctuations. After cleaning the line, operation was resumed at a temperature of 783 K for 1.8 h before the bed temperature drop—first to 755 K for 50 min and then to 705 K for the remaining 3.1 h. A time-temperature average was used to evaluate the oil yield from the run. Similar temperature changes were observed in run HC-14. During the first 3.3 h of operation, the bed temperature was 866 K. It then dropped to 847 K for 1.1 h and to 816 K for the last 1.5 h. The loss of temperature control apparently resulted from a change in the quality of bed circulation.

Run HC-25 was conducted using a recirculating bed with a 0.022-m-ID x 0.74-m-long draft tube. A system pressure of 1136 kPa was used, as compared to 2170 kPa used for the other recirculating fluidized-bed runs. The system operated smoothly throughout the run at a temperature of 844 K.

### E.1.3 Rapid hydrolysis run

For Run HC-28, the reactor was modified to give rapid disengagement and quenching of the volatile products. This was done by attaching the draft tube directly to a cyclone, as shown in Fig. 3.5. Run HC-28 was conducted using the revised circulation system to study rapid hydrolysis of Wyodak coal at 854 K and 2170 kPa. The system operated very smoothly throughout the run.

Design of the char recirculation system for the reactor was based on studies performed in the 0.1-m-ID Lucite mock-up. The draft tube measured 2.67 m long and was constructed of 0.022-m-ID stainless steel tubing. The coal feed was introduced through a 0.0048-m-OD line that entered the bottom of the draft tube through 0.0077-m-ID tubing. The annular space between the two lines was used to introduce additional

gas to the draft tube. Char from the fluidized bed enters the bottom of the draft tube through a side arm having a 0.016-m-ID opening. The upper end of the draft tube is attached to a open cyclone (0.05-m ID) in which the char is disengaged from the gas stream and returned to the fluidized bed for recirculation. The gas stream passes through a second cyclone (0.024-m ID) before entering the scrubber, where it is rapidly quenched to 305 K by a water spray.

The recirculation system was tested in the mock-up before being installed in the reactor. At gas velocities equivalent to those used in run HC-28, the char circulated smoothly at a rate of 272 kg/h. The cyclone efficiency was  $\sim 99.8\%$ , resulting in a char carry-over of  $\sim 0.5$  kg/h. Although a lower char entrainment rate would be desirable to reduce the amount of solids collected with the oil product, the rate was considered acceptable for the run.

Run HC-28 was made at a pressure of 2170 kPa and a draft tube temperature of 847 K. The average temperature of the fluidized bed was 854 K. The total hydrogen flow rate to the system was  $0.65 \text{ std m}^3/\text{min}$ , with  $0.48 \text{ std m}^3/\text{min}$  going to the draft tube and  $0.17 \text{ std m}^3/\text{min}$  to the fluidized bed. The superficial gas velocity in the draft tube was 2.9 m/s, giving a gas residence time in the draft tube of  $\sim 1$  s. The coal feed stream to the draft tube ( $0.14 \text{ std m}^3/\text{min}$ ) was preheated to 477 K, while the remaining draft tube gas ( $0.34 \text{ std m}^3/\text{min}$ ) was preheated to 644 K. The run duration was 6 h and 56 min, during which time 42.7 kg of coal was fed at an average rate of 6.2 kg/h.

The system operated very smoothly throughout the run. The temperature, pressures, and gas flow rates remained steady. The temperatures in the reactor were uniform, indicating good fluidization and char circulation. The temperatures in the upper section of the reactor above the char overflow line and the off-gas line between the reactor and scrubber were higher than those attained in previous runs because of the circulation of char to the top of the reactor.

## E.2 Description of Runs with Untreated Illinois No. 6 Coal

Some unique problems are encountered when processing caking coals in a high-temperature fluidized bed. Caking coals such as Illinois No. 6 have a Free-Swelling Index in the upper part of the 1 to 10 range. They soften at temperatures that exceed  $\sim 672$  K.<sup>1</sup> The outer surface of the particle becomes plastic, and small bubbles appear in the coal. As the temperature is increased, the walls surrounding the bubbles may rupture. At still higher temperature, referred to as the resolidification point, the particle becomes a hard, porous mass. Resolidification occurs at a temperature of  $\sim 783$  K.

When a highly caking coal is introduced into a fluidized bed maintained at a temperature above the initial softening point, it becomes plastic and begins to swell. Individual coal particles contacting one another tend to adhere and form agglomerates. Thus, the incoming coal stream must be rapidly diluted with inert char to avoid agglomeration. The recirculating fluidized bed can be extremely effective in accomplishing this dilution because of the high char recirculation rate through the draft tube into which the coal feed stream is introduced.

Eight operability tests (runs HC-15 through HC-20, HC-22, and HC-27) with Illinois No. 6 caking coal were conducted. Table E.3 summarizes the experimental conditions for each experiment.

Illinois No. 6 coal diluted with char (devolatilized at 922 K in the atmospheric pressure carbonizer) was fed to the reactor, which was operated at a hydrogen pressure of 2170 kPa and bed temperatures ranging from 714 to 872 K. Three char-to-coal dilution ratios were investigated — 6/1, 5/1, and 3/1. During run HC-17 (reactor bed temperature of 714 K), a sustained feed period, with good reactor bed recirculation, of 7 h at a feed rate of 4.4 kg/h was achieved. For the other runs, reactor bed recirculation was limited by agglomeration on the hot reactor wall or by equipment problems. Since the reactor feed was diluted with char and the quantities of coal fed to the reactor were small, the amount of oil produced was not sufficient to determine liquid yields.

Table E.3. Summary of experimental conditions for runs using Illinois No. 6 caking coal

Experiment	HC-15	HC-16	HC-17	HC-18	HC-19	HC-20	HC-22	HC-27
Coal feed								
Char/Illinois No. 6 coal ratio wt/wt	5/1	5/1	6/1	6/1	3/1	3/1	3/1	<u>a</u>
Total weight fed, kg	1.9	7.8	33.1	38.3	17.4	20.9	1.3	2.3
Total feed period, h	0.4	1.5	7.6	10.0	4.5	5.4	0.6	1.7
Uninterrupted feed period, h	0.2	1.3	7.0	9.0	4.0	4.5	0.3	0.5
Feed rate, kg/h	4.4	5.2	4.4	3.9	3.9	3.9	3.2	1.4
Reactor								
Total H <sub>2</sub> input, std m <sup>3</sup> /min	0.30	0.54	0.54	0.54	0.57	0.62	0.57	0.57
To coal transport tube	0.07	0.20	0.20	0.18	0.20	0.31	0.14	0.14
To draft tube nozzle	0.05	0.03	0.03	0.04	0.03	0.06	0.03	0.03
To downcomer plenum	0.18	0.31	0.31	0.32	0.34	0.25	0.40	0.40
Temperature of H <sub>2</sub> entering downcomer plenum, K	783	839	727	783	866	824	855	761
Bed temperature at start of feed, K	866	714	714	797	769	839	852	872
Wall temperature at start of feed, K	922	769	797	866	805	900	839	880
Estimated maximum temperature reached by coal in draft tube during noncirculation period, K	<u>b</u>	<u>b</u>	<u>b</u>	589	561	505	836	861

aUndiluted Illinois No. 6 coal.

bData not available.

A recurrent problem in runs HC-18, -19, and -20 in which the reactor bed temperature was in the range of 769 to 839 K was blockage of the downcomer region by agglomerated solids adhering to the hot ( $\sim 866$  K) reactor wall. Although coal was fed to the reactor for considerable periods, this blockage prevented proper bed circulation and resulted in incomplete devolatilization of the coal feed. Since much of the reactor heat load was supplied by the electrical heaters on the exterior of the reactor wall, a substantial temperature differential existed between the reactor wall and the reactor bed.

The first two experiments (HC-15 and HC-16) were basically shakedown tests with caking coal. No system modifications were made for HC-15. The feed mixture consisted of five parts char to one part Illinois No. 6 coal. When the feed was introduced in run HC-15, the reactor was at a temperature of 866 K and a pressure of 2170 kPa. Three attempts were made to feed coal, but each attempt was terminated after a few minutes by plugging of the coal transport tube at the entrance to the reactor. Several modifications were made before the next run (HC-16). The hydrogen supply to the draft tube nozzle, which blankets the coal transport tube as it enters the reactor, was not heated in order to provide cooling for the transport tube. The 0.017-m-ID draft tube was replaced with a 0.022-m-ID draft tube since experience with the atmospheric pressure carbonizer had shown the latter to be less prone to agglomeration buildup.

The modification improved system operation. Run HC-16 was the first successful attempt to feed caking coal to the reactor. A mixture of one part Illinois No. 6 coal to five parts char was fed to the reactor at a rate of 5.2 kg/h for a period of 1.25 h. The temperature and hydrogen pressure of the reactor bed were 714 K and 2170 Pa, respectively. To aid in the handling of agglomerating coal, the hydrogen feed rate was increased from 0.30 std  $\text{m}^3/\text{min}$  used in run HC-15 to 0.54 std  $\text{m}^3/\text{min}$ . The higher hydrogen supply rate improved recirculation of the char bed in the reactor. The axially spaced reactor-bed temperature measurements were reasonably uniform during the feed period. The run was terminated

by plugging of the transport line. Post-run inspection showed that thermal stresses had caused the transport line to break free of the draft-tube nozzle screen and slip under it, causing a restriction in the flow through the transport line.

Prior to run HC-17, the internal cyclone was removed from the reactor since it had been the site of some agglomeration. For run HC-17, a mixture of one part Illinois No. 6 coal to six parts char was fed at a rate of 4.4 kg/h for 7 h without interruption. The temperature and hydrogen pressure of the reactor were 714 K and 2170 kPa, respectively. A partial blockage in the char overflow line occurred after 7 h of steady operation. The axially spaced reactor bed-temperature measurements were very uniform, indicating excellent bed recirculation. The hydrogen flow rates were the same, and a char starter bed was used as in run HC-16. Although the system operated well during the run, the operating temperature of 714 K was not sufficient to achieve good devolatilization of the coal, and higher operating temperatures were needed to obtain good oil yields.

During the next three runs (HC-18, -19, and -20), reactor bed temperatures up to 839 K and a decreased char dilution ratio (3/1, char/Illinois No. 6 coal) were investigated. Uninterrupted feed periods of 9 h for run HC-18, 4 h for run HC-19, and 4.5 h for run HC-20 were achieved with a nominal feed rate of 3.9 kg/h. As mentioned previously, agglomeration blockages of the downcomer region prevented extensive devolatilization during these runs.

For run HC-18, coal diluted to a 6/1 ratio with char was fed at a rate of 3.9 kg/h to the 797 K, 2190-kPa reactor bed. The reactor temperature was uniform at 797 K when coal feeding was initiated. After the feed was introduced, the bed temperature dropped to 714 K in 50 min. After 10 min of steady operation at 714 K, there were indications that the downcomer region may have become blocked by agglomerate material adhering to the hot (866 K) reactor wall. The blockage was indicated by a loss of reactor-bed differential pressure and scattering of the axially spaced bed-temperature measurements. There was apparently very little circulation through the downcomer for the

remainder of the run (9 h), and the main solids flow path was a single pass through the draft tube and out the overflow port. With this flow pattern, the solids residence time in the reactor was less than  $\sim 10$  s, whereas the solids residence time with normal bed recirculation is  $\sim 60$  min. Without the benefit of recirculating char to heat the coal rising through the draft tube and with essentially all of the hydrogen that entered the reactor flowing through the draft tube, the maximum temperature reached by the coal was calculated to be  $\sim 589$  K. This temperature is not sufficient for extensive devolatilization of the coal. Agglomerated material blocking the char overflow line terminated the run after 10 h of operation.

A lower char-to-Illinois No. 6 coal ratio (3/1) was used in run HC-19. Attempts were made to ensure that there was an adequate starter bed in the reactor at the beginning of the run; however, much of the bed was discharged to the overflow line while the system was being pressurized and depressurized to remove air. The temperature of the hydrogen entering the downcomer plenum was increased to 866 K to reduce the heat load on the reactor. The behavior of the bed during run HC-19 was similar to run H-18, with the downcomer apparently becoming blocked  $\sim 25$  min after the feed operations were initiated. Under these conditions, the feed was continued at 3.9 kg/h for 4 h.

Run HC-20 was made with the 3/1 char-to-Illinois No. 6 coal feed mix as in run HC-19. To minimize loss of the char starter bed, a deflector plate was installed at the reactor char overflow port, and the experimental procedure was modified so that the char starter bed could be introduced after completion of the purge cycles. The hydrogen flow rates into the reactor were chosen to give maximum bed recirculation based on recent ambient mock-up work. The reactor pressure was 2170 kPa. About half of the char starter bed remained and was recirculating at 839 K after the coal feed was introduced. As in the previous two runs, the bed temperature dropped to 714 K 20 min after the feed was initiated. The temperature measurements of the bed remained within a few degrees of 714 K for the next 40 min. Then, the downcomer apparently became blocked as before, the bed temperatures showed a wider

variation, and the bed differential pressure went to zero. The feed was continuous at a rate of 3.9 kg/h for 4.5 h. The maximum temperature reached by the coal during the last 3.5 h of operation was calculated to be 505 K. The run was terminated by a plug at the char overflow port.

The main objective of run HC-22 was to determine whether the caking problems in the reactor that had been experienced in previous runs with Illinois No. 6 coal could be eliminated by ensuring that the material leaving the draft tube had been heated above 811 K. To accomplish this, a preheater was installed in the coal transport line to the reactor, and a thermocouple was installed to measure the temperature inside the draft tube. A started bed of char was added to the reactor before the run was started. The feed was a 3/1 mixture of char and Illinois No. 6 coal. Hydrogen flow rates of 0.14 std m<sup>3</sup>/min to the transport line, 0.40 std m<sup>3</sup>/min to the downcomer, and 0.03 std m<sup>3</sup>/min to the draft tube were used. The flow rates were based on conditions that gave good char circulation and fluidization in mock-up studies. The initial bed temperature in the reactor was 852 K. All the temperatures in the fluidized bed were fairly close, and the temperature of the material flowing through the draft tube was 836 K, indicating that there was good fluidization in the bed and good circulation through the draft tube. The coal preheater performed well, heating the feed stream to 469 K before it entered the reactor. Coal feed was started at a relatively slow rate of 1.1 kg/h. The rate was increased to 2.3 kg/h after 5 min; 12 min later, the rate was increased to 3.2 kg/h. During this period, the system appeared to perform well, and there was a high gas evolution rate, indicating that the coal was being devolatilized. After ~20 min of operation, however, the temperature of the material passing through the draft tube began to decrease, and the bed temperatures began to diverge, indicating that caking had occurred. Operation was continued until the draft tube became plugged after ~35 min of run time. Post-run inspection showed that the downcomer area was caked around the top of the draft tube. Evidently, the coal had not been sufficiently devolatilized in the draft tube to prevent caking after it was discharged into the downcomer region.

An objective of run HC-27 was to determine whether increased residence time in the reactor would sufficiently devolatilize coal in the draft tube so that the caking problems at the top of the draft tube which had occurred in previous runs with untreated Illinois No. 6 coal could be eliminated. To accomplish this, the length of the fluidized-bed section of the reactor and the draft tube were increased by 1.52 m, as shown in Fig. 3.4. Operating conditions for the run were similar to those used in runs HC-23, HC-24, and HC-26, with the exception that the bed temperature was  $\sim 28$  K higher (872 K). The operating pressure was 2170 kPa, and the total hydrogen flow to the system was  $0.57 \text{ std m}^3/\text{min}$ , with  $0.17 \text{ std m}^3/\text{min}$  being fed to the draft tube and  $0.40 \text{ std m}^3/\text{min}$  to the distributor plate. Assuming that  $\sim 80\%$  of gas from the distributor plate entered the draft tube, as observed in mock-up studies, the gas residence time in the draft tube was  $\sim 0.8$  s. The feed material was undiluted Illinois No. 6 coal. Before beginning the run, 8.5 kg of char was fed to the reactor as a starter bed. With the starter bed in the reactor and with the hydrogen flow at the desired ratio, temperatures in the downcomer were uniform, indicating good circulation of the char. The transport gas stream was preheated to 461 K. The temperature of material leaving the draft tube was  $\sim 861$  K, or  $\sim 11$  K cooler than the bed in the downcomer. Coal feed to the reactor was started at a slow rate of  $\sim 1.4$  kg/h. Almost immediately after the feed was started, the temperature profile in the reactor changed, probably as a result of caking. The transport line plugged 30 min after the coal feed was started, and it was necessary to reduce the system pressure to clear the line. Coal was fed to the reactor during three other periods for a total time of 1 hr and 40 min, during which time a total of 2.3 kg of coal was fed; however, operation was erratic, and bed circulation and fluidization were poor. The run was therefore terminated. The reactor was examined after the run, and caking was found to have occurred both at the top and bottom of the fluidized-bed section. We have not determined at what location the caking first began to occur. Performances of the system with caking coal could probably be improved by more vigorous fluidization of the downcomer and by improving mixing and the method of introducing coal at the bottom of the draft tube.

### E.3 Description of Runs with Treated Illinois No. 6 Coal

Three experiments (HC-23, HC-24, and HC-26) were made using Illinois No. 6 coal that had been pretreated to eliminate the caking tendencies of the coal. Treatment methods similar to those developed at Battelle Memorial Institute were used. Coal for run HC-23 was prepared by pretreatment with CaO and NaOH, and coal for run HC-24 was pretreated with  $\text{Na}_2\text{CO}_3$ . Both pretreatments were done in an autoclave. Before run HC-26, scouting tests were performed to find a pretreatment method that could be conducted at atmospheric pressure. Based on these tests, a  $\text{Na}_2\text{CO}_3$ -CaO pretreatment was developed for use in run HC-26. Operating conditions for the runs are given in Table E.4. A more detailed description of the coal pretreatment methods is given below.

#### E.3.1 Coal pretreatment method

Coal for run HC-23 was prepared by mixing 1.8 kg of coal (-45 +170 mesh) with 0.24 kg of CaO, 1.3 kg NaOH, and 7.3 kg of water. The mixture was heated in a rocking autoclave at temperatures in the range of 473 to 548 K for ~1 h. After removal from the autoclave, the coal was washed with water, filtered, and dried in a vacuum dryer. The treated coal had a Free-Swelling Index of <1 and exhibited only a slight tendency to agglomerate. The treated coal was passed through a Sweco Separator to remove oversize (+38 mesh) particles. After the oversize particles had been removed, the remaining coal contained ~31% fines (~140 mesh). Apparently, the caustic treatment had caused considerable comminution of the coal particles. A small portion of the material was tested in the feeder to the Bench-Scale Hydrocarbonization System and was found to have poor flow characteristics. The fines content of the coal was then reduced to 25% by one pass through the Sonic Sifters. The resulting material had acceptable flow characteristics and was used as the feed for the run. The sulfur and ash content of the coal before and after treatment is given in Table E.5. Approximately half of the sulfur content of the coal was removed by the pretreatment.

Feed for run HC-24 was prepared by heating 1.8- to 2.3-kg batches of Illinois No. 6 coal (-50 +170 mesh) with 0.9 kg of  $\text{Na}_2\text{CO}_3$  and 7.0 kg of

Table E.4. Summary of experimental conditions for runs with pretreated Illinois No. 6 coal

Run No.	Bed temperature (K)	Reactor pressure (kPa)	Coal feed rate (kg/h)	Hydrogen rate (std m <sup>3</sup> /min)	Run time (h)
HC-23	844	2170/2032 <sup>a</sup>	2.1	0.57	13.3
HC-24	844	2170	4.3	0.57	7.7
HC-25	841	2170	3.9	0.54	12.8

<sup>a</sup>Reactor pressure was 2170 kPa for the first 4.0 h and 2032 kPa for the remaining 9.3 h.

Table E.5. Sulfur and ash content of CaO-NaOH-treated coal used in run HC-23

	Illinois No. 6 coal before treatment (%)	Illinois No. 6 coal after CaO-NaOH treatment (%)
Organic sulfur	2.31 (2.70 maf)	0.90 (1.47 maf)
Total sulfur	3.86 (4.51 maf)	1.38 (2.26 maf)
Calcium	0.94	4.55
Sodium	0.09	4.46
Ash	12.2	23.5

water in a batch autoclave. The slurry was heated to 573 K and held at that temperature for 2 h. After cooling, the coal was washed with water, filtered, and dried in a vacuum dryer. Free-Swelling Index measurements indicated that the treated coal had only a slight tendency to agglomerate. Analysis of the coal before and after treatment with Na<sub>2</sub>CO<sub>3</sub> is given in

Table E.6. The results indicate that the treatment removed a small amount of the sulfur. The treated coal contained 2.9% sodium and had a higher moisture and ash content than the original coal.

Prior to run HC-26, scouting tests, as shown in Table E.7, were performed to investigate methods of pretreating Illinois No. 6 at atmospheric pressure to reduce the caking tendencies. Such a pretreatment should be much easier and less expensive than treatments requiring the use of high pressure. In these tests, mixtures of Illinois No. 6 coal (-45 +170 mesh), water, and other materials were heated for ~24 h. Following the treatment, the coal was filtered, rinsed with water, and vacuum dried. As shown by the Free-Swelling Index results, CaO, char, activated carbon, and  $\text{FeCl}_3$  and mixtures of these materials eliminated caking under some of the conditions used, while  $\text{Na}_2\text{CO}_3$ , NaOH,  $\text{Fe}_2(\text{SO}_4)_3$ , and  $\text{H}_2\text{SO}_4$  alone did not. Treatment No. C-1, using a mixture of CaO and  $\text{Na}_2\text{CO}_3$ , was selected for pretreating the feed for run HC-26. Approximately the same concentrations of CaO and  $\text{Na}_2\text{CO}_3$  are used in this treatment as were used in runs HC-23 and HC-24, respectively. The CaO is effective in reducing the caking tendencies of the coal and for reaction with sulfur. The  $\text{Na}_2\text{CO}_3$  is expected to be useful in improving liquid yields and making the char more reactive.

Table E.6. Analyses of Illinois No. 6 coal before and after treatment with  $\text{Na}_2\text{CO}_3$  for run HC-24

	Illinois No. 6 coal before treatment (%)	Illinois No. 6 coal after treatment with $\text{Na}_2\text{CO}_3$ (%)
Moisture	2.2	4.2
Ash	12.2	16.8
Volatile matter (maf) <sup>a</sup>	37.4	33.0
C	81.0	82.5
H	6.4	5.8
N	1.3	1.4
Total S	4.5	4.2
Organic S	3.2	3.1
Na	0.09	2.9

<sup>a</sup>Moisture and ash free.

Table E.7. Scouting tests to determine a coal pretreatment method for run HC-26

Sample No.	Amount of Illinois No. 6 coal (g)	Amount of water (ml)	Chemicals Added	Results of Free-Swelling Index
<u>Samples heated to 80°C for 24 h</u>				
A-1	15	75	None (control)	3-1/2
A-2	15	75	15 g HC-14B char	1
A-3	15	75	30 g HC-14B char	1
A-4	15	75	15 g HC-23 char	No caking
A-5	15	75	30 g HC-23 char	No caking
A-6	15	75	15 g HC-24 char	2-1/2
A-7	15	75	30 g HC-24 char	No caking
A-8	25	75	6 g CaO	No caking
A-9	25	75	3 g CaO	No caking
A-10	25	75	5 g activated carbon	No caking
A-11	25	75	5 g NaOH	3-1/2
A-12	25	75	2 g NaOH	2-1/2
A-13	25	75	10 g Na <sub>2</sub> CO <sub>3</sub>	2
A-14	15	75	15 g FeCl <sub>3</sub> ·6H <sub>2</sub> O	1-1/2
A-15	15	75	30 g Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	3
A-16	15	75	5 ml conc. H <sub>2</sub> SO <sub>4</sub>	3-1/2
A-17	15	75	15 g HC-14B char (powdered before mixing)	1-1/2
<u>Samples below refluxed for 24 h</u>				
B-1	50	400	131 g FeCl <sub>3</sub> ·6H <sub>2</sub> O	No caking, crusty
B-2	50	400	103 Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	1-1/2
B-3	50	400	6.5 g CaO, 5 g Na <sub>2</sub> CO <sub>3</sub>	No caking
B-4	50	400	5 g NaOH, 5 g Na <sub>2</sub> CO <sub>3</sub>	2
<u>Samples heated at 80°C for 17 h</u>				
C-1	300	1000	30 g CaO, 128 g Na <sub>2</sub> CO <sub>3</sub>	No caking

Feed for run HC-26 was prepared by treating Illinois No. 6 coal (-45 to +170 mesh) with CaO, Na<sub>2</sub>CO<sub>3</sub>, and water at ~353 K for 16 h. The treatment was performed in two batches. Each batch consisted of 31.2 kg coal, 3.12 kg CaO, 13.13 kg Na<sub>2</sub>CO<sub>3</sub>, and 104 ℓ of water. The mixture was agitated in a 55-gal drum containing a steam coil. The coal was washed with water, filtered, and dried in a vacuum dryer after treatment. The treated coal had a Free-Swelling Index of zero. Analysis indicates that this coal contained ~3.4% sodium and 2.6% calcium, as shown in Table E.8. Sulfur was not removed by the pretreatment.

### E.3.2 Description of runs with pretreated Illinois No. 6 coal

The draft tube in run HC-23 was used to recirculate the reactor bed. Prior to the run, 4.2 kg of char was fed to the reactor for the starting bed. The reactor temperature was held at 844 K throughout the run. The average hydrogen flow rate to the coal transport line was 0.12 std m<sup>3</sup>/min, and the hydrogen rates to the downcomer and draft tube were 0.40 and 0.05 std m<sup>3</sup>/min, respectively. The coal feed stream entering the reactor was preheated to 464 K. Operation of the system was generally good, with the exception that the coal feed rate was lower than had been planned, possibly due to the large amount of fines present in the feed. Fluidization of the bed appeared to be good throughout the run, as indicated by uniform temperatures in the bed and a constant pressure differential across the bed. The temperature of the material circulating through the draft tube was only ~8 to 11 K lower (833 K) than that of the downcomer region, indicating good circulation of char through the draft tube. There were no indications of caking of the bed with the treated coal, as had been observed in previous runs with untreated Illinois No. 6 coal. From the start of the run, the coal feed rate was low. The feed hopper was pressurized slightly in an attempt to increase the feed rate. After 4 h of operation, the system pressure was reduced from 2170 kPa to 2032 kPa to avoid the possibility of blowing a ruptured disc. The run continued for 13.3 h until all the coal (29 kg) had been fed. The average feed rate for the run was 2.1 kg/h.

Table E.8. Analysis of Illinois No. 6 coal before and after treatment with CaO and Na<sub>2</sub>CO<sub>3</sub> for run HC-26

	Illinois No. 6 coal before treatment (%)	Illinois No. 6 coal after CaO-Na <sub>2</sub> CO <sub>3</sub> treatment (%)
Moisture	0.2	2.78
Ash	11.0	27.1
Volatile matter	39.7	35.1
C (maf)	77.7	81.7
H (maf)	5.9	5.8
N (maf)	1.4	1.5
Total sulfur (maf)	4.1	4.4
Organic sulfur (maf)	2.9	2.8
Ca	0.6	3.4
Na	0.07	2.6

Run HC-24 was made with the draft tube in place to provide a recirculating fluidized bed in the reactor. The run duration was 7.7 h, during which time 33 kg of coal was fed. The run proceeded very smoothly with no interruptions. The fluidized-bed temperature was uniform at 844 K, and the top of the draft tube was at 830 K, indicating that good fluidization and char recirculation had been achieved. The system pressure for the run was 2170 kPa. The total hydrogen flow rate to the reactor was 0.57 std m<sup>3</sup>/min, with 0.40 std m<sup>3</sup>/min going to the downcomer, 0.14 std m<sup>3</sup>/min to the coal transport line, and 0.03 std m<sup>3</sup>/min to the draft tube nozzle. The coal feed was preheated to 461 K before entering the reactor. No caking or agglomeration problems occurred during the run.

In run HC-26, the reactor was also operated as a recirculating fluidized bed. The starter bed consisted of 2.45 kg of char from run HC-25. During the run, the temperature of the fluidized bed was uniform

at 841 K, and the temperature of material leaving the draft tube was 819 K. The operating pressure was 2170 kPa. The total H<sub>2</sub> flow rate was 0.54 std m<sup>3</sup>/min, with 0.37 std m<sup>3</sup>/min going to the downcomer and 0.17 std m<sup>3</sup>/min to the draft tube. The run duration was 12 h and 50 min, during which time 50.6 kg of coal was fed at an average rate of 3.9 kg/h. Operation of the system was generally good. The coal was somewhat more difficult to feed than usual, which was possibly due to the lime particles that were present. A small nitrogen purge was used in the feed hopper to assist in feeding the coal. The reactor bed appeared to be uniformly fluidized during the run, and there was no evidence of caking. Inspection of the reactor after the run showed it to be free of cakes or deposits.

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155. A. Theodore Stewart, Jr., Chief Scientist, Research and Engineering, Bechtel Corporation, 50 Beale St., San Francisco, CA 94105
156. J. D. Sullivan, System Development Corporation, 2500 Colorado Ave., Santa Monica, CA 90604
157. J. Todd, Department of Materials Science and Mineral Engineering, Hearst Mining Building, University of California, Berkeley, CA 94720
158. Raymond E. Vener, DOE Scientific Representative, U.S. Embassy, Bonn, APO, New York, NY 09080
159. D. Weeter, Civil Engineering Department, University of Tennessee, Knoxville, TN 37916
160. J. R. Thurgood, Utah Power and Light Co., P. O. Box 899, Salt Lake City, UT 84110
161. R. F. Weimer, Air Products & Chemicals, Inc. P. O. Box 538, Allentown, PA 18105
162. Richard A. Wolfe, Vice President, Research and Development, United Coal Companies, P. O. Box 1280, Bristol, VA 24201
163. James C. Young, Civil Engineering Department, Iowa State University, Ames, IA 50011
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