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RESEARCH AND DEVELOPMENT OF RAPID HYDROGENATION FOR COAL CONVERSION TO SYNTHETIC MOTOR FUELS

(RISER CRACKING OF COAL)

Second Quarter Report
For the Period July 1 to September 30, 1978

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ABSTRACT

Over the reporting period, work in the bench-scale unit has been directed at exploring methods for handling caking coals. Throughout this work, a sample of Illinois No. 6 coal having an FSI of 4-1/2 has been used, and the methods explored included the use of dry diluents, extractive solvents, and additives.

Both silica sand and devolatilized char have been successfully used as dry diluents, but large amounts are required, tending to make processing inefficient. Slurrying with a solvent carrier comprised of 20% by weight naphthalene, 40% by weight toluene, and 90% by weight phenol is in the evaluation stage, as is the use of additives which are used at the level of 10% by weight additive with 90% by weight coal. One of the most promising systems is coal treated in water with calcium hydroxide with subsequent evaporation of the water to obtain dry solids for feeding. The bench-scale unit was modified to permit liquids and slurries to be pumped from atmospheric pressure to reactor pressure in a single step. In the experimental work, it has been found that the mixture of naphthalene, toluene, and phenol can be fed to the reactor at temperature and pressure without plugging the reactor.

Site preparation for the PDU is approximately half finished, and a contract for fabrication of the major vessels is being let. The Incoloy 800 tubing for the preheater and riser reactor has been received, and the pressure shell for the riser should be delivered in December.

A low pressure simulator of a PDU combustor section has been built and operated; there does not appear to be any critical relationship between the mainstream velocity and the entering oxygen velocity, allowing considerable latitude in sizing the air/oxygen injection needle. For temperature changes of 300°F, the use of ceramic shields does not appear to be necessary, but this will be evaluated in further tests.

I. OBJECTIVE AND SCOPE OF WORK

The objective of the research and development program described in this report is to develop the technology of short residence time hydropyrolysis of lignites and coals for optimized yields of high-octane gasoline blending stock constituents. The scope of the investigation will include the design, construction, and operation of a bench-scale unit (5-10 lb/hr) and a process development unit (50-100 lb/hr). The process under development is called "Riser Cracking of Coal." In the final phase of the project, the technical and economic aspects of large-scale operation will be evaluated.

II. ACHIEVEMENT OF PROJECT OBJECTIVES

Task 1 (Planning) has been completed, and Task 2 (Construction and Operation of a Bench-Scale Unit) is continuing in its operating phase. Task 3 (Design of a Process Development Unit) has been completed, and Task 4 (Construction of a Process Development Unit) is in the procurement and initial construction stage.

In the on-going bench-scale unit investigations, the recent efforts have been to explore methods for processing caking coals through the use of dry diluent solids, solvent carriers, and pretreatments with additives such as lime or bentonite clay. Both fine silica sand and devolatilized char have been used successfully as dry diluents, but the large quantities required (80% to 90% by weight of the dry feed) tend to make processing inefficient. Slurry feeding with solvent carriers is in the evaluation stage together with additives deposited on the coal in water or toluene slurries.

By relatively minor changes, the operating pressure of the PDU has been increased to 2600 psig; the site preparation has been 50% completed, a contract for the fabrication of the major pressure vessels is being let, and instrumentation and control purchasing will be completed in the next month. A local supplier has been found who can provide a hydrogen supply system capable of operating at 3000 psig and delivering hydrogen and other gases to the PDU in the volumes needed.

III. SUMMARY OF PROGRESS TO DATE

During the reporting period, 12 runs were made in the bench-scale unit; the overall objectives and results of these runs are summarized in Table 1, and reflect our commitment to explore methods of processing caking coals as outlined in the work plan for the project compiled in the Task 1 report.

As reported previously, using silica sand as a dry diluent, successful runs were made using 20% by weight Illinois No. 6 coal (FSI = 4-1/2) with 80% by weight sand. Devolatilized char was not as efficient a diluent, and a successful run was obtained using 10% by weight coal with 90% by weight char, but not with a mixture of 20% by weight coal with 80% by weight char.

Prior work performed by the U.S. Bureau of Mines[4] showed that by using heating rates of from 6°C/min to 75°C/min, caking coals could be rendered nonagglomerating by fluidization with hydrogen. An attempt was made to extend this finding to the bench-scale unit operation by recycling Illinois No. 6

Table 1. SUMMARY OF RUNS MADE FROM JULY 1 THROUGH SEPTEMBER 30, 1978

Run/Date	Objective	Results
BC-15/6-29-78	Operate with 20 wt % of caking coal and dead-burned char at coil outlet temperature of 1450°F and 2000 psig to determine yields from bituminous coal.	Unsuccessful; aborted after 1 minute of operation because of plug in coil.
BC-16/7-14-78	Operate with 10 wt % of caking coal and dead-burned char at coil outlet temperature of 1450°F and 2000 psig to determine yields from bituminous coal.	Successful; run terminated after 53 minutes of operation due to plug in coil.
BC-17/7-20-78	To perform a hydrogen pretreatment of a caking coal at coil outlet temperature of 800°F and 2000 psig.	Partially successful; aborted after 26 minutes of operation because of plug in coil.
BC-18/7-25-78	To perform a hydrogen pretreatment of a caking coal at coil outlet temperature of 700°F and 2000 psig.	Technically successful; however, material balance incomplete due to incomplete data.
BC-19/7-27-78	To perform an additional hydrogen pretreatment of the caking coal previously treated in Run BC-18 at coil outlet temperature of 800°F and 2000 psig.	Successful; operated for 75 minutes with voluntary shutdown.
BC-20/8-8-78	To perform an additional hydrogen pretreatment of the caking coal previously treated in Run BC-19 at a coil outlet temperature of 850°F and pressure of 2000 psig.	Unsuccessful; run terminated when the coil plugged after a few minutes of operation.
SF-1/8-21-78	To feed a slurry of 20% lignite in toluene using a coil outlet temperature of 1450°F and pressure of 1500 psi.	Successful.
SF-2/8-24-78	To repeat Run SF-1 for a longer operating period.	Partially successful; run terminated when check valve in feed pump malfunctioned.

Table 1. SUMMARY OF RUNS MADE FROM JULY 1 THROUGH SEPTEMBER 30, 1978, Cont.

Run/Date	Objective	Results
SF-3/8-31-78	To test the feeding of solvent system of naphthalene, toluene, and phenol at 1500 psig and coil outlet temperature of 1400°F.	Successful; run ended when sample bombs were filled.
SF-4/9-7-78	Operate with slurry of 20% by weight bituminous coal at 1500 psig and coil outlet temperature of 1450°F. Slurry solvent consisted of 40% by weight phenol, 40% by weight toluene, and 20% by weight naphthalene.	Unsuccessful; plug formed in coil after 1 minute of operation.
SF-5/9-15-78	Repeat of SF-4. Prior to run slurry was autoclaved at 680°F and 2000 psig for 2 hours.	Unsuccessful; plug formed in coil after 1 minute of operation.
CT-1/9-21-78	Operate with bituminous coal pretreated with calcium hydroxide at 1800 psig and soaking temperature profile at 1475°F.	Unsuccessful; plug formed in coil after 1 minute of operation.
CT-2/9-28-78	Operate with Illinois No. 6 coal pretreated with calcium hydroxide sized to -100 mesh at 2000 psig and coil outlet temperature of 1475°F.	Unsuccessful; plug formed in feed end of coil after 1 minute of operation.

coal through the reactor, heating it to successively higher temperatures in successive passes through the bench-scale unit. Successful runs were obtained when the coil outlet temperature was limited to 700° and 800°F, but the coil plugged when the outlet temperature was raised to 850°F. It was concluded that a successful treatment, if possible, was beyond the limits of the coil-tube reactor.

The notion, however, is not without merit, because our commercial concept will involve a fluidized bed in which slurrying solvent is flashed off, and appropriate modification of processing conditions might lead to the desired conversion of agglomerating coals to non-caking coals. It would be necessary, however, to pursue the investigation in a fluidized bed rather than an entrained flow system.

An attempt to feed caking coal to the coil-tube reactor using a solvent carrier was made. Because there was some doubt that wet slurries could be processed without plugging the unit, a slurry of 20% by weight lignite in toluene was processed first in the reactor modified for slurry feeding. These runs were successfully taken through the "dry point" without plugging.

The solvent carrier system of interest was comprised of 20% by weight naphthalene, 40% toluene, and 40% phenol. A quantity of this system was made up, and was successfully run in the bench-scale unit using the slurry feeding equipment, although in the turn-around, some solids were found in the char trap. The residue from the char trap was combined with the liquids recovered from the sample bombs and cold trap to evaluate change in the chemical composition of the solvent system induced by the pyrolysis treatment.

A quantity of Illinois No. 6 coal was then ball milled to -200 mesh size, and a slurry of 20% by weight milled coal with 80% by weight solvent system prepared. Portions of this slurry were autoclaved at 680°F and 2010 psig, and 720°F and 1950 psig for subsequent evaluation in the bench-scale unit. At this writing, the untreated slurry and one autoclaved sample have been tried in the bench-scale unit, but these runs were unsuccessful, with plugs forming in the first minutes of operation.

A number of processes described in the literature were developed for reducing the sulfur content of coals[1-3] which also reduce the caking tendency of the parent coal; these processes involve the treatment of a coal in an aqueous slurry with various additives. It would seem reasonable to redevelop this kind of a process to render caking coals nonagglomerating.

A number of additive materials including sodium carbonate, calcium hydroxide, calcium oxide, calcium carbonate, bentonite clay* and burnt sienna pigment (a clay rich in Fe_2O_3) were tested in various treatments to alter the caking properties of Illinois No. 6 coal. In all of these treatments, 10% by weight additive was mixed with 90% by weight coal.

The treatments consisted of dry-mixing the additive with the coal, mixing with water to obtain a slurry that was subsequently evaporated to dryness, and mixing with toluene to obtain a slurry that was subsequently evaporated to dryness to obtain dry solids for testing.

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* Predominantly montmorillonite, a highly absorptive aluminosilicate. Sodium (or Wyoming) types absorb many times their own weight of water. Used as filler in paper, oil well drilling muds, grease thickener, decolorizing, etc. Found in large deposits world-wide.

Two methods were used to evaluate the caking property of treated coals. In a pipe test, a quantity of test material was placed in a 1/4-inch pipe which was heated to a dull red heat until the evolution of volatile matter ceased. The pipe was then cooled to room temperature and the solid residue examined. The solids were considered non-caking if the residue would flow freely from the pipe used in the test.

In the second test method, a sample of treated coal was placed in a boat which was heated to approximately 1300°F in flowing hydrogen at atmospheric pressure. The treated coal was considered non-caking if the solid residue was free flowing.

None of the additives tested were effective when dry mixed with the coal, or deposited on the coal from a toluene slurry. When deposited on the coal from a water slurry, calcium oxide, calcium hydroxide, and bentonite clay were effective in rendering caking coals non-caking. Approximately 4 pounds of Illinois No. 6 coal was then treated with calcium hydroxide in a water slurry for evaluation in the bench-scale unit.

The design of the PDU has been completed and procurement of the long-delivery items has been started. After reviewing bids, a contract for fabrication of the major process vessels was let. Several local suppliers of hydrogen have been contacted, and one has been found who can provide a system for supplying hydrogen at 3000 psig in volumes sufficient for operation of the PDU.

Detailed drawings of the instrumentation and controls have been completed, and suppliers contacted; instrumentation purchasing should be completed this month. Due to a shortage of electric power, a gas-fired preheater will be used instead of the electrically heated device described in the Task 3 design report.

Our approximate position in the technical program is shown on the progress chart (Figure 1).

IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 2. Build and Operate a Bench-Scale Unit

1. Work Accomplished

a. Bench-Scale Unit Operations

During the reporting period, 2 runs were made in the bench-scale unit (Figure 2) using mixtures of Illinois No. 6 coal (FSI = 4-1/2) and devolatilized char as feedstock, and 4 runs were made using Illinois No. 6 coal by itself as feedstock. The sieve analyses of these materials are shown in Table 2, and the operating conditions and main results are summarized in Table 3. The bench-scale unit was then modified as shown in Figure 3 to permit the feeding of slurries to the reactor; 5 runs were made feeding liquid/solid slurries to the reactor; two final runs were made using Illinois No. 6 coal treated with calcium hydroxide as feedstock.

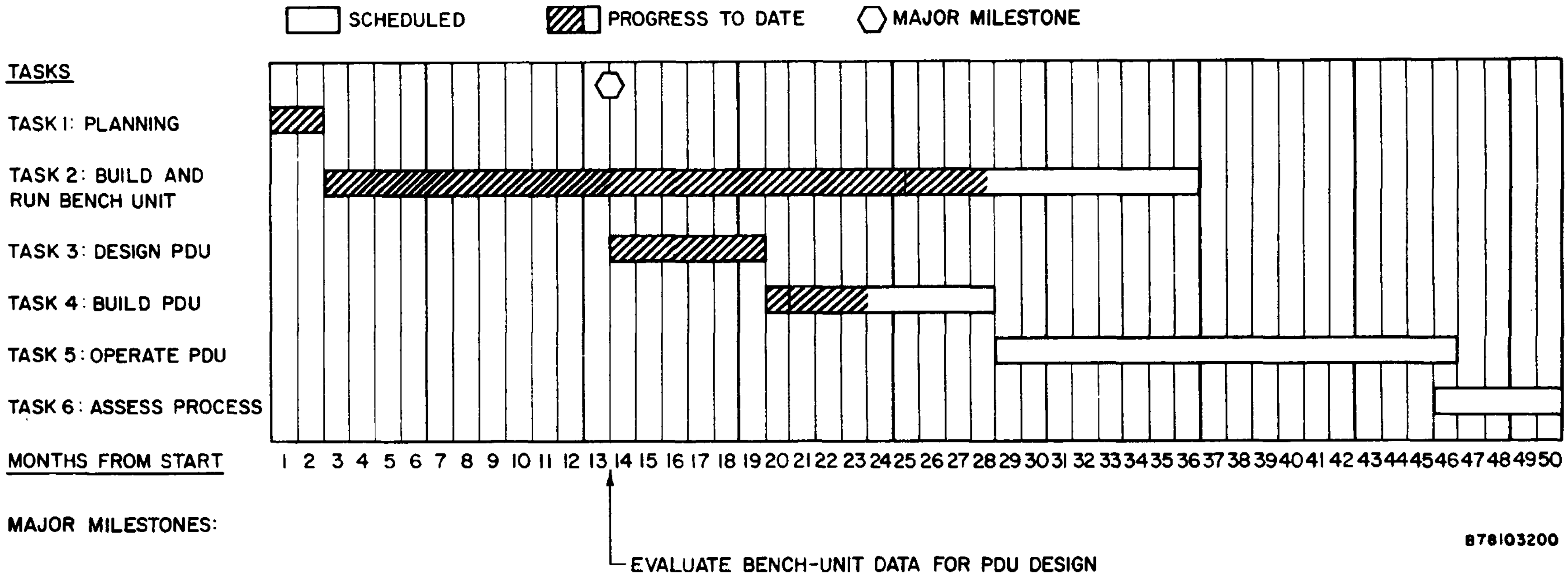

Figure 1. PROGRESS CHART

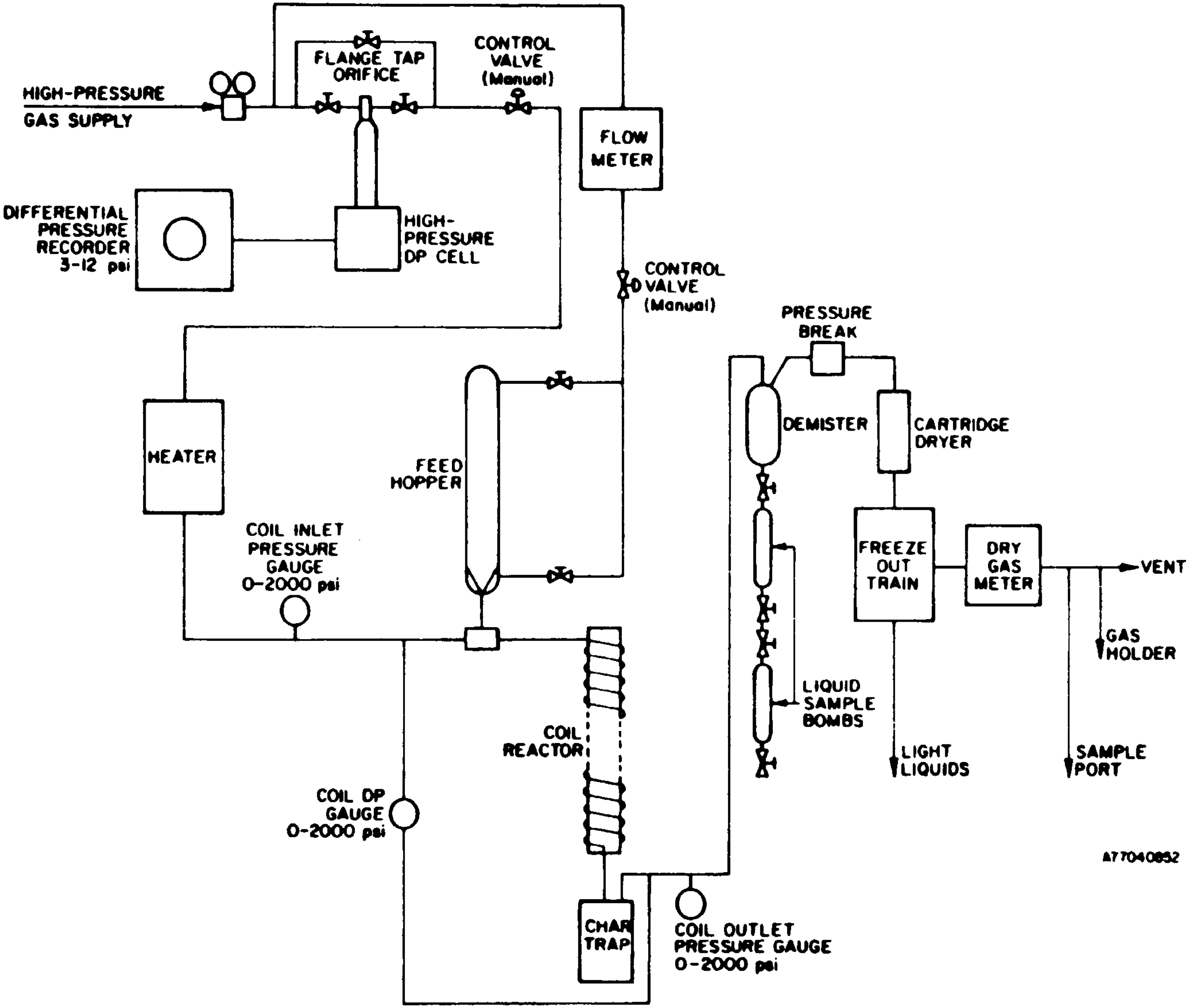

Figure 2. REVISED EQUIPMENT LAYOUT

Table 2. SCREEN ANALYSES OF MATERIALS USED FROM JULY 1 THROUGH SEPTEMBER 30, 1978

Size, U.S. Mesh	North Dakota Lignite	Illinois No. 6 Coal	Coal* and Devolatilized Char
>60	0	0.5	3.4
60 x 80	1.2	24.1	13.3
80 x 100	1.9	12.0	18.4
100 x 200	13.6	40.5	33.3
200 x 325	34.4	21.4	17.3
pan	48.9	1.5	14.3
	100.0	100.0	100.0

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* 20% (by weight) Illinois No. 6 coal with 80% devolatilized char.

Table 3. OPERATING CONDITIONS AND RESULTS OF RUNS MADE FROM JULY 1 THROUGH SEPTEMBER 30, 1978

Run No.	BC-16	BC-18	BC-19	SF-2	SF-3
System Outlet Pressure, psig	2000	2000	2000	1500	1500
Coil Outlet Temperature, °F	1450	700	800	1400	1400
Residence Time, s	2.9	4.0	3.8	2.2	2.2
Solids Feed Rate, lb/hr	8.3	3.6	3.8	2.9	0
Run Length, min	53	75	70	25	19
Solids in Feed Gas, wt %	82.6	76.7	76.2	25.0	0
H_2/MAF Coal Weight Ratio	1.1*	0.304	0.313	1.459	0
Balances, wt %					
Ash	85.6	100.0	100	76.0	--
Carbon	**	--	--	**	--
Hydrogen	**	--	--	**	--
Overall	99.6	100.0	100	84.6	92.3
Carbon Distribution, wt %					
Liquids	6.96*	0	0	**	--
Carbon Oxides	7.61*	0	0	**	--
Methane	21.44*	0	0	**	--
Light Gases	5.25*	0	0	**	--
Char	--	100	100	**	--

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* Based on feed coal fraction.

** In process.

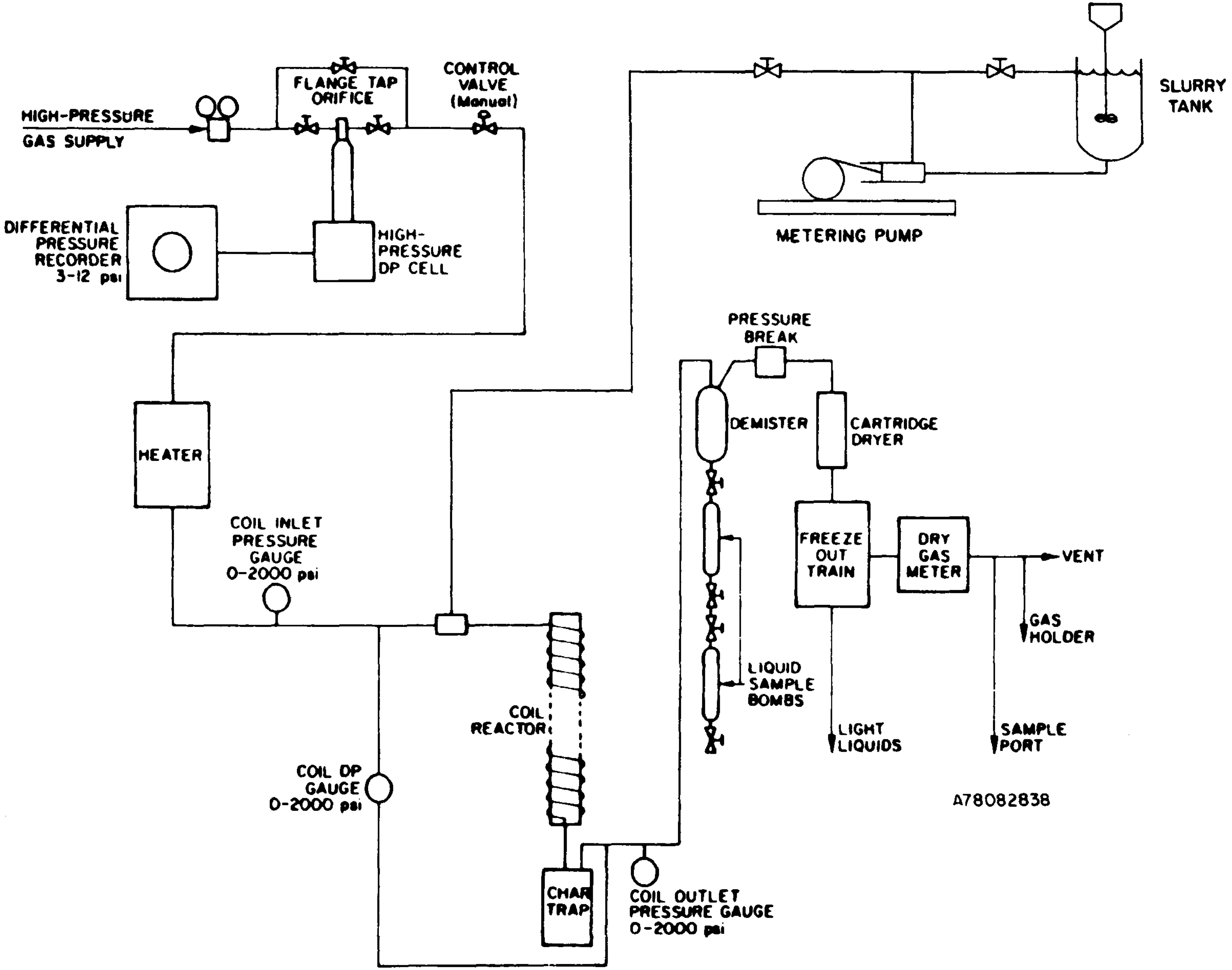

Figure 3. BENCH-SCALE UNIT REVISED FOR SLURRY FEED

The two runs using Illinois No. 6 coal mixed with devolatilized char were made to determine the degree to which the coal would have to be diluted with char to obtain successful processing in the bench-scale unit. The run in which 10% by weight coal was mixed with 90% by weight char (BC-16) was successful, but the run (BC-15) using a mixture of 20% by weight coal with 80% by weight char was not successful, indicating that the maximum amount of Illinois No. 6 coal that could be successfully processed in the bench-scale unit is between 10% and 20% by weight when mixed with dry devolatilized char.

The proximate and ultimate analyses of the feed and spent solids for Run BC-16 are shown in Tables 4 and 5 together with analytical results from other runs which have been unreported up to now. The mass balance and product distribution are shown in Table 6, and the average makegas analyses are shown in Table 7. The available chemical analyses of the main liquid product, the gasoline fraction of the main liquid product, light liquids condensed in the freeze-out train, and fuel oil fraction of the main liquid product are summarized in Tables 8, 9, 10, and 11.

It was anticipated in the IGT proposal covering the work of this project that a combination of reactor residence time and temperature pathway might be found that would permit hydrogenation of caking coal without sticking and agglomeration. In addition, some work reported by Kawa et al.[4] suggested that at low heating rates, caking coals could be made non-caking by fluidization with hydrogen. The next several runs (BC-17, 18, 19, and 20) were made to explore this theory. In BC-17, Illinois No. 6 coal was passed through the reactor at 2000 psig and a coil outlet temperature of 800°F. This run was only partially successful, with a plug forming in the coil after 26 minutes of operation.

In the next run (BC-18), the coil outlet temperature was reduced to 700°F; this run was successful. The treated coal was recycled through the reactor in Run BC-19, in which the reactor was operated at 2000 psig and a coil outlet temperature of 800°F. This run was also successful, with a voluntary shutdown being made after 75 minutes of operation. The pretreatment made in Run BC-18 appears to have had some effect, because the reactor plugged under similar operating conditions with untreated coal (Run BC-17).

A final run was made (BC-20) using the solids recovered from BC-19 as feed, a reactor pressure of 2000 psig and a coil outlet temperature of 850°F. This run was unsuccessful, with a plug forming after a few minutes of operation. It was concluded at this point that while treatments described by Kawa et al.[4] were effective at heating rates of from 6°C/min to 75°C/min, such slow rates are beyond the practical limits of an entrained flow system.

It should be remembered that the commercial embodiment of riser cracking of coal will involve an operation in which slurrying solvent is flashed from the feed solids at temperatures and pressures appropriate to the treatments described by Kawa et al.[4] The investigation should be pursued in terms of a fluidized bed treatment rather than an entrained flow system, however.

The bench-scale unit was then modified as shown in Figure 3 for feeding slurries directly to the reactor. In the first run (SF-1), a slurry of 20% by weight lignite in toluene was used as feed slurry. In modifying the

Table 4. ANALYSIS OF FEED SOLIDS

Run No.	BC-9	BC-11	BC-12	BC-13	BC-16	SF-2
	wt %					
Proximate Analysis						
Moisture	1.1	1.1	1.2	1.1	2.6	19.7
Volatile Matter	8.0	7.6	7.3	7.5	6.4	34.2
Ash	81.3	81.6	82.0	81.8	18.5	8.5
Fixed Carbon	9.6	9.7	9.5	9.6	72.5	37.6
Total	100.0	100.0	100.0	100.0	100.0	100.0
Ultimate Analysis (Dry Basis)						
Ash	82.22	82.54	82.99	82.78	18.99	10.56
Carbon	13.50	13.20	13.10	13.20	74.60	60.90
Hydrogen	0.97	0.95	0.95	0.96	1.04	4.10
Sulfur	0.71	0.72	0.71	0.72	2.38	0.79
Nitrogen	0.09	0.16	0.12	0.17	0.74	0.82
Oxygen (by difference)	2.51	2.43	2.13	2.17	2.25	22.83
Total	100.00	100.00	100.00	100.00	100.00	100.00

Table 5. ANALYSIS OF SPENT SOLIDS

Run No.	BC-9	BC-11	BC-12	BC-13	BC-16	BC-18	SF-2
				wt %			
Proximate Analysis							
Moisture	0.2	0.2	0.2	0.0	0.3	0.6	5.3
Volatile Matter	2.0	1.6	1.5	1.8	3.0	38.5	20.9
Ash	88.5	90.5	90.9	90.9	18.3	10.5	13.4
Fixed Carbon	9.3	7.7	7.4	7.3	78.4	50.4	60.4
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Ultimate Analysis (Dry Basis)							
Ash	88.68	90.68	91.04	90.94	18.39	10.58	14.10
Carbon	10.00	8.50	8.30	8.20	77.60	69.50	79.00
Hydrogen	0.48	0.32	0.32	0.33	0.92	5.02	3.28
Sulfur	0.27	0.20	0.18	0.20	2.04	4.50	0.69
Nitrogen	0.08	0.07	0.00	0.06	0.62	1.29	0.82
Oxygen (by difference)	0.49	0.23	0.16	0.27	0.43	9.11	2.11
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 6. MASS BALANCE AND PRODUCT DISTRIBUTION IN RECENT RUN

Run No.	BC-16
Component	
Feed Solids	3345
Feed Hydrogen	319
Feed Methane	30
Feed CO	19
Feed Nitrogen	19
Feed Argon	318
Total Mass In	4050
Spent Char/Solids	2890
Liquids	196
Light Liquids	4
Gases	944
Total Mass Out	4034
Distribution of Products	
Hydrogen	334
Nitrogen	28
Argon	350
Methane	73
Ethane	29
Propane	3
Light Gases (C_2-C_4)	1
Carbon Oxides	77
Hydrocarbon Liquids	
Main Liquid Product (MLP)	15
Freeze-Out	2
Make-Gas	4
Gases (MLP work-up)	3
Char	2890
Water (by difference)	225
Total Mass Out	4034

Table 7. AVERAGE MAKE-GAS COMPOSITIONS

Run No.	BC-16	BC-18	BC-19	SF-3
	mol % (wet basis)			
Component				
CO	1.1	0.7	0.7	0.5
CO_2	0.2	0	0	0
Hydrogen	85.9	93.9	93.9	93.3
Methane	1.9	0.5	0.5	0.4
Ethane	0.4	0	0	0
Propane	Tr	0	0	0
Butane	0	0	0	0
Ethylene	0	0	0	0
Propylene	0	0	0	0
Acetylene	0	0	0	0
Benzene	Tr	0	0	0
Argon	4.6	4.4	4.5	4.7
Nitrogen	0.5	0.5	0.4	1.1
Steam	5.4	Tr	Tr	0
Total	100.0	100.0	100.0	100.0

Table 8. ANALYSES OF MAIN LIQUID PRODUCT

Run No.	PP-11	PP-12	BC-1	BC-3	BC-7,9	BC-11, 12,13	BC-16
Specific Gravity	1.051	1.051	1.093	1.065	1.079	1.080	1.074
IBP, °F	120	115	179	156	149	152	*
Ultimate Analysis, wt %							
C	80.61	81.23	82.80	79.79	80.00	81.56	80.71
H	7.53	6.11	6.47	6.56	6.62	6.05	6.37
S**	2.21	1.38	2.72	3.26	2.57	2.71	3.24
N	0.45	0.52	0.68	0.85	0.83	0.84	0.70
O (by difference)	9.20	10.76	7.33	9.54	9.98	8.64	8.98
Ash	0.0	0.0	0.0	0.0	0.0	0.20	0.0
C/H Weight Ratio	10.70	13.29	12.80	12.16	12.08	13.48	12.67
Fraction, wt %							
C_5-400°F	46.1	37.3	43.1	43.9	44.8	29.9	*
400°F	53.9	62.7	56.9	56.1	55.2	70.1	*

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* Insufficient sample.

** Sulfur values seem high and will be re-run to verify.

Table 9. ANALYSES OF GASOLINE FRACTION OF MAIN LIQUID PRODUCT

Run No.	BC-11,12,13
	— wt % —
Component	
Benzene	12.10
Toluene	15.40
Ethylbenzene	1.30
Xylenes	3.25
C_9 Aromatics	1.07
Indans	3.48
Indene	0.05
Naphthalenes	20.31
Phenol	35.20
Cresols	2.99
C_8 Phenols	0.11
Unidentified	4.74
Total	100.00

Table 10. ANALYSES OF COLD-TRAP LIQUIDS

Run No.	BC-16
Component	—wt%—
Benzene	21.60
Toluene	49.20
Xylene	6.17
Indene & Indan	1.90
Ethylbenzene	4.16
Naphthalene	13.09
Unidentified*	3.88
Total	100.00

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* Unidentified fraction 90% thiophene and derivatives of thiophene.

Table 11. ANALYSES OF FUEL OIL FRACTION OF MAIN LIQUID PRODUCT

Run No.	PP-5	PP-11	PP-12	BC-1	BC-11, 12,13
Ultimate Analysis, wt %					
C	90.31	89.46	91.44	84.90	87.40
H	5.82	5.77	6.04	5.48	5.68
S	--	--	--	--	**
N	--	--	--	--	**
O (by difference)	--	--	--	--	**
Ash	--	--	--	--	1.1
C/H Weight Ratio	15.52	15.50	15.14	15.49	15.39
CC Residue, wt %	13.2	*	**	*	13.8

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* Insufficient sample.

** In process.

equipment, much difficulty was experienced in getting knife-edge check valves to operate; these were replaced with Ball check valves which performed much better, allowing the slurry to be pumped from ambient pressure to reactor operating pressure (1500 psig) without difficulty. A successful run was obtained which was repeated (SF-2) to obtain a better material balance. The char recovered from the char trap smelled strongly of toluene, however.

To prevent a caking coal from plugging the reactor, a solvent carrier system of 20% by weight naphthalene with 40% by weight toluene and 40% by weight phenol was devised. Illinois No. 6 coal was then ball milled to -200 mesh size to avoid jamming the check valves on the slurry pump, the milled coal was then mixed with the solvent to obtain a slurry containing 20% by weight coal. In the first caking coal trial (SF-3), the solvent system was fed by itself to identify problems in operation, particularly with plugs forming in the coil, and material condensing in the char trap. The run was successful, but in performing the turn-around, some solids were found in the char trap. To evaluate any change in solvent composition, the residue in the char trap was combined with the liquids recovered from the sample bombs and cold trap. These are being analyzed at this time.

In Run SF-4, the slurry of 20% by weight Illinois No. 6 coal in the 80% by weight solvent system was run using a reactor pressure of 1500 psig and a coil outlet temperature of 1450°F; this trial was not successful, with the coil plugging in the first minutes of operation. The slurry was then recovered, and a portion autoclaved at 680°F and 2010 psi for two hours; the autoclaved slurry was then loaded, and tried at the same conditions as those used in Run SF-4. This trial also was not successful, with the coil plugging in the first minutes of operation.

A second portion of the slurry was autoclaved at 720°F and 1950 psia for 1 hour.

The two slurry samples are being held in sealed containers for further testing.

Work with additives such as calcium hydroxide or bentonite clay has shown some promise, and a quantity of Illinois No. 6 coal was pretreated with the calcium hydroxide, the most promising material, from a water slurry. The slurry was then dried, and screened to -60 mesh, prior to loading into the reactor.

The first trial (CT-1) was made using a reactor pressure of 1800 psig and a coil outlet temperature of 1975°F. This run was not successful because of a plug which formed rapidly in the cold head of the coil. The feed solids were recovered and ground to -100 mesh, since it appeared that the feed had defluidized, plugging the coil. The run was repeated (CT-2) with the -100 mesh feed, and the coil again plugged, again in the cold end. Further examination showed that the autoclaved slurry had left tar deposits on the walls of the tube, which could pick up the pulverized coal, and plug the reactor. In both of these runs, the plug was readily removed. The coil was then cooled, and flushed with toluene and acetone to remove the tar deposits.

b. Data Analysis

The net hydrogen consumption for the P, TP, and RT series of runs was calculated and is summarized in Figure 4. The net hydrogen consumption appears to be essentially linear with carbon conversion but is not independent of residence time or temperature profile. The ultimate analyses of the gasoline boiling range liquids obtained from North Dakota lignite are summarized in Table 12. The carbon and hydrogen content are typical of highly aromatic liquids; a sharply upsweeping temperature profile appears to favor high oxygen content, while relatively severe thermal treatment favors low sulfur and oxygen content.

c. Simulation of PDU Combustor

A low-pressure simulator of a riser cracking PDU combustor section (Figure 5) was built and operated to uncover any potential problems in the operation of the PDU combustors. These potential problem areas involved the inlet velocity of air or oxygen relative to the mainstream velocity, possible burning of the air/oxygen needles, and the shielding of the tube walls adjacent to the combustion area with ceramic inserts to prevent damage by radiant heating. In the tests conducted thus far, the air/oxygen needle has remained undamaged, so that the velocity of inlet oxygen relative to the process stream does not appear to be critical. Precise sizing of the injection needle is not required.

Several ceramic shields were broken by thermal shock, but it has been found that when the bulk stream temperature rise is limited to 300°F, the combustor can be operated without ceramic shields. The entrained solids mask the walls, and prevent melting by radiant heating. Some further tests without ceramic shields will be made to confirm this. In addition, better process temperature measurement can be made in the absence of the ceramic shields.

d. Non-Caking Additives and Diluents

The investigation of additives and diluents to render agglomerating coals non-caking was continued, evaluating the products by means of a simple caking test, in which a sample of the prepared solids was heated in a section of 1/4-inch pipe essentially in the absence of air to a dull red heat, until the evolution of volatile matter ceased. The solids are considered non-caking if the residue solids in the pipe are free flowing. In this test, untreated Illinois No. 6 coal forms a hard rod-like mass having the same diameter as the pipe.

The results of the additives and treatments evaluated thus far by this test are summarized in Table 13. The various additives considered were calcium oxide, calcium hydroxide, calcium carbonate, bentonite clay, and burnt sienna (Fe_2U_3). In the tests, 10% by weight of additive was mixed with 90% by weight Illinois No. 6 coal, in addition to dry mixes, water or toluene was added to make a slurry which was then dried to obtain treated solids for testing.

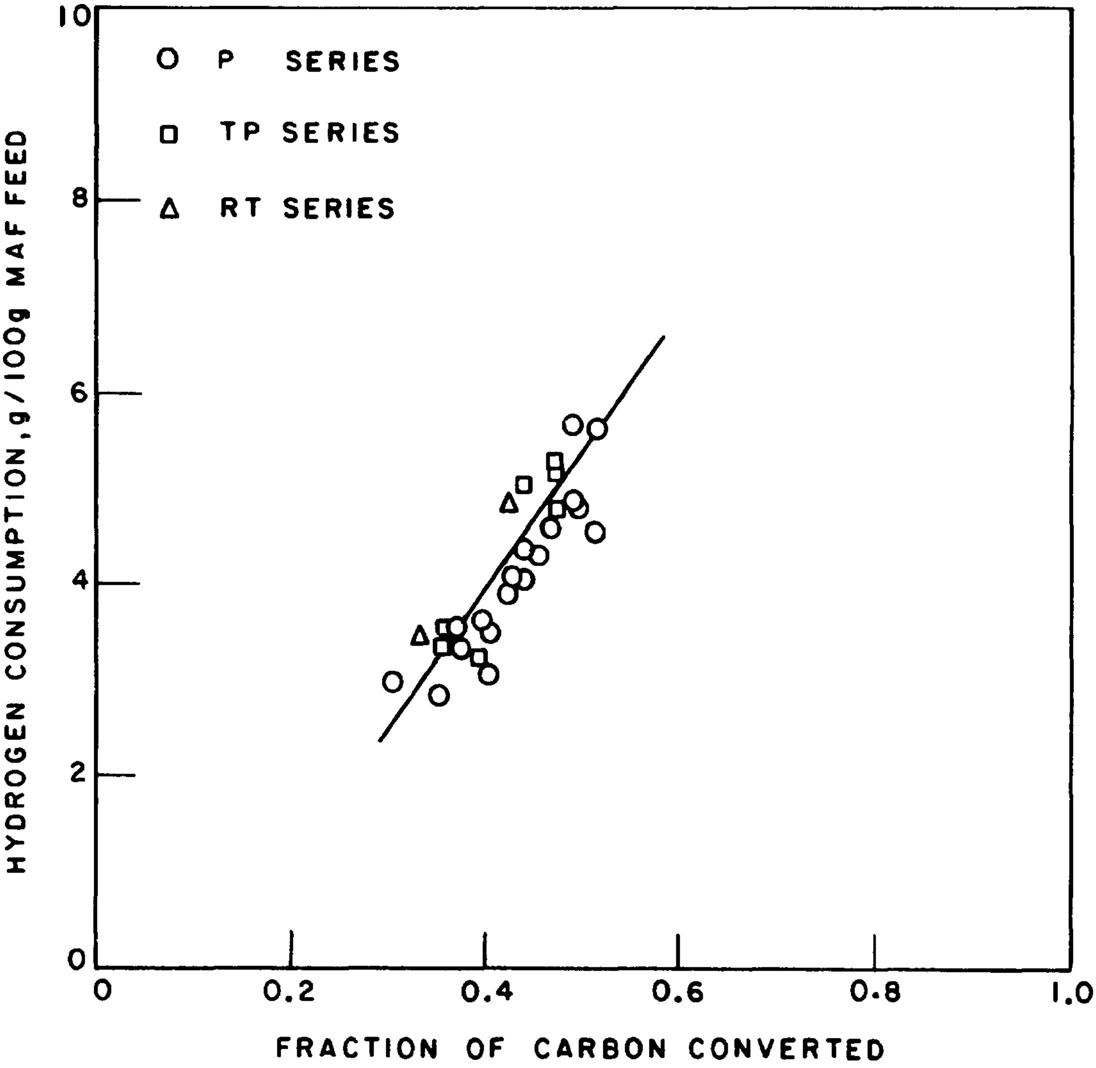

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Figure 4. NET HYDROGEN CONSUMPTION, EXPRESSED AS GRAMS OF HYDROGEN PER 100 GRAMS MAF LIGNITE

Table 12. ULTIMATE ANALYSIS OF GASOLINE BOILING RANGE LIQUIDS OBTAINED FROM NORTH DAKOTA LIGNITE

Run No.	P-10	P-11	P-12	P-13	P-14	P-15	P-16	P-17	P-19	P-21	P-22	P-26
Component												
C	90.21	90.58	87.00	87.59	87.41	89.99	90.63	90.85	89.91	88.21	90.12	88.95
H	7.99	7.86	7.24	7.67	8.35	7.80	7.64	7.64	7.63	7.66	7.38	7.40
S	0.10	0.10	0.15	0.13	0.11	0.10	0.08	0.06	0.08	0.13	0.07	0.05
N	--	--	0.48	0.44	0.51	0.39	0.34	0.23	0.47	0.49	0.35	0.08
O	1.70	1.46	5.13	4.17	3.62	1.72	1.31	1.22	1.91	3.51	2.08	3.52
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Run No.	P-27	P-28	TP-1	TP-2	TP-3	TP-4	TP-5	TP-6	TP-8	TP-10	TP-11	RT-1	RT-2
Component													
C	90.83	91.00	91.66	88.97	89.58	89.93	90.81	90.47	79.84	92.21	82.99	90.81	89.42
H	7.36	7.89	7.70	7.79	7.72	7.68	7.64	7.81	9.06	7.27	7.41	7.78	7.63
S	0.03	0.02	0.01	0.09	0.05	0.07	0.11	0.01	0.09	0.08	0.09	0.09	0.26
N	0.04	0.06	0.02	0.24	0.11	0.06	0.39	0.42	0.14	0.16	0.14	0.27	0.53
O	1.74	1.03	0.61	2.91	2.54	2.26	1.05	1.29	10.87	10.28	9.37	1.05	2.16
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

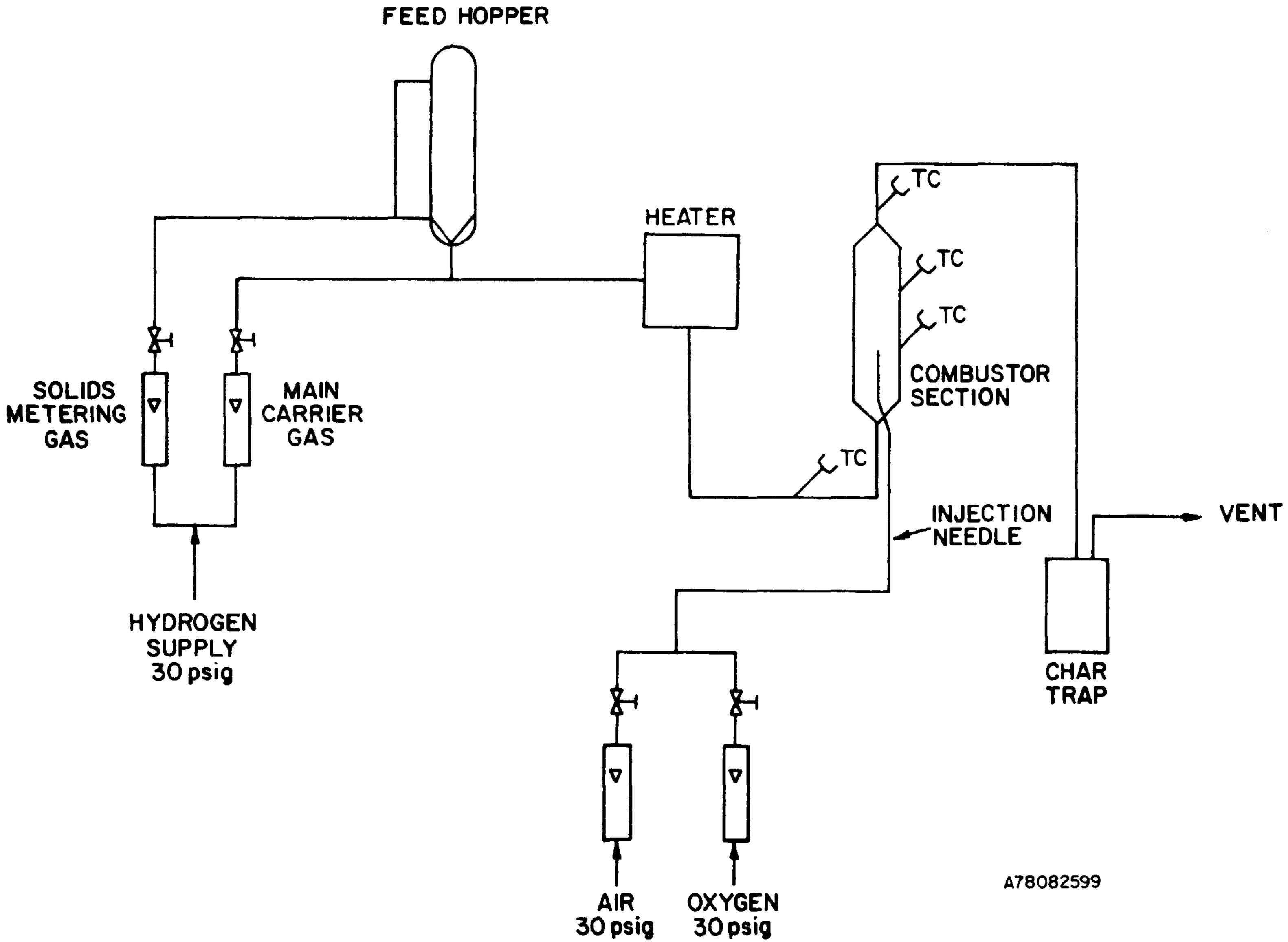

Figure 5. FLOW DIAGRAM OF PDU COMBUSTOR SIMULATOR

Table 13. SUMMARY OF PIPE TESTS OF VARIOUS ADDITIVES TO ILLINOIS NO. 6 COAL (FSI = 4-1/2)

Additive	Dry Mix	Toluene Slurry	Water Slurry
CaO	C*	C	NC**
$Ca(OH_2)$	C	C	NC
$CaCO_3$	C	C	C
Bentonite Clay	C	C	NC
Burnt Sienna (Fe_2O_3)	C	C	C
Control	C	C	C

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* C = Caking.

** NC = Non-Caking.

None of the additives tested were effective when mixed dry with the coal, or slurried with toluene after being dry-mixed with the coal. When slurried with water, with subsequent drying, calcium oxide, calcium hydroxide and bentonite clay produced a non-caking product, while calcium carbonate and burnt sienna pigment were not effective.

Some of these materials were tested further by a boat test in which a sample of treated solids was heated to approximately 1300°F in flowing hydrogen at atmospheric pressure for 50 minutes. The results of these tests are summarized in Table 14. The effects of the additives and treatments were the same as those observed in the pipe test; coal treated with calcium oxide, calcium hydroxide or bentonite clay in a water slurry was non-caking. In further tests, coal treated with calcium hydroxide in a water slurry with subsequent drying was reslurried with toluene, dried and tested. The solid residue was free flowing, showing that the non-caking property, once imparted, is not lost upon reslurrying with toluene.

In an additional test, coal treated with calcium hydroxide in a water slurry was dewatered by filtration; the dewatered solids were mixed with toluene which was evaporated away by heating. The dry solids were found to be non-caking, showing that the drying of the water slurry is not a part of the process that destroys the caking properties of the coal.

2. Work Forecast

Tests of autoclaved slurries of Illinois No. 6 coal and naphthalene, toluene and phenol will be completed, and a trial of a promising pretreatment of Illinois No. 6 coal will be made in the bench-scale unit. A tentative on-going near-term experimental program has been formulated, and will be completed when the preliminary runs with slurries and pretreated coals are completed.

Trials with the PDU combustor simulator will be continued to investigate the need for ceramic shields. Correlation of data with modifications of the Johnson model will be explored further.

B. Task 3. Design a PDU

The PDU design has been issued and approved.

C. Task 4. Construction of a PDU

1. Work Accomplished

Detailed drawings of the major pressure vessels of the PDU were revised to reflect actual dimensions of certain features such as nozzle lengths, and three bids for fabrication were obtained. At this writing, a contract is being let for fabrication of the major vessels. The pressure shell to contain the riser reactor will be shipped to IGT in December. Preparation of the PDU site is approximately half completed; the major steel beams and stairs have been installed and about one-fourth of the floor grating has been welded into position.

Table 14. RESULTS OF BOAT TEST
(50 Minutes at 1300°F in Flowing Hydrogen)
USING VARIOUS ADDITIVES WITH ILLINOIS NO. 6 COAL
(FSI = 4-1/2)

Treatment	Result
CaO in water slurry	Non-caking
$Ca(OH)_2$ in water slurry, dried and reslurried with toluene	Non-caking
Bentonite clay in water slurry	Non-caking
$CaCO_3$ in water slurry	Caking
Control	Caking

Drawings for instrumentation and control have been completed, and purchasing of instruments and controls will be completed next month. The tubing for fabricating the preheater coil and riser reactor has been received.

Due to the cost of supplying additional electric power and the high cost of a temperature control system, a gas-fired preheater will be used instead of the electrically-heated preheater described in the PDU design report. A hydraulic motor has been ordered; this will be installed inside the feed hopper, and will drive a vertical screw which will prevent bridging in the feed hopper.

2. Work Forecast

Site preparation will be finished soon, and equipment erection will be started in late November or early December. The design of the gas-fired preheater will be finished, and procurement of needed equipment will be continued.

V. CONCLUSIONS

The main findings from the work performed during the reporting period can be summarized as follows:

1. The caking properties of Illinois No. 6 coal can be destroyed by depositing calcium oxide or bentonite clay on the coal in a water slurry.

2. The net hydrogen consumption in coal hydropyrolysis is essentially linear with carbon conversion, but is not independent of residence time or time-temperature history.

3. It is possible to feed liquids and slurries directly to the reactor using a Hills-McCanna piston pump.

4. Mixtures of naphthalene, toluene, and phenol can be processed in the reactor without plugging, showing that naphthalene and phenol, if desired, can be recycled for conversion to monoaromatics.

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