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TWO-STAGE, CLOSED COUPLED CATALYTIC LIQUEFACTION OF COAL

SIXTEENTH QUARTERLY REPORT FOR THE PERIOD

1 JULY 1992 - 30 SEPTEMBER 1992

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E.S. Johanson
W.F. Karolkiewicz
L.K. Lee
R.H. Stalzer

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DE-AC22-88PC-88818

HYDROCARBON RESEARCH, INC.
100 OVERLOOK CENTER, SUITE 400
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DECEMBER 1992

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ABSTRACT

This quarterly report covers activities of the Two-Stage, Close-Coupled Catalytic Liquefaction of Coal Program during the period July 1 - September 30, 1992, at Hydrocarbon Research, Inc. in Lawrenceville and Princeton, New Jersey. This DOE contract period is from October 1, 1998 to December 31, 1992.

The overall purpose of the program is to achieve higher yields of better quality transportation and turbine fuels and to lower the capital and production costs in order to make the products from direct coal liquefaction competitive with other fossil fuel products.

The quarterly report covers work on Laboratory Testing, Bench Scale Studies and PDU Activities focusing on scale-up of the CTSL processing of sub-bituminous Black Thunder Coal.

SUMMARY

The major activities during this period were preparation and testing of FeOOH-impregnated Black Thunder coal for a Bench Scale run (CC-15) and PDU operations on Black Thunder sub-bituminous coal.

Using a procedure developed by Pittsburgh Energy Technology Center approximately 1100 lbs. of iron-impregnated coal was prepared. This coal exhibited higher conversions than that of the untreated coal in microautoclave reactivity tests under thermal conditions. The iron impregnated coal will be tested in a 50 lb/day bench unit in October.

A PDU run was conducted to scale-up the CTSL "Extinction Recycle" process to produce an all-distillate product using Black Thunder Mine coal. A vertical leaf filtration system was used to separate solid residuals, while a vacuum tower was employed to produce recycle liquid for the "Extinction" operation. Apart from some initial pumping and bypassing problems, the filter performed well in 30 filtration cycles under both on-line and off-line modes of operation.

The PDU operated 13 days on coal feed with four interruptions before shutdown at the beginning of Period 14. Most interruptions were caused by high level in the hot separator. During shutdown inspections fine catalyst particles were found in the letdown valves of the hot separator. Also, a significant amount of paraffinic wax was present in the recycle solvent.

INTRODUCTION

The studies conducted in this quarterly report are presented by task and in sequence.

Task 1 is the Management Plan. *Task 2* is for Laboratory Studies and includes microautoclave and micro-reactor work. *Task 3* is for Bench-Scale studies. *Task 4* is for Mini PDU Scale-up. *Task 5* is the Technical Assessment, including Modelling, Design and Economics. *Task 6* is Program Administration.

The contract period was October 1, 1998 to September 30, 1992 and has been extended to December 31, 1992.

TASK 2 - LABORATORY SCALE STUDIES

Two series of microautoclave studies were conducted in support of the PDU (Run 260-03) and the bench-scale run CC-15 on iron-impregnated coal.

A program of 40 microautoclave tests was conducted to evaluate the reactivity of Black Thunder Mine coal feeds, the Criterion C-317 catalyst, and the start-up solvents used in the course of PDU Run 260-03, along with some reference runs with catalysts, coals and solvents used in other CTSL operations. Impact of high temperature exposure to an atmosphere of high water content on catalyst strength was also evaluated.

The latter study was to evaluate the reactivity of iron-impregnated coal and untreated Black Thunder Mine coal in both thermal and catalytic mode of operation. In thermal mode the iron-impregnated coal showed slight improvement over the untreated coal in both coal and residuum conversions. However, in the presence of supported catalyst the impact of iron on conversions was masked by the performance of the supported catalyst.

SUPPORTIVE MICROAUTOCLAVE TESTS FOR THE MINI PDU RUN

A. COAL EVALUATION

The feed coal to the PDU Run 260-03 (designated as HRI-5991) was Black Thunder Mine coal which was ground and dried by Empire Coke Co. Various portions of this shipment were tested over a period of nine months to monitor any possible aging of the coal.

Several samples were taken and tested between the period November 1991 and July 1992. A description of these samples are as follows:

<u>Designation</u>	<u>Description</u>
HRI-5991 1991	A coal sample (Bag 5) taken shortly after receipt of the coal in November, 1991 and stored in a closed metal can since then.
Run 260-03 Period 1 Feed	A feed coal sample taken during Period 1 of the run, in November, and stored in a closed metal can.

Run 260-03
Period 14 Feed

A feed coal sample taken during Period 14
after the final operation of the run in July.

HRI-5991
Bag 1,3,6, & 8

Samples taken in July, 1992 of the coal
from the 1,000 lb. shipping modules in which they had
been stored since November 1991.

The current program also tested the HRI-5887 shipment of Black Thunder Mine
which had also been prepared by Empire Coke Co. for qualification of their
operations.

The standard coal evaluation conditions were:

Temperature	800°F
Pressure (hot)	2000 psig H ₂
Time	30 minutes
Solvent/Coal	8g/2g
Catalyst/Coal	1/1 (in catalytic tests)

There were some tests at 825°F.

The following tabulation compares the microautoclave results for the HRI-5991 coal
samples, in the standard coal evaluation tests using HRI-5198 solvent and
HRI-5394 presulfided Shell S-317 1/32" Ni/Mo catalyst, with those of the earlier
shipment of Black Thunder Mine coal. The table gives number of tests, the
average coal conversion of those tests, and statistical significance of the difference
from the average for the pooled data of the tests of the earlier shipments.

<u>SHIPMENTS</u>	<u>THERMAL EVALUATION</u>			<u>CATALYTIC EVALUATION</u>		
	No. of Tests	Coal Conversion	Average Significance	No. of Tests	Coal Conversion	Average Significance
All HRI-5991 Samples	11	70.2	99.3	6	85.9	87.5
HRI-5991 1991 Sample	1	66.8	98.8	1	87.4	23.5
Run 260-03 Period 1	1	70.8	92.6	1	85.7	79.4
Run 260-03 Period 14	5	74.6	89.6	1	80.4	99.9
HRI-5991 1992 From Storage	4	70.0	99.6	3*	87.4	35.9
HRI-5887	2	77.0	39.8	2	91.5	98.7
Pooled HRI-5613,5630, 5713	5	78.6	---	8	87.9	---

* Discarding result for Bag 3 in Run XX-026 (73.7% conversion)

These results indicate that the HRI-5991 shipment was less reactive than average of the earlier shipments, by 2.0% in the catalytic tests (87.5% statistical confidence level) and 8.4% in the thermal tests (99.3% statistical confidence level).

The HRI-5887 shipment from Empire Coke Co. was more reactive than the HRI-5991 shipment, also prepared by them, and gave the highest catalytic conversion results, 3.6% higher than obtained with earlier shipment (98.7% confidence level), although the thermal conversions with HRI-5887 shipment were slightly lower than obtained with those of reference coals. Expressing the HRI-5887 results relative to those of the HRI-5991 results, indicates 5.6% higher catalytic test conversion (99.1 confidence level for the difference), and 5.1% higher thermal test conversion (88.6% confidence level of the difference).

The Run 260-03 Period 14 coal sample gave the lowest catalytic conversion result of the these tests, but the thermal conversion results were in the general range of the other samples of the HRI-5991 shipment. Microautoclave tests using the Run 260-03 Period 14 coal with other solvents and catalysts gave conversions in the general range obtained with the other HRI-5991 samples, see below.

B. COAL EVALUATION WITH VARIOUS SOLVENTS AND CATALYSTS

Tests were conducted to evaluate the HRI-5991 shipment of Black Thunder Mine Coal and various solvent and catalysts. Four solvents were used. The origin of these solvents are described in the following table:

<u>Designation</u>	<u>Description</u>
HRI-6002	Wilsonville Solvent (V-123): Recieved Dec. 4, 1991. Boiling range: 450-985°F
HRI L-769	Start-up solvent for Run 260-03 Topped HRI-6002 (650°F*) Boiling range: 540-985°F)
HRI L-769 7/92	Material from the PDU Solvent Tank (Tank #4) sampled in July/92 consisting of the original L-769 and process solvent generated from Run 260-03.
HRI-5198	Solvent used in the microautoclave coal evaluation tests, produced during Wilsonville operations with Illinois coal.

The following table summarizes the results of tests with the HRI-5991 shipment of Black Thunder Mine coal and various solvents and catalysts.

Catalyst HRI No.	Solvent	Number of Tests	Coal Conversion [W%]	Residuum Selectivity [W% coal conv.]
HRI-5394P S-317	HRI-5198	6	85.9	24.7
HRI-5394 S-317	HRI-6002	2	88.6	27.2
HRI-5903 C-317	HRI-5198	1	88.3	30.0
HRI-5903 C-317	HRI-6002	2	88.0	29.6
HRI-5903 C-317	HRI L-769	1	90.8	22.2
HRI-6043P AO-60	HRI-6002	1	83.0	31.6
HRI-5394P S-317P	HRI-5198	6*	87.9	22.0
HRI-5394 S-317P	HRI-5198	2**	91.5	24.2

* Tests with earlier shipment of Black Thunder Mine Coal

** Tests of HRI-5887 shipment of Black Thunder Mine Coal

These results indicate the relative performance of the catalysts in terms of lower residual yield was in the order:

S-317P > S-317 > C-317 > AO-60

However, the greatest difference in residual oil yield, 7.2% lower for the S-317P catalyst than for the AO-60 catalyst, has a relatively low statistical confidence level of 72.6%.

Similarly, the relative performance of the solvents in terms of lower residual oil yield was in the order:

L-769 > HRI-6002 equivalent HRI-5198

with a statistical confidence level of 82.2% for the 7.8% lower residual oil yield with the L-769 solvent.

The pattern of coal conversions similarly was improved coal conversion with L-769 solvent with the equivalent performance of the HRI-6002 and HRI-5198 solvents, again with a low statistical confidence level, 55.5%.

C. SOLVENT EVALUATION

In *Table 1*, the results of the current microautoclave solvent evaluation tests are compared with the results of the other solvents which have used as start-up solvents for CTSL Bench Unit operations. The conditions for these tests are 30 minutes, 750°F with a solvent/coal ratio of 2/1 in 2000 psig nitrogen. The tests determine the conversion of the test coals which are HRI-5174 Illinois No. 6 coal, and HRI-5613 Black Thunder Mine coal.

With Illinois coal, the HRI-5198 solvent (the solvent for microautoclave coal conversion evaluations) gave a solvent evaluation results in the higher part of the range of results for the earlier solvent tests, and both the HRI-5969 (Wilsonville solvent V-124 used in the November startup of the PDU Run) and the HRI-6002 solvent (from which the L-769 start-up oil for Run 260-03 was distillate) gave a mild range result. The initial L-769 start-up oil had result slightly below the lowest value obtained previously, while the L-769 solvent as developed during the course of operations through July, 1992 has an exceptionally low solvent quality result.

With the Black Thunder Mine coal, only the initial L-769 material and the HRI-6002 solvent had results in the range of values obtained earlier and the result was higher than that of only one of the previous tests. The HRI-5198 results was slightly lower than those values, while, again, the L-769 solvent in July, 1992 had an exceptionally low result.

The essential conclusion is that L-769 materials used during Run 260-03 had poor solvent quality performance, which deteriorated even further as the run continued.

D. REACTIVITY OF FILTER FEED SLURRIES

Table 2 summarizes the results of catalytic microautoclave tests using the filter feed slurries from Period 10A and Period 13A of Run 260-03. The test conditions were those used in the standard coal evaluation tests and the liquid/catalyst and coal solids/catalyst ratios corresponded closely to the ratios that are used in the standard coal evaluation tests.

The solids content of slurries were 23.6 W% (Period 10 sample) and 16.7 W% (Period 13 sample), and a composition corresponding to 80-82% conversion of the maf coal that had been fed to the PDU operation. TGA analysis of the liquid components indicated residuum contents of 7.2 W% (Period 10A) and 3.8 W% (Period 13A). The atomic hydrogen to carbon ratio of the liquids were about 1.6/1.

In both the microautoclave tests about 57% of the moisture-ash-free (maf) coal fed in the microautoclave feed was reacted, which results in solids composition corresponding to about 92% conversion of the maf coal originally fed to the PDU operation. The residual oil content of liquid products for both tests was higher than that in the liquid feed, by an amount that corresponded to about 20% of amount of coal converted in the test. This amount of residual oil formation is slightly below the amounts formed in the various catalytic coal evaluation tests.

E. RECOVERED CATALYST EVALUATION

A series of eight microautoclave tests were performed to determine the effect upon catalyst strength of high temperature exposure to an atmosphere of high water content. Four catalysts, including Criterion C-317, Shell S-317, Davison GR-14 and AO-60, were tested at 800°F and 2,000 psig for 64 hours in an atmosphere which contained 25-30 V% water vapor. The test was a static test, without reactor agitation, to avoid mechanical breakage of the catalyst during the extended test. In addition, the C-317 and S-317 catalysts were tested in 30 minutes tests, with four parts of oil to catalyst, both with calcined catalyst and catalysts containing about 9.0 W% water. Crush strength and attrition losses were determined on the charged and treated catalysts.

The high temperature treatment lowered the crush strength, and caused attrition losses, with a greater change where there was water in the reactor, either presence as free water or water adsorbed upon the charged catalyst. The following table compares the crush strength and attrition losses of the variously treated catalysts with the values for the fresh catalysts;

Water in Reactor W% Catalyst	Crush Ratio		Attrition Ratio	
	C-317	S-317	C-317	S-317
0.0 (calcined)	0.79	0.83	1.88	1.62
9.0 (adsorbed)	0.71	0.82	2.77	1.84
13.3 (free water)	0.73	0.73	2.74	2.25

The water treatment had the greatest effect upon the Davison GR-14 catalyst and possibly least effect, although considerable, upon the S-317 catalyst as summarized in the following tabulation:

Catalyst	Crush Ratio	Attrition Ratio
GR-14	0.59	4.15
AO-60	0.62	2.58
C-317	0.73	2.74
S-317	0.73	2.25

TABLE 1
MICROAUTOCLAVE EVALUATION OF SOLVENTS

Coal Conversions in Tests at
750°F for 30 Minutes
Solvent/Coal Ratio: 2/1
2000 psig Nitrogen Atmosphere

TEST COAL	ILLINOIS NO. 6 HRI-5174	BLACK THUNDER HRI-5613
SOLVENT		
HRI-5969 ⁽¹⁾	55.6	52.0
L-769 1991 ⁽²⁾	51.3	48.9
L-769 1992 ⁽³⁾	42.2	35.3
HRI-6002 ⁽⁴⁾	59.8	47.7
HRI-5198 ⁽⁵⁾	66.3	44.8
HRI-5910	70.2	53.8
HRI-5648	70.1	61.5
L-742	67.4	65.9
HRI-5911	65.8	51.7
HRI-5757	61.9	58.8
L-721	60.8 (61.6)	63.7
HRI-5658	59.3	57.0
HRI-4907	58.0	69.4
HRI-5443	69.4 (57.8)	54.7
227-25 Shut-Down	53.4	53.0
	55.3	47.2

- (1) Wilsonville Solvent (V-124) used in the startup of PDU in November 1991. (recieved Oct. 9/91).
- (2) Topped HRI-6002 for Run 260-03 Start-up in Nov. 1991
- (3) Sample of oil in July, 1992, after replenishing original inventory of L-769 by returning oil from PDU operations.
- (4) Coal derived distillate from Wilsonville (V-123), recieved Dec. 4/92.
- (5) Test Solvent for coal evaluation tests. Hydrotreated solvent from Wilsonville operations on Illinois Coal. Received November, 1985.

TABLE 2
MICROAUTOCLAVE TESTS ON FILTER FEED SLURRY
FROM PDU RUN 260-03 OPERATIONS

Tests at 825°F, 2000 psig H₂, 30 minutes
5 gm slurry per gm of HRI-5903 Criterion C-317 Catalyst

MICROAUTOCLAVE RUN	XX11	XX12
Feed Slurry Inspection		
Period No.	10A	13A
Composition, W%		
Ash	7.20	4.78
Coal	16.39	11.88
Liquid	76.40	83.33
Liquid Component Analysis, W%		
Carbon	88.18	88.28
Hydrogen	11.63	11.80
Nitrogen	0.24	0.17
Sulfur	0.02	0.03
TGA Analysis		
"THF"		
Residuum	7.24	3.84
Microautoclave Product		
Composition, W% of Feed		
Ash	7.42	4.64
Coal	7.22	4.95
Liquid	83.62	87.11
Total	98.26	96.27
Liquid Component Analysis, W% *		
Carbon	88.26	88.46
Hydrogen	10.98	11.26
Nitrogen	0.24	0.20
Sulfur	0.03	0.03
TGA Analysis, W%		
Residuum	9.10	5.32
Conversion (Ash balanced)		
Coal fed to Microautoclave	57.2	57.1
Conversion Level, W% of Coal		
to PDU Operation		
Microautoclave Feed	81.9	80.2
Microautoclave Product	92.3	91.5

* Rotoevaporated liquid washed from autoclave with THF.

SUPPORTIVE MICROAUTOCLAVE TESTS FOR BENCH RUN CC-15

The supportive microautoclave study for Run CC-15 consisted of 26 coal reactivity tests. The initial 10 tests were designed to evaluate two HRI prepared laboratory samples (approximately 2500 ppm of iron) and a higher iron loading sample (5000 ppm) supplied by PETC. These initial tests were conducted mostly in catalytic mode using a solvent/coal ratio of 4/1. The remaining 16 were devoted to the testing of representative coal samples taken from the bulk Fe-impregnated feedstock prepared for Run CC-15. The latter tests were carried out in the absence of supported catalysts at a lower solvent/coal (2/1) ratio with the intention of highlighting any possible impacts that may be evolved from the addition of iron catalyst precursor.

Analyses of the untreated and various samples of Fe-impregnated coals are given in *Table 3*, while results from the microautoclave reactivity tests are summarized in *Tables 4 and 5*.

A. LABORATORY SAMPLES

The conditions used in the reactivity tests on the laboratory samples were standard coal evaluation conditions of 800°F, 30 minutes, 2000 psig H₂ at coal/solvent ratio of 1/4. Both catalytic mode (Tests 1 to 6) and thermal mode (Tests 7 and 8) were performed.

Coal conversion and resid yields are compared in *Figures 1 and 2*, respectively. In the presence of supported catalysts at the standard solvent/coal ratio of 4/1, there were no significant difference in coal conversions and resid yields between the iron-treated samples and untreated sample. Also, The lower iron containing HRI samples (2500 ppm) had similar coal conversion (86.6 and 87.3 W% maf coal) as the PETC sample (87.5 W%) which had twice as much iron catalyst precursor.

However, there were noticeable differences in the quality of the liquid product between the iron-treated and the untreated coal. Liquid products generated from the iron-treated coal contained 15 to 20% more nitrogen than products from the untreated coal, refer to *Table 5*. Examining the nitrogen content of the feed coals (*Table 3*) suggested additional nitrogen containing compounds, in forms of ammonia and/or nitrate, were being adsorbed onto the coal matrix during the impregnation procedure. The nitrogen content of the two iron-treated coals was 1.78 and 2.13%; and was 2.2 to 2.6 times higher than that of the untreated coal, 0.81%. Similar difference in nitrogen contents was observed between the bulk iron-treated coal and untreated coal.

B. IRON-IMPREGNATED FEEDSTOCK FOR RUN CC-15

Several iron-treated coal samples were taken from different batch of the feedstock prepared for Run CC-15. These samples were:

HRI-5828	Untreated coal from which all L-780 coal prepared
L-780A	1st batch (50 lbs dry coal) of Fe-treated coal
L-780B	2nd batch (100 lbs dry coal) of Fe-treated coal
L-780A	Washed Fe-treated coal; in an attempt to
Washed	reduce the amount of adsorbed nitrogen compounds
L-780 9/26	subsequent 7 batches of 100-150 lbs batches as
L-780 9/28	identified by its date of preparation
L-780 9/29	
L-780 10/8	
L-780	Recovered solids from the decanted liquid
Decanted	

In view of the lack of sensitivity in using the standard coal evaluation conditions for evaluating the iron-treated and untreated coals, the microautoclave reactivity test conditions were modified as follows:

Temperature:	800°F
Time:	30 minutes
Supported catalyst:	None
Solvent/coal ratio:	6g/3g

Coal conversions of untreated and iron-treated coal are compared in *Figure 3*. The untreated coal (HRI-5828) gave coal conversions ranging from 69.9 to 73.3 W% (average of 72.2 W%) and was about 10.5 W% lower than that of another untreated coal (HRI-5887) tested under the laboratory sample evaluation series. (Test YY-8).

These results indicate that the iron-treated coal performed better in terms of coal conversion. However, the first batch of iron-treated coal (average conversion of 75.2 W%) was less reactive than the subsequent batches of treated coals which had a conversion level ranging from 80.4 to 83.3 W%). It is possible that the iron impregnation technique used in preparing these bulk samples was not optimum in the first 50 lbs. batch and was improved gradually as more feedstock were processed.

As discussed in tests with the laboratory samples, a higher nitrogen content was detected in products derived from iron-treated coals in all the bulk samples tested, *Table 5*. Using a lower solvent/coal ratio of 2/1 in the absence of the supported catalyst, the removal of nitrogen was much less than for the catalytic cases. The nitrogen content (THF-free basis) of liquid product from treated coal ranged from

0.71 to 0.84 W%), as compared to the untreated coal cases of 0.38 to 0.56 W%).

An attempt was made to re-wash the L-780A treated coal sample to lower its nitrogen content. The washed sample of iron-treated coal did not yield exceptional lower nitrogen content suggesting that the bonding between the additional nitrogen compounds and the coal matrix was much stronger than what is considered as physical adsorption. These nitrogen compounds were chemically bonded to the coal matrix and would not be removed easily without the assistance of effective catalysts.

TABLE 3

Analysis of FeOOH-Impregnated Black Thunder Coals

Coal HRI Sample #	Untreated 5887	Treated 5991A	Treated 5991B	PETC 6050	Untreated 5828	Treated L-780A	Treated L-780B	Treated L-780A (Washed)
Proximate Analysis (By TGA Method)								
Moisture, W%	7.24	3.96	2.80	2.62	21.88	7.18	7.12	
Ash, mf W%	6.82	6.86	6.84	8.56	7.08	5.76	5.69	
Volatile Matter, mf W%	n/a	n/a	n/a	45.21	n/a	44.60	44.71	
Fixed Carbon, mf W%	n/a	n/a	n/a	46.23	n/a	49.64	49.60	
ASTM Ash, mf W%	6.82	6.86	6.84	6.38	7.23	6.07	6.24	6.06
Fe in Ash, W% Ash	2.03	3.56	3.89	7.95	2.84	10.68	9.15	9.35
Fe in Ash, W% mf Coal	0.138	0.244	0.266	0.507	0.205	0.648	0.571	0.567
Elemental Analysis, W%								
Moisture	8.01	9.39	9.32		8.01	7.31	7.28	4.00
Carbon	62.38	62.13	62.23		62.38	62.01	62.02	64.66
Hydrogen	4.89	4.81	4.94		4.89	5.02	4.92	4.70
Nitrogen	0.81	2.13	1.78		0.81	2.24	2.18	2.30
Sulfur	0.38	0.35	0.35		0.38	0.39	0.39	0.35
Oxygen (By Diff)	17.26	14.91	15.11		17.26	17.29	17.24	18.19
Ash	6.27	6.28	6.27		6.27	5.74	5.97	5.81
Total	100.00	100.00	100.00		100.00	100.00	100.00	100.00

Note: HRI-5991A and 5991B were labelled previously as HRI-5828A and 5828B , respectively.

HRI, Inc.

11/24/92

TABLE 4

CTSL PROGRAM: Bench Run CC-15
 Supportive Microautoclave Tests
 (Series YY-001 to 024)

Test No.	Catalyst	Solvent	Coal	Temp [F]	Time [min]	Coal [g]	Solvent [g]	Coal Conversion [W% Coal]	TGA Resid Yied [W% Coal]
1	S-317	HRI-6002	HRI-5991A	825	30	2.00	8.00	90.78	22.80
2	S-317	HRI-6002	HRI-5887	825	30	2.00	8.01	92.69	24.10
1A	S-317	HRI-6002	HRI-5991A (0.12 g DMDS)	800	30	2.00	8.00	87.25	23.20
2A	S-317	HRI-6002	HRI-5887 (0.1 g DMDS)	800	30	2.00	8.01	82.63	20.20
3	S-317	HRI-6002	HRI-5991B (0.1 g DMDS)	800	30	2.00	8.01	88.56	21.00
4	S-317	HRI-6002	HRI-5887 (0.1 g DMDS)	800	30	2.00	8.01	90.90	22.50
5	S-317	HRI-6002	HRI-6050 (0.12 g DMDS)	800	30	2.00	8.00	87.51	19.00
6	S-317	HRI-6002	HRI-5887 (0.11 g DMDS)	800	30	2.00	7.99	88.47	19.00
7	—	HRI-6002	HRI-6050 (0.09 g DMDS)	800	30	2.00	7.99	83.66	37.26
8	—	HRI-6002	HRI-5887 (0.09 g DMDS)	800	30	2.00	8.00	82.58	36.00
9	—	HRI-6002	L-780A (0.15g DMDS)	800	30	3.00	6.00	74.65	32.90
10	—	HRI-6002	HRI-5828 (0.15g DMDS)	800	30	3.00	6.00	69.91	33.90
11	—	HRI-6002	L-780B (0.16g DMDS)	800	30	3.00	6.00	80.43	32.60
12	—	HRI-6002	HRI-5828 (0.14g DMDS)	800	30	3.00	6.01	72.84	38.90
13	—	HRI-6002	L-780A (0.11g DMDS)	800	30	2.00	8.01	79.65	31.20
14	S-317	HRI-6002	L-780A (0.11g DMDS)	800	30	2.00	8.01	90.00	18.40
15	—	HRI-6002	L-780A (0.16g DMDS)	800	30	3.00	6.01	75.84	36.90
16	—	HRI-6002	L-780A Washed (0.15g DMDS)	800	30	3.00	6.00	77.42	32.10
17	—	HRI-6002	L-780A (0.15g DMDS)	527/800	15/30	3.00	5.99	79.00	38.10
18	—	HRI-6002	HRI-5828 (0.15g DMDS)	527/800	15/30	3.00	6.01	73.00	33.00
19	—	HRI-6002	L-780LO 9/26 (0.15g DMDS)	800	30	3.00	6.00	82.76	36.34
20	—	HRI-6002	L-780B1/4 9/29 (0.15g DMDS)	800	30	3.00	6.00	83.27	37.22
21	—	HRI-6002	L-780B3 9/28 (0.15g DMDS)	800	30	3.00	5.98	80.88	37.91
22	—	HRI-6002	L-780 Decanted (0.15g DMDS)	800	30	3.01	6.00	88.55	29.92
23	—	HRI-6002	L-780 10/08 (0.15 DMDS)	800	30	2.99	6.00	80.39	24.15
24	—	HRI-6002	HRI-5828 (0.15 DMDS)	800	30	3.00	6.01	73.20	17.62

Note: HRI-5991A and 5991B were originally labelled as HRI-5828A and 5828B.

11/24/92

TABLE 5
Microautoclave Coal Evaluation (YY-Series)
Product Liquid Inspections

Run No.	Coal Type	THF Content W%	Elemental Analysis, W%			
			Carbon	Hydrogen	Nitrogen	Sulfur

Untreated Coal, Catalytic Mode						
2a	5887	8.79	88.32	9.61	0.30 (0.33)	0.0255
4	5887	9.69	89.38	9.79	0.36 (0.40)	0.034
6	5887	6.26	88.75	9.91	0.33 (0.35)	0.017
Untreated Coal, Thermal Mode						
8	5887	4.73	87.83	9.40	0.41 (0.43)	0.181
10	5828	5.19	86.62	8.82	0.45 (0.47)	0.203*
12	5828	5.32	86.72	8.76	0.44 (0.46)	0.251*
18	5828	4.60	87.23	8.93	0.36 (0.38)	0.246*
24	5828	6.80	86.74	8.91	0.52 (0.56)	0.386*
Fe-treated Coal, Catalytic Mode						
1a	5991A	6.24	88.40	9.78	0.43 (0.46)	0.0247
3	5991B	14.53	88.64	9.68	0.38 (0.44)	0.020
5	6050	5.84	88.99	9.78	0.39 (0.41)	0.039
14	L780A	5.50	88.22	9.62	0.44 (0.46)	0.010
Fe-treated Coal, Thermal Mode						
7	6050	5.58	86.91	9.48	0.50 (0.53)	0.252
13	L780A	5.11	88.19	9.56	0.51 (0.54)	0.200
9	L780A	4.53	87.13	9.06	0.68 (0.71)	0.300*
15	L780A	12.97	85.36	9.07	0.68 (0.78)	0.258*
16	L780A Washed	4.90	87.04	8.96	0.68 (0.72)	0.298*
17	L780A	5.34	86.71	8.71	0.72 (0.76)	0.362*
11	L780B	4.45	87.18	9.16	0.71 (0.74)	0.317*
19	L780 9/26	5.84	86.46	8.91	0.77 (0.82)	0.255*
20	L780 9/29	7.10	86.51	8.94	0.77 (0.83)	0.287*
21	L780 9/28	4.93	86.47	8.91	0.80 (0.84)	0.362*
23	L780 10/8	8.83	85.93	9.08	0.74 (0.81)	0.407*
22	L780 Decanted	4.75	86.61	9.53	0.70 (0.73)	0.255*

* DMDS was added in these tests.

Values in bracket are in THF-free basis.

Run YY-17 & 18 : simulated two-stage tests at 527/800° F for 15/30 minutes.

FIGURE 1

FIGURE 2

FIGURE 3

Run CC-15 Iron-treated Feed Coal
Microautoclave Reactivity Test

TASK 3 - BENCH SCALE STUDIES

RUN CC-15 EVALUATION OF A PRE-DISPERSED IRON OXIDE HYDROXIDE CATALYST (FeOOH)

A 14 day study is scheduled with FeOOH-Impregnated Black Thunder Mine Coal that includes a comparison with untreated coal in thermal/catalytic mode of operation. An additional pretreating step will be incorporated for conditioning of the iron catalyst precursor.

EXPERIMENTAL PLAN

The run plan (*Table 6*) consists of four process conditions, three with iron-treated coal and one an untreated coal. The space velocity, backpressure, H₂S addition rate, oil/coal ratio, and temperature at both the thermal and catalytic stage will be held constant through the entire run. Two pretreatment temperatures of 527°F (Condition 1) and 570°F (Condition 2) will be tested. The lower pretreating temperature is the same pretreating temperature used in Run CC-14 for processing Illinois #6, while the higher temperature (570°F) is the optimum temperature for processing Black Thunder Mine coal, as determined by PETC.

An iron loading of 5000 wppm is chosen to maximize the effect of the iron catalyst precursor on process performance.

TABLE 6**RUN CC-15 EVALUATION OF IRON-IMPREGNATED COAL****EXPERIMENTAL PLAN**

Condition	1	2	3	4
Periods	1-5	6-8	9-11	12-14
Feed	Fe-coal	Fe-coal	Untreated	Fe-coal

Temperatures, °F				
Pretreatment	527	570	570	570
Thermal Stage	800	800	800	800
Catalytic	775	775	775	775

Other

Feed Coal:	Black Thunder Mine Coal
H ₂ S Addition:	3 W% dry coal
Oil/Coal Ratio:	1.6
Space Velocity:	44 lb dry coal/hr/ft ³ catalyst
Supported Catalyst:	Shell S-317 1/32" (HRI-5394)
Dispersed iron:	5000 ppm

A. FEEDSTOCK PREPARATION

Approximately 1100 lbs of FeOOH-impregnated Black Thunder Mine coal has been prepared according to a recipe, an incipient wetness impregnation/precipitation technique developed by DOE-PETC. The PETC recipe calls for 8 parts of $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ in 400 parts of distilled water for wetting 500 parts of coal to incipient wetness (paste). The wet paste is then added into a solution containing 100 parts of ammonium hydroxide (29% NH_3) dissolving in 2500 parts of distilled H_2O . The iron is precipitated as FeOOH and bond to the coal matrix. The treated coals are then recovered from the coal/water mixture and subsequently dried to a desired moisture level.

Since the amount of water required to bring the coal to an incipient wetness state is very much depended on the initial moisture of the pulverized coal, the amount of water used to dissolve ferric nitrate was reduced from the original PETC recipe. A comparison of the two procedures is given as the following:

DOE-PETC FeOOH-Impregnation Procedures (Basis: 500 parts of Dry Coal)

	Original	Modified*
Iron Loading wppm dry coal	2500	5000
Coal	500	500
<u>Impregnation Step</u>		
Ferric Nitrate	8	18
Water	400	125
<u>Precipitation Step</u>		
Ammonium Hydroxide	100	113
Water	2500	2825

(* Procedure modified by HRI according to initial moisture of the feed coal)

A total of eight drums of FeOOH-Impregnated coal, approximate weight of 1100 lbs, were prepared. The moisture, ash and elemental analyses of the treated coals are given in the *Table 7*.

With the exception of Drum #4, all feedstock contained less than 10% of moisture. Also, the iron loading of selected drums (Drums 1, 2, 3, 4, & 8) were inspected. The iron loading was consistently above 5000 ppm and ranged from 5900 (Drum #5) to 7800 (Drum 4) ppm on a dry coal basis. Similar to the samples used in the microautoclave reactivity tests, the nitrogen content of the iron-impregnated coals were generally 2.6 to 3.0 times higher than that of the untreated coal.

TABLE 7

Analyses of FeOOH-Impregnated Coal

	DRUM #1	DRUM #2	DRUM #3	DRUM #4	DRUM #5	DRUM #6	DRUM #7	DRUM #8
Date Drummed	9/1	9/26	9/28	9/29	9/30	10/4	10/5	10/8
Amount, Lbs	68	128	143	157	150	157	157	137
<hr/>								
TGA Analysis, W%								
Moisture	5.42	9.74	8.33	11.61	6.36	6.12	9.36	7.91
Ash (as is)	6.28	6.11	6.08	5.94	6.20	6.58	6.10	6.15
ASTM Ash, mf	6.24	6.7	6.95	6.94				6.45
S in Ash	N/A	5.13	5.60	5.49				4.81
Fe in Ash	10.7	9.6	10.6	11.3				9.1
% mf coal	0.67	0.64	0.74	0.78				0.59
Elemental Analysis, maf W%								
Carbon	71.49	72.47	72.33	73.44				71.64
Hydrogen	4.74	4.35	4.21	4.44				4.74
Nitrogen	2.51	2.51	2.47	2.53				2.86
Sulfur	0.38	0.42	0.48	0.49				0.39
Oxygen	20.88	20.22	20.51	19.11				20.37

TASK 4 - PDU SCALE-UP

A. OBJECTIVE

Scale-up the CTSL "Extinction Recycle" process to produce an all-distillate product using Black Thunder Mine, Sub-Bituminous Coal.

B. EXPERIMENTAL PLAN

The original plan specified an 28 day operation, however due to several mid-run interruptions, the number of mass balance periods were reduced to 13. A vertical leaf filtration system was evaluated in both on-line and off-line modes.

The target operating conditions are as follow:

Temperature, °F	
Preheater	650
1st Stage	750
2nd Stage	825
Back Pressure, psig	2500
Space Velocity	56
lb/hr/ft ³ catalyst/stage	
DMDS, W% dry coal	3
Catalyst Replacement	
Rate, lbs/ton dry coal	1.5

Two approaches in reaching the target process conditions were tested. A slow approach to the target reactor temperatures was initially chosen to ensure that the catalyst could reach equilibrium at a gradual pace. This approach was adapted in the four restarts prior to Period 11. In the last restart (Period 12) a faster approach to the desired reactor temperature was used.

RUN PLAN PDU 260-03

Period	Temperature, °F			Catalyst Addition, lb/hr	
	Preheater	1st Stage	2nd Stage	1st Stage	2nd Stage
0	650	700	750	3.6	3.6
1	650	715	765	0.0	0.0
2	650	730	780	1.8	1.8
Restart					
3	650	745	795	0.0	0.0
4	650	760	810	1.8	1.8
Restart					
5	650	745	795	0.0	0.0
6	650	760	810	1.8	1.8
7	650	760	810	0.0	0.0
Restart					
8	650	715	765	0.0	0.0
9	650	730	780	1.8	1.8
10	650	740	790	0.0	0.0
11	650	750	810	1.8	1.8
Restart					
12	650	750	815	0.0	0.0
13	650	750	825	0.0	0.0

C. OPERATION PERIOD

Nov-Dec 1991	Periods 1 & 2 (Startup Solvent HRI-5969)
Jan-May 1992	Filter Modification and Off-line testing
June-July 1992	Periods 3 to 13 (Startup Solvent L-769)

D. OPERATING SUMMARY

The PDU (Unit 260) was modified for CTSL demonstration operation. Major modifications to the unit were completed by the first week of November 1991. Black Thunder Mine coal, topped Wilsonville solvent as start-up oil, and 1/16" Criterion C-317 catalyst were utilized for this run.

During the 1991 operations, several filtration issues were encountered. Operations were halted after two operating periods for troubleshooting requirements.

After it was established that the filter was functional, Run 260-03 operations resumed in June 1992. Operations proceed well during this demonstration except for seven unscheduled shutdowns. Shutdowns were effected due to difficulties with catalyst bed level and hot separator liquid level control. Catalyst and carbonaceous materials resembling unreacted coal were found in the ebullating lines, hot separator and letdown valves during each shutdown inspections. Catalyst withdrawn from the reactor was also observed to be smaller than average particle size. Thirteen operating days were completed in this run. The temperature of reactors 1 and 2 for each Period are plotted in *Figure 4*. Each break in the line connecting the temperature points represent an interruption in the operation.

Operating difficulties were suspected to be process related and not due to equipment malfunction. Microautoclave and cold flow catalyst attrition/carryover studies were undertaken to gain additional insight into the situation surrounding the shutdowns.

Duration of the coal feed into the reactor ranged from about 18 hours to 79 hours before shutdowns were initiated. Due the number of start-up and shutdown the mass recovery of some of the Periods deviated considerably from 100%. For the reason mentioned completed analyses were performed only on two Periods, Periods 10A and Period 13.

E. FILTRATION

During the November filter operations, two major problems areas were identified. The filter feed pump could not operate for an extended time and massive bypassing of the filter media was occurring. The resolution of these issues extended into June 1992.

The filtration section, shown in *Figure 5*, was ready to be integrated with the PDU at Period 3 restart in early June. As experience was gained through PDU operations, additional modifications were added to the filtration system. A failure of the filter cake withdrawal valve to seal, led to the development and installation of a pressure liquid jets to clean the valve sealing area.

Approximately 30 separate filtration operations were completed from July 2nd through July 18. *Tables 8 and 9* summarize the on-line and off-line performance of the filtration system. During on-line operation, the amount of ash remaining in the filtrate declined from 1.7 (period 5) and 3.3 (period 5) to solid free at the of the

run. The filter cakes generally contained slightly less than 50% of residual oils. The filter performed better during the off-line operation in July in which the quinoline soluble, oil content in the filter cakes was less than 30%.

F. COAL CONVERSION

Coal Conversion was calculated for selected Periods and reported in *Figure 6*. Conversions for this PDU operation ranged from 78.1 and 88.2 W% maf coal and were generally lower than the values projected from CTSL data under similar conditions. It seems that the conversion decreases with the progression of the run reflecting possible degeneration in solvent quality. This conclusion was also suggested by microautoclaves tests conducted separately in HRI and Consol and from proton analysis conducted by Consol, *Table 10*.

G. PRODUCT YIELDS (PERIOD 10 AND 13)

Tables 11 and 12 summarize the normalized yields for Run 260-03 Periods 10 and 13 which have been calculated using four methods. The tables include some collected yield parameters for comparison with the results of the various normalization techniques.

The normalization results presented in the second column of the tables is based on the "net" method. Here, the weight of normalized NET product is equal to the weight of the feed quantities plus calculated hydrogen consumption after appropriate ash balance, carbon, nitrogen, and sulfur balances. In this calculation, the normalized vacuum bottoms yields was taken to be the same as the collected vacuum bottoms yield, the filter cake yield was obtained by ash balance, and the other carbon containing streams were adjusted for carbon balance closure by a common "carbon normalization factor" given in the table, which in this case was only 0.545 times the collected quantities if those streams.

The third column of the tables summarizes the "gross" normalization, that is the total of the net products plus the recycled vacuum bottoms and recycled vacuum overhead is equal to the weight of the coal, seal oil, DMDS, coal moisture plus the recycled vacuum bottoms and recycled vacuum overhead.

The fourth column of the tables is a "net" normalization, similar to that of the second column, excepting the vacuum bottoms yield was adjusted in common with the other products.

The fifth column of the tables is a "gross" normalization, similar to that of the third column, excepting the vacuum bottoms yield was adjusted in common with the other products. this method of normalization is similar to that used in normalizing the results of the CTSL Bench Unit operations.

As indicated in the tables, the collected yields from both Periods were characterized by very low ash recoveries (32 and 42%), high total weight recovery (100%), associated with the carbon recovery, again over 100%. The deviations from closure are exacerbated when filter cake yields are increased to obtain an ash balance, with increase in the filter cake weight corresponding to 28 and 30 W% of the coal fed, and a consequent increase in the carbon recovery to over 130% of the carbon in the net feed. Normalization, with carbon closure (in order to obtain reasonable water yields which were essentially calculated by an oxygen-by-difference balance) then requires very large downward adjustment of the products other than the filter cake. For Period 10 this adjustment, the "carbon normalization factor" given in the tables, was as low as 0.545 for the net normalization without adjustment of the vacuum bottoms yields. For the "gross" normalization, and adjustment of the vacuum bottoms yield, this factor increases to 0.845.

Consequently, normalized gas yields were always lower than the collected gas yields, with the gross normalization (including vacuum bottoms adjustment) corresponding most closely to the collected quantity. This normalization method resulted in the lowest residual yields (actually, with virtually no net residual oil yield in the Period 13 calculation). The normalized yield of C_4 -975°F distillate was the highest by this gross normalization technique, more markedly for the Period 13 calculations where there was essentially the same distillate obtained by the four calculations techniques.

Tables 13 to 15 summarize the quality of the liquid product and filter cake from Periods 10 and 13.

H. RECOVERED CATALYST INSPECTION

Tables 16 and 17 compare the properties of the catalysts recovered from the first and second stages during Periods 11 and 13.

The catalysts recovered from the two stages after Period 11 contained moderate amounts of carbon, 12.2 and 12.4 W%. The first stage catalyst had lost the longer particles, over 6.3 mm, which appeared principally in the intermediate 2.5-6.3 mm length range, with only slight increases in the amounts of the shorter particles. In contrast the second stage catalyst, despite the shorter duration of coal operations, had a very considerable increase in the proportion of the particles shorter than 2.5 mm, by a factor of over 3, to about 30 W% of the catalyst.

The catalyst recovered from two stages after Period 13 contained slightly lower amount of carbon, 10.1 and 10.5 W%. This first stage catalyst sample had a small amount of the longer particles, over 6.3 mm, and slightly greater amounts of the particles shorter than 2.5 mm. This second stage catalyst sample indicated no loss of the particles longer than 2.5 mm remaining. The drum attrition test loss for both of the recovered catalyst samples was about twice that of fresh catalyst. The unusually lower molybdenum analysis of the recovered second stage catalyst is being checked.

TABLE 8

FILTER STREAMS PRELIMINARY INSPECTIONS

Period	1	2	3	4	5	6	7
Filter Feed, Wt%							
Ash			1.10		2.26	1.83	
Filtrate, Wt%							
Ash			1.69			3.31	
Filter Cake, Wt%							
Quinoline Insol.		38.85				54.89	

FILTER STREAMS PRELIMINARY INSPECTIONS

Period	8	9	10	11	12	13
Filter Feed, Wt%						
Ash						4.52
Filtrate, Wt%						
Ash						0.0
Filter Cake, Wt%						
Quinoline Insol.	55.30	53.47	55.42			56.84

TABLE 9
FILTER PRELIMINARY INSPECTIONS
OFF LINE TESTING

DATE	5/23	7/12	7/14	7/14
TIME		1900	0600	1840
<hr/>				
Filter Feed, Wt%				
Quinoline Insol.	14.78		20.48	20.97
Filtrate, Wt%				
Quinoline Insol.	0.17	0.27	0.52	0.12
Filter Cake, Wt%				
Quinoline Insol.	49.17	84.22		71.77

TABLE 10
PROTON DISTRIBUTION AND PHENOLIC-OH CONCENTRATION

HRI NO. LO	PROTON DISTRIBUTION (%)							PHENOLIC-OH	
	COND. AROM.	UNCOND. AROM.	CYCLIC ALPHA	ALKYL ALPHA	CYCLIC BETA	ALKYL BETA	GAMMA	CONC. MEG/G	om
6040	6.7	5.8	13.5	9.1	20.7	27.1	17.1	0.35	3315
6041	5.4	4.7	9.8	7.3	19.1	33.2	20.6	0.18	3316
6042	4.9	3.9	10.3	7.7	20.0	34.3	19.0	0.10	3322
6045	3.1	4.2	8.7	7.1	20.7	35.0	21.2	<0.10	3330
6046	4.3	2.6	7.9	5.6	18.6	39.4	21.5	<0.10	3325
6047	6.0	2.9	9.9	6.3	20.8	36.0	18.1	0.10	3309
6048	5.6	2.8	7.0	5.6	18.1	38.0	22.8	0.11	3311
6049	5.6	3.0	7.7	6.3	18.8	36.9	21.8	0.12	3306
6097	6.3	2.6	9.6	7.3	19.9	35.9	18.4	0.13	3306

Date obtained 9/14/92

Date obtained 10/25/92

TABLE 11

PDU RUN 260-03 PERIOD 10
 CTSL WYOMING COAL
 PRELIMINARY DATA - VARIOUS NORMALIZATION METHODS

PERIOD	10T				
PERIOD START DATE	07/05/92				
PROCESS CONDITIONS					
REACTOR #1 TEMPERATURE DEG F	746.				
REACTOR #2 TEMPERATURE DEG F	794.				
CALC. HYDROGEN INLET PARTIAL PRESSURE, PSIG	2929.				
CATALYST SP. VEL., LB/HR/FT3 (EACH STAGE)	52.				
HYDROGEN PURITY AT REACTOR #1 INLET, MOL %	87.3				
CALC. HYDROGEN EXIT PARTIAL PRESSURE, PSIG	2050.				
UNIT BACK PRESSURE, PSIG	2890				
REACTOR #1 CAT AGE, LB DRY COAL/LB CAT	175				
REACTOR #2 CAT AGE, LB DRY COAL/LB CAT	52				
MATERIAL BALANCE RECOVERY, W% OF TOTAL FEEDS					
EXCESS RECOVERY, W% OF DRY COAL	11.8				
NORMALIZATION METHOD					
VACUUM BOTTOMS YIELD	Collected	Net	Gross	Net	Gross
CARBON NORMALIZATION FACTOR		--Unadjusted--		Normal.	Normal.
		0.545	0.754	0.591	0.838
STREAM YIELDS, W% of Dry Coal					
C1-C7 Gases (DMDS adjusted)	8.87	4.31	6.40	4.77	7.22
Naphtha Still Bottoms	33.08	18.04	24.97	19.54	27.73
Vacuum Still Overhead (net)	25.17	13.73	4.55	14.87	11.66
Vacuum Still Bottoms (net)	17.56	17.56	17.56	10.37	-7.31
Filter Cake	3.93	34.27	34.27	38.47	48.80
Water (less Injection Water)	35.00	25.83	25.75	25.76	25.54
Carbon Recovery	107.76	100.00	100.00	100.00	100.00
Ash Recovery	31.82	100.00	100.00	100.00	100.00
NORMALIZED YIELDS, W % OF DRY COAL					
H2S		0.26	0.26	0.27	0.28
NH3		0.75	0.75	0.77	0.82
H2O		19.22	19.03	19.03	18.82
CO+CO2		0.11	0.14	0.11	0.16
C1-C3 (Ex CH4 from DMDS)	6.56	3.07	4.68	3.42	5.32
C4-390 F		10.50	14.53	11.37	16.14
390-500 F		5.45	6.67	5.90	7.80
500-650 F		11.07	13.13	11.98	12.87
650-850 F		17.56	13.23	17.35	14.01
850-975 F		8.72	8.63	8.15	6.69
975 F+ (SOLIDS-FREE)		6.93	6.93	5.33	1.39
UNCONVERTED COAL		16.33	16.33	16.33	16.34
ASH (SO3-FREE)	2.10	6.60	6.60	6.60	6.60
TOTAL (100 + H2 CONS)		106.30	106.77	106.61	107.24
PROCESS PERFORMANCE					
975 + CONVERSION, W % MAF		75.1	76.3	76.8	81.0
COAL CONVERSION, W % MAF		82.5	82.5	82.5	82.5
TOTAL C4-975F, W % MAF COAL		57.1	55.7	58.6	61.6
HYDROGEN CONSUMPTION, W % FRESH FEED		6.30	6.77	6.61	7.24

NORMVAR2600310.TAB

TABLE 12

PDU RUN 260-03 PERIOD 13
 CTSI WYOMING COAL
 PRELIMINARY DATA - VARIOUS NORMALIZATION METHODS

PERIOD	131				
PERIOD START DATE	07/17/92				
PROCESS CONDITIONS					
REACTOR #1 TEMPERATURE DEG F	745.				
REACTOR #2 TEMPERATURE DEG F	807.				
CALC. HYDROGEN INLET PARTIAL PRESSURE, PSIG	2755.				
CATALYST SP. VEL., LB/HR/FT3 (EACH STAGE)	48.				
HYDROGEN PURITY AT REACTOR #1 INLET, MOL %	93.7				
CALC. HYDROGEN EXIT PARTIAL PRESSURE, PSIG	2365.				
UNIT BACK PRESSURE, PSIG	2880				
REACTOR #1 CAT AGE, LB DRY COAL/LB CAT	248				
REACTOR #2 CAT AGE, LB DRY COAL/LB CAT	52				
MATERIAL BALANCE RECOVERY, W% OF TOTAL FEEDS					
EXCESS RECOVERY, W% OF DRY COAL	102.3				
	4.9				
NORMALIZATION METHOD					
VACUUM BOTTOMS YIELD	Collected	Net	Gross	Net	Gross
CARBON NORMALIZATION FACTOR		--Unadjusted--		Normal.	Normal.
		0.694	0.742	0.675	0.867
STREAM YIELDS, W% of Dry Coal					
C1-C7 Gases (DMDS adjusted)	10.79	7.10	7.68	6.86	9.19
Naphtha Still Bottoms	83.74	58.09	52.14	56.50	72.63
Vacuum Still Overhead (net)	6.86	4.76	-0.63	46.3	3.01
Vacuum Still Bottoms (net)	-6.99	-6.99	-6.99	-4.72	-24.86
Filter Cake	20.17	47.62	47.62	47.62	48.80
Water (less Injection Water)	20.11	25.66	25.63	25.61	26.01
Carbon Recovery	111.38	100.00	100.00	100.00	100.00
Ash Recovery	42.42	100.00	100.00	100.00	100.00
NORMALIZED YIELDS, W % OF DRY COAL					
H2S		0.26	0.26	0.26	0.26
NH3		0.79	0.79	0.78	0.82
H2O		18.89	18.93	18.84	19.24
CO+CO2		0.21	0.23	0.20	0.26
C1-C3 (Ex CH4 from DMDS)	7.06	4.51	4.91	4.35	5.95
C4-390 F		14.90	15.94	14.49	18.64
390-500 F		10.81	11.46	10.49	13.65
500-650 F		20.26	18.32	19.39	26.08
650-850 F		7.64	7.58	8.97	-2.89
850-975 F		-0.16	-0.16	0.03	-1.69
975 F+ (SOLIDS-FREE)		1.66	1.66	1.88	-0.08
UNCONVERTED COAL		20.46	20.46	20.46	20.46
ASH (SO3-FREE)	2.80	6.60	6.60	6.60	6.60
TOTAL (100 + H2 CONS)		106.56	106.97	106.76	107.31
PROCESS PERFORMANCE					
975 + CONVERSION, W % MAF		86.3	76.3	76.1	78.2
COAL CONVERSION, W % MAF		78.1	78.1	78.1	78.1
TOTAL C4-975F, W % MAF COAL		57.2	56.9	57.2	57.6
HYDROGEN CONSUMPTION, W % FRESH FEED		6.56	6.97	6.76	7.31

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TABLE 13

PDU Run 260-03 Product Inspections
Boiling Point Distributions

Analysis	Period 10			Period 13		
	Naphtha Stabilizer Bottoms	Vacuum Still Overheads	Vacuum Still Bottoms	Naphtha Stabilizer Bottoms	Vacuum Still Overheads	Vacuum Still Bottoms
Yield, W% Liquid Product						
Boiling Point [F]						
IBP	156	414	741	175	463	588
5 V%	201	491	779	240	514	628
10 V%	219	541	807	278	521	638
20 V%	247	584	834	358	544	656
30 V%	281	606	859	436	554	680
40 V%	326	628	(Cracked)	493	573	702
50 V%	372	650		528	588	718
60 V%	414	668		558	600	738
70 V%	462	692		585	610	764
80 V%	506	714		610	626	810
90 V%	562	746		644	646	917
95 V%	604	779		672	660	963
FBP	630	821		691	702	
Volume %						
@ 390 F	55			24		
@ 500 F	79	6		42		
@ 650 F	98	51		92	90	
@ 850 F			30			86
@ 975 F			(cracked)			93
Weight %						
IBP-390 F	51.30			21.20		
390-500 F	24.70			17.40		
500-650 F	20.40	49.84		50.70		15.01
650-850 F	2.70	48.64	25.44	9.70	99.12	66.70
850-975 F		0.98	72.70		0.66	7.61
975 F+						9.76
Loss	0.90	0.54	1.86	1.00	0.22	0.92
Total	100	100	100	100	100	100

Note: Period 10B Sample contains solids (Filter operation was bypassed)

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TABLE 14

PDU Run 260-03 Product Inspections

Boiling Point Distributions

Analysis	Period 10						Analysis	Period 13					
	Distribution [W%]	Carbon [W%]	Hydrogen [W%]	Nitrogen [Wppm]	Sulfur [Wppm]	API		Distribution [W%]	Carbon [W%]	Hydrogen [W%]	Nitrogen [Wppm]	Sulfur [Wppm]	API
Naphtha Stabilizer Bottoms							Naphtha Stabilizer Bottoms						
IBP-390 F	52.2	85.60	14.09	144.0	204.2	50.8	IBP-390 F	22.2	86.80	14.08	141.0	136.9	50.3
390-500 F	24.7	86.66	12.70	383.0	355.3	33.9	390-500 F	17.4	86.80	12.73	343.0	191.7	33.1
500-650 F	20.4	87.41	12.36	396.0	140.0	26.6	500-630 F	50.7	87.66	12.28	324.0	64.7	25.7
650 F+	2.7	88.31	11.93	474.0	130.0	---	630 F+	9.7	87.41	11.87	374.0	154.0	20.3
Whole Sample	100	86.14	13.30	276.0	314.7	40.7	Whole Sample	100	86.93	12.61	322.0	304.6	31.5
Vacuum Still Overheads							Vacuum Still Overheads						
IBP-650 F	50.38	87.62	12.21	314.5	90.5	24.5	IBP-702 F	99.34	87.58	12.25	214.7	172.0	24.1
650-821F	48.64	87.43	11.69	340.2	170.2	19.5	702F+	0.66	---	---	---	---	---
821F+	0.98	---	---	---	---	---	Whole Sample	100	87.77	12.14	231.6	183.0	24.4
Whole Sample		88.03	12.00	344.0	38.4	22.1							
Vacuum Still Bottoms							Vacuum Still Bottoms						
IBP-859F	27.3	88.61	11.60	1768.0	130.0	18.1	IBP-850F	15.93	87.94	11.84	824.0	67.9	
859F+	72.7	74.35	6.59	5700.0	4100.0	-14.4	650-850F	66.7	88.61	11.41	1821.0	68.4	
Whole Sample	100	80.52	8.19	5000.0	2730.0	-6.1	850-963F	7.61	88.75	6.50	1300.0	88.8	
							963F+	9.76	53.27	3.27	5100.0	7890.0	
							Whole Sample	100	86.35	11.05	1800.0	500.0	

Note: Period 10B Sample contains solids (Filter operation was bypassed)

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TABLE 15

FILTER CAKE INSPECTIONS

	Period 10A2	Period 13B1
Elemental, W%		
Carbon	72.55	73.82
Hydrogen	7.49	7.48
Nitrogen	0.45	0.46
Sulfur	0.527	0.521
ASTM Ash, W%	16.63	14.02
S in Ash, W%		3.12
Molybdenum, Wppm	3980	TBD
Quinoline Filtration		
Insolubles, W%	52.89	56.84
Ash, W%	17.08	15.57
S in Ash, W%	4.34	4.39
Resid Content (TGA Method)	25.22	18.95

TBD: To be Determined

TABLE 16

RECOVERED CATALYST ANALYSES
PDU RUN 260-03, July 7, 1992 After Period 11

Stage	1	2	Fresh
Catalyst Age, Lbs Coal/Lb Catalyst	175	52	0
Screen Analysis of oil-free catalyst			
Lumps, W%	0.0	0.0	
+20 mesh, W%	99.8	90.3	
20-30 Mesh, W%	0.06	2.5	
30-100 mesh, W%	0.11	7.5	
-100 mesh, W%	0.01	0.4	
Analysis of oil-free			
+20 mesh catalyst, W%			
Carbon	12.21	12.42	
Hydrogen	1.16	0.96	
H/C Ratio	1.14	0.93	
Nitrogen	0.26	0.32	
Calcium	0.13	0.18	
Length Distribution			
< 0.5 mm, W%	0.0	0.3	0.0
0.5-1.0 mm, W%	0.3	4.4	0.8
1.0-1.5 mm, W%	3.1	7.2	2.3
1.5-2.5 mm, W%	8.0	17.4	6.9
2.5-6.3 mm, W%	88.6	63.4	83.7
> 6.3 mm, W%	0.0	7.2	6.2
Analysis of 30-100 mesh oil-free solids			
Molydenum, W%		7.09	

Notes:

First stage catalyst - Dull charcoal luster, with less than 1% tan (young). Tips of extrudates were slightly rounded.

Second Stage Catalyst - Slightly shiny charcoal luster, with 3-5% tan(young). Tips of extrudates were not rounded. There were a few 3-8 mm diameter lumps.

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TABLE 17

RECOVERED CATALYST ANALYSES
 PDU RUN 260-03, July 18, 1992 After Period 13

Stage	1	2	Fresh
Catalyst Age, Lbs Coal/Lb Catalyst	248	52	0
Oil In Original Sample, W%	31.1	27.3	
Screen Analysis of oil-free catalyst			
Lumps, W%	0.0	0.0	
+20 mesh, W%	94.7	99.0	
20-30 Mesh, W%	1.4	0.3	
30-100 mesh, W%	3.6	0.8	
-100 mesh, W%	0.8	0.5	
Analysis of oil-free +20 mesh catalyst, W%			
Carbon	10.05	10.49	
Hydrogen	0.97	0.93	
H/C Ratio	1.16	1.06	
Nitrogen	0.25	0.17	
Calcium	0.05	0.02	
Molybdenum	10.06	4.92	10.1
Drum Attrition Test Loss, W%	5.3	5.9	2.7
Length Distribution			
< 0.5 mm, W%	0.0	0.0	0.0
0.5-1.0 mm, W%	1.9	0.6	0.8
1.0-1.5 mm, W%	3.1	1.0	2.3
1.5-2.5 mm, W%	8.1	0.0	6.9
2.5-6.3 mm, W%	83.9	91.7	83.7
> 6.3 mm, W%	3.0	6.7	6.2
Analysis of 30-100 mesh oil-free solids			
Molydenum, W%	0.62	5.50	
Ash, W%	87.2	77.0	
Analysis of -100 mesh oil-free solids			
Molydenum, W%	0.74	2.22	
Ash, W%	82.4	75.1	
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FIGURE 4

Reactor 1 & 2 Temperature Vs. Period

—■— Reactor 1 —+— Reactor 2

FIGURE 5

TITLE: PDU 260 Simplified Flow Diagram Run 003 Filtration Section			HYDROCARBON RESEARCH, INC.		DATE: 5/18/91
JOB NO.			DRAWING NUMBER 260SF004		ISSU: 9/21/92
FORM RND-AL1			CHECKED:		RFL/

FIGURE 6

PDU Run 260-03
Black Thunder Mine Coal
Coal Conversion

TASK 5 - TECHNICAL ASSESSMENT

No activity during this reporting period.

TASK 6 - ADMINISTRATION

In the balance of the current contract two CTSL remains. Topical reports for the Mini PDU Run, the Bench-Scale and Laboratory-Scale Studies are being prepared.

A paper entitled "PDU Scale-up of CTSL Processing of Sub-bituminous Coal" was presented at the Liquefaction Contractors' Review Conference in Pittsburgh on September 23, 1992.

The attached schedule shows the run activities for the reminder of the contract.

FIGURE 7

<div><div><div>HRI[®]</div><div>HRI, INC. PRINCETON, N.J.</div></div></div>		REVISED CC-CTSL SCHEDULE										DATE: 10/30/92	
		1992											
		APR	MAY	JUNE	JULY	AUG	SEPT	OCT	NOV	DEC			
		CC-15											
		CC-16											
								</					