

**OPTIMIZATION OF REACTOR CONFIGURATION
IN COAL LIQUEFACTION****THIRD QUARTERLY REPORT FOR THE PERIOD****1 APRIL 1992 - 30 JUNE 1992****A.G. Comolli
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JANUARY 1992

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TABLE OF CONTENTS

	<u>PAGE NO.</u>
ABSTRACT	1
SUMMARY	2
TASK 2 - LABORATORY SUPPORT	3
TASK 3 - LABORATORY SCALE OPERATIONS-REACTOR CONFIGURATION	7
TASK 4 - TECHNICAL ASSESSMENT	13
TASK 5 - PROJECT MANAGEMENT	13

LIST OF FIGURES AND TABLE

<u>FIGURES</u>	<u>TITLE</u>	<u>PAGE NO</u>
1	Pore Size Distribution of Shell S-317 1/20" Trilobe Catalyst - Cumulative Pore Volume	5
2	Pore Size Distribution of Shell S-317 1/20" Trilobe Catalyst - Differential Pore Volume	6
3	Microautoclave Test Results	10
4	Schematic Diagram of the 3/8" Fixed Bed Reactor System	12
5	Phase I - Schedule (Year 1)	14

<u>TABLES</u>		
1	Catalyst Properties	4
2	Microautoclave Tests Using L-772 Partially Converted Slurry from PDU Run 260-03	9

ABSTRACT

This report summaries the work in the third quarter of the optimization of reactor configuration in direct coal liquefaction.

The microautoclave screening test program to determine the ultimate conversion of Black Thunder Mine coal has been initiated. Fabrication and assembly of the small scale fixed bed unit are underway and scheduled to complete by the end of July.

SUMMARY

During the third quarter of the program, experimental work had commenced on microautoclave evaluation of partially converted coal slurry obtained from PDU Run 260-03. Additional conversion of coal in the non-catalytic and catalytic tests was observed. However, the increase in coal conversion was lower than previous tests on the HRI-5887 shipment of Black Thunder Mine coal prepared by Empire Coke Company. Microautoclave tests on coal used as feed in the PDU Run 260-03 are being evaluated under the CTSL program.

Retrofitting of a small continuous flow unit for fixed bed processing of partially converted coal slurry had commenced in June and expected to completed by the end of July. The fixed bed test program is scheduled to start in mid-August.

A batch of presulfided Shell S-317 1/20" trilobe catalyst had been obtained from Wilsonville and was characterized during this period. The Mo/Ni ratio of the presulfided trilobe catalyst was very similar to that of the fresh Shell S-317 1/32" extrudates. As a result of the presulfiding procedure, part of the pore structure (24%) was blocked by carbonaceous deposits. However, the pore size distribution of the trilobe catalyst remained about the same as the fresh 1/32" extrudates.

A paper on reactor configuration in coal liquefaction was presented at the 206th ACS National Meeting held in San Francisco, California on April 7.

PROGRESS REPORT

Task 2 - Laboratory Support

A trilobe catalyst has been selected as the first catalyst to be evaluated in the fixed bed mode. The trilobe catalyst is known to give lower pressure drop than catalyst of other shapes, eg. extrudates and beads. A batch of Shell S-317 1/20" presulfided trilobe catalyst (HRI-6030) was obtained from Wilsonville for this purpose.

Selected chemical and physical properties of the Shell 1/20" trilobe catalyst are compared with that of fresh Shell 1/32" (HRI-5394) and Criterion 1/16" (HRI-5903) extrudates in *Table 1*.

The presulfided trilobe catalyst was stored in oil during shipment and was washed with toluene to an "oil-free" state prior to being characterized. The oil-free sample contained 7.35 W% of sulfur. The Mo/Ni ratio of the trilobe catalyst (5.1) was similar to the Shell 1/32" extrudate catalyst (5.2) and were both higher than that of the Criterion catalyst (4.2).

The presulfided trilobe catalyst had a higher bulk and particle densities, but lower pore volume and surface area than the other two catalysts. The pore volume of the trilobe catalyst was 24.8% less than that of the Shell 1/32" extrudate, while the difference in surface area was only 19%. The pore size distribution of these catalysts are presented in *Figures 1 and 2*. Although similar analyses on a fresh trilobe sample were not available for direct comparison, it is very likely that the fresh trilobe catalyst may have similar properties as the Shell S-317 extrudate. The observed difference in physical properties between the two Shell catalysts was a result of carbon deposition from the presulfiding procedure.

Although the two extrudate catalysts (HRI-5903 and 5394) had similar chemical and physical properties, there were considerable differences in its pore size distribution.

The 1/16" Criterion catalyst (5903) contained more meso and macropores in the range of 200-10,000 angstroms. However, the model micropore diameter was only 46 angstroms in the Criterion catalyst while that of the 1/32" Shell catalyst (5934) was higher (slightly above 100 angstroms).

The 1/16" Criterion catalyst will be evaluated in the second fixed bed test.

TABLE 1

**CATALYST PROPERTIES - Presulfided Shell S-317 1/20" Trilobe
Comparison with Catalysts Used in the CTSL Program**

	Shell Trilobe Persulfided	Shell Extrudate e	Criterion Extrudate
HRI NUMBER	6030	5394	5903
Nominal Diameter, inches	1/20	1/32	1/16
CHEMICAL ANALYSIS (W% mf)			
Molybdenum	7.91	11.4	10.11
Nickel	1.55	2.2	2.38
Mo/Ni Ratio, w/w	5.1	5.2	4.2
Carbon	3.03		
Hydrogen	0.85		
Nitrogen	0.07		
Sulfur	7.35		
PHYSICAL PROPERTIES			
Bulk Density, lb/ft ₃	43.8	36.7	38.1
Particle Density, g/cc	1.090	0.966	0.938
Pore Volume, cc/g	0.490	0.652	0.645
Surface Area, M ₂ /g			
Hg Porosimetry	160	197	283
BET Method	166	N/A	314
PORE SIZE DISTRIBUTION, cc/g			
> 30 Å	0.490	0.65	0.64
> 100 Å	0.276	0.39	0.30
> 250 Å	0.140	0.19	0.27
> 500 Å	0.122	0.16	0.24
> 1500 Å	0.084	0.11	0.18
> 4000 Å	0.018	0.02	0.08
Modal Diameter, Mesopores Å	90	95	46
Modal Diameter, Macropores, Å	3300	2800	4200

FIGURE 1

CATALYST PORE SIZE DISTRIBUTION

Criterion (HRI 5903) And Shell S-317 (HRI 5394, 6-30) Catalyst

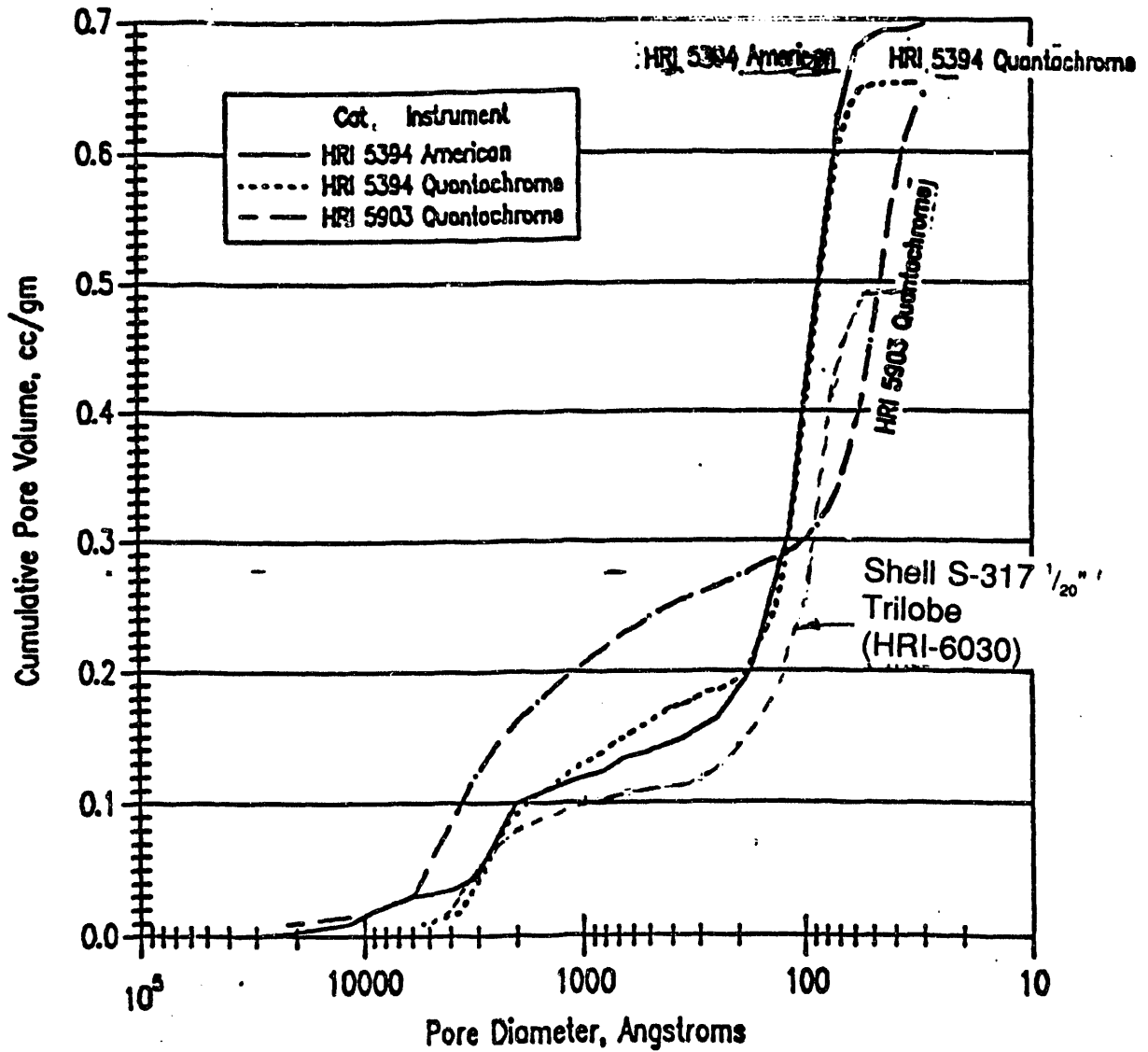
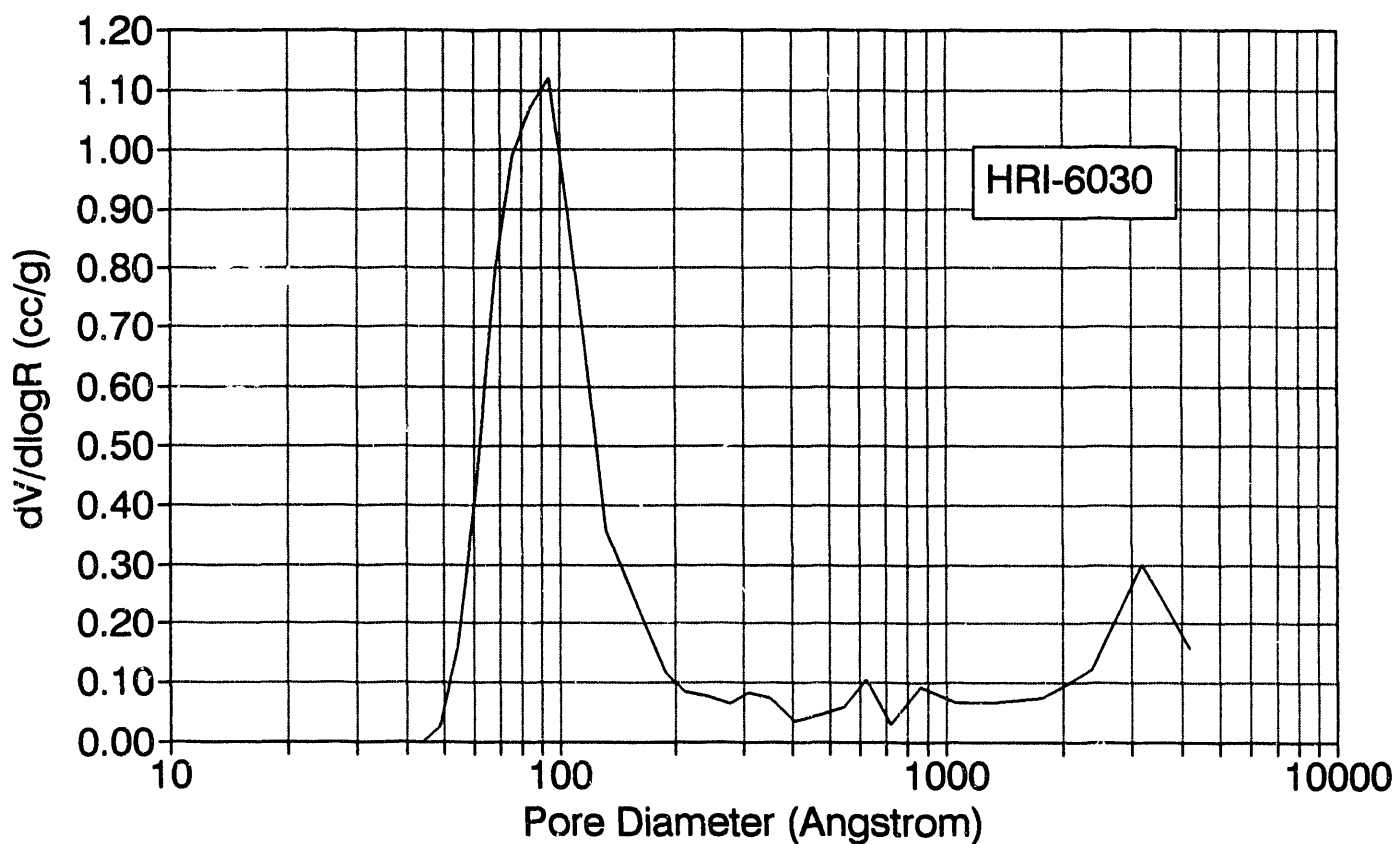


FIGURE 2

Shell S-317 1/20" Trilobe Catalyst

$dV/d\log R$ vs Pore Diameter



Task 3 - Laboratory Scale Operations-Reactor Configuration

A. Microautoclave Screening Test

The partially converted coal slurry (L-772) retained from the November, 1991 operations using Black Thunder Mine coal in PDU Run 260-03, and which is to be used in small scale fixed bed tests, has been tested in a 20 cc Microautoclave comparing the performance in tests with and without catalyst.

The tests used the L-772 slurry directly in the tests which was for 30 and 60 minutes, at 800° F, and 2,000 psig hydrogen pressure. Where catalyst was used, it was HRI 5359P2, Shell S-317 catalyst that had been presulfided in a fixed bed using TNPS as the sulfiding agent. The catalyst quantity was 2 grams, with an L-772 charge of 10 grams. The L-772 contained about 17.1 W% solids, which consisted of mineral matter and unconverted coal corresponding to a conversion of 75.7 W% of the coal fed to the PDU operation.

Table 2 summaries the results of the tests on slurry L-772.

The catalytic tests had higher coal conversions and lower residual oil yields than were obtained in the non-catalytic tests. The apparent coal conversion rate in the catalytic tests was higher by a factor of about 1.75 than in the non-catalytic tests. However, conversion levels were considerably lower than had been obtained in similar tests with bench unit product solids. The analyses of liquid products indicated that there was about 2/3 as much net residual oil formation in the catalytic tests. However, the hydrogen contents of the product liquids indicated no specific advantage for the catalytic tests.

Coal Conversion

The additional conversions in the catalytic tests were higher than in the corresponding non-catalytic test, although the difference was narrower for the longer tests. The non-catalytic tests increased the conversion level from 75.7 W% to 88.9 and 90.8 W% for the 30 and 60 minute tests, respectively, while the corresponding conversion levels for the catalytic tests were 1.7 and 0.4 W% higher, at 90.6 and 91.2 W%. Assuming first order kinetics, the change in conversion with time for both types of tests indicate a limiting conversion level of about 91.2 W% (ostensibly the rest of the coal is inert), with the specific rate for the catalytic tests about 1.75 times that for the non-catalytic tests.

The relatively low conversion levels obtained in these tests and the apparently high proportion of inert coal is surprising. The HRI 5887 shipment of Black Thunder Mine coal prepared by Empire Coke Company gave 91.4 and 94.4 W% conversion in 30 and 60 minute microautoclave tests, respectively, also at 800° F and 2000 psig using a gas oil solvent in approximately the same oil/solid ratio that obtained in tests using the L-772 slurry (refer to Figure 3). Previous microautoclave tests with partially converted Black Thunder Mine bench unit product solids increased the conversion level of a first stage product from 65.4 to 93.5 W% (the test was at 825° F, but otherwise similar). Conversion levels of over 95 W% were obtained in similar tests with the bench unit second stage product solids.

Product Liquid Analyses

The hydrogen content of the oil was lowered by 0.6 to 1.0 W%, which is more or less in line with the relatively low hydrogen content of the additional material dissolved. The hydrogen contents correlate with the material having a hydrogen content of 2.1 W%. The essential conclusion is that the catalyst did not have any specific impact upon hydrogen content.

Residual oil contents (by thermogravimetric analysis) in the liquid products were all higher than the residual oil content of liquid in the feed. However, these contents were lower in the catalytic product than in the thermal product. For the thermal tests the increase in residual oil content was 0.56-0.60 times as great as the amount of coal dissolved, while for the catalytic tests this ratio was 0.34-0.38. This ratio in the thermal tests is very close to that indicated in correlation of microautoclave and bench unit yields as the proportion of residual oil formed in the primary liquefaction of the coal, so that these thermal results indicate virtually no secondary reaction of the residual oil.

Microautoclave tests using hexahydropyrene as a solvent have also been completed. Analyses are being carried out and will be reported in the next quarterly report.

TABLE 2

Advanced Coal Liquefaction Concepts Program
Reactor Configuration

Microautoclave Tests Using L-772 Partially Converted Slurry from PDU Run 260-03

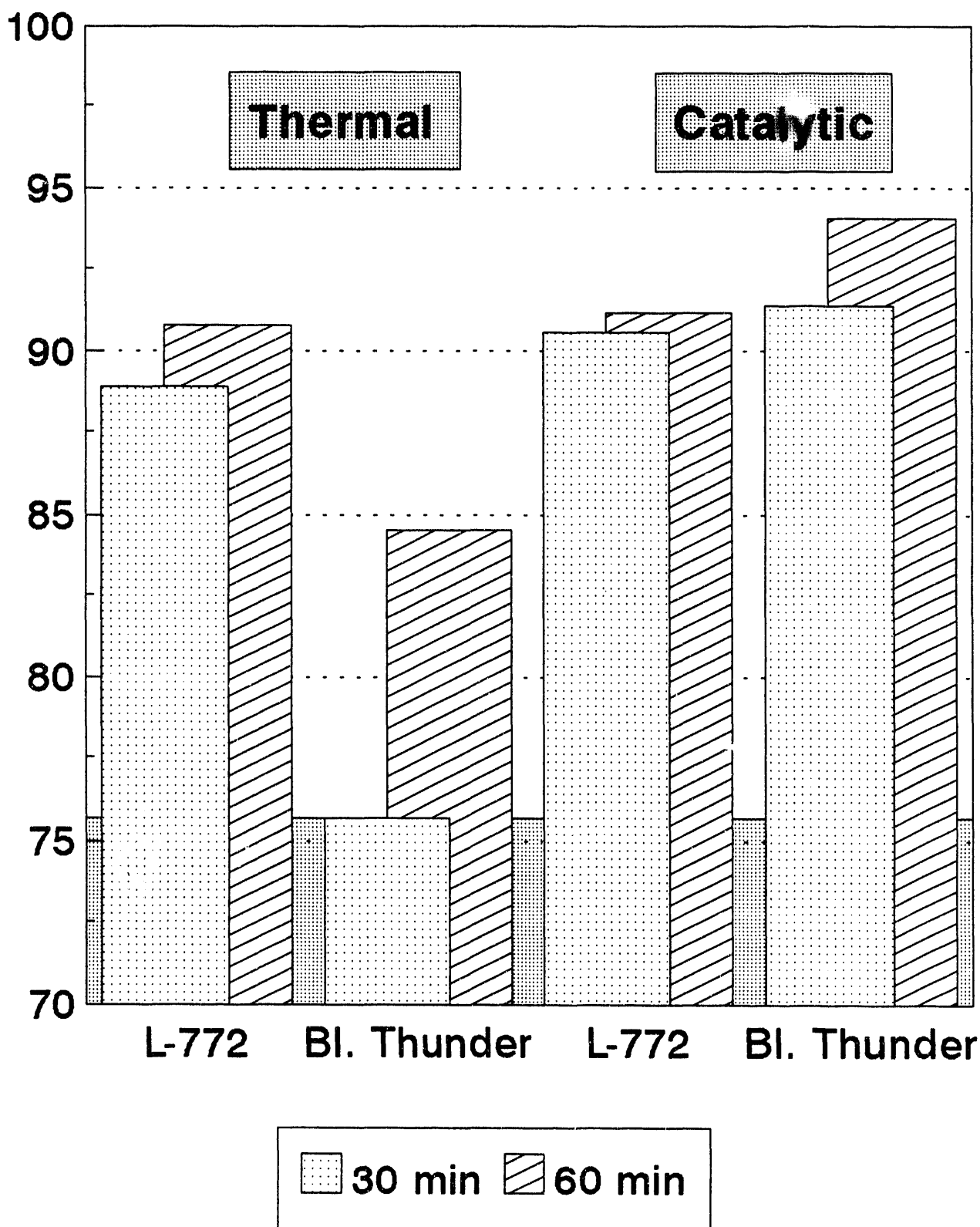
	Black Thunder Coal	L-772 Slurry Feed	CM115	CM117	CM116	CM118
Temperature, F			800	800	800	800
Pressure (hot), psig			2000	2000	2000	2000
Time, min			30	60	30	60
Catalyst, g/g Slurry			0	0	0.2	0.2
Coal Conversion, W%		75.7	88.9	90.8	90.6	91.2
Analysis of Liquid Product, W%						
Carbon	68.65	88.65	87.89	87.94	88.33	87.21
Hydrogen	4.56	11.14	10.55	10.39	10.32	10.19
Nitrogen	0.87	0.05	0.46	0.07	0.07	0.06
Sulfur	0.5	0.019	0.028	0.053	0.08	0.07
H/C	0.80	1.51	1.44	1.42	1.40	1.40
Residuum (TGA), W%		5.14	10.26	10.67	8.8	8.65
Incremental Residuum g/g coal dissolved			0.6	0.56	0.38	0.34

FIGURE 3

Microautoclave Test Results (800 F, 2000 psig)

Black Thunder Coal

Raw Coal vs Partially Converted Coal Slurry (L-772)



B. Fixed Bed Reactor Configuration

A small continuous flow unit is being retrofitted for fixed bed processing of partially converted coal slurry or CTSL 2nd stage feed. A schematic diagram of the 3/8" diameter fixed bed is given in *Figure 4*.

The fixed bed unit (Unit 254) consists of two 3/8" diameter tubular reactors connected in series. Pressure drop across each reactor is monitored by a DP cell for detection of possible solid build up in the catalyst bed.

Two 2-day tests were designed to evaluate the solid handling ability of the fixed bed packed with the Shell S-317 1/20 trilobe catalyst (Run 254-01) and the Shell S-317 1/16" extrudate catalyst (Run 254-02) in an upflow mode.

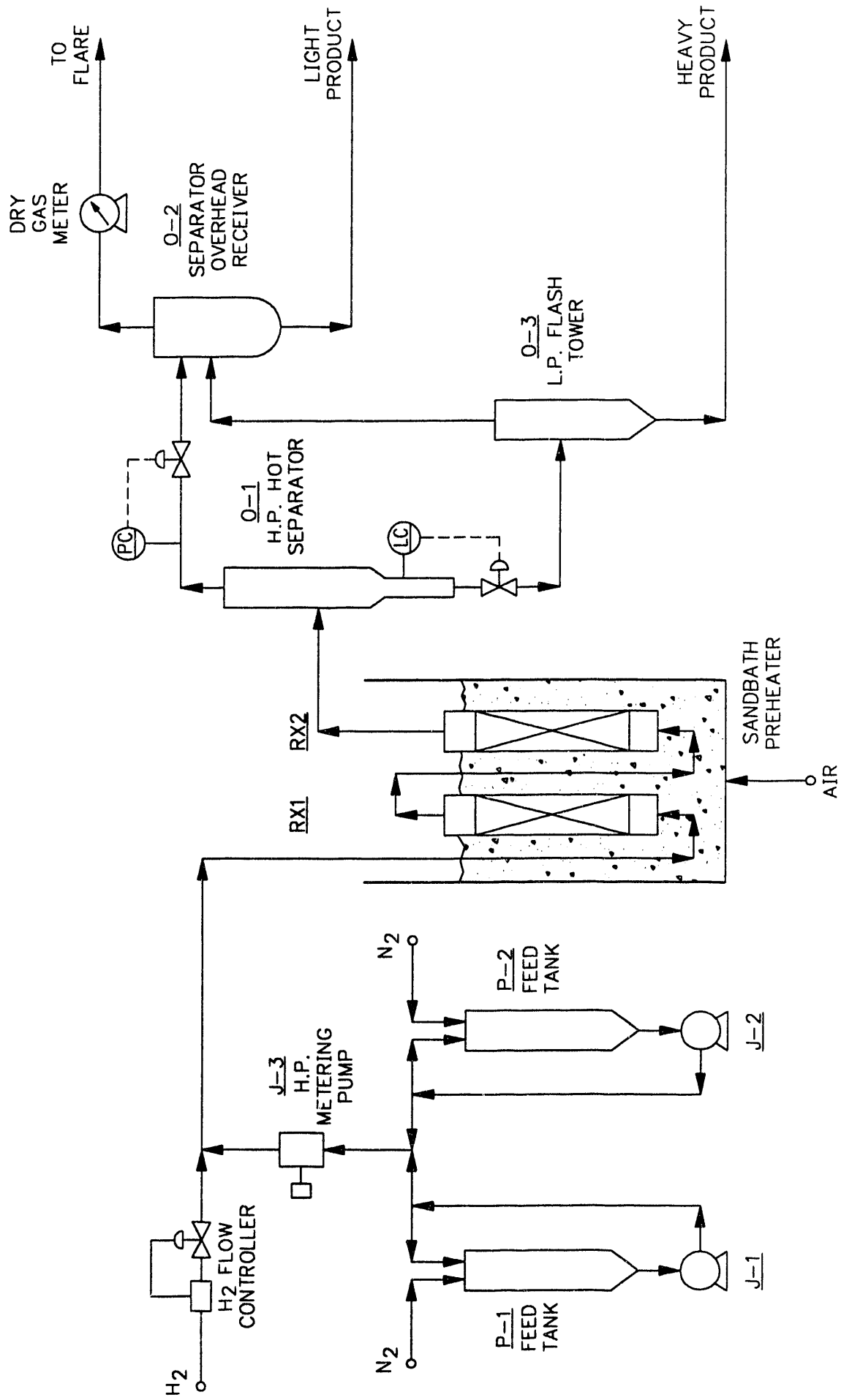
For each test the following process conditions will be evaluated:

Condition	1	2
Period	1-2	3-4
Feed Slurry	PDU 260-03 O-47 Slurry (L-772)	
Catalyst	Shell S-317 1/20" trilobe in Run 254-01 1/16" extrudate in Run 254-02	
Pressure, psig	2500	2500
Temperature, ° F	800	800
Space Velocity lb/h/ft ³	155	78

Note: Duration of each period is 12 hours.

It is anticipated the equipment retrofitting and commissioning of the unit will be completed by the end of July. The test program is scheduled to commence in mid-August.

FIGURE 4



HRI 3/8" FIXED BED REACTOR SYSTEM - UPFLOW MODE
(UNIT 254)

Task 4 - Technical Assessment

No activity was undertaken during this reporting period.

Task 5 - Project Management

Approval had been granted on the Environmental Assessment.

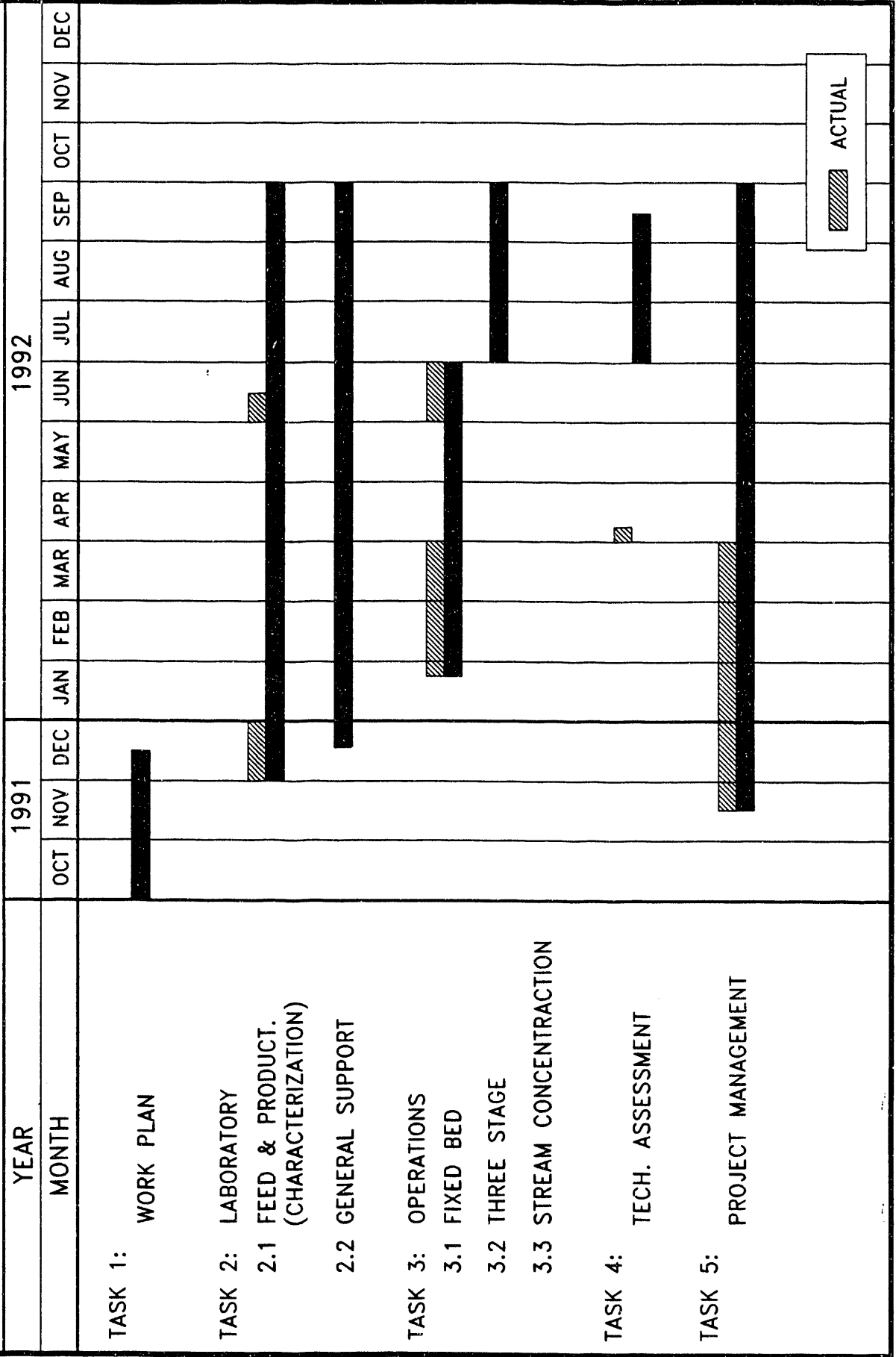
A technical paper was presented at the 206th ACS National Meeting held in San Francisco on April 7.

An updated work plan is attached, *Figure 5*.

FIGURE 5



OPTIMIZATION OF REACTOR CONFIGURATIONS



**DATE
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