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OPTIMIZATION OF REACTOR CONFIGURATION IN COAL LIQUEFACTION

NINTH QUARTERLY REPORT FOR THE PERIOD

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1 OCTOBER 1993 - 31 DECEMBER 1993

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WORK PERFORMED UNDER CONTRACT

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HYDROCARBON RESEARCH, INC.
100 OVERLOOK CENTER, SUITE 400
PRINCETON, NJ 08540

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TABLE OF CONTENT

LIST OF FIGURES AND TABLES

ABSTRACT

This quarterly report covers the activities of Optimization of Reactor Configuration in Coal Liquefaction during the Period October 1 to December 31, 1993, at Hydrocarbon Research, Inc. in Lawrenceville and Princeton, New Jersey. This DOE Contract Period was from October 1, 1991 to September 30, 1993 and has recently been extended to March 31, 1994.

The overall objective of this program is to achieve a new approach to liquefaction that generates an all distillate product slate at a reduced cost of about $25 per barrel of crude oil equivalent.

This quarterly report covers work on laboratory Support, Laboratory-scale Studies and Project Management.

SUMMARY

During this reporting period, a simulated three-stage coal liquefaction continuous flow test was attempted using a two-stage Robinson-Mahoney reactor system. The objective of this test was to compare the performance of a two-stage fully backmixed system with a three-stage system with and without interstage stream re-concentration on processing Illinois No. 6 coal from Crown II Mine. Coal was fed continuously to the unit for 60 hours. However, due to mechanical problem encountered with the letdown and high differential temperature between the furnace and the reactor, the run was aborted.

The run will be repeated after modification on the letdown system has been completed.

INTRODUCTION

This is the ninth progress report of a two-year contract to study and optimize various reactor configurations for direct coal liquefaction. The studies conducted during this quarter are reported by task.

Task 1 - Project Work Plan, had been completed.

Task 2 - Laboratory Support, covers feedstocks characterization and general analytical supports for Task 3.

Task 3 - Laboratory-Scale Studies, evaluates three reactor configurations, namely, fixed-bed reactor as a "finishing reactor", three-stage close coupled backmixed reactor system and interstage product stream concentration.

Task 4 - Technical Assessment, includes modelling and comparative assessments of the three reactor configurations.

The Contract Period, which was originally from October 1, 1991 to September 30, 1993, has now been extended to March 31, 1994.

TASK 2 - LABORATORY SUPPORT

Properties of the feed coal and vehicle oil used in the simulated three-stage run (245-22) are discussed.

Vehicle Oil (L-802)

The vehicle oil for the simulated three-stage test was a blend of makeup oil (L-794) and pressure filter liquids (L-795) from Bench Run 227-78 (CMSL-02). The blending ratio was 1 part of L-794 to 3 parts of L-795. Analysis of the composite oil, L-802, is given in **Table 1**. The composite oil contained 24.0 W% of 524C (975F) residuum and 2.89 W% of toluene insolubles.

Feed Coal (HRI-6158)

The feed coal was a bituminous coal, Illinois No. 6 Crown II Mine coal from Macoupin County. The pulverized coal was prepared by Empire Coke Company and shipped in nitrogen purged container truck to HRI for the Proof of Concept program. The drying was accomplished by hot inert gases containing less than 3 W% oxygen. The analysis of a sample (HRI-6156) taken from a grinding test prior to the preparation of the bulk shipment is given in **Table 2**.

The feed coal contained 3-5 W% of moisture. The characteristic of this coal was typical of Illinois No. coal. However, the chlorine content, 0.12 W%, is considered to be in the high range. The total sulfur content was 4.48 W%, of which pyritic sulfur is slightly more than 25% (1.2 W% maf coal).

The re-activity of the feed coal was tested under standard microautoclave conditions (Temperature of 427°C for 30 minutes under 13.8 MPa of hydrogen over-pressure; solvent/coal/catalyst ratio of 4/1/1). THF conversion ranged from 95.1 to 95.2 W% was observed suggesting this coal is 3 to 3.5 W% more active than previously tested Illinois No. 6 coals from Burning Star No. 2 Mine.

TASK 3 - LABORATORY SCALE OPERATIONS: REACTOR CONFIGURATION

During this reporting period, a continuous flow test to evaluate the three stage reactor configuration and interstage stream concentration concept was attempted using a 1-liter two-stage Robinson-Mahoney reactor system. However, due to mechanical problem encountered, the test was aborted 60 hours after coal was introduced to the unit. An account of this attempt is described in this report.

Objective

To evaluate the three-stage and interstage stream concentration concepts using Illinois No. 6 coal.

Background

The addition of a third back-mixed catalytic ebullated bed reactor in series to two close-coupled reactor will bring the performance of the process closer to the ideal plug flow configuration. An elementary first -order kinetic model, with equal temperatures in all stages, indicates that a three-stage system would require 26% less total volume than the two-stage configuration at a conversion level of 95 %.

The concentration of primary reactants declines progressively stage by stage in a close-coupled, multistage fully back-mixed system. More effective use of reactor space for the conversion liquid and solid phase reactants would be promoted if their concentrations in the liquid phase could be maintained at higher levels and the hydrogen partial pressure increased. Based on first-order kinetic model, it is projected that a three-stage system of back-mixed reactors with reconcentration of the second-stage product going to the third-stage require only 43% as much total reactor volume to attain 95% conversion as would be needed to a conventional two-stage system with no interstage feed concentration.

Run Plan

A two-stage Robinson-Mahoney reactor system was used for simulating the three-stage operations. The simulation will be achieved by two consecutive **once-through** tests. In the first test, two reactors will be used and the partially converted, slurry product from the this test will then served as feed material for the second test, which uses only a single reactor.

This run consists of four operating conditions extending over a 16 days duration, as shown in **Table 3**. Conditions 1 one of the two conditions to be evaluated in is the first half of the non-integrated three-stage test with the first and second temperature to be controlled at 399 and 429C, respectively. The slurry product from Condition 1 will then be further processed in Conditions 3 and 4 (the second half of the test), with or without removal of lighter product. Process conditions chosen for Condition 2 are typical CTSL operating conditions. The process performance from Condition 2 serves as a basecase for comparing with the simulated three-stage operations Condition 1-3 and Condition 1-4.

Robinson-Mahoney Reactor

The Robinson-Mahoney dual-reactor system, employed for this coal liquefaction study, was supplied by Autoclave Engineering, Inc. With the exception of the stationary catalyst cage, the internals of the reactor were the original design. The cage was modified to hold approximately 128 cc of extrudate catalysts by increasing the wide of the annulus space. Heat is provided by a single zone 1.7 Kw electric furnace. The reactor internal temperatures are measured at two locations (14 and 19 cm. below the top flange).

The top and the body flanges were insulated to minimize the heat lost through the top section, the unheated section, of the reactor. In spite of this effort, the temperature gradient in the vapor phase was as great as 2.5-2.8°C/cm (12-13F/in.). The agitation speed was 1200 rpm.

A schematic process flow diagram is shown in Figure 1. The vehicle oil, feed coal and hydrogen are mixed and preheated to about 344C before entering the first reactor through a bottom port. The gas/liquid interface is controlled by the height of an overflow tube. The interface is usually slight above the overflow tube as suggested by reactor axial temperature profiles measured under system pressure and temperature.

Feed Coal and Vehicle Oil

Illinois No. 6 coal from the Crown II Mine was used in this test. This coal was also used in the Proof of Concepts program (POC-01). The vehicle oil was a blend of makeup oil (L-794) and pressure filter liquids (L-795) from Bench Run 227-78 (CMSL-02). The analysis of the feed coal and vehicle oil is given in **Table 1**.

Operating Summary

Run preparation started on November 12, 1993. Each of the two reactors was charged with 128 cc of Akzo AO-60 1/16" extrudate catalyst recovered from the first stage of Bench Run 227-76 (CC-16). The characteristics of the fresh and recovered catalysts are compared in **Table 3**. The recovered catalyst contained 12.4 W% of carbon and 1.94 W% of metal contaminants. Also, the surface area was reduced from 286 m^2/g in the fresh catalyst to 189 m^2/g in the recovered catalyst.

The unit was heated up on No. 2 fuel oil on November 15; switched to startup oil L-769 and followed by L-802, the vehicle oil, as the reactor temperatures approaching the desired steady temperature for Condition 1. Coal feed was introduced to the system at 2400 hours of November 16. Coal feed was maintained for about 60 hours prior to shutdown which was caused by high furnace temperature required to sustain the desired temperature in second stage reactor. Also, as a result of failures of letdown valve several system upsets, loss of pressure ranging from 3.5-13.8 MPa (500-2000 psi) were experienced during this operating periods. However, four 12-hour material balance periods were completed.

Unit inspection indicated the following:

1. Both the first and second stage reactors had approximately 1/2" thick layer of some unreacted coal or coke deposits on top of the catalyst cages. The thermowell and the agitator were also covered with dry coke-like solids.

2. The agitator blade assembly became disengaged from the magnetic drive. The agitator would not turn with the magnetic drive.

Temperature in both reactor was very stable in the first 24 hours of operator on coal feed. Reactor 1 temperature was controlled well between the range of 399-405C, while Reactor 2 temperature was within a tighter range 426-430C. Approximately, 25 hours on coal feed both reactor temperatures started to decrease, while the external furnace temperature took a step jump of 20-25C and then increased steadily thereafter. The sudden increase in the differential temperature between the furnace and the reactor liquid at 25-28 hours suggested either a fast buildup of solid materials on the reactor well or/and the loss of mixing in the reactors.

Material Balance and Product Inspection

Table 5 summarizes the input rates, output rates and yield of net products for the four material balance periods. With the exception of sub-period 2B, the overall mass recoveries were within 94.0 to 101.0 W%. The mass balance of sub-period 2B was very poor (79.2 W%). A significant amount of the Separator Overhead and Bottom products were not accounted for in this sub-period.

Products form the Period 2B are being analyzed and preliminary results are listed in **Table 6**. The coal conversion was estimated to be 92.6 W%. The conversion level approaches the highest value of 96.0 W% observed in a larger scale two-stage operation (PDU) at higher reaction severity of 413 and 433C.

Recommendations and Future Plan

The simulated three stage run will be repeated in late February or early March time frame. Prior to the repeated test the existing stellite trim on the Hot Separator letdown valve will be replaced by tungsten carbide. Also, a short series of cold model study is planned to evaluate the solid and liquid mixing pattern in the reactor using a "see through" mockup model.

TASK 4 TECHNICAL ASSESSMENT

No activity was undertaken during this reporting period.

TASK 5 PROJECT MANAGEMENT

Updated work schedule is attached (Figure 2)

Table 1

Inspection of Vehicle Oil (L-802)

API Gravity	7.8	
ASTM-D1160 Distillation		
	[C]	[F]
IBP	82	179
5 V%	224	435
10 V%	329	625
13 V%	343	650
20 V%	349	660
30 V%	373	704
40 V%	391	735
50 V%	409	769
60 V%	438	820
64 V%	454	850
70 V%	468	875
78 V%	524	975
Distribution		
	W%	**V%**
IBP-343C	12.69	13
343-454C	48.23	51
343-524C	15.06	14
524C+	24.02	
Elemental Analysis [W%]		
Carbon	87.95	
Hydrogen	8.57	
Nitrogen	0.36	
Sulfur	0.21	
Solubility [W%]		
Cyclohexane Insol.	6.73	
Toluene Insol.	2.89	

Table 2

Inspection of Illinois No. 6 Crown II Mine Coal

Moisture, W%	3.39
Proximate Analysis, W% dry basis	
Volatile Matter	41.40
Fixed Carbon	49.18
Ash	9.42
Elemental Analysis, W% dry-ash free basis	
Carbon	79.32
Hydrogen	5.85
Nitrogen	1.58
Sulfur	4.48
Oxygen (by diff.)	8.77
Chlorine	0.12
H/C	0.89
Sulfur Forms, W% dry-ash free basis	
Sulfate	1.00
Pyritic	1.20
Organic	3.26
Mineral Analysis, W% Ash	
P2O5	0.23
SiO2	49.98
Fe2O3	16.34
Al2O3	18.64
TiO2	0.95
CaO	4.05
MgO	0.87
SO3	3.38
K2O	2.27
Na2O	1.48
SrO	0.03
BaO	0.01
Mn3O4	0.10
Underdetermined	1.67

Table 3

Simulated Three-Stage Liquefaction Run: Run Plan

Illinois No. 6 Coal (HRI-6107)
Shell S-317 Ni/Mo 1/32" Catalyst (HRI-5394)

Condition	1	2	3	4
Periods	1-8	9-11	12-14	15-16
No. of Reactor	2	2	1	1
Temperature, °F				
Reactor #1	750	750	825	825
Reactor #2	805	825	n/a	n/a
Space Velocity lb MAF coal/h/ft^3 cat. per 1st stage	66	44	66	66
Feed Type	Coal	Coal	Cond. 1 Whole Product	Cond. 1 Topped Product
Solvent/Coal Ratio	1.2	1.2	n/a	n/a
Coal and Solvent Flowrates:				
Pat I				
dry coal, g/h	136	90	n/a	n/a
wet coal, g/h @ 3W% moisture	140	93	n/a	n/a
solvent, g/h	168	111	n/a	n/a
Total Slurry, g/h	308	204	n/a	n/a
Part II				
Slurry, (dry) g/h	n/a	n/a	195*	210**
Water,g/h	n/a	n/a	21*	n/a
Hydrogen and Water Injection Rates:				
Hydrogen, scfh	11	7.0	8.0	8.0

* To be confirmed to match the production rate of separator bottoms from Condition #1.

** To match the production of topped separator bottoms from Condition #1

Table 4

Analysis of Fresh and Recovered AO-60 Catalyst

Catalyst	Fresh	Run CC-16 1st Stage
Catalyst Age, Kg coal/Kg cat.	0	253
Bulk Density, gm/cc	0.557	0.758
Analyses of Oil Free +20 mesh Catalyst, W%		
Carbon		12.43
Hydrogen		0.90
Nitrogen		0.32
Sulfur		5.59
H/C Ratio		0.87
Molybdenum	12.25	7.59
Nickel	2.60	1.80
Titanium		1.021
Iron		0.372
Calcium		0.056
Sodium		0.493
Total Metal Contaminants		1.94
Loss on Ignition, W%		20.82
Particle Density, gm/cc particle*	3.547	2.412
Pore Volume, cc/gm	0.874	0.489
Surface Area, m2/gm	286	190
Modal Pore Diameter, Angstrom		
Macropores		875
Mesopores	125	80

Table 5

Advanced Coal Liquefaction Program

Simulated Three-Stage Continuous Flow Test

Part I Condition I

Period No.		1A	1B	1	2A	2B	2
Operating Conditions							
Temperature [C]	Reactor 1	401	401	401	388	396	392
	Reactor 2	425	427	427	420	409	415
Unit Back Pressure [MPa]		17.0	16.3	16.6	16.8	24.3	16.8
Space Velocity [lb/h/ft3 Cat./Stage]		66.9	65.3	66.1	67.5	67.5	67.6
Avg. Catalyst Age [Kg/Kg coal]		270	287	287	340	358	358
Veh. Oil/Coal Ratio		1.24	1.24	1.24	1.24	1.24	1.24
Material Recovery [W%]		101.0	94.0	97.5	99.3	79.2	89.1
Mass Balance [gm/hr]							
INPUTS							
Coal (wet)		141.6	138.1	139.8	142.8	142.8	142.8
Vehicle Oil		169.8	165.7	167.7	171.4	171.3	171.3
Hydrogen		26.5	27.3	26.9	26.5	26.5	26.5
Water to Separator		101.0	93.4	97.2	75.4	88.3	81.9
Total Input		438.9	424.4	431.6	416.1	428.9	422.5
OUTPUTS							
H2		22.3	19.8	21.0	16.0	18.0	17.0
Product Gas		9.6	8.8	9.2	32.0	34.4	33.2
Separator Water		109.4	108.3	108.9	83.3	91.7	87.5
Separator Overheads (Oil)		51.3	35.0	43.2	63.0	8.2	35.6
Separator Bottoms		250.6	226.9	238.8	219.0	187.2	203.1
Total Output		443.2	398.8	421.0	413.3	339.5	376.4
NET PRODUCTS [w% Fresh Feed]							
Gases: COx		0.3	0.3	0.3	0.8	0.9	0.9
	C1-C3	4.1	3.8	3.9	9.8	10.6	10.2
	C4-C7	1.6	1.5	1.6	8.6	9.2	8.9
	H2S	1.0	0.9	1.0	3.9	4.2	4.0
Water		6.1	11.1	8.6	5.7	2.5	4.1
Separator Overheads (Oil)		37.4	26.1	31.7	45.5	5.9	25.7
Separator Bottoms		58.85	45.71	52.3	34.3	11.48	22.9
Total		109.32	89.46	99.4	108.56	44.7	76.6
Coal Conversion, W% maf Coal							92.6

Table 6

Simulated Two-stage Robinson Mahoney Test (Run 245-22)

Inspection of Separator Bottoms

Pressure Filtration:

Filter Liquids:	83.19 W%
Solids:	16.81 W%

Pressure Filtered Liquid

API	7.6
IBP [C]	226

	W%
IBP-343C	23.01
343-454C	41.20
343-524C	12.68
524C+	23.11

Filter Cake

	W%
Quinoline Insolubles	29.73
Ash in QI	17.99
Sulfur in QI Ash	0.94
Coal Conversion	92.6

Whole Sample

	W%
IBP-343C	21.86
343-454C	39.14
343-524C	12.05
524C+	21.95
Unreacted Coal	1.97
Ash	3.02

Figure 1

A Schematic Process Diagram of the Two-Stage Robinson Mahoney Unit

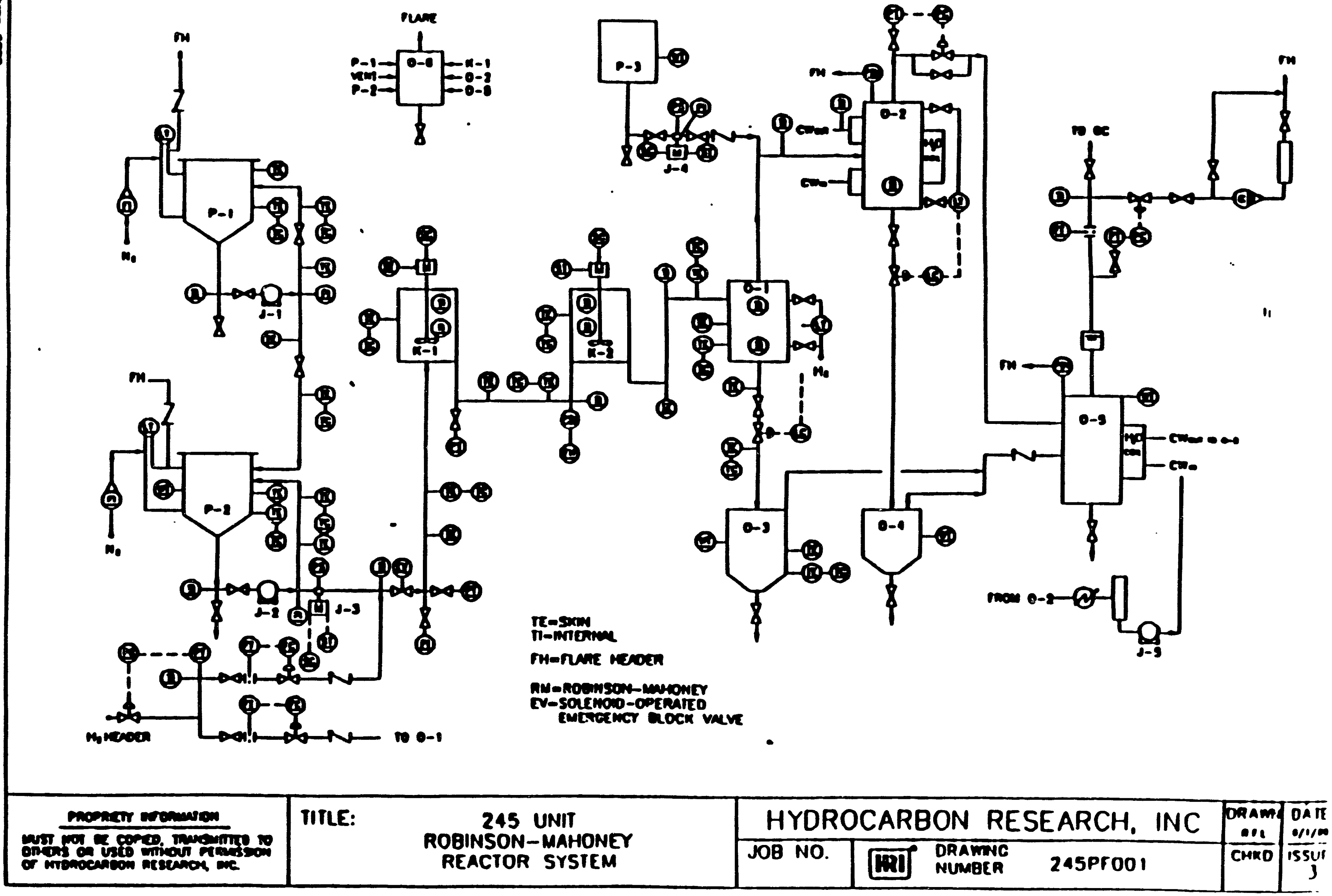
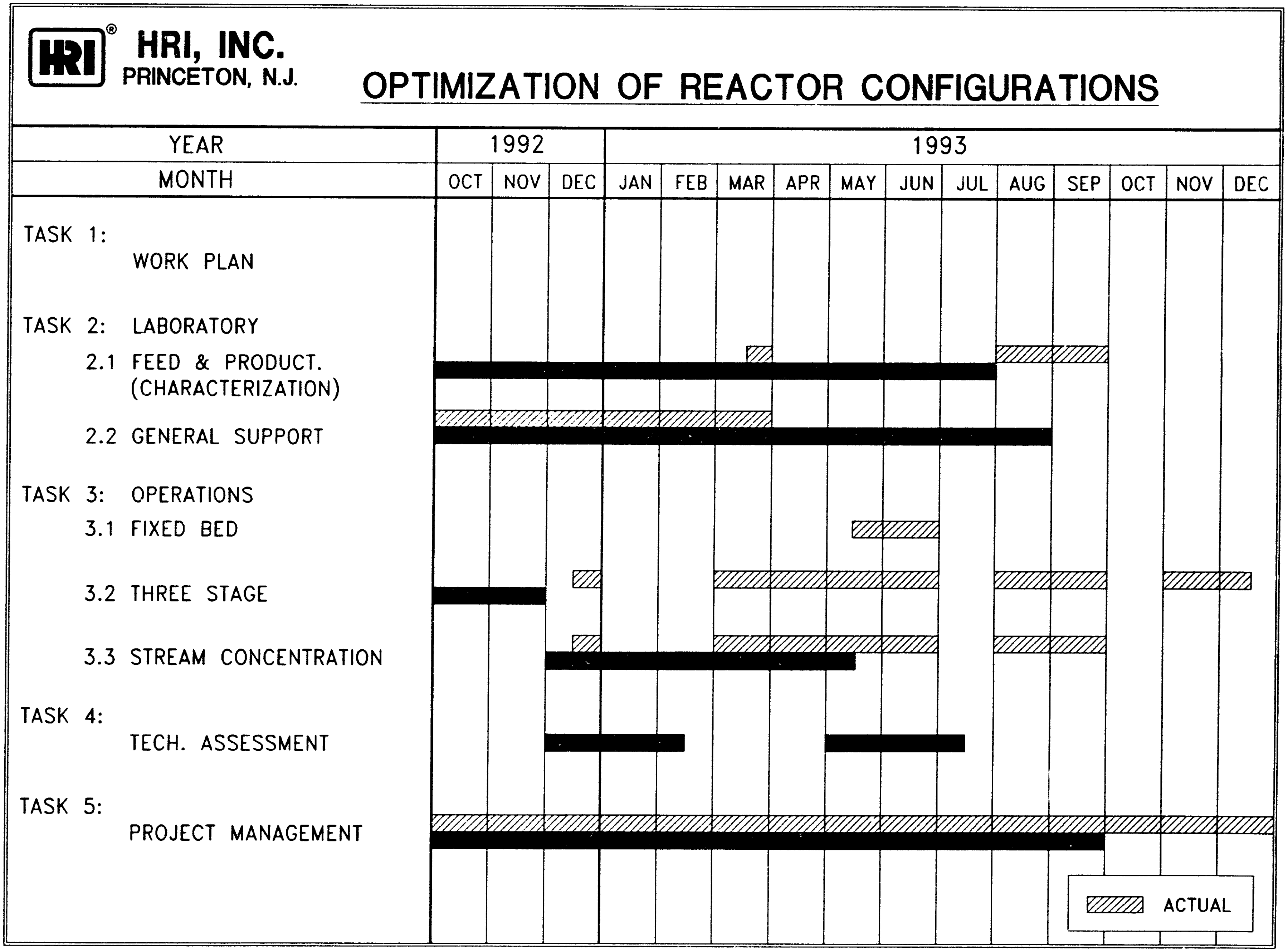


Figure 2


HRI, INC.
PRINCETON, N.J.
OPTIMIZATION OF REACTOR CONFIGURATIONS
YEAR
1992
1993
MONTH
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JAN
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MAR
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MAY
JUN
JUL
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OCT
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DEC
TASK 1:
WORK PLAN
TASK 2: LABORATORY
2.1 FEED & PRODUCT. (CHARACTERIZATION)
2.2 GENERAL SUPPORT
TASK 3: OPERATIONS
3.1 FIXED BED
3.2 THREE STAGE
3.3 STREAM CONCENTRATION
TASK 4:
TECH. ASSESSMENT
TASK 5:
PROJECT MANAGEMENT
ACTUAL

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