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**U.S. Department of Energy
Pittsburgh Energy Technology Center**

**Refining and End Use Study of
Coal Liquids**

Contract No. DE-AC22-93PC91029

**Quarterly Report
April - June 1996**

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Section 1

Introduction and Summary

This report is Bechtel's tenth quarterly technical progress report and covers the period of March 25, 1996 through June 30, 1996.

1.1 Introduction

Bechtel, with Southwest Research Institute, Amoco Oil R&D, and the M.W. Kellogg Co. as subcontractors, initiated a study on November 1, 1993, for the U.S. Department of Energy's (DOE's) Pittsburgh Energy Technology Center (PETC) to determine the most cost effective and suitable combination of existing petroleum refinery processes needed to make specification transportation fuels or blending stocks, from direct and indirect coal liquefaction product liquids. This 47-month study, with an approved budget of \$4.4 million dollars, is being performed under DOE Contract Number DE-AC22-93PC91029.

A key objective is to determine the most desirable ways of integrating coal liquefaction liquids into existing petroleum refineries to produce transportation fuels meeting current and future, e.g., year 2000, Clean Air Act Amendment (CAAA) standards. An integral part of the above objectives is to test the fuels or blends produced and compare them with established ASTM fuels. The comparison will include engine tests to ascertain compliance of the fuels produced with CAAA and other applicable fuel quality and performance standards.

The final part of the project includes a detailed economic evaluation of the cost of processing the coal liquids to their optimum products. The cost analyses is for the incremental processing cost; in other words, the feed is priced at zero dollars. The study reflects costs for operations using state of the art refinery technology; no capital costs for building new refineries is considered. Some modifications to the existing refinery may be required. Economy of scale dictates the minimum amount of feedstock that should be processed.

To enhance management of the study, the work has been divided into two parts, the Basic Program and Option 1.

The objectives of the Basic Program are to:

- Characterize the coal liquids
- Develop an optimized refinery configuration for processing indirect and direct coal liquids
- Develop a LP refinery model with the Process Industry Modeling System (PIMS) software.

The work has been divided into six tasks.

- Task 1 - Development of a detailed project management plan for the Basic Program
- Task 2 - Characterization of four coal liquid feeds supplied by DOE
- Task 3 - Optimization of refinery processing configurations by linear programming

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Task 4 - Pilot plant analysis of critical refinery process units to determine yield, product quality and cost assumptions. Petroleum cuts, neat coal liquids, and coal liquids/petroleum blends will be processed through the following process units: reforming, naphtha and distillate hydrotreating, catalytic cracking and hydrocracking.

- Task 5 - Development of the project management plan for Option 1
- Task 6 - Project management of the Basic Program and Option 1

The objectives of Option 1 are to:

- Confirm the validity of the optimization work of the Basic Program
- Produce large quantities of liquid transportation fuel blending stocks
- Conduct engine emission tests
- Determine the value and the processing costs of the coal liquids

This will be done by processing the coal liquids as determined by the optimization work, blending and characterizing the product liquids, and running engine emission tests of the blends. Option 1 has been divided into three tasks.

- Task 1 -Based on the pilot plant and linear programming optimization work of the Basic Program, production runs of pilot plants (hydrotreating, reforming, catalytic cracking, and hydrocracking) will be conducted to produce sufficient quantities for blending and engine testing.
- Task 2 -The pilot plant products will be blended, characterized, and engine tested
- Task 3 -An economic analysis will be conducted to determine the costs of processing the coal liquids through the existing refinery

Table 1-1 shows which organization has the primary responsibility for each task.

1.2 Summary

The major efforts conducted during the second quarter of 1996 were in the areas of:

- DL2 naphtha hydrotreating
- Option 1 planning

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Table 1-1 Project Task Primary Responsibility Chart

Task	Description	Bechtel	SwRI	Amoco	Kellogg
1	Project Management Plan (PMP) development	x			
2	Feed characterization		x		
3	Linear programming	x			
4	Pilot plant analysis - Cat cracking of DL liquids Cat cracking of indirect wax Hydrocracking of wax Fractionation, reforming, hydrotreating, etc.			x x	x
5	Option 1 PMP development	x			
6	Project management	x			
Option 1 - Task 1	Pilot plant production - Cat cracking of DL liquids and wax All other production work				x
Option 1 - Task 2	Fuel blending, characterizing, engine testing		x		
Option 1 - Task 3	Economic analysis	x			

- x = key participant

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2.0 Hydrotreating of DL2 Naphtha (Run 56)

The Direct Coal Liquid No. 2 (DL2) was distilled into four components: light naphtha, medium naphtha, light distillate, and heavy distillate. The upgrading of the medium naphtha (sample designation FL-2561) is complete. Results of the tests will be incorporated in the PIMS linear programming model by Bechtel for direct liquid refining. The results of hydrotreater Run 56 with the DL2 are described below with commentary based on the experience with DL1 naphtha hydrotreating.

2.1 Technical Objectives

The DL2 naphtha fraction was hydrotreated at SwRI in Run 56 between February 21 and 28, 1996. The objective for the DL2 medium naphtha hydrotreating experiment was to produce an appropriate feed for a modern reformer, and obtain process data at the surrounding operating conditions. This objective required reducing the sulfur concentration to less than 0.5 ppmw at the most severe operating condition. In addition, product properties and the processing data were needed for input to the PIMS model of the combined coal liquid-petroleum refinery. Hence, the objectives of the test were to:

- Reduce the sulfur content to less than 0.5 ppmw to protect the reforming catalyst
- Obtain process data and operating efficiency data at various operating conditions
- Compare the processing with DL1.

The nitrogen content was low in DL2, requiring little reduction. In addition, normal processing for sulfur reduction will result in decreases in nitrogen concentrations.

2.2 Experimental Setup

Figure 2-1 illustrates the pilot plant hydrotreating apparatus configured for this experiment, which was similar to that used for Run 53, DL1 naphtha hydrotreating. Feedstock was pumped from a weighing tank, heated to 350°F in a feed pre-heater, and passed to the reactor. On the way to the feed pre-heater, make-up and recycle streams of high pressure (250 - 760 psig) hydrogen joined the feedstock. The make-up hydrogen flowrate was set at 1200 SCFB and the recycle was held constant at 2400 SCFB. The aggregate hydrogen flows constituted a gas contacting rate of 3600 SCFB.

The small, single-stage reactor was packed with 0.211 gallons of nickel-molybdenum catalyst, Criterion HDN-60. The processed feedstock was cooled and depressurized after leaving the reactor, first in a high pressure, then a low pressure, separator. Hydrogen gas was recovered in the separators, scrubbed, and returned to the reactor via the recycle stream. The liquid was delivered to a small stripper through which warm, countercurrent nitrogen passed to remove

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any residual, volatile material. The liquid effluent was weighed in the bottoms receiver, while the vent gas flowrate was measured and its content analyzed periodically.

2.3 Experimental Conditions

Several factors were considered in determining the points in the experimental matrix for hydroprocessing the medium naphtha DL2 feed. The DL2 feed contains lower concentrations of heteroatoms than the DL1 feed. In addition, the results of the DL1 naphtha hydrotreater runs showed excess severity for the hydroprocessing over much of the DL1 matrix; further, the results were difficult to model. For example, in the DL1 matrix, the lower severity processing fully removed the sulfur, leaving no changes observable through the higher severity points. Because of the high concentration of naphthenes, the combination of high temperature, low LHSV, and low hydrogen pressure provided little, if any, aromatics hydrogenation; in fact, one point exhibited a slight dehydrogenation. Other factors affecting the selection of experimental conditions included the processing extremes available with the current equipment, which have been summarized previously.

Based on the feed properties and the DL1 naphtha hydrotreating experience, the matrix of DL2 test conditions was designed to include lower temperatures and pressures, and higher space velocities. Comparing the ranges of variables in the two matrixes, the DL2 matrix covers wider ranges in temperature and space velocity, and about the same range of pressures. One point in the DL1 matrix was common to the DL2 matrix: the point with lowest severity in the DL1 matrix provided a link to a pressure-temperature plane of the DL2 matrix.

Unexpected results early in the run prompted a deviation from the planned sequence of processing conditions. The range of conditions planned was believed sufficient to produce products with a range of sulfur concentrations decreasing from the lowest severity operating point, and becoming low enough to meet the target at the most severe point. However, the lowest severity product contained less than 1.6 ppmw sulfur by direct measurement, and may have been less than 0.5 ppm as inferred from the raw data traces. As a result, all the more severe processing points were omitted and some data were obtained at conditions less severe than the least severe condition in the original plan. However, even at a decreased severity of 250 psig, 380°F, and 2.8 Hr⁻¹ LHSV, the sulfur removal appeared to be essentially complete.

Figure 2-2 shows the final DL2 experimental matrix, along with an outline of the corresponding DL1 matrix for comparison. Point K represents the typical refinery conditions. The skip in the letter designations of the points resulted from the adjustments to the planned matrix made during the run. Table 2-1 lists the experimental conditions for each of the points in Figure 2-2 and the other points in the original plan.

The reactor pressure was varied from 250 psig to 760 psig. The reactor temperature was varied from 380 to 680°F. The flow rate was also varied between 0.56 gph and 0.84 gph, which for

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this pilot plant operation, represents an equivalent liquid hourly space velocity of 2.67 to 4.0 hr^{-1} . [Liquid hourly space velocity (LHSV) is an inverse measure of residence time in the reactor equal to the flowrate divided by the reactor volume expressed in consistent units.]

Two feedstocks were used in the naphtha hydrotreating. The first was a petroleum feedstock (FL-2310). This material was selected in consultation with Amoco as a typical refinery naphtha normally used as hydrotreater feedstock. The second experimental feed was the neat DL2 naphtha fraction (FL-2561).

2.4 Test Results

During the course of the experiment, pressures, temperatures, and flow rates were varied over a matrix of conditions. These conditions were selected to achieve the experimental objectives of the naphtha hydrogenation and remain in the vicinity of typical refinery conditions. System conditions were monitored at each point, and when sufficiently stabilized, a sample was drawn from the stripper outlet. The specific test conditions and the data collected at those conditions is summarized in Table 2-2. The table records the individual sample designations, the actual conditions at which the points were taken, and the measured values for density, hydrogen content, and sulfur concentration. These properties were provided for the feed materials at the bottom of the table. The sulfur results were uniformly so low, that not all samples were submitted for analysis. Some of those from the more severe processing conditions were omitted.

Figure 2-3 charts how the pressure, temperature, and flow rate varied during the run. It shows a continuous record of the pressure, flowrate, and reactor temperature. Samples (denoted by letters) were drawn after conditions had stabilized for typically three hours. The times when each of the feedstocks was introduced are also shown in the figure.

The density was measured with a density meter, and the hydrogen content was determined by ASTM D 3701. Gas samples were also taken from the high pressure vent, high pressure separator, recycle stream, and the stripper sample ports for gas chromatographic analyses. Two conditions limited the information obtained from the GC analyses during the run. The gas chromatograph was operating outside of desired performance parameters, and following the run, it was replaced. In addition, the low processing severity and the low concentration of sulfur in the DL2 feed naphtha meant that the gas samples were expected to be low in all components except hydrogen, or nitrogen in the case of the stripper gas. This, in fact, was the case, and after the gas samples taken for the more severe conditions showed no other components beside hydrogen or nitrogen, analyses of several of the least severe points were omitted.

Mass balances were calculated for each experimental point. An automated process control system regulated and recorded most of the processing parameters and other functions of the

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pilot plant. It also obtained process data at regular intervals, typically each 10 seconds, and this data was downloaded into a computer file. This data was later retrieved, averaged over approximately five minute intervals, and imported into a spreadsheet for calculating the mass balances. The liquid volumes and flow rates were based on weight-scale measurements, and the gas flows were based on several types of flow meters appropriate to the pressure and flow range of the particular stream and calibrated individually. Pressures were measured with electronic meters employing strain gage technology, and temperatures were measured with thermocouples. The values reported for temperature, pressure, LHSV, and hydrogen flows are averages over the two- to four-hour period for each mass balance calculation. The hydrogen consumption was the hydrogen feed less the hydrogen leaving the system, via the vents. Gas composition was measured on samples by gas chromatograph, but as noted previously, components other than the majority hydrogen or nitrogen were mostly undetected. Sulfur in the liquid products was analyzed by inductively coupled plasma (ICP) spectroscopy, and nitrogen was measured by chemiluminescence with an Antek instrument.

The petroleum points at the beginning and the end of the run were obtained at different conditions to provide greater variability for later comparisons of computations in the refinery modeling. Very good sulfur removal was noted for the much higher level of sulfur in the petroleum material.

2.5 Discussion

The DL2 medium naphtha was remarkable for the low severity required to affect the heteroatoms and density. Forms of sulfur which are particularly easy to remove include hydrogen sulfide, low molecular weight compounds, and elemental sulfur. A Doctor test indicated no hydrogen sulfide in the feed. A brief run of untreated feed through the stripper only (no reactor) did not remove the sulfur, indicating that the sulfur source was not volatile. The measured value may have been elemental sulfur, or some other form, but it was not an obdurate form of sulfur since the severity during the run was a small fraction of the severity experienced in the in-line hydrotreater. If the sulfur compounds were the residual from the kinetic processes during production processing, then a mix of typical compounds could be present, which at the 15 ppm concentration level should disappear readily with only a modest severity of processing.

A summary of the mass balance data is shown in Tables 2-3 and 2-4. The overall closures, in terms of weight, were quite good, most points showing a small percent loss (negative gain). The hydrogen consumption figures seem a little high, because the chemical hydrogen consumption itself was very low. The data points were in two groups, one at about 400 SCFB, and the other at about 650 SCFB. Since most of the hydrogen leaving the system left through the high-pressure vent, an error in that flow rate would have a significant effect on the calculated hydrogen consumption. It was necessary throughout the investigation to operate at low liquid flow rates to conserve feed stocks, because of their limited supply. As a result, the

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meter in the high pressure vent line was operating in the lowest part of its range, even though the absolute feed contacting rate was fairly high. At the low end of its range, the meter may read too low, causing the hydrogen consumption calculation to be high. If that were the case, the hydrogen consumption reported may better represent an upper limit, rather than a typical value.

2.5 Conclusions

The hydrotreating tests on the DL2 medium naphtha was very successful, emphasizing the high quality (low sulfur concentrations) of the product from the close-coupled, two stage liquefaction process with in-line hydrotreating. In these tests, the sulfur concentrations were further reduced to levels which would be acceptable to any modern reforming catalyst, showing at least a 97% reduction. The nature of the sulfur present was not revealed, but was readily removed even at the lowest severities - all of which are less severe than would be encountered in petroleum hydrotreating.

The DL2 naphtha was more readily processed than the DL1 naphtha. This is the case even considering that the DL1 naphtha was a perfectly acceptable feedstock. It is not clear if this resulted from the operation of the in-line hydrotreater or the different source coal used for DL2.

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Table 2-1 - Planned Test Sequence for DL2 Naptha Hydrotreating

Item	Operation	Feed	LHSV, Hr ⁻¹	Pressure, Psig	Temperature, °F
A	Initial activity check	NTFpet	2.7	760	600
B	Coal liquid data	MN1c	2.7	760	600
C	Coal liquid data	MN1c	1.85	760	600
D	Coal liquid data	MN1c	2.7	450	520
E	Coal liquid data	MN1c	1.0	1170	680
F	Coal liquid data	MN1c	1.0	1170	520
G	Coal liquid data	MN1c	1.0	450	520
H	Coal liquid data	MN1c	2.7	1170	520
I	Coal liquid data	MN1c	1.85	1170	600
J	Coal liquid data	MN1c	1.85	450	600
K	Coal liquid data	MN1c	2.7	450	680
L	Coal liquid data	MN1c	2.7	1170	680
M	Coal liquid data	MN1c	1.0	450	680
N	Blend data	NTFb	1.0	450	680
O	Blend data	NTFb	1.0	1170	680
P	Blend data	NTFb	2.7	450	520
Q	Final activity check	NTFpet	2.7	760	600

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Sample ID	Feed Type	Avg Temp, °F	Feed Rate, GPH	Press., Psig	Sp. Gr., g/mL	NMR H ₂ , wt%	Sulfur, ppmw
56-A-22	MN1pet*	596	0.560	761	0.7661		30.7
B-35	MN1c**	602	0.568	760	0.7830		
D-48	MN1c	520	0.575	451	0.7822		<1.6*
D-53	MN1c	416	0.572	450	0.7827	13.83	<1.6*
D-56	MN1c	470	0.572	449	0.7839	13.83	<1.6*
D-57	MN1c	465	0.572	450	0.7843	13.65	<1.6*
D-59	MN1c	480	0.572	449	0.7825	13.90	<1.6*
R-62	MN1c	381	0.590	250	0.7843	13.84	<1.6*
S-66	MN1c	682	0.572	760	0.7826	13.87	<1.6*
T-74	MN1pet	680	0.579	449	0.7664	14.05	
Feeds:							
FL-2310	MN1pet	N/A	N/A	N/A	0.7673	13.95	4280
FL-2561	MN1c	N/A	N/A	N/A	0.7824	13.86	15
* Lower limit of resolution via standard used. Observed limit ~0.5 ppm.							

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Table 2-3 - Mass Balance Summary for DL2 Naphtha Hydrotreating Experiments, Part 1

ID	Feed Type	Feed s.g.	Reactor Temp, °F	Reactor Pres. psig	LHSV, Hr ⁻¹	H ₂ Feed SCFB	Recycle SCFB	H ₂ Cons. SCFB	LiqF-Lb	TotF-W%
56A	NTFpet	0.7673	597.4	760	2.607	1241	2492	407	21.875	102.46
56B	MN1c	0.7824	601.7	760	2.696	1208	2411	386	37.726	102.34
56D48	MN1c	0.7824	519.8	450	2.731	1185	2373	372	31.534	102.30
56D53	MN1c	0.7824	417.3	450	2.690	1197	2411	667	12.654	102.32
56D56	MN1c	0.7824	467.7	450	2.646	1229	2476	683	18.757	102.38
56D59	MN1c	0.7824	379.0	450	2.710	1198	2388	667	10.433	102.32
56D62	MN1c	0.7824	377.1	450	3.973	819	1635	453	15.293	101.59
56R	MN1c	0.7824	382.6	250	2.794	1160	2325	645	8.194	102.25
56S	MN1c	0.7824	679.8	760	2.684	1218	2399	681	10.495	102.37
56K	MN1c	0.7824	679.7	450	2.737	1142	2348	635	10.201	102.22
56T	NTFpet	0.7673	680.2	450	2.758	1184	2377	658	18.182	102.34

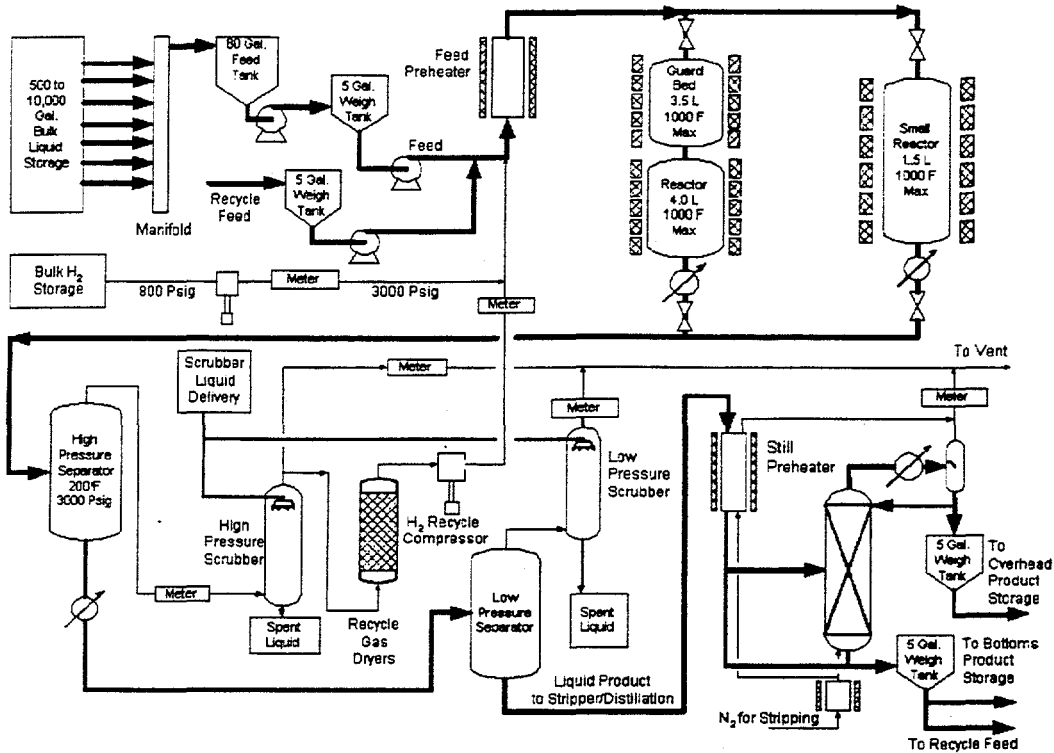
Table 2-4 - Mass Balance Summary for DL2 Naphtha Hydrotreating Experiments, Part 2

ID	BtmL s.g.	BtmL-Lb	BtmL-Ga	TotP-Lb	TotP-Gal	Gain wt%	Feed S in Btms, %	Feed N in Btms, %	Gain S wt%	Gain N wt%
56A	0.7661	21.551	3.3779	21.907	3.3779	-2.31	1.87	0.00	-98.13	-100.00
56B	0.7830	36.833	5.6485	37.643	5.6801	-2.57	3.25	0.00	-96.75	-100.00
56D48	0.7822	30.884	4.7411	31.423	4.7451	-2.65	3.26	0.00	-96.74	-100.00
56D53	0.7827	12.423	1.9059	12.501	1.9106	-3.53	3.27	0.00	-96.73	-100.00
56D56	0.7839	18.991	2.9090	19.115	2.9165	-0.48	3.37	0.00	-96.63	-100.00
56D59	0.7825	10.253	1.5733	10.303	1.5748	-3.57	3.28	0.00	-96.72	-100.00
56D62	0.7826	14.941	2.2924	15.022	2.2954	-3.36	3.26	0.00	-96.74	-100.00
56R	0.7843	8.537	1.3071	8.586	1.3094	2.53	3.47	0.00	-96.53	-100.00
56S	0.7826	10.119	1.5526	10.179	1.5570	-5.37	3.21	0.00	-96.79	-100.00
56K	0.7825	10.277	1.5770	10.327	1.5777	-0.98	0.00	0.00	-100.00	-100.00
56T	0.7664	17.661	2.7670	17.811	2.7779	-4.38	m	0.00	-100.00	-100.00

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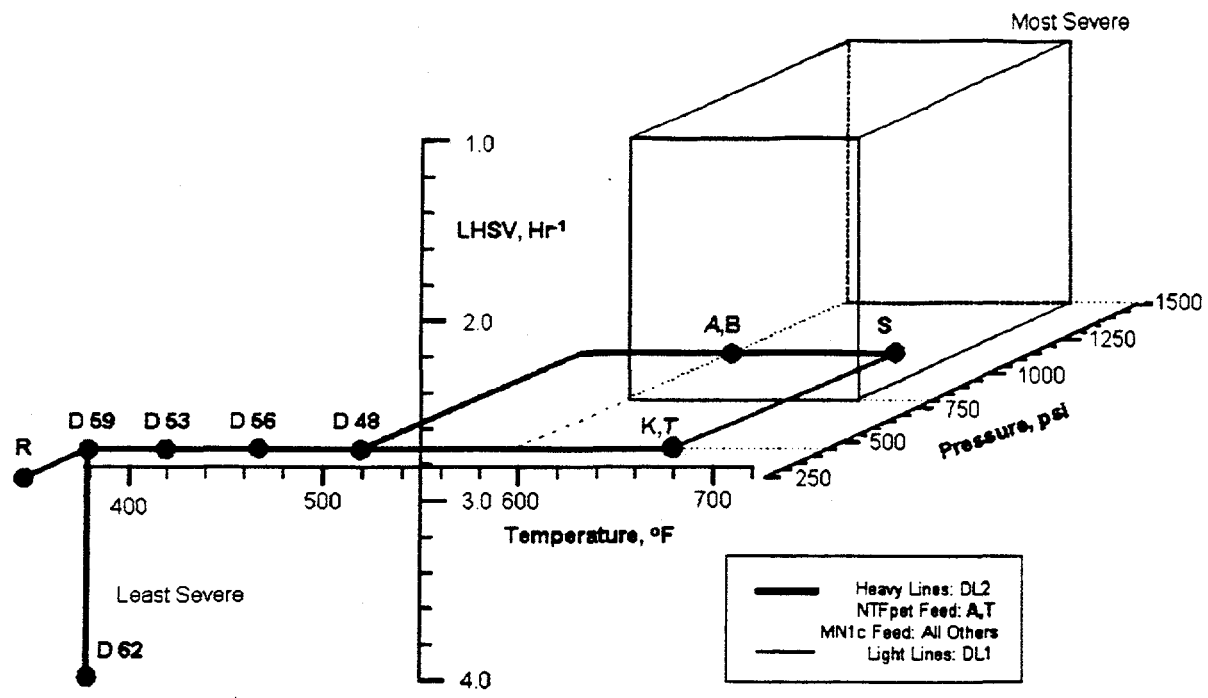
Figure 2-1 - Hydrogenation Pilot Plant



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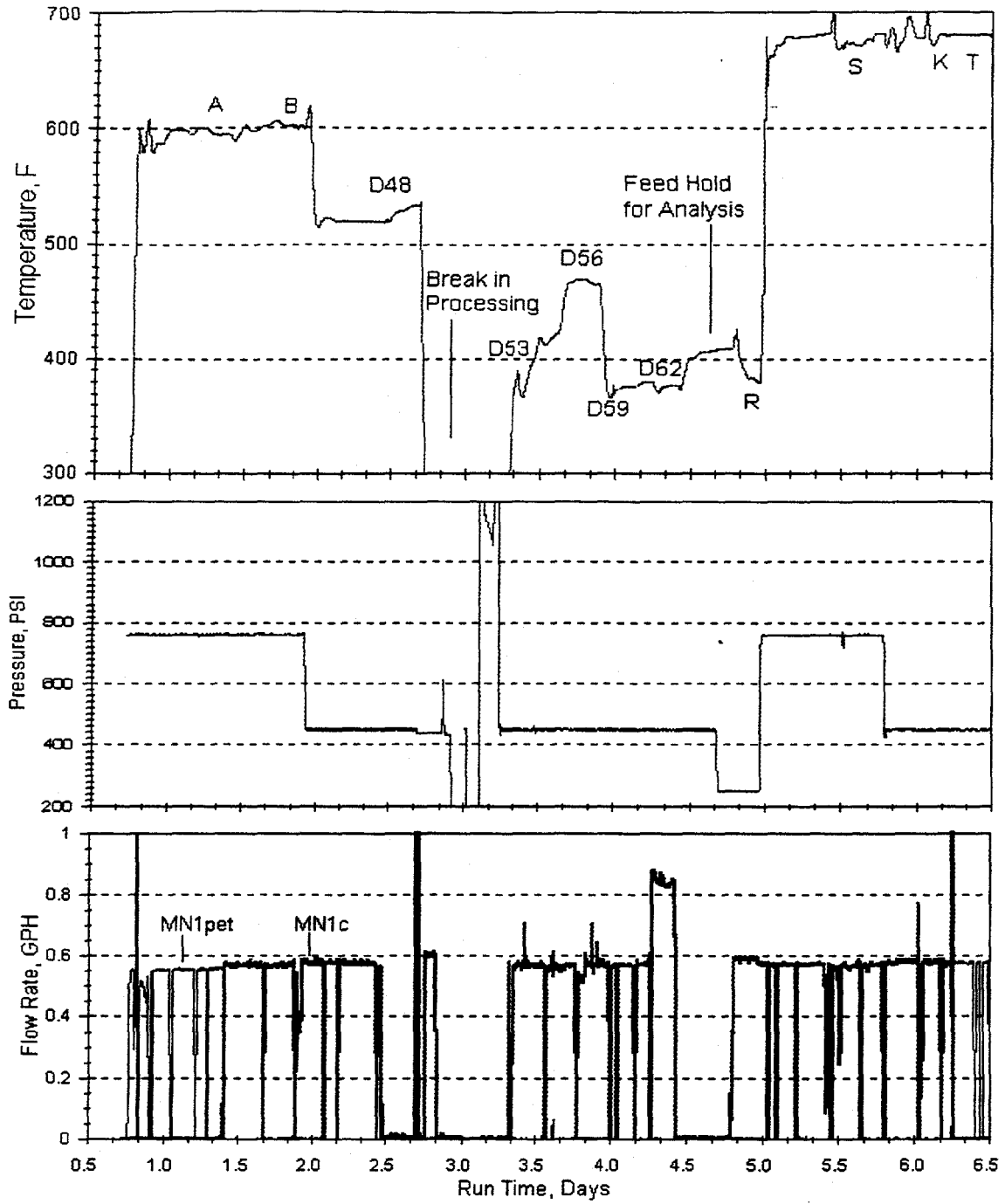
Figure 2-2 - Matrix of Experimental Points for DL2 Naphtha Hydrotreating



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Figure 2-3 - Timeline of DL2 Naphtha Hydrotreating



Section 3

Bechtel Activities

3.1 Option 1 planning

Activities primarily centered around developing a work plan for the production of the fuels that will be testing in Option 1.

A separate linear programming refinery model was created and was used to determine feed blends to the four DL2 production runs.

- Naphtha hydrotreating - reforming
- Light distillate hydrotreating
- Heavy distillate hydrotreating
- Catalytic cracking

The LP results also provided preliminary recipes for fuel blends that will be tested in Option 1. The volume of material that requires processing in each production run was based on:

- The preliminary fuel blending recipes
- The amount of each fuel required emission and performance testing
- The expected yields from each of the production runs

Currently, the property data for the fuel blendstocks are primarily derived from the PIMS database. This data will be replaced by actual property measurements on the products from the Option 1 production runs and on other blendstocks. Once this data has been incorporated into the LP model, the final fuel blending recipes can be determined.

The work plan for Option 1 will be issued as a separate document.

Section 4

Amoco Activities

There was no project activity for this reporting period.

Section 5

M.W. Kellogg Activities

There was no project activity for this reporting period.

Section 6

Project Management

6.1 Plans

6.2 Reports and Schedules

The milestone schedule and status for the Basic Program and Option 1 is shown in Figure 6-1.

Figure 6-1 Milestone Schedule for Basic Program & Option 1

PLAN STATUS REPORT

1. TITLE		2. REPORTING PERIOD		3. IDENTIFICATION NUMBER												
Refining and End Use Study of Coal Liquids		3/25/96 to 6/30/96		DE-AC22-93PC91029												
4. PARTICIPANT NAME AND ADDRESS		5. START DATE		6. ESTIMATED COMPLETION DATE												
Bechtel Corporation 50 Beale Street San Francisco, CA 94105		11/1/93		9/30/97												
7. ELEMENT CODE	8. REPORTING ELEMENT	93		FY94		FY95		FY96		FY97		10. PERCENT COMPLETE				
		D	M	J	J	D	S	D	S	D	S	M	J	S	a. Plan	b. Actual
Task 1	Project Work Plan	1												100	100	
Task 2	Feed Characterization	2												100	70	
Task 3	Linear Programming (LP) Analysis	3												94	81	
Task 4	Pilot Plant Analysis	4												97	67	
Task 5	Option 1 Work Plan	5												100	55	
Task 6	Administration Task	6												68	68	
Option 1 Task 1	Pilot Plant Analysis (Produce Fuels)	7												55	0	
Option 1 Task 2	Characterization, Blending, and Testing	8												0	0	
Option 1 Task 3	Economic Study	9												0	0	

1 Submit Final Work Plan	7 Input IL pilot plant data	12 Production runs for DL1 (deleted from program)
2 Characterize DL1 liquid	8 Conduct evaluation runs	13 Production runs for IL
3 Characterize IL liquid	9 Conduct DL1 pilot plant tests	14 Production runs for DL2
4 Characterize DL2 liquid	10 Conduct IL pilot plant tests	15 ASTM tests for DL1 (deleted from program)
5 Develop LP model	11 Conduct DL2 pilot plant tests	16 ASTM tests for IL
6 Input DL pilot plant data		17 ASTM tests for DL2

11. SIGNATURE OF PARTICIPANT'S PROJECT MANAGER AND DATE
Cheryl Ann 8/1/96