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Pittsburgh Energy Technology Center**

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

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## Introduction and Summary

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This report is Bechtel's sixth quarterly technical progress report and covers the period of December 19, 1994 through March 26, 1995.

### 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

## Section 1

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- Task 2 - Characterization of four coal liquid feeds supplied by DOE
- Task 3 - Optimization of refinery processing configurations by linear programming
- 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 first quarter of 1995 were in the areas of:

- Linear programming model development - The petroleum version of the model was completed. Data acquired to date from the Task 4 pilot plant work on Direct Coal Liquid 1 (DL1) were incorporated into the model.
- Direct coal liquid preliminary evaluation - Preliminary evaluation studies showed that in a refinery expansion scenario, DL1 would have a margin of \$3-4 per barrel higher than the base petroleum crude. In addition, the higher

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quality of DL1 resulted in a \$1 per barrel increase in value over previous coal liquids.

- DL1 hydrotreating testing - The naphtha and heavy distillate hydrotreating tests were completed. The cause of the high sulfur concentrations in the hydrotreated naphtha was identified and corrected.
- DL1 catalytic cracking - Pilot plant and micro activity tests showed that the DL1 heavy distillate was an excellent catalytic cracking feedstock with good gasoline production properties. Gasoline yield increased with higher hydrotreating severity.
- IL catalytic cracking - Pilot plant tests showed that the indirect liquid (IL) wax was also an excellent catalytic cracker feed.
- Indirect wax cleanup - Approximately 150 gallons of clean FT wax was produced.

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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	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		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 DL1 Naphtha and Distillate Fractions

Direct Coal Liquid No. 1 (DL1) was distilled into five components: light naphtha, medium naphtha, heavy naphtha, light distillate, and heavy distillate. SwRI has studied upgrading the medium naphtha (sample designation FL-2385) and the heavy distillate (FL-2372) by hydrotreating at the DOE Synthetic Fuel Center at SwRI. The hydrotreater experiments examined changes in the properties of the treated naphtha and heavy distillate fractions over a range of operating conditions. Results of the tests will be used to calibrate and verify the PIMS model by Bechtel for DL1 refining. The results of hydrotreater Runs 49, 51, and 53 are summarized below in the order that they would be encountered on the PIMS diagram.

#### 2.1 DL1 Naphtha Hydrotreating (Run 51)

##### 2.1.1 Objectives and Experimental Conditions

The DL1 naphtha fraction was hydrotreated at SwRI in Run 51 between December 7 and 14, 1994. The objectives of the test were to:

- Reduce the sulfur content to less than 0.5 ppm by weight to protect the reforming catalyst
- Reduce the nitrogen content to less than 0.5 ppm by weight
- Increase the hydrogen content of the naphtha
- Obtain process data and operating efficiency data at various operating conditions

Figure 2-1 illustrates the pilot plant hydrotreating apparatus configured for this experiment. Feedstock is pumped from a weighing tank, heated to 400°F in a feed preheater, and passed to the reactor. On the way to the feed heater, make-up and recycle streams of high pressure (770 - 1400 psig) hydrogen join the feedstock. The reactor is composed of two stages; a 3.5 liter guard bed, followed by a 4.0 liter reactor. The reactor is packed with a nickel-molybdenum catalyst, Criterion HDN-60. The processed feedstock is cooled and depressurized after leaving the reactor first in a high, then in a low, pressure separator. Hydrogen gas is recovered in the separators, scrubbed, and returned to the reactor.

For the coal liquid naphtha which was in limited supply, a smaller parallel reactor (not shown in Figure 2-1) was installed and used for the test matrix (described below). The make-up hydrogen flowrate was set at 10 SCFH and the recycle was held constant at 20 SCFH. The aggregate hydrogen flows constituted a gas contacting rate of 2208 - 4258 SCFH (contacting rates varies as the feed rate changes). The larger reactor was used for the production Run 52.

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During the course of the experiment, pressures, temperatures, and flow rates were varied over a matrix of conditions selected to achieve the experimental objectives of the naphtha hydrogenation. System conditions were monitored and, when sufficiently stabilized, a sample was drawn from the low pressure separator outlet. The specific gravity was measured with a density meter and hydrogen content was determined by the ASTM D3701 method. A stripper column was not used during the run in order to conserve DL1 feedstock. Instead, the samples were caustic washed to remove H<sub>2</sub>S and submitted for sulfur by x-ray fluorescence (XRF) and Inductively Coupled Plasma (ICP), and nitrogen by chemiluminescence (Antek) analyses. Gas samples were also taken from the vent sample port for gas chromatographic analyses.

The operating conditions in the hydrotreater were varied between a low severity condition, designated condition B, set to match current refinery practice, and a high severity condition C set so that the expected sulfur and nitrogen contents of the treated material would be below 0.5 PPM. A test matrix considering high and low settings of pressure, temperature, and flow rate was used to systematically examine conditions between the two severity extremes. Low pressure, temperature, and residence time were selected for the low severity condition. High pressure, temperature, and residence time were used for the high severity condition. Pressures were varied from 762 psig to 1400 psig. Temperatures were varied from 600 to 720°F. The flow rate was also varied between 0.571 gph and 0.317 gph, which for this pilot plant operation, represents an equivalent liquid hourly space velocity of 1.4 to 2.7 hr<sup>-1</sup>. 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.

Three 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 is the neat DL1 naphtha fraction (FL-2385). The third is a blend of 67% petroleum and 33% coal liquid by volume.

The test sequence began with the petroleum feedstock at the low severity condition A. At steady state (determined by reaching constant density and hydrogen contents), a product sample was drawn at this and each subsequent condition. The petroleum feed was tested first to provide a benchmark for the PIMS library data and to perform startup on a more abundant feed to conserve DL1 naphtha. The neat coal liquid was then introduced at the low severity condition B. The temperature, pressure, and residence time were increased to the high severity level C, and a sample was drawn and tested to assure that the nitrogen was below 0.5 PPM. (Since desulfurization takes place more readily than denitrification, only the nitrogen content was determined) Once this had been established, the neat coal liquid was tested at five additional conditions with



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varying pressure, temperature, and flow rate at severities between the two extremes. The petroleum/coal liquid blend was then tested at three conditions (I, J, and K) and the petroleum feedstock was reintroduced as the process was brought back to its initial, low severity condition L. Comparison of this last test condition to the first shows whether there has been significant catalyst deactivation. The petroleum sample was then run at condition M to test for catalyst response to changes in severity.

Figure 2-2 charts how the pressure, temperature, and flow rate varied during the run. This is a two-page plot showing a continuous record of pressure, flowrate, and reactor temperature with periodic measurements of specific gravity of the product liquid. Samples (denoted by letters A through M) were drawn after conditions had stabilized for approximately three hours. The times when each of the feedstocks was introduced is also shown in the figure.

### 2.1.2 Test Results

The specific test conditions and the data collected at those conditions are summarized in Table 2-1. In general, there is a narrow range of product properties. For the neat DL1 naphtha, the density differs by only 0.008 gm/ml and the hydrogen content differs by 0.37 wt% between the extremes of process severity. The inherent variability within the data, from random causes and limitations of instrumentation, are significant in comparison to the small variation between the samples, which was restricted by the relatively narrow range of process severity. Subsequent naphtha hydrotreating tests showed that the measured hydrogen content may vary by as much as +/- 0.10% wt (see Section 2.2). This limits the ability of the data analysis to accurately predict the product properties.

The hydrotreating step produced good hydrodenitrogenation, with product nitrogen values at or below the target value (0.5 ppm) under most of the conditions. The measured sulfur levels were high and inconsistent with the nitrogen measurements and were above the target. The open-to-the-air collection and caustic washing method used in preparing the product samples was found to introduce "elemental sulfur" contamination. This problem has been resolved, and an improved sampling procedure has been adopted. The revised procedure is described in Section 2.2.

The relative values of the temperature, pressure, and flow rate for the neat coal liquid tests are shown in a wire frame diagram in Figure 2-3. The figure illustrates how direct comparisons may be made between sample points sharing common values of two test parameters, but differing in the third. Table 2-2 compares points differing in only one parameter, and presents the main average effects of increasing pressure, temperature, and flow rate from the low to the high value. Pressure influenced the hydrogenation more strongly than

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temperature or flowrate in the ranges studied. The hydrogen content increased by an average of 0.22% wt when the pressure was increased from 770 to 1400 psig. The pressure also had the greatest effect on density, decreasing the density by an average of -0.0037 gm/ml when the pressure was increased from 770 to 1400 psig. The changes in specific gravity generally confirmed the change in hydrogen content. Increasing the temperature from 600° to 720°F consistently increased the hydrogen content, but reducing the LHSV from 2.7 to 1.4 hr<sup>-1</sup> increased the hydrogen content only at high pressure (1400 psi). At low pressure (770 psi) the hydrogen content decreased.

There is a three step progression in temperature between points B, F, and H. The points share a common pressure (770 psig) and LHSV (2.7 hr<sup>-1</sup>). In this case, the consumption of hydrogen is greater and the specific gravity is lower at the intermediate temperature, point F. This would suggest that there may be a critical temperature between 600 and 720°F where the processing efficiency is maximum. At higher temperatures, the reverse or dehydrogenation reactions are favored.

The experimental results show that the catalyst lost activity during the sequence of experiments. The usual measure of catalyst deactivation, the change in temperature required to restore product quality, did not fit into the experimental plan. Aromatics hydrogenation and heteroatom removal in a petroleum feed were observed before and after the sequence (samples A and L), with the objective to indicate whether a major activity loss, which could complicate the modelling effort, had occurred. The data on Table 2-1 clearly showed a decrease in activity. It must be noted that most studies of catalyst activity are done with the same feedstock over specially prepared catalyst over a long period of time. These conditions were not possible with the current experimental matrix, which changed both feedstock and temperature, including high temperature excursions.

While no objective measure was made, intuitively, the changes in catalyst activity seem high for the time on stream. The effect of high naphthenes concentration in the feed probably caused some local dehydrogenation at hot spots within the reactor during operation in the low hydrogen pressure and high temperature part of the matrix. Some of the hydrogen concentration data does show a decrease under those conditions. One difficulty in interpreting the extent of deactivation is the thermal cycle of the experimental matrix. In addition, activity reduction can come from the high temperature levels alone without regard to the specific feedstocks.

The selection of the experimental matrix was influenced by the expected increase in processing severity over current refinery practice that would be expected in the timeframe of interest to the current study (year 2010). The naphtha results indicate that the increase in severity went too far, and caused little improvement

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in product quality and may have contributed to catalyst deactivation. A different matrix shape with lower severity levels should provide the required product quality and experimental results without catalyst deactivation.

### **2.2 DL1 Naphtha Hydrogenation with Stripping (Run 53)**

Based on the unexpected high sulfur content in the hydrotreated DL1 naphtha in Run 51, an experiment was devised to see if air contact was the cause of the high sulfur concentrations observed in the product naphthas. The effluent of the low pressure separator was directed to a specially made distillation/stripper column modified to permit nitrogen stripping. A brief run was conducted on 2/28-3/3/95 in the hydrogenation pilot plant using the small (~1 liter) reactor. The new, small stripping column provides an appropriate residence time for flows in the small reactor.

#### **2.2.1 Background**

The hydrogenation samples in naphtha hydrotreater Run 51 were collected directly from the low pressure separator ahead of the point where the liquid usually would proceed to the stripper column. This collection site differs from the usual sample point for product samples which is after the stripper column. This sampling practice had been used successfully with the large reactors. The low pressure separator contains "sour" product, saturated in hydrogen sulfide which is one of the products of the hydrogenation reaction. This H<sub>2</sub>S is normally removed in the stripper to complete the sulfur removal process started in the packed bed reactor, thereby "sweetening" the naphtha. In the previous experiment (Run 51), a caustic wash was substituted for the stripper to accomplish the removal. This technique was used to conserve the scarce feedstock, to simplify the equipment operation, and because the stripper volume was too large for the small reactor flow.

As described in Section 2.1, the samples were submitted for sulfur and nitrogen analyses. Good removal of nitrogen to below 1 ppm was observed. Sulfur, however, was reduced to only the 60 - 180 ppm range, far higher than the target of < 0.5 ppmw. The high sulfur concentration did not seem reasonable, considering the good nitrogen removal, and suggested the possibility of an unusual selective catalyst deactivation with respect to the desulfurization reactions.

Discussions of this work quickly centered on the sample collection method. The experience of the project participants with a rare "elemental sulfur contamination" in refinery products matched the circumstances of the sampling method. Exposing the sour product to air during sampling at moderate temperature (>70°F) provided the chance for dissolved sulfur species to form. This "dissolved sulfur" was not reactive with caustic and was less volatile than

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H<sub>2</sub>S (thereby not strippable). A test of this idea was needed. Another concern was the time allotted to reach steady state at a given experimental condition, and this would also be tested.

### **2.2.2 Equipment Modifications**

A convenient vessel to utilize as a stripper for use in conjunction with the small reactor was available in the form of the feed preheater of the original distillation/stripper column. Its volume was suitably sized for the smaller volume of the new reactor. With the addition of a tee for nitrogen addition at the bottom of the vertical preheater as well as a "U" tube to maintain a liquid level, the down-flowing naphtha coming from the low pressure separator could be stripped of H<sub>2</sub>S. A vacuum break was placed at the top of the "U" tube to prevent siphoning from the new little stripper to the product collection vessel. At the top of the preheater, a tee was added to remove the stripping gas. This stream went through a total condenser (water cooled) before venting. The existing temperature control for the preheater was used to operate the stripper in service. The effluent liquid was conducted by flexible tube to a glass accumulator resting on the product weigh scale. This glass vessel had a nitrogen purge to restrict contact with air. Figure 2-4 shows the new stripper system.

### **2.2.3 Experiment with Stripping**

Three points from Run 51 were selected for the investigation. Later, a fourth point was added to illustrate the effect of pressure. Condition A represents the most severe condition, point C the least severe, and point D an intermediate severity condition from the Run 51 matrix. Point B duplicates point A, except for the lower pressure. Table 2-3 gives the planned operating conditions.

This work, which ran between 28 February and 3 March 1995, included extended periods on each condition to assess the approach to steady state.

### **2.2.4 Results**

Table 2-4 is the sample log from the stripping experiment and Figure 2-5 shows the timeline. It includes the process information collected during the run as well as the analytical results obtained afterward for hydrogen and sulfur. The preponderance of the samples contained less than 0.4 ppm sulfur. This value is the current detection limit of the in-house ICP method and depends on the purity of the material that the lab uses for a blank. The objective of <0.5 ppm was readily met. A wire frame diagram of the experimental points is shown in Figure 2-6.

Sample 53-B14 was taken from the low pressure separator. This was an attempt to recreate the conditions of the sampling conducted in Run 51. No increased sulfur was observed for this caustic washed sample. The next sample taken had a

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slightly elevated sulfur concentration, 2 ppm. This increase may have been caused by the disturbance caused by sampling from the low pressure separator.

Only the first condition (point A) showed that additional time may be required to reach steady state. It is proposed that point A (being the most severe condition) required the longest time to flush out any adhering sulfur compounds from the surfaces of the equipment or the catalyst bed itself. The only other time dependent behavior came in point D when the pressure was increased.

Although the trend was toward low values, no obvious reason was found for the increase in sulfur. A shift in the physical conditions arising from the pressure variation may have disturbed a "pocket" of impurity, which was seen in the product.

### **2.2.5 Discussion**

The results show that stripping allowed the limited matrix to be completed and to achieve the sulfur removal objective. The severities were all sufficiently great to decrease sulfur concentration to such a low level that its variation with severity could not be observed.

For most of the points steady state was achieved quickly (1-2 hours), but the first point showed that when going to conditions of low sulfur concentration, more time must be allowed to flush prevailing sulfur from the system.

The catalyst performed adequately to effect the desired desulfurization. This would indicate that this charge of catalyst or a similar one can be used to finish the DL1 matrix of experiments.

## **2.3 DL1 Heavy Distillate Hydrotreating (Run 49)**

### **2.3.1 Objectives and Experimental Conditions**

The DL1 heavy distillate fraction was hydrotreated in Run 49. The test was conducted between November 14 and 28, 1994. The objectives of the test were to:

- Reduce the sulfur content to less than 380 ppmw
- Reduce the nitrogen content to less than 380 ppmw
- Increase the hydrogen content to 12 wt% or higher for FCC pretreatment
- Reduce aromatics content, improving ignition quality
- Obtain process data and operating efficiency data at various operating conditions

The pilot plant hydrotreating configuration was identical to the one used in the naphtha processing. The hydrogen was circulated at a slightly greater flow rate than in the naphtha processing: make-up hydrogen rate was set at 12 SCFH and the recycle hydrogen rate was set at 24 SCFH. The make-up hydrogen rate varied

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from 1084 to 2981 SCFB, and the recycle hydrogen rate was added at between 2167 and 5961 SCFB. Pressures, temperatures, and flow rates were adjusted to attain 17 different conditions, A through Q. Process conditions were monitored, and once the system had sufficiently stabilized, a sample was drawn from the outlet of the low pressure separator. The specific gravity of each sample was measured with a density meter, and the hydrogen content was determined by ASTM D 3701. The samples were caustic washed to remove hydrogen sulfide and ammonia, and submitted for sulfur analysis by ICP and nitrogen analysis by chemiluminescence, D 4629. Gas samples were also taken from the vent sample port for gas chromatographic analyses.

The operating conditions of the hydrotreater were varied between a low severity condition, set to match current refinery practice, and a high severity condition set so that the sulfur and nitrogen contents of the treated heavy distillate would be well below 380 ppmw. A test matrix considering high and low settings of pressure, temperature, and flow rate were used to systematically examine conditions between the two extremes. Low pressure, temperature, and high LHSV were selected for the low severity condition. High pressure, temperature, and low LHSV were used for the high severity condition. Pressures were varied between 700 psig and 1350 psig. Temperatures were varied from 620 to 688°F. The LHSV was also varied between 0.8 and 2.2 hr<sup>-1</sup>.

Three feedstocks were used in the heavy distillate hydrotreating. The first was a petroleum feedstock(FL-2338). The second was the DL1 heavy distillate fraction (FL-2372). The third was a blend of the two (67% petroleum/ 33% coal liquid by volume).

The test sequence began with the petroleum feedstock at the low severity condition A. A sample was drawn at this and each subsequent condition. The neat coal liquid was then introduced at the low severity condition B. The temperature, pressure, and residence time were then increased to their high level states, Condition C, and a sample was drawn and tested to assure the sulfur and nitrogen were below 380 PPM. After several adjustments, this was established. The neat coal liquid was tested at nine additional conditions with varying pressure, temperature, and flow rate at severities between the two extremes of Conditions B and C. The petroleum/coal liquid blend was then tested at three conditions (M, N, and O), and the petroleum feedstock was reintroduced as the process was brought back to its initial, low severity condition P. Comparison of this last test condition to the first showed whether there had been significant catalyst deactivation, and this was checked by increasing the severity on the petroleum feedstock to Condition Q.

Figure 2-7 charts how the pressure, temperature, and flow rate varied during the run. Samples (denoted on the plot by letters A through Q) were drawn after

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conditions had stabilized for approximately three hours. The times that each of the feedstocks was introduced is also shown in the figure.

### 2.3.2 Test Results

The test setpoints and the data collected are summarized in Table 2-5. The hydrogen content of the processed DL1 heavy distillate were consistently above 12 wt%, satisfying the test objective. The exception was Condition L, whose high flow rate made the condition effectively less severe than point B. Multiple tests of the hydrogen content of Sample L show an average hydrogen content of the product of 11.98 wt%.

The range of product properties for the DL1 heavy distillate is narrower than it was in the naphtha processing. The density differs by only 0.006 gm/ml and the hydrogen content differs by 0.24% wt between the extremes of process severity. As with the naphtha data, trends in the heavy distillate hydrotreating are clouded by variability in the data. It should be noted that the experimental matrix was chosen to include typical refinery conditions and the least radical severities believed to achieve the processing objectives.

Hydrotreating reduced the sulfur and nitrogen content in the coal liquid to below the 380 ppmw target required for product stability.

The relative values of the temperature, pressure, and flow rate for the neat coal liquid tests are shown in a wire frame diagram in Figure 2-8. Table 2-6 compares points differing in only one parameter, and presents the effects of increasing pressure, temperature, and flow rate from the low to the high value of each parameter. As with the naphtha hydrotreating, the most influential control parameter was an increase in pressure from 700 to 1350 psig, which resulted in the predominant effect of increasing the hydrogen content by 0.105 wt%. An increase in hydrogen content was usually, but not always, accompanied by a decrease in density, but over the narrow range of the data, no inference about resulting hydrocarbon composition should be made. There is an occasional inconsistency between these two effects. Increasing either the temperature (from 620 to 688°F) or LHSV (from 1.4 to 2.7 hr<sup>-1</sup>) changed the hydrogen content and specific gravity by lesser amounts, and in inconsistent ways. A decrease in the LHSV should not decrease the hydrogen content. This information suggests that the variation within the data is obscuring the effects caused by varying the process conditions over a limited range of severity.

As in the naphtha hydrotreating tests, there are clear indications that the catalyst experienced deactivation. The distillate petroleum was treated at the same conditions at the start (Point A) and the end of the run (Point P). A comparison of these two points shows that there was a significant decrease in hydrogen uptake and sulfur and nitrogen removal. In addition, the product sulfur

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concentrations at the lowest severity condition (Point B) is less than the sulfur contents of samples taken later, but at generally higher severities (Points G,H, I, J, and L).

### 2.4 Analysis of Hydrotreater Data

Both the naphtha and the heavy distillate hydrotreater tests (Runs 49 and 51) included three levels of operating temperature. In both cases, the intermediate temperature was about 650°F. The effect on hydrogen consumption of a temperature increase below 650°F, compared to a temperature increase above 650°F are considered in Table 2-7. The table shows that for each of the three cases where the temperature was raised from 650°F to a greater level, the hydrogen content decreased by an average of 0.06 wt%. On the other hand, a temperature increase below 650°F increased the hydrogen content by an average of 0.4 wt% in two of three cases. The small changes in specific gravity for those same points do not contradict the trend.

This would suggest that a critical temperature may exist somewhere between the temperature limits tested. At temperatures above this critical value, the reverse reaction rate (which is temperature dependent) is reducing the net rate of the hydrotreating below the maximum level. This may indicate that some of the selected matrix conditions were beyond the thermodynamic limit for the hydrogenation reaction.

Regression analyses were performed on the data from Runs 49 and 51. Predictive linear models of the specific gravity and hydrogen fraction were generated in the form:

$$SG = K + a_1 (T - T_0) + a_2 (P - P_0) + a_3 (LHSV - LHSV_0).$$

The results of these regressions were presented at the February Project Meeting in San Francisco. Since that time, the data have been reevaluated. Rather than relating the product properties linearly to the three operating parameters, a simplified model using a single plotting parameter, an index of severity was used. The severity term, *S*, is the combination of the control parameters:  $S = P \cdot T / LHSV$ . In general, as the pressure, temperature, or processing duration (1/LHSV) increases, the products are processed more fully, whether for desulfurization, denitrogenation, or hydrogenation. Consequently, as the severity term increases, the hydrogen content should increase and the specific gravity decrease. Figure 2-9 shows the increase in hydrogen content (relative to the feedstock) for the naphtha and heavy distillate hydrotreater runs. The figure shows a generally linear relationship between the hydrogen content and the severity term, considering the experimental error. There is some scatter in the



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data, but the strong correlation is evident. The same holds true for the specific gravity vs. severity as shown in Figure 2-10.

The correlation coefficient,  $r^2$ , which is one measure of the goodness of fit of a model to data, has been calculated for the models as shown in Table 2-8. The numbers show that the severity model has a slightly stronger correlation to the data than the linear model.

### 2.6 Conclusions and Recommendations

Naphtha and heavy distillate portions of the DL1 have been hydrotreated to increase their hydrogen content and to reduce nitrogen and sulfur concentrations to within acceptable limits. Hydrotreating was conducted over a range of conditions, with varying pressure (700 to 1350 psig), temperature (596 to 720 °F) and flow rate (Liquid Hourly Space Velocity between 0.8 and 2.7 hr<sup>-1</sup>). The tests roughly followed a 2<sup>3</sup> factorial format, which considers each of the variables at two different values.

The tests satisfied the experimental objectives of increasing hydrogen content and decreasing the nitrogen and sulfur contents below a prescribed level. The recorded initial sulfur levels in the naphtha hydrotreating exceeded the 0.5 ppmw criteria. The high levels were caused by contamination during caustic washing of the samples. The apparatus has been modified to include a stripping column, and has been demonstrated in naphtha hydrotreater Run 53 to give sulfur readings within the criterion. While catalyst aging was observed, the products were still within tolerance.

The influence of the control parameters on the product properties was examined and modeled. The most influential parameter on changes in hydrogen content and specific gravity was the pressure. Doubling the pressure produced about a 50% increase in the hydrogen consumption in both the naphtha and heavy distillate hydrotreating runs. The effects of temperature and flow rate were less significant over the limited range of severity tested. There was some suggestion in the data that an optimum temperature for hydrogen addition may fall between the temperature extremes tested.

Two models were constructed for predicting the specific gravity and hydrogen consumption of the hydrotreated DL1 naphtha and heavy distillate. The first was a linear model using pressure, temperature, and LHSV as parameters. The second model related the change in material properties to a simplified process severity term (P·T/LHSV). The severity term models gave an improved correlation of the data, suggesting that the effects of these variables are not additive.

## **SwRI Activities**

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In terms of severity, future work should cover lower severity levels. Based on the test work completed so far, it has been determined that the objectives can be met. It is not known, however, what minimum levels are required to meet the objectives. In other words, the DL1 coal liquid may have been "over-treated" in these tests. By examining lower severity levels, the severity level required to meet, but not exceed the objectives could be determined.

A limited amount of testing at higher severity levels may also be appropriate to confirm the relationship between the severity parameter and hydrogen uptake. As shown in Figures 2-9 and 2-10, there is very limited data at the high severity levels.

A catalyst deactivation test should be conducted with either the DL1 naphtha or heavy distillate. The test should be conducted at a constant pressure and feed rate. Temperature would then be adjusted to maintain a constant heteroatom removal or aromatic saturation. The required rise in temperature is an indication of catalyst deactivation.

**SwRI Activities**

Table 2-1. DL1 Naphtha Hydrotreating Summary - Run 51								
SAMPLE#	Feed	Avg. Processing			Density g/mL	H Wt% NMR	Sulfur	Nitro- gen
		Deg F	Psig	LHSV			PPMW	PPMW
FL-2385	Feed DL1				0.794	13.62	690	219
FL-2310	Feed Petr				0.767	13.95	1630	<1
A	Petr	599	770	2.6	0.765	14.06	160	<1
B	DL1	596	770	2.7	0.787	13.89	130	3
C	DL1	723	1397	1.4	0.780	14.21	60	<1
D	DL1	722	762	1.4	0.784	13.84	120	2
E	DL1	602	1397	2.7	0.786	13.98	140	<1
F	DL1	656	762	2.7	0.786	13.97	130	<1
G	DL1	720	1396	2.7	0.782	14.13	150	3
H	DL1	718	762	2.8	0.788	13.94	180	3
I	Blend	722	764	1.5	0.768	14.25	190	10
J	Blend	722	1400	1.3	0.761	14.80	250	<1
K	Blend	603	766	2.6	0.771	14.12	230	<1
L	Petr	607	768	2.7	0.771	13.34	460	<1
M	Petr	721	772	1.5	0.760	14.39	400	<1

## SwRI Activities

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Effect	Sample Points	Change in H Content	Effect on SG	Average Change in H Content	Average Effect on SG
Temperature (600 to 720°F)	B to H E to G	+0.05% +0.15%	+0.001 -0.004	+0.010%	-0.0015
Pressure (770 to 1400 psig)	B to E H to G D to C	+0.09 +0.19 +0.37	-0.001 -0.006 -0.004	+0.22%	-0.0037
LHSV (1.4 to 2.7 hr-1)	C to G D to H	-0.08 +0.10	+0.002 +0.004	+0.01%	+0.003

Item	Feed	Flow Rate		Pressure psig	Temperature, °F
		GPH	LHSV		
Warm Up	FL-2310	~0.27		1600	722
A	FL-2385	0.271	1.28	1600	722
B	FL-2385	0.271	1.28	400	722
C	FL-2385	0.567	2.68	770	596
D	FL-2385	0.419	1.98	1185	660

## Section 2

**SwRI Activities**

Table 2-4. DL1 Naphtha Hydrotreater Sample Log - Run 53											
DATE 28 Feb. 1995					FEED: FL-2385						
Sample ID	DATE	TIME	Log Bk/Pg	Qty Oz	Temp Rx Av °F	LHSV	Pres psig	Feed	Liquid Density g/mL	Hydrogen Wt% NMR	Sulfur (ICP)
53-A 1	28 Feb 95	10:24	32/38	4	720	1.3	1600	DL1	0.78	14.20	6.12
53-A 2	28 Feb 95	11:55	32/39	4	720	1.3	1600	DL1	0.78	14.18	1.48
53-A 3	28 Feb 95	13:22	32/40	4	720	1.3	1600	DL1	0.78	14.14	1.9
53-A 4	28 Feb 95	14:40	32/40	4	719	1.3	1604	DL1	0.78	14.35	<0.4
53-A 5	28 Feb 95	15:50	32/41	4	720	1.3	1608	DL1	0.779	14.31	<0.4
53-B 6	1 Mar 95	06:00	32/44	4	721	1.3	405	DL1	0.788	13.65	<0.4
53-B 7	1 Mar 95	07:30	32/44	4	721	1.3	401	DL1	0.789	13.69	<0.4
53-B 8	1 Mar 95	10:30	32/45	4	717	1.3	398	DL1	0.788	13.64	<0.4
53-B 9	1 Mar 95	11:25	32/46	4	719	1.3	403	DL1	0.789	13.72	<0.4
53-B10	1 Mar 95	12:53	32/46	4	720	1.3	401	DL1	0.788	13.68	<0.4
53-B11	1 Mar 95	13:55	32/47	4	720	1.3	401	DL1	0.788	13.57	<0.4
53-B12	1 Mar 95	15:12	32/47	4	717	1.3	400	DL1	0.788	13.66	<0.4
53-B13	1 Mar 95	16:30	32/48	4	718	1.3	396	DL1	0.788	13.58	<0.4
53-B14	1 Mar 95	16:30	32/48	4	718	1.3	396	DL1	0.788	13.67	<0.4
53-B15	1 Mar 95	17:50	32/48	4	719	1.3	397	DL1	0.788	13.60	2.04
53-C16	2 Mar 95	01:40	32/50	4	601	2.7	775	DL1	0.786	13.88	<0.4
53-C17	2 Mar 95	04:25	32/51	4	601	2.7	770	DL1	0.786	13.90	<0.4
53-C18	2 Mar 95	06:59	32/52	4	602	2.7	773	DL1	0.785	14.01	<0.4
53-D19	2 Mar 95	12:41	32/54	4	660	2.0	1179	DL1	0.784	13.96	<0.4
53-D20	2 Mar 95	21:21	32/56	4	658	2.0	1177	DL1	0.784	13.95	3.72
53-D21	2 Mar 95	22:52	32/57	4	661	2.0	1181	DL1	0.784	13.90	2.06
53-D22	3 Mar 95	02:10	32/58	4	662	2.0	1182	DL1	0.784	13.91	0.74

## Section 2

**SwRI Activities****Table 2-5. DL1 Heavy Distillate Hydrotreating Summary - Run 49**

SAMPLE No.	Feed DL1/Petr	Avg. Processing			Density	Hydrogen Wt%	Sulfur	Nitrogen
		Deg F	Psig	LHSV	g/mL	NMR	PPMW	PPMW
FL-2372	DL1Feed				0.919	11.87	314	590
FL-2338	Petr Feed				0.868	12.22	6380	109
A	Petr	619	700	1.9	0.851	13.20	286	<1
B	DL1	624	700	2.0	0.914	12.06	5.2	351
C	DL1	687	1350	0.8	0.909	12.23	17	2
D	DL1	688	1350	1.3	0.913	12.14	12	44
E	DL1	649	1345	1.4	0.913	12.14	16	115
F	DL1	654	1025	1.4	0.914	12.09	59	218
G	DL1	650	700	1.4	0.915	12.07	20	300
H	DL1	620	1345	1.4	0.913	12.17	9.7	238
I	DL1	622	1351	2.0	0.914	12.20	24	303
J	DL1	653	700	2.2	0.914	12.13	16	355
K	DL1	684	1351	2.1	0.911	12.10	7	129
L	DL1	685	700	2.2	0.915	11.98	30	321
M	Blend	686	699	2.0	0.875	12.57	244	53
N	Blend	685	1351	0.7	0.859	13.08	446	<1
O	Blend	618	700	1.9	0.876	12.55	836	119
P	Petr	620	699	1.9	0.854	12.87	564	53
Q	Petr	652	700	1.4	0.847	12.80	36	11

## Section 2

**SwRI Activities****Table 2-6. DL1 Heavy Distillate Hydrotreating Effects - Run 49**

Effect	Points	Change in H content	Effect on SG	Average Change in H	Average Effect on SG
Temperature (620 to 688°F)	H to D I to K	-0.03% -0.10%	0 -0.003	-0.065%	-0.0015
Pressure (700 to 1350 psig)	B to I G to E	+0.14% +0.07%	0 -0.002	+0.105%	-0.001
LHSV (1.4 to 2 hr <sup>-1</sup> )	H to I D to K	+0.03% -0.04%	-0.001 -0.002	-0.005%	-0.0015

**Table 2-7. Effect of Increasing Temperature Above and Below 650 F**

Feedstock	Points	Temperatures	Change in SG	Change in H <sup>2</sup> %
DL1 Hvy Distillate (Run 49)	J to L E to D	653 to 685°F 649 to 688°F	+0.001 0.00	-0.15 % -0.0 %
DL1 Naphtha (Run 51)	F to H	656 to 718°F	+0.002	-0.03 %
Average Effect of Temperature Increase Above 650°F			+0.001	-0.06 %
DL1 Hvy Distillate (Run 49)	B to J H to E	624 to 653°F 620 to 649°F	0.00 0.00	+0.07 % -0.03 %
DL1 Naphtha (Run 51)	B to F	596 to 656°F	-0.001	+0.08 %
Average Effect of Temperature Increase from 620 to 650°F			-0.0003	+0.04 %

**SwRI Activities**

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	R <sup>2</sup> (P,T,LHSV)	R <sup>2</sup> (Severity)
Specific Gravity	0.59	0.59
H <sub>2</sub> Wt%	0.37	0.52



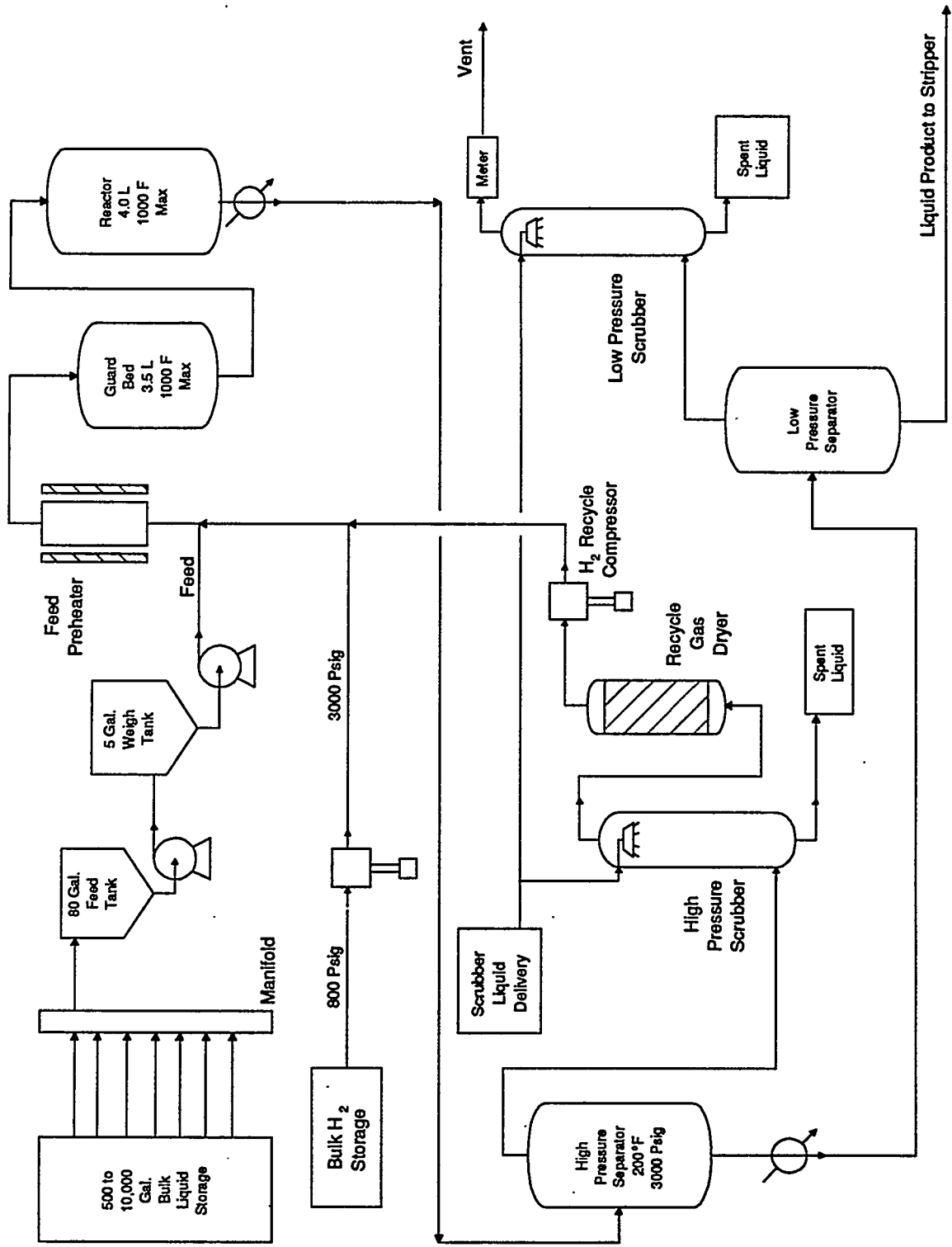


Figure 2-1. Flow Diagram of Pilot-Scale Hydrotreating Apparatus

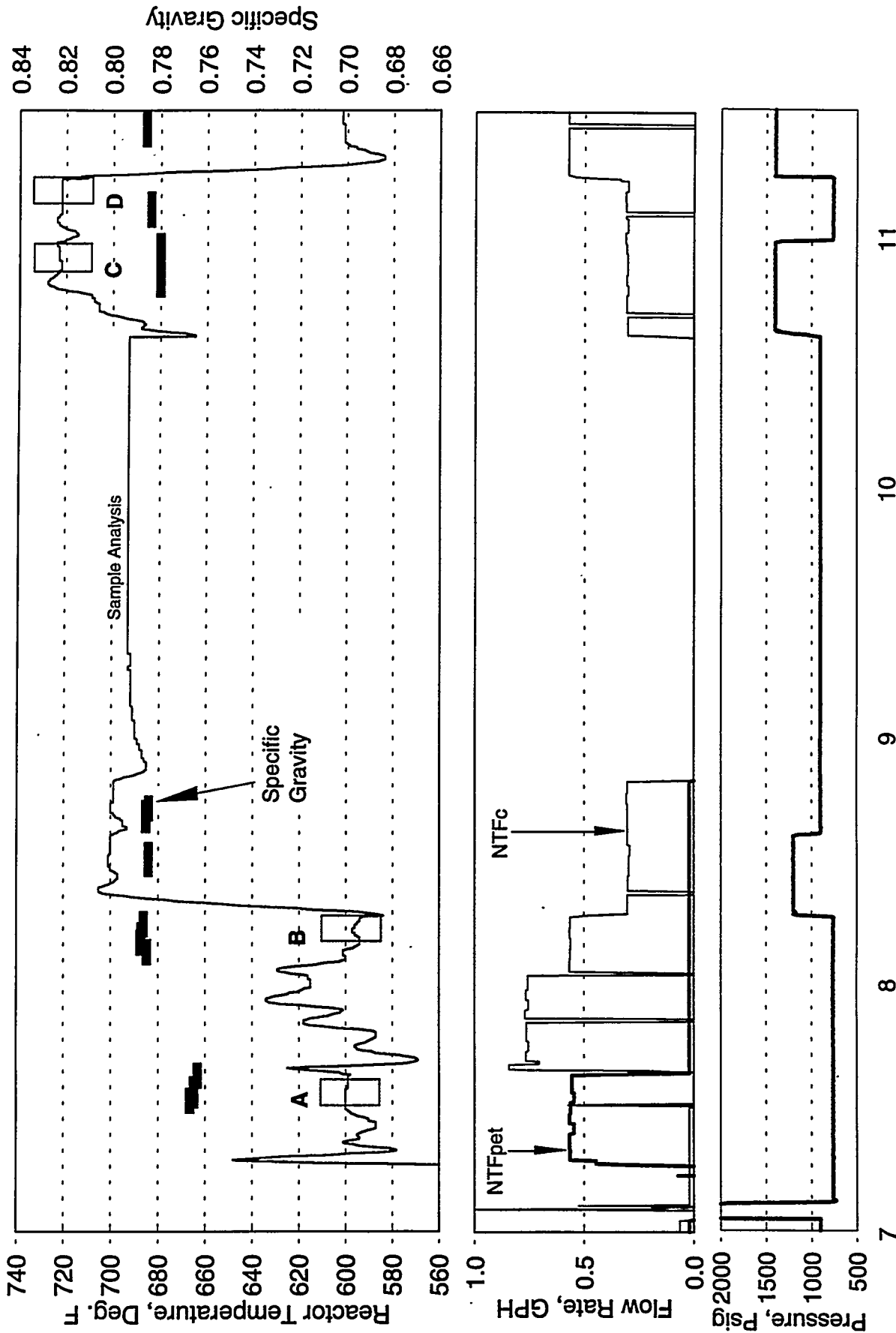


Figure 2-2. DL1 Naphtha Hydrotreating Timeline, Run 51

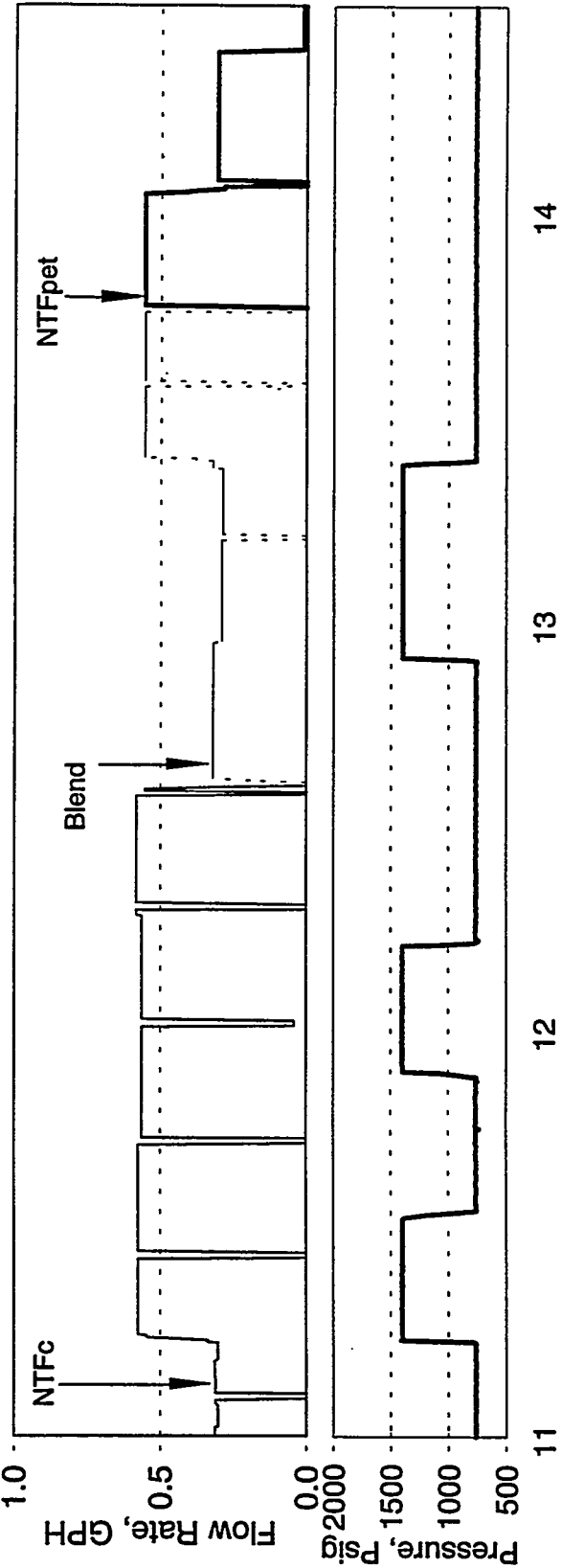
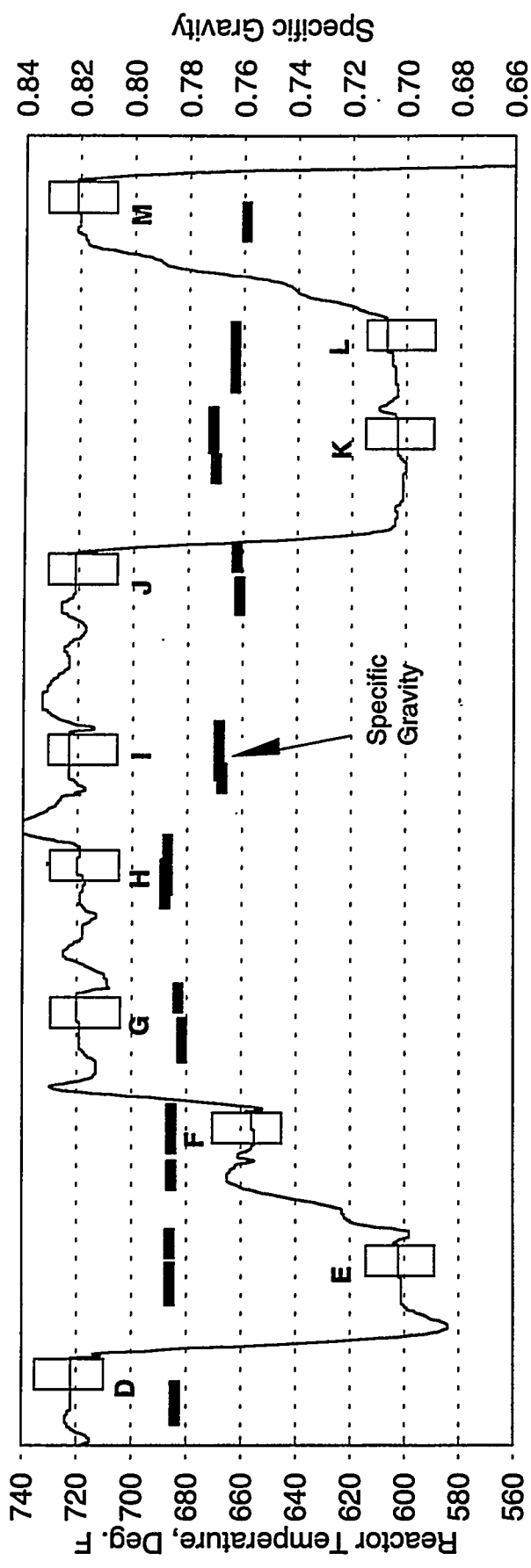


Figure 2-2. (Cont'd) DL1 Naphtha Hydrotreating Timeline, Run 51

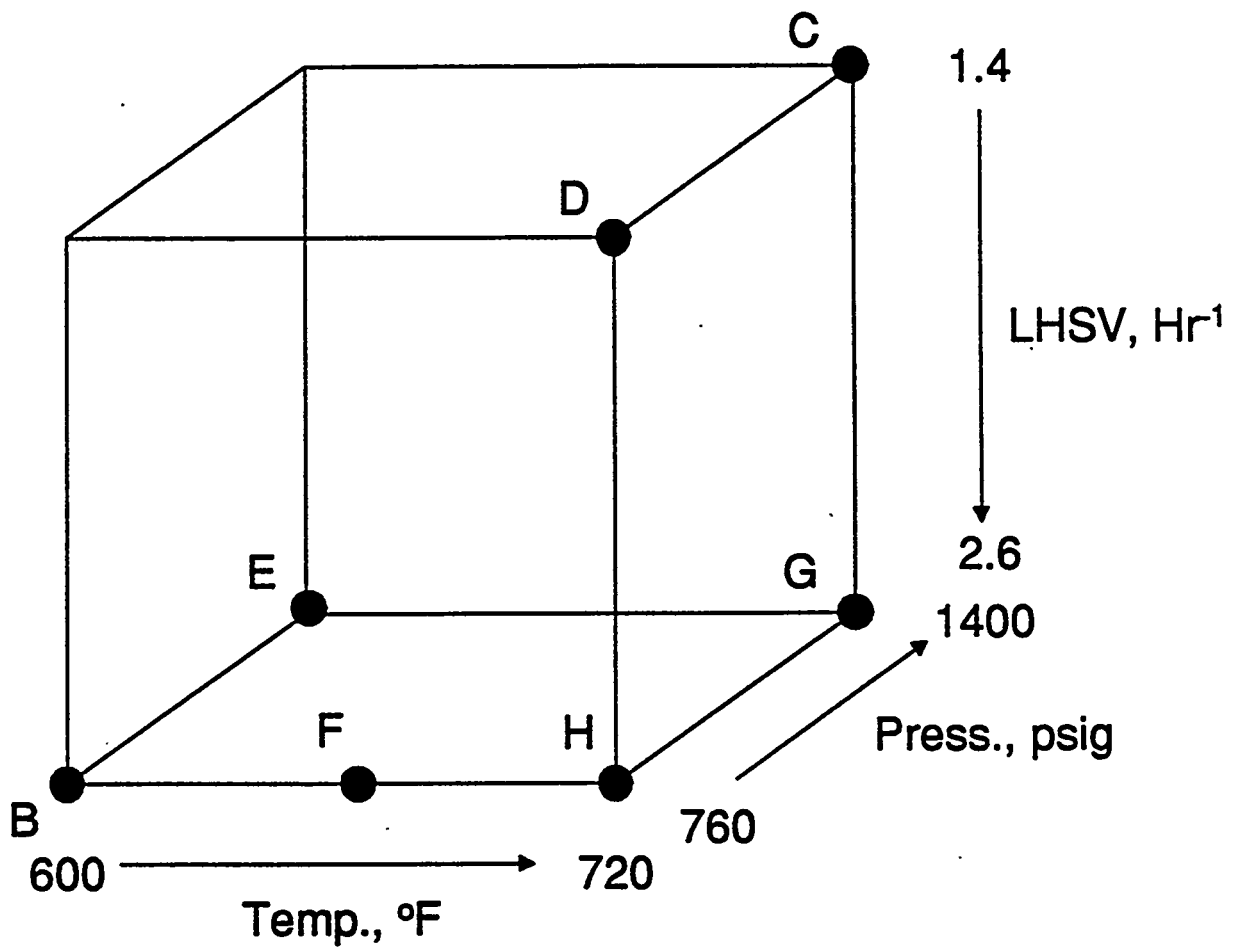


Figure 2-3. Experimental Matrix for DL1 Naphtha Hydrotreating

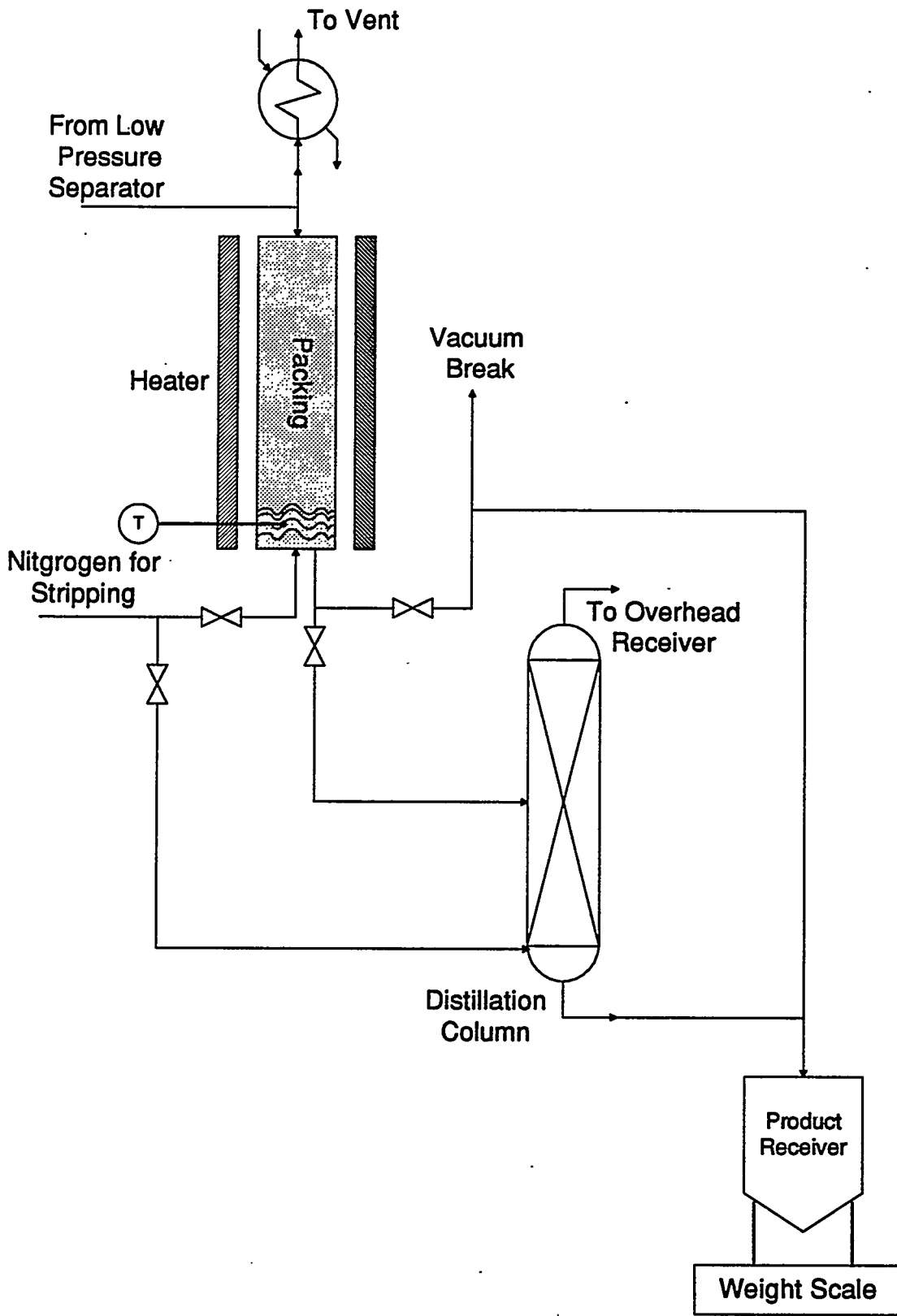


Figure 2-4. Product Stripper Modification

# DL1 Medium Naphtha Hydrotreating, Confirmation

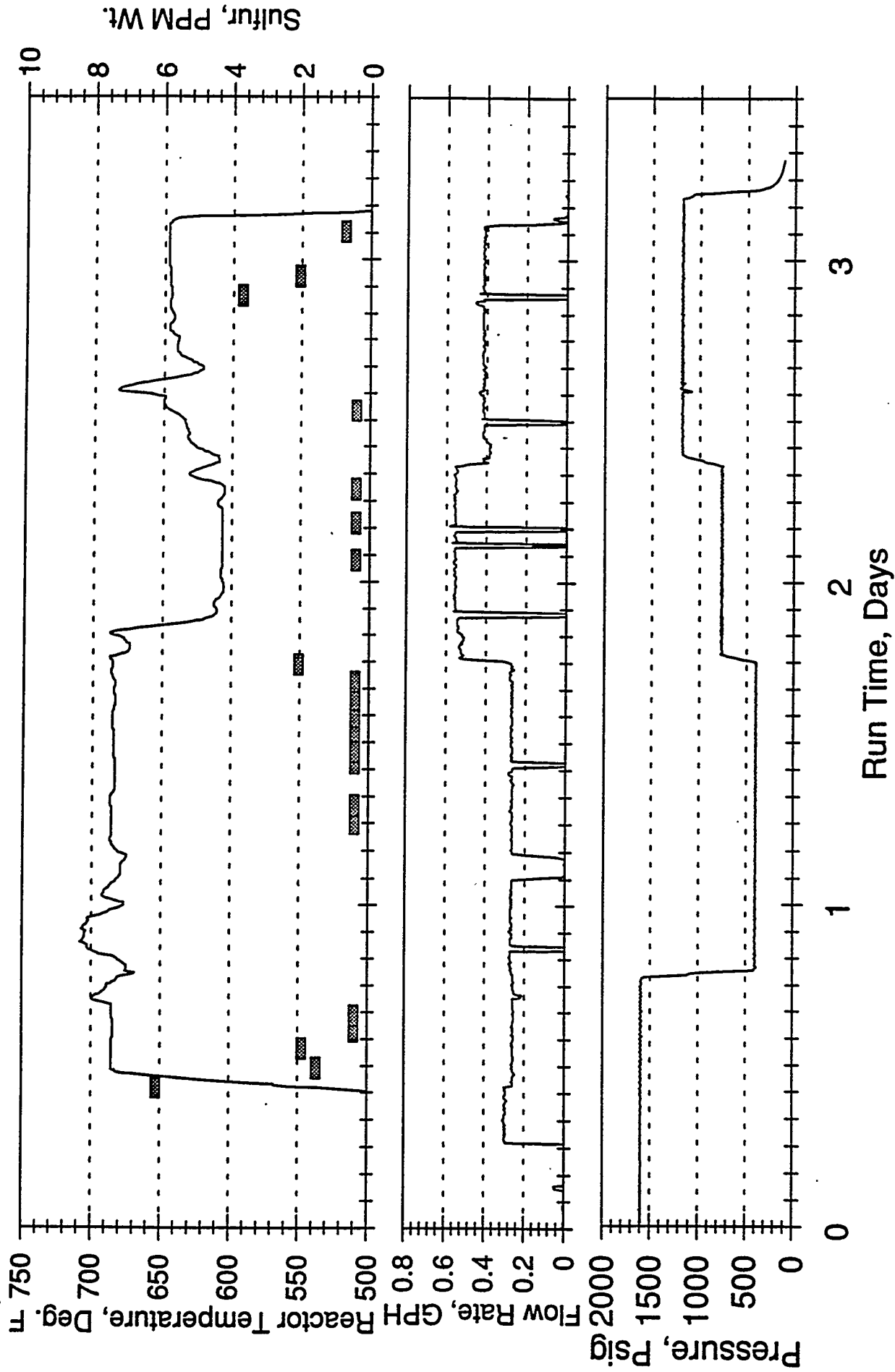
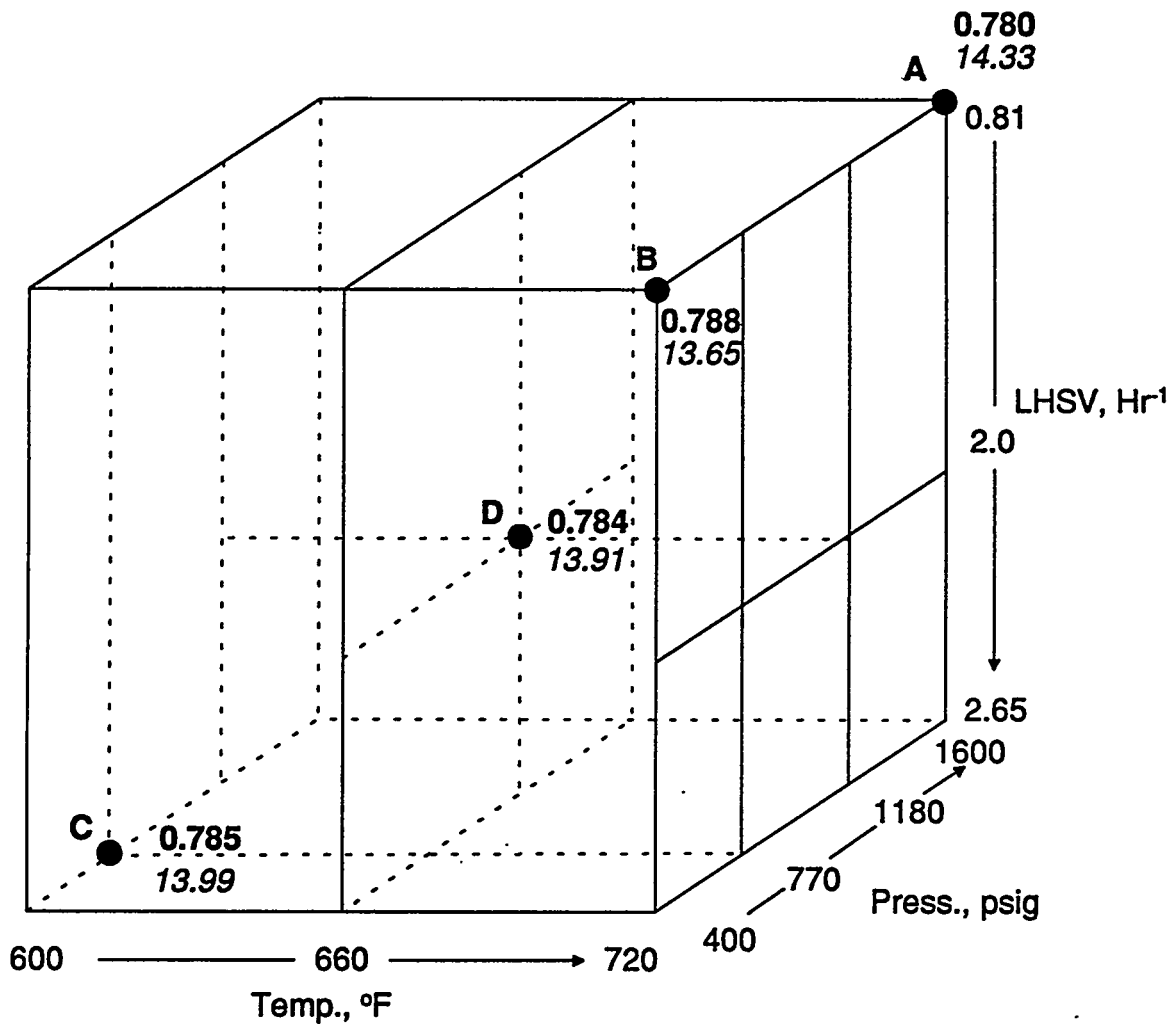


Figure 2-5. DL1 Naphtha Hydrotreating with Stripping Timeline, Run 53



DL1 Medium Naphtha Hydrotreating Confirmation,  
 Density (**Bold**), g/mL, and Hydrogen Concentration, (*Italics*), %

Figure 2-6. Experimental Points in Hydrotreating with Stripping, Run 53

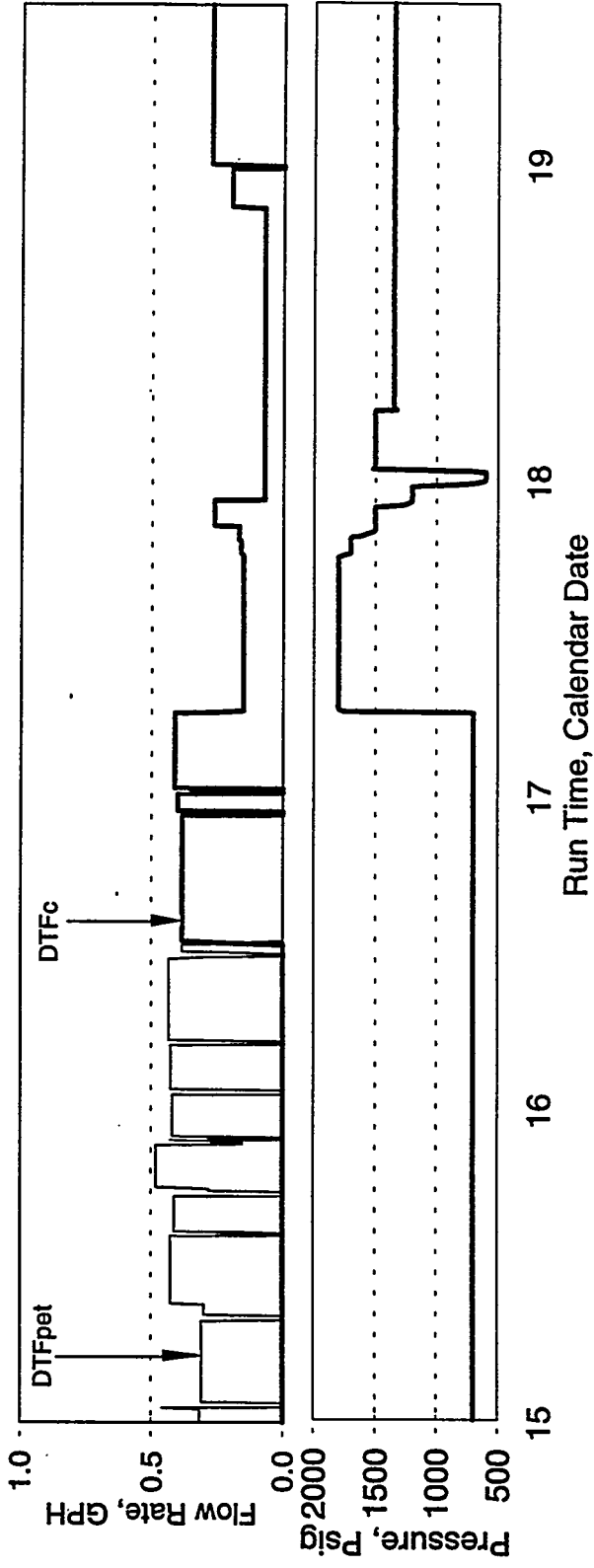
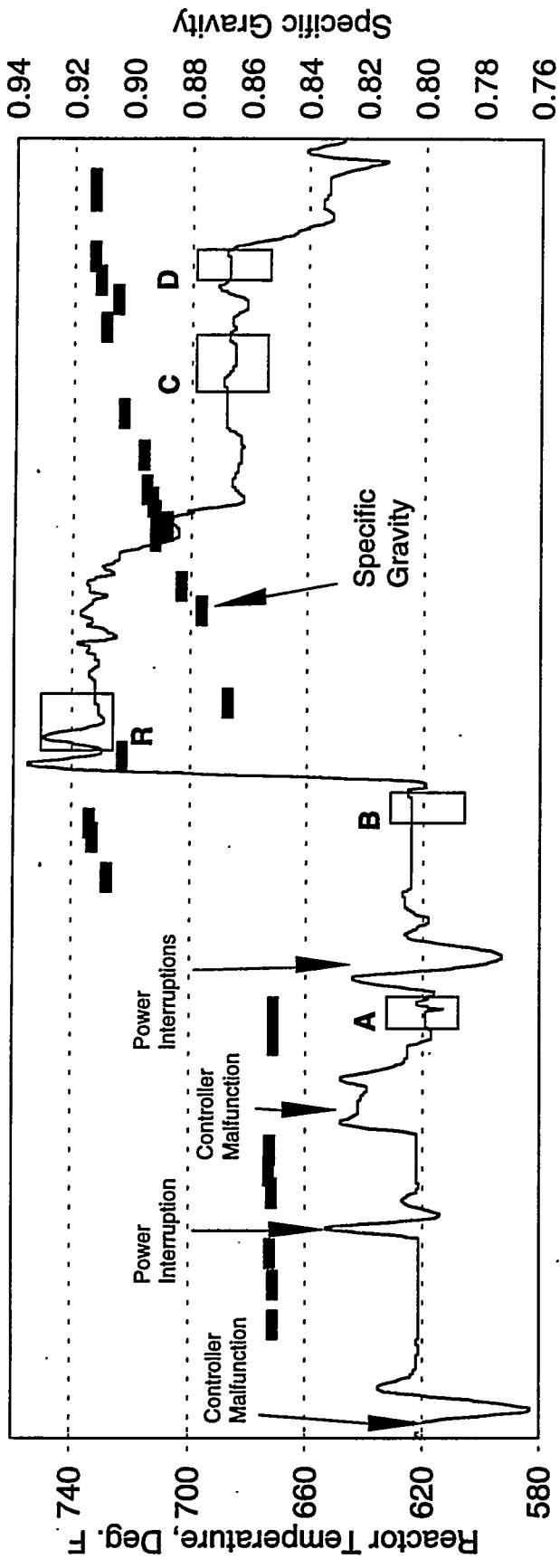


Figure 2-7. DL1 Heavy Distillate Hydrotreating Timeline, Run 49



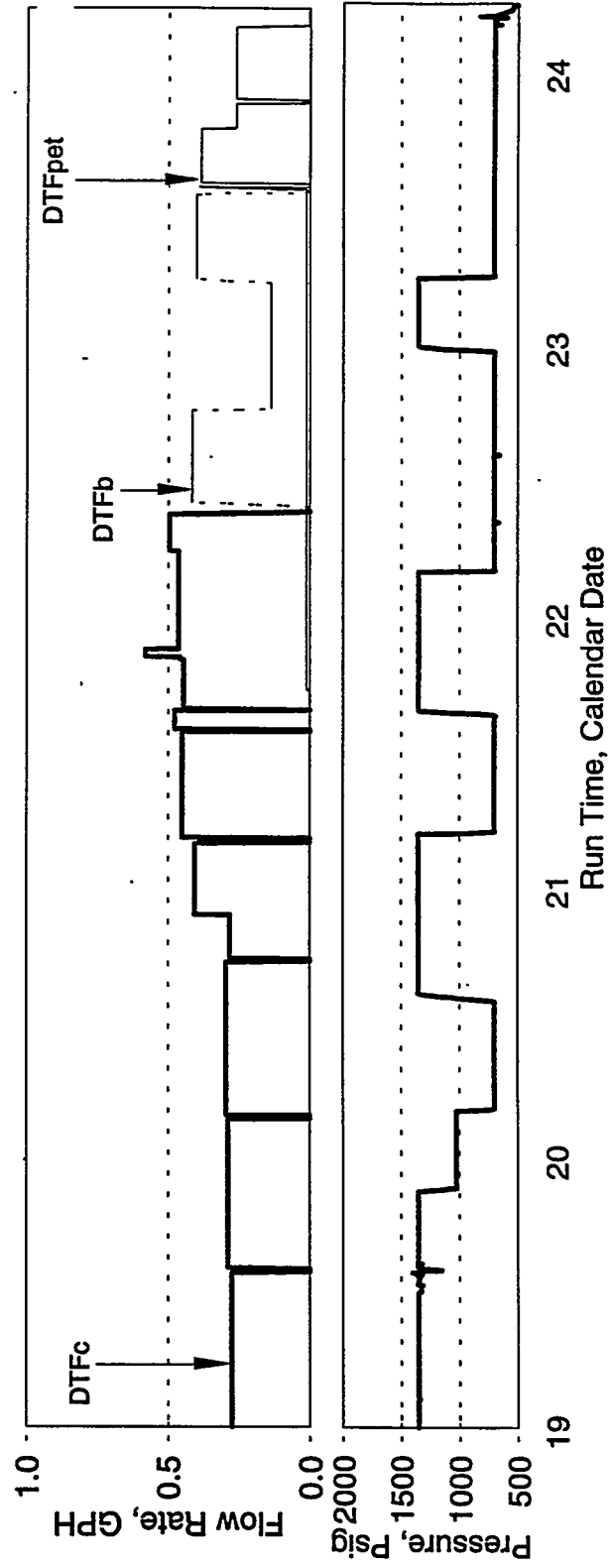
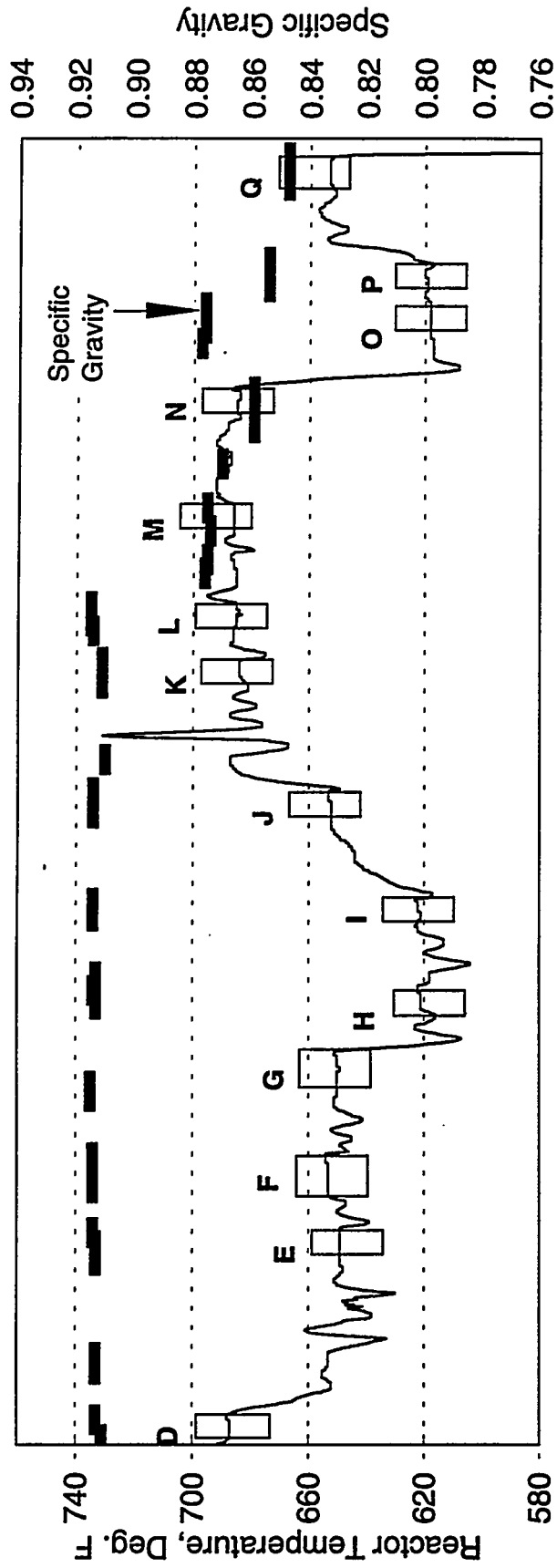


Figure 2-7. (Cont'd) DL1 Heavy Distillate Hydrotreating Timeline, Run 49

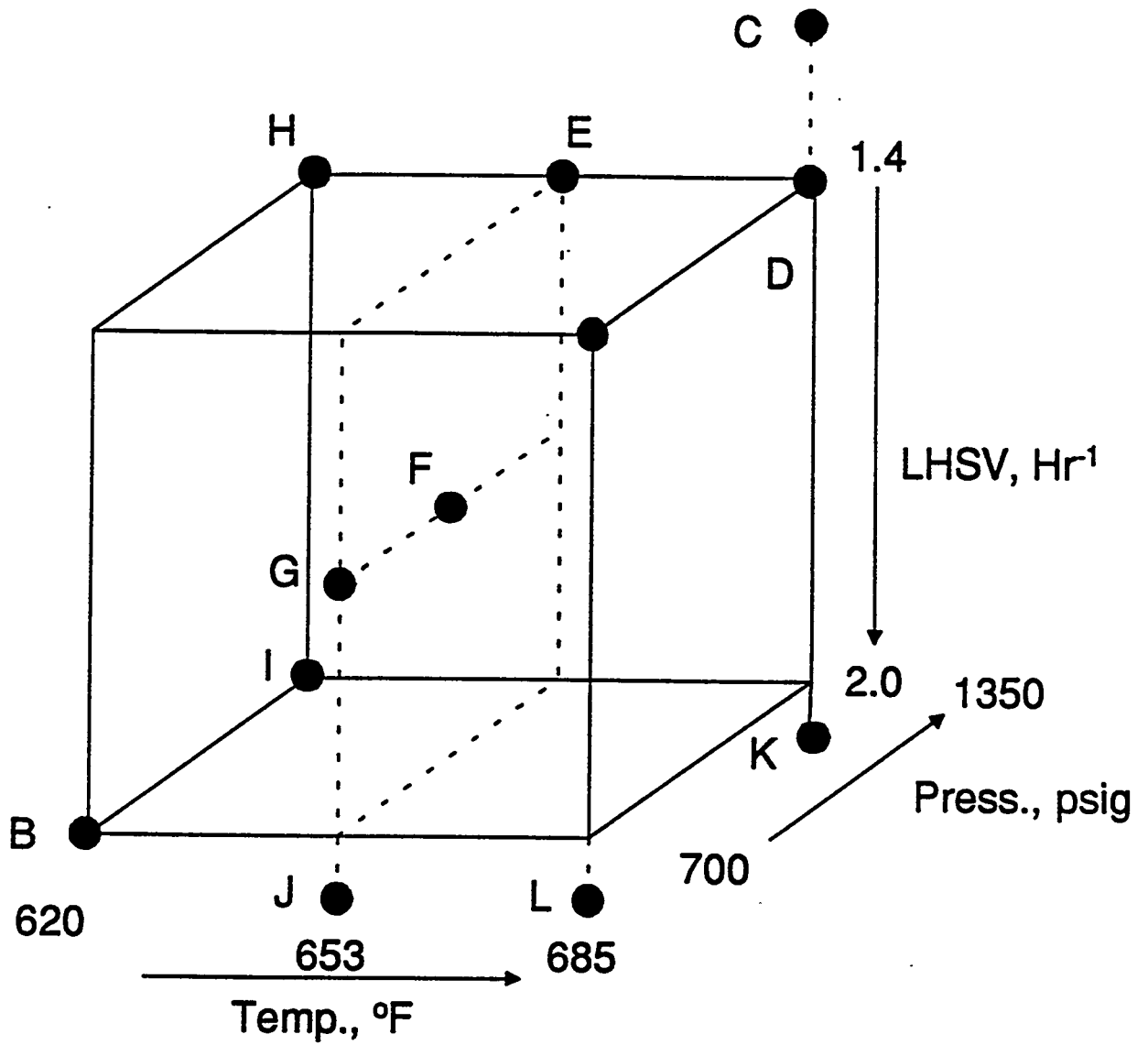
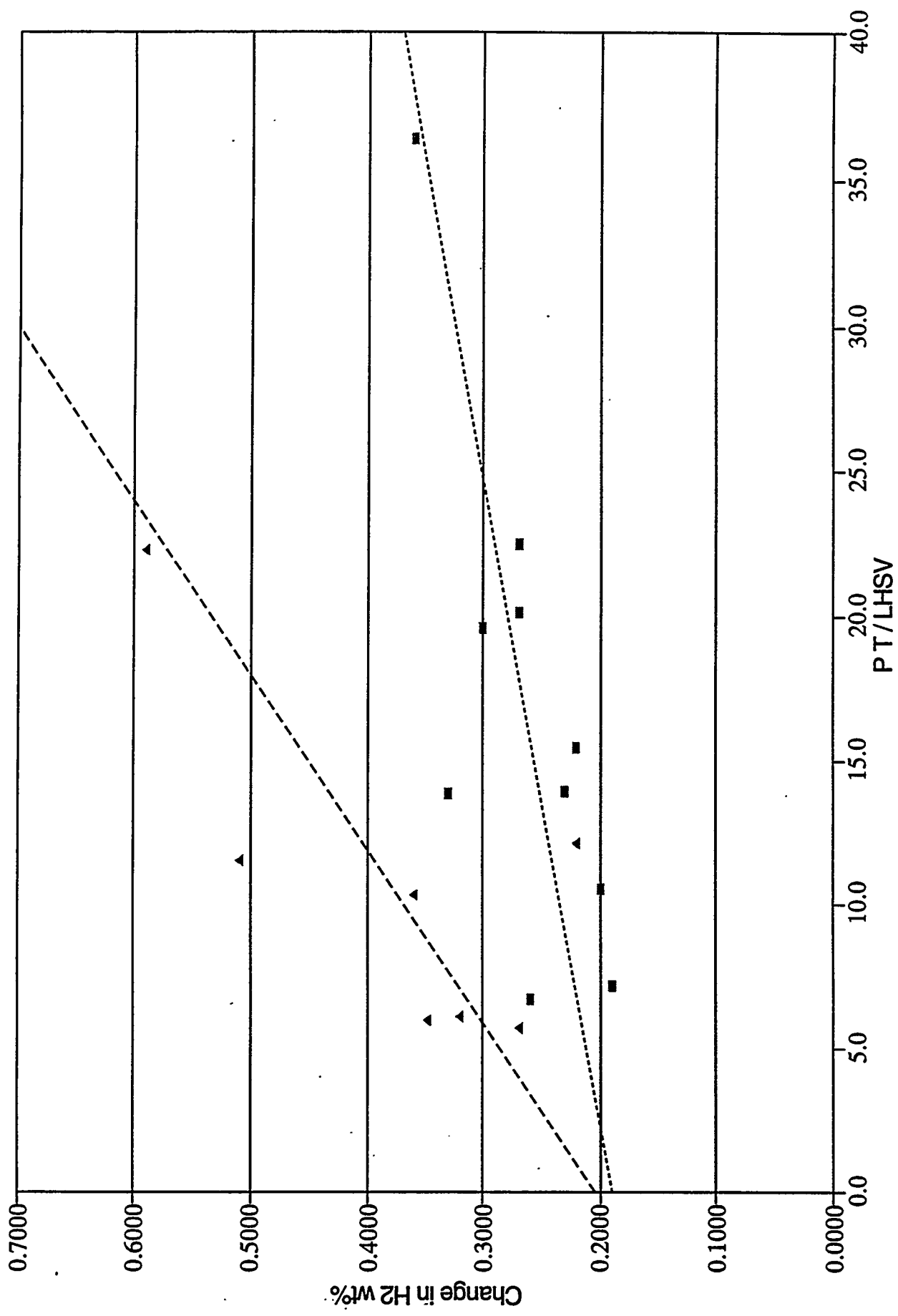
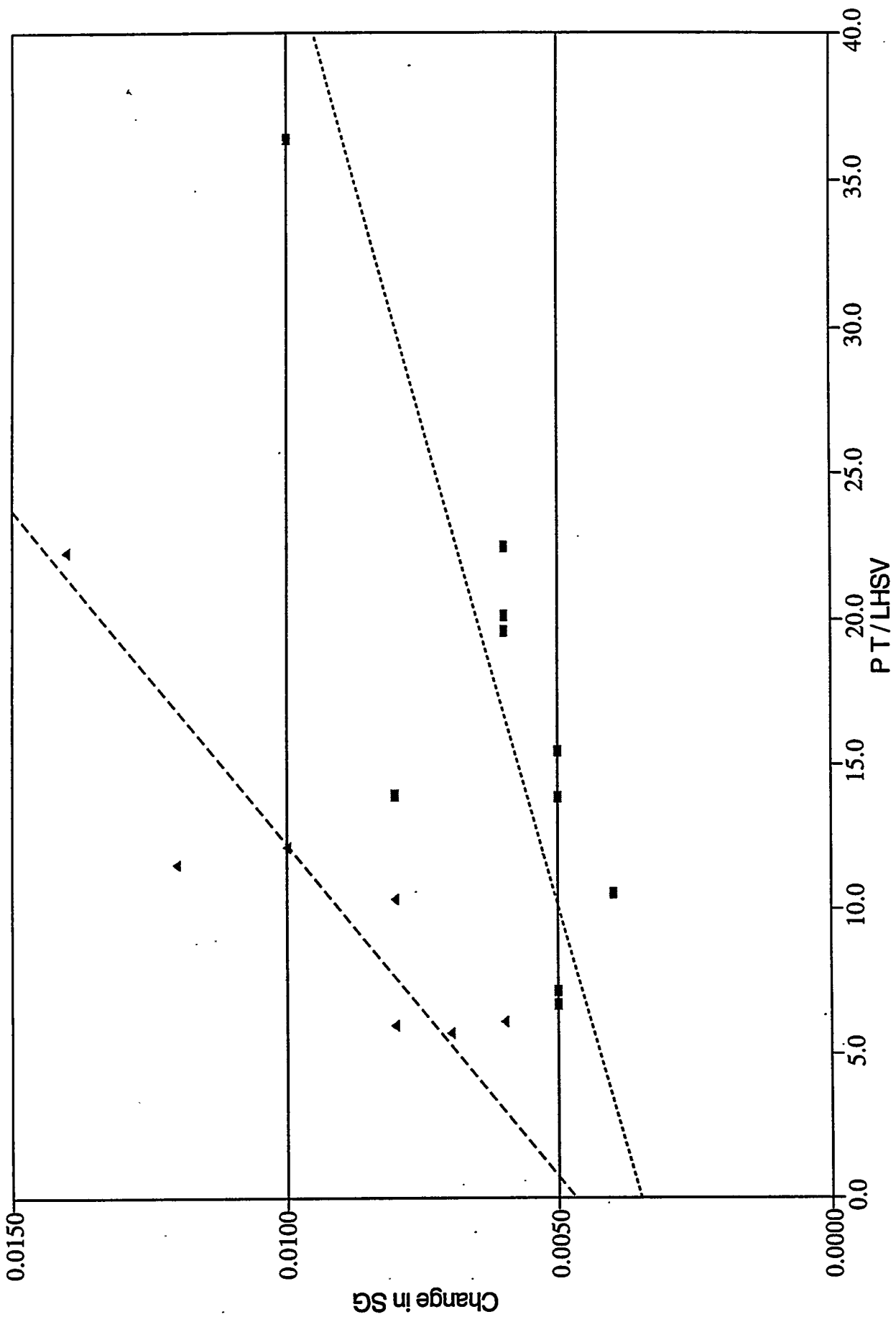


Figure 2-8. Experimental Matrix for DL1 Heavy Distillate Hydrotreating, Run 49



■ Distillate Run 49 ▲ Naptha Run 53

Figure 2-9. Hydrogen Concentration in Weight Percent vs. PT/LHSV



■ Distillate Run 49 ▲ Naphtha Run 53

Figure 2-10. Specific Gravity vs. PT/LHSV