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DEVELOPMENT OF A CORRELATION BETWEEN
SLURRY OIL COMPOSITION AND
PROCESS PERFORMANCE.

Topical Report 2.

ANALYSES OF SLURRY RECYCLE OILS FROM
H-COAL PDU RUN 8

MASTER

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ABSTRACT

Daily samples of the slurry recycle oils from H-Coal PDU Run 8 (Illinois 6 coal, Fuel Oil and Intermediate modes) were analyzed by ^1H -NMR spectroscopy, GC/MS, and liquid chromatographic techniques. The residual recycle material (975°F^+ , THF soluble) is much higher in preasphaltenes than corresponding material from the Syncrude mode with the same coal. This may have caused, or been caused by operability problems in PDU 8, many of which involved plugging at various points in the PDU. In any case, the combination of high preasphaltenes and operability problems can combine to significantly accelerate catalyst deactivation. Because of these factors, and the segmented nature of PDU Run 8 it is not possible to make any statement regarding the attainment of steady-state in either the Fuel Oil or Intermediate modes.

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Section 1

INTRODUCTION

This is the second of three reports of analyses of H-Coal slurry recycle oils. Daily samples of the clean oil tank (COT) inventory and hydroclone overflow (HO) were taken during Run 8 of the H-Coal PDU operated by HRI at Trenton, New Jersey. This run was made in the Fuel Oil and Intermediate modes (coal space velocities 78 and 50 lb/hr/ft³) with Illinois 6 coal. A previous report⁽¹⁾ detailed analyses of similar samples from PDU Run 5 (Illinois 6 coal, Syncrude mode). Samples were analyzed by ¹H-NMR spectroscopy, GC/MS, and liquid chromatographic techniques to obtain a molecular characterization of the slurry recycle oils. The composition data obtained are used to determine the relationship between slurry oil composition and process performance. Specifically, the data from PDU Run 8 and PDU Run 5 are compared in this report to determine the effect of space velocity on slurry oil composition for runs using the same coal. The final report, on samples from PDU Run 9 (Kentucky 11 coal, Syncrude mode) will compare data from different coals in the same mode, by reference to PDU Run 5. The final report will also be a comprehensive summary of the project.

Section 2

SUMMARY

A. DESCRIPTION OF PDU RUN 8

PDU Run 8 consisted of 15 days operation in the Fuel Oil mode (SV = 78 lb/hr ft³) followed by 7 day operation in the Intermediate mode (SV = 50 lb/hr/ft³) with Illinois 6 coal. Analyses of the coal and start-up solvent (Allied Chemical 24CB creosote oil) are given in Tables 2-1 and 2-2, respectively. The coal analysis is compared to that of the Illinois 6 coal fed to PDU Run 5.

PDU Run 8 consisted of 23 run periods (days) although operational difficulties, and attendant shutdowns, along with the reduction in space velocity during the last seven days of the run, divided the run into four shorter periods of operation.

The first restart of the run (Period 3) ended in a shutdown on day 6 when recycle flow in the reactor was lost. The run was restarted on day 7, but coal feed was terminated on day 9 when a leak occurred in a pressure relief valve. The third segment of the run (days 10-15) was interrupted by a minor fire in the vapor collection system for slurry mix tank section. Start-up oil was fed to the reactor while the coal slurry feed was stopped. The run was restarted on day 16, and the space velocity decreased to the intermediate mode velocity during days 17 and 18. On days 18-23 the unit was operated in the Intermediate mode. For convenience we will refer to these four segments as A,B,C and D, each spanning the run days shown below.

<u>Run Segment</u>	<u>Run Days</u>	<u>Mode</u>	<u>Space Velocity</u>
A	3-6	Fuel Oil	78
B	7-9	Fuel Oil	78
C	11-15	Fuel Oil	65
D	17-23	Intermediate	50

Complete details of the run history are given in HRI's report of PDU 8⁽²⁾, from which the above was abstracted. It is important to note that much of the operational difficulty was caused by plugging at various points in the system, including the slurry charge pump, the internal recycle pump, the hydroclone, and the catalyst addition and withdrawal system. We believe this is related to the high preasphaltene content of the recycled residuum, perhaps inherent to operation in the high space velocity fuel oil mode. This will be discussed below.

B. RESULTS OF ANALYSES OF SLURRY RECYCLE OILS

- The recycle distillates from PDU Run 8 have much the same proton distribution (by ¹H-NMR spectroscopy) as the corresponding distillates from PDU 5. The distillates recycled during operation in

Table 2-1

Analyses of Illinois 6 (Burning Star Mine) Coals
Fed to PDU Runs 5 and 8^a

	<u>PDU Run 5</u>	<u>PDU Run 8</u>
<u>Proximate Analyses, Dry Basis, wt %</u>		
Ash	10.66	11.29
Volatile Matter	38.34	37.50
Fixed Carbon	51.00	51.21
<u>Ultimate Analyses, Dry Basis, wt %</u>		
Carbon	70.01	68.43
Hydrogen	5.01	4.41
Nitrogen	1.31	1.25
Sulfur (LECO)	3.54	3.44
Ash	10.66	11.29
Oxygen (Difference)	9.39	11.18

^aData taken from References (2) and (3).

Table 2-2

Analysis of Allied Chemical 24CB Creosote Oil^a
Start Up Solvent, PDU Run 8

	<u>Wt %</u>
<u>Elemental Analysis</u>	
Carbon	85.97
Hydrogen	6.12
Sulfur	0.61
Nitrogen	0.99
<u>Vacuum Distillation</u>	<u>T, °C</u>
<u>ASTM D1160, modified</u>	
IBP	216
10, Vol %	257
30	285
50	292
70	330
90	381
End Point	463

^a From reference (2).

the Fuel Oil mode are more aromatic than the distillates recycled in the Intermediate mode. The change in mode results in a significant increase in alkyl beta and gamma protons. Since the aliphatic protons are indicative of a poorer physical solvent, we would expect this change to have a negative impact on process performance.

- Analyses of the THF soluble, 975°F⁺ fraction of the HO show it to be much higher in high molecular weight, functional components than the corresponding material from PDU Run 5. The concentration of this refractory material decreased with a decrease in space velocity. For example, the solubility fractionation (LCF) shows an average preasphaltene content (normalized) of 19.5% in the recycled resid from PDU Run 5. The preasphaltene content is 39.4% and 32.7% for the Fuel Oil and Intermediate space velocity modes of PDU 8, respectively.
- The weight average molecular weight of the THF soluble resid in the Fuel Oil mode of PDU 8 was 584 amu, and 578 amu in the intermediate mode. The average molecular weight in PDU 5 was 527 amu in the Syncrude mode. These values were determined by GPC and are probably valid only as relative numbers.
- Because of the segmented nature of this run, it is not possible to analyze the data for evidence of steady-state performance as was done with the PDU 5 data. It is unlikely that the process reached steady-state during the Fuel Oil mode. The data during the last five days of the Intermediate mode operation show less variation, and may represent steady-state values. However, the preceding events in the runs (i.e., the catalyst history) make this questionable.
- Based on the ¹H-NMR data, the quality of the recycle distillate as a liquefaction medium is comparable to that of the PDU 5 recycle distillate. These distillates were shown to be good hydrogen donors.
- The ratio of phenanthrene to selected n-alkyl naphthalenes, used as a measure of catalyst activity, shows little variation for the COT samples throughout the run, and the average value is comparable to the steady-state value from PDU 5. This suggests a rapid catalyst deactivation early in PDU Run 8, possibly accelerated by the operability problems, as opposed to the slower deactivation seen in PDU Run 5.
- The high preasphaltene content of the recycle resid, particularly during the periods of upset during the beginning of the run, may have caused rapid catalyst deactivation. This large content of refractory material may have contributed to the operability problems in the run, many of which involved plugging of various components. These results suggest that a preferable approach to operation in a high space velocity mode is to start the run at a low space velocity, and to increase space velocity while monitoring the preasphaltene content of the recycle resid. In this way it may be possible to establish an upper limit on the recycle rate of preasphaltenes which can be operable in the process. The H-Coal PDU has been operated successfully in the Fuel Oil mode (PDU Run 3), although this 12-day run did not involve catalyst replacement. In comparing these runs it is noteworthy that PDU 3 had an average resid yield of 32.4%, while the resid yield in the fuel oil segment of PDU Run 8 was near 40%. We

cannot say that the high space velocity is directly responsible for the operability problems in PDU 8, but it is clear that a combination of high space velocity and independent operability problems can have a significant effect on overall unit performance.

Section 3

EXPERIMENTAL

A. SAMPLE HANDLING AND PREPARATION

Samples were taken by HRI during days 3 through (23) of PDU Run⁸ and shipped to CCDC in one-quart metal containers, blanketed with argon. Samples were stored at ambient temperatures until analysis.

Clean oil tank samples were analyzed by ¹H-NMR and GC/MS without any further treatment.

Hydroclone overflow samples were distilled in a 1" x 3' jacket heated Vigreux column to an endpoint of 290°C pot and column temperature at 1 torr. 290°C, 1 torr corresponds to an atmospheric boiling point of 535°C. The distillate was analyzed by ¹H-NMR and GC/MS. The 535°C residue was ground using a mortar and pestle and a 5-g sample pressure filtered with freshly distilled tetrahydrofuran (THF) through Whatman No. 42 paper at ambient temperature. The filter cake was washed with THF until the filtrate was colorless. The solids were weighed to determine the insolubles (unconverted coal and mineral matter) then combusted for 1 hr at 800°C in an electric muffle furnace to convert the mineral matter to oxidized ash. The THF was removed from the filtrate by rotary vacuum evaporation. The resultant THF soluble HO resid was analyzed by SESC, LCF, GPC, and ¹H-NMR. These experimental techniques are described below.

B. LIQUID CHROMATOGRAPHIC SEPARATIONS

The 290°C⁺/1 torr THF-soluble fraction of the hydroclone overflow was characterized by three separation procedures. LCF (liquid column fractionation) separates primarily by solubilities. SESC (sequential elution solvent chromatography) separates by solubility and functionality, and GPC (gel permeation chromatography) separates by molecular size.

The apparatus used for all three procedures consists of a Milton-Roy Laboratory Mini-Pump, a Rheodyne 7010 loop-type on-line injector, and a Pye Unicam LCM2 flame ionization detector (FID). The Pye FID response is quantitative for the detection of carbon. It is, therefore, well suited for coal-liquids work, since it will respond equally well to alkyl groups and aromatic compounds. A UV detector, for example, would not respond to alkanes or unconjugated alkenes.

The Pye detector operates by passing a moving stainless steel wire of fine gauge through the effluent stream from the column. Small amounts of column effluent are carried by the wire into an evaporator oven, where the solvent is stripped, leaving the sample deposited on the wire. Since some volatiles can be lost at this point, the detector response decreases with increasing sample volatility. However, the materials analyzed in this work were all non-volatile (535°C⁺).

Upon leaving the evaporator oven, the coated wire passes into a heated (850°C) quartz tube, where the deposited sample is burned in an air stream. The resultant CO₂ passes into a molecular entrainer, where H₂ is mixed with the stream. This mixture is carried into a Ni catalyst chamber. The CO₂ is reduced to CH₄, which is analyzed by the FID.

Because detector response is dependent upon the sample and chromatographic solvent, response factors are determined for LCF and SESC by making preparative runs on large scale columns, with proportional increases in solvent flow and sample size. Fractions obtained are rotary evaporated, vacuum dried and weighed. Response factors are calculated as the ratio of detector response to fraction weight. Given the relatively minor variations in hydrocyclone overflow residuum composition for a given PDU run, it was assumed that one set of response factors was adequate for all samples from that run. LCF and SESC response factors were determined for each PDU run. Since GPC uses only one solvent, no factors were required.

1. LCF

Liquid column fractionation (LCF) is a method which separates THF soluble coal extracts into the following categories. (1) oils (hexane-solubles), (2) asphaltenes (benzene-soluble/hexane insoluble) and (3) preasphaltenes (pyridine-soluble/benzene insoluble). The LCF procedure⁽⁴⁾ consists of injecting a THF dissolved sample onto a 2 x 1000 mm glass column packed with glass beads (Analabs, 70/80 mesh). The solvents are then pumped through the column sequentially at a flow rate of 1.5 ml/min; hexane (5 min), benzene (8 min) and pyridine (8 min) to elute oils, asphaltenes, and preasphaltenes, respectively. Sample size is 20 µl and the sample concentration is approximately 0.050 g/ml in THF. Peak areas were measured with an LDC computing integrator in the digitize mode. Response factors were applied to the peak areas (raw data) to obtain weight percentages of the three fractions.

The LCF method is not expected to reproduce the more conventional Soxhlet methods. However, it is a rapid, reproducible, and of acceptable analytical precision⁽⁴⁾. Its rapidity (~ 20 min) makes it much more suitable for process monitoring than the Soxhlet methods which have a turnaround time of several days.

2. SESC

SESC (sequential elution solvent chromatography) is an adsorption technique, in which stepwise increases in solvent strength elute seven discrete fractions, each corresponding to a different compound functionality type, from the stationary phase (Woelm silica gel, 63 x 100 µ, Brockmann activity I, with 4% H₂O added). The procedure for this project is a modified version of the method developed by Farcasiu⁽⁵⁾. Seven solvents are used in the sequence, which, along with the compounds eluted in each fraction, are listed below.

<u>Fraction</u>	<u>Solvent</u>	<u>Flow Time, min</u>	<u>Content</u>
1	85/15 Hexane/Benzene	17	Saturates + aromatics
2	Chloroform	19	Polar aromatics, furans, thiazoles, non-basic N

<u>Fraction</u>	<u>Solvent</u>	<u>Flow Time, min</u>	<u>Content</u>
3	90/10 Chloroform/Et ₂ O	17	Monophenols
4	97/3 Et ₂ O/EtOH	17	Basic nitrogen, heterocycles
5	MeOH	10	Highly functional material, 10% w/w heteroatoms
6	THF	14	Increasing basic functionality
7	Pyridine	15	Increasing molecular weight

Note that 3% EtOH is added to solvent 4, diethyl ether. This deactivates the silica gel, allowing more highly polar compounds to be eluted by THF and pyridine. Even after deactivation, however, some compounds remain permanently adsorbed. Recoveries from current H-Coal preparative column SESC runs have averaged about 94%, indicating a loss of about 6%.

Run conditions are similar to LCF: flow rate of 1.5 ml/min detector evaporator oven set at 150°C, integration in the digitize mode. The column 2 x 1000 mm glass, is dry-packed with silica gel to 15 cm below the top of the column. The remaining volume is packed with glass beads (70/80 mesh). Due to deactivation and residual adsorption, the column must be repacked for each run with fresh silica gel. Sample size is 100 µl and sample concentrations are about 0.040 g/ml.

The raw data are corrected for THF and pyridine baseline plateaus as well as baseline drift. Response factors determined by preparative runs are used to determine final weight percentages.

3. GPC

Gel permeation chromatography (GPC) is a commonly employed method of obtaining molecular weight distributions^(6,7). A polymer, usually polystyrene or similar inert material, with a specified degree of crosslinking, is the fractionation medium. Depending on the molecular size, molecules passing through the crosslinked polymer structure are retained to a greater or lesser extent, with the largest molecules eluting first. Molecules which are too large to penetrate the polymer structure are excluded. This exclusion produces a peak which appears as a fairly sharp shoulder on the leading edge of the distribution. This distribution is based on effective molecular size rather than molecular weight. Usually, gel permeation columns are standardized with linear medium chain-length oligomers of known average molecular weight. Since coal liquids are made up primarily of aromatic structures, the relationship between the molecular weight and molecular size which exists for the oligomer standards does not hold for coal liquids.

Standardization was accomplished instead by use of field ionization mass spectrometry (FIMS) data obtained on residual coal liquids in other work. FIMS provides a weight distribution vs. molecular weight, which, when fitted to the distribution curve produced by the GPC on the same sample, allows an empirical relationship between elution time and molecular weight to be established. This takes the form:

$$M = e^{(-At + B)} \quad (1)$$

where t is the elution time, M is the molecular weight, and A and B are empirical constants. This relationship is valid only for those molecular weights which elute after the exclusion volume. For the column used, this uppermost weight was 700 amu. Above this weight was the exclusion peak and a small fraction of the distribution ($\sim 5\%$). The remainder of the distribution was arbitrarily divided into 4 cuts, 700 $\rightarrow$ 550 amu, 550 $\rightarrow$ 400 amu, 400 $\rightarrow$ 250 amu, and < 250 amu.

The GPC column was pressure packed with a pre-swelled gel/pyridine slurry. The gel used was Bio-Beads S-X2, 200-400 mesh (Bio-Rad Laboratories, Richmond, California), which is a styrene-divinylbenzene copolymer with 2% crosslinkage. Column dimensions were 3 x 1000 mm. Solvent flow (pyridine) was 0.85 ml/min. Sample size was 20 μ l, with a sample concentration of 0.020 g/ml in pyridine. Column performance was monitored with daily injections of a standard squalane solution. Detector and integrator parameters were the same as those used for LCF and SESC.

C. ^1H -NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (^1H -NMR)

^1H -NMR spectra were recorded on a Varian EM-360L 14 kG instrument. Homogenized COT and HO distillate samples were dissolved in chloroform- d , to make a $\sim 12\%$ v/v solution, then filtered. Homogenized HO THF soluble residue samples were dissolved in pyridine- d to ~ 190 g/l then filtered. An internal tetramethylsilane (TMS) reference was used to lock the RF field. Samples were spun at ~ 50 rpm in 5 mm OD precision sample tubes. Spectra were scanned from 10.5 to 0 ppm over 5 min at 0.5 mG RF power.

We investigated the use of elevated sample temperatures for the HO THF soluble residue but determined there to be no significant improvement. All samples were, therefore, run at ambient temperature.

Integrations for the distillate fractions (COT and HO 290°C, 1 torr) were performed in duplicate on the instrument using a sweep rate of 2 min. The integrations were divided into seven regions corresponding to seven proton types.

<u>Chemical Shift</u> <u>(TMS), ppm</u>	<u>Proton Type</u>	<u>Description</u>
10.5 $\rightarrow$ 7.15	Condensed Aromatics	Proton attached to a condensed aromatic ring
7.15 $\rightarrow$ 4.6	Uncondensed Aromatics and Hydroxyl	Proton attached to an uncondensed aromatic ring or to oxygen
4.6 $\rightarrow$ 2.5	Cyclic Alpha	Proton on naphthenic carbon adjacent to fused aromatic ring of naphtheno-aromatics
2.5 $\rightarrow$ 2.0	Alkyl Alpha	Methyl or non-cyclic methylene or methylenidene proton adjacent to aromatic ring

2.0	1.4	Cyclic Beta	Naphthenic protons. Naphthenic protons two positions from the aromatic ring of naphtheno-aromatics.
1.4	1.0	Alkyl Beta	Interior protons of paraffins. Methyl protons two positions from an aromatic ring. Non-cyclic methylene protons two or more positions from an aromatic ring.
1.0	0.5	Gamma	Terminal methyl protons of paraffins or alkyl sidechains three or more positions from an aromatic ring.

Integrations of the spectra of the HO THF soluble residue samples were performed by planimetry in triplicate. This method makes it possible to subtract the effects of pyridine peaks and any remaining THF. The integrations were divided into four regions corresponding to four proton types as previously described.

<u>Chemical Shift (TMS)</u>	<u>Proton Type</u>
10.5 → 4.6 ppm	Aromatics and Hydroxyl
4.6 → 2.0 ppm	Alpha
2.0 → 1.0 ppm	Beta
1.0 → 0.5 ppm	Gamma

D. GC/MS

Each distillate sample was analyzed by gas chromatography/mass spectrometry (GC/MS) using a Hewlett-Packard 5992 GC/MS with a 60 m x 0.25 mm SP-2100 glass WCOT column. An internal standard (~ 2 wt %) of indan was added for quantitation. The temperature program ran from 100 to 270°C @ 4°/min and was then held at 270°C for 25 min. The carrier gas (99.9999% helium) was held at a constant head pressure of ~48 psig and gave a flow of 2.6 ml/min @ 100°C. Neat samples were injected without splitting (10 nl of ~5% sample in THF).

The mass spectrum of each GC peak and that of its background were stored on flexible disc. Each background spectrum was subtracted from its corresponding peak spectrum and the background subtracted mass spectrum of each GC peak was searched for matches vs. our library of ~ 300 coal-related compounds. Typically there were between 150 and 300 GC peaks of which ~ 60 matched our library spectra. Identifications of those peaks which did not match were based on their mass spectra and retention times and are occasionally only tentative.

Quantitation is based on the peak height of the background subtracted peaks relative to the internal standard assuming uniform response. The data area, therefore, semi-quantitative.

Section 4

RESULTS AND DISCUSSION

A. RECYCLE COMPOSITION

The normalized distribution of the hydroclone overflow components (distillate, resid and solids) is given in Table 4-1. The recycle rates of these components, the clean oil tank material and makeup solvent are given in Table 4-2. We did not receive samples for days 10 and 16 and the data from day 7 (possibly days 8 and 9) suggest that the samples were not representative. Table 4-3 compares the average data from each of the four run segments of PDU 8 with average data from periods 12-30 of PDU Run 5. As noted in the previous report PDU 5 had made a reasonable approach to steady-state by day 12. As in PDU 5, the hydroclone overflow was rich in distillate for the first few days of the run. After the first shutdown the HO sample we received was high in resid, and as will be shown below, this resid was high (> 50%) in preasphaltenes. This may have accelerated catalyst deactivation and enhanced plugging problems which occurred during the run, if we accept these as being representative samples.

The third run segment, "C", was plagued by catalyst addition and removal problems. The concentration of resid and solids in the HO was still high, although the concentration of preasphaltenes in the resid dropped to around 40% during this part of the run.

The segment of the run in the Intermediate mode, "D", showed improved operability corresponding to a drop in the resid content of the HO, and a drop in the preasphaltene content of the HO resid to around 33%. The average values for the HO composition during this stage of the run (Table 4-3) are similar to those during PDU 5 although the resid was higher in preasphaltenes.

B. LIQUID CHROMATOGRAPHIC SEPARATIONS OF THF SOLUBLE HO RESID (975°F⁺)

1. Solubility Fractionation

The normalized LCF data are given in Table 4-4. In Table 4-5 these data have been put on a wt % hydroclone overflow basis. They show a gradual increase in the preasphaltene content of the recycle resid during the first six days of the run. The sample from day 7, which contained 72% distillate, was not representative. On day 8 the percent resid in the hydroclone overflow and the concentration of preasphaltenes in the resid were very high. The preasphaltene content dropped on day 9, but the % resid was still very high. After restarting on day 11 the preasphaltene content of the HO decreased through day 15, and further declined during operation in the Intermediate mode.

Table 4-6 compares the solubility fractionations of the HO resids from the Fuel Oil (SV = 78) and Intermediate (SV = 50) modes of PDU 8 with the Syncrude mode (SV = 31) used in PDU 5. The higher quality of the recycled

Table 4-1

Distribution of Hydroclone Overflow Components
H-Coal PDU Run 8

<u>Run Period</u>	<u>Wt % of Hydroclone Overflow</u>			
	975°F ⁺			
	975°F ⁻ <u>Distillate</u>	THF Soluble <u>Resid</u>	Unconverted <u>Coal</u>	<u>Ash</u>
2	57.8	34.5	2.5	4.6
3	47.7	42.3	3.8	5.8
4	45.3	43.7	4.4	5.6
5	45.1	44.0	4.5	5.7
6	45.5	42.9	5.5	5.5
7	72.3	23.7	1.6	1.4
8	31.9	51.0	7.7	8.2
9	31.9	50.8	8.3	8.5
10	--	--	--	--
11	41.3	47.9	5.0	5.4
12	36.8	48.4	7.7	6.5
13	31.5	49.0	10.5	8.6
14	31.8	47.9	9.4	10.3
15	26.2	47.5	12.9	11.8
16	--	--	--	--
17	31.1	49.0	10.0	10.3
18	36.5	46.0	7.5	8.1
19	43.7	42.0	7.5	6.3
20	43.2	42.2	7.6	6.4
21	40.5	42.0	8.7	8.2
22	44.2	42.9	6.1	6.3
23	42.2	43.5	6.2	7.1

Table 4-2

Recycle Rates of Slurry Oil Components
H-Coal PDU Run 8

Run Period	Recycle Rate, lb/lb Coal					
	COT	Makeup Oil	HO Distillate	HO, THF Soluble Resid	Unconverted Coal	Ash
2	1.38	0.00	0.52	0.41	0.02	0.04
3	1.25	0.00	0.55	0.49	0.04	0.07
4	1.02	0.00	0.52	0.50	0.05	0.06
5	0.92	0.00	0.55	0.54	0.06	0.07
6	1.02	0.00	0.52	0.49	0.06	0.06
7	0.71	0.00	0.56	0.18	0.01	0.01
8	1.03	0.00	0.38	0.60	0.09	0.10
9	1.03	0.00	0.40	0.63	0.10	0.11
10	0.85	0.00	--	--	--	--
11	1.02	0.00	0.43	0.50	0.05	0.06
12	0.91	0.00	0.37	0.48	0.08	0.06
13	0.81	0.00	0.36	0.56	0.12	0.10
14	0.86	0.05	0.36	0.55	0.11	0.12
15	1.17	0.06	0.43	0.79	0.21	0.20
16	1.35	0.00	--	--	--	--
17	0.93	0.01	0.45	0.70	0.14	0.15
18	0.87	0.02	0.50	0.63	0.10	0.11
19	0.97	0.02	0.60	0.58	0.10	0.09
20	0.77	0.02	0.61	0.59	0.11	0.09
21	0.91	0.04	0.73	0.75	0.16	0.15
22	0.60	0.36	0.64	0.62	0.09	0.09
23	0.62	0.24	0.63	0.64	0.09	0.11

Table 4-3

Distribution of Hydroclone Overflow Components
H-Coal PDU Runs 5 and 8

<u>Run Segment</u>	<u>Run Period</u>	<u>Average Wt % for Run Segment</u>			
		<u>975°F⁻</u>	<u>975°F⁺ THF Soluble</u>	<u>Unconverted Coal</u>	<u>Ash</u>
A	3-6	45.9	43.2	4.6	5.6
B	8-9	31.9	50.9	8.0	8.4
C	11-15	33.5	48.1	9.1	8.5
D	17-23	40.5	43.9	7.7	7.5
PDU Run 5	12-30	42.5	43.4	5.4	8.3

Table 4-4

LCF Fractionation of Hydroclone Overflow THF Soluble Resid
H-Coal PDU Run 8

<u>Run</u> <u>Period</u>	<u>Wt %, Normalized</u>		
	<u>Oils</u>	<u>Asphaltenes</u>	<u>Preasphaltenes</u>
2	40.5	29.3	30.2
3	40.4	28.9	30.7
4	37.1	29.2	33.7
5	32.3	30.1	37.6
6	26.9	31.0	42.0
7	22.2	25.4	52.4
8	32.4	11.7	55.9
9	32.6	32.0	35.4
10	--	--	--
11	25.5	31.3	43.3
12	26.5	31.9	41.7
13	28.7	33.7	37.5
14	28.9	33.4	37.7
15	32.2	33.9	33.9
16	--	--	--
17	33.2	34.1	32.7
18	32.3	33.3	34.4
19	33.0	33.5	33.5
20	33.4	33.3	33.3
21	34.6	33.3	32.1
22	32.9	33.4	33.7
23	36.2	34.2	29.7

Table 4-5

LCF Fractionation of Hydroclone Overflow
on a Wt % HO Basis
H-Coal PDU Run 8

Run Period	Wt % of Hydroclone Overflow		
	Oils	Asphaltenes	Preasphaltenes
2	14.0	10.1	10.4
3	17.1	12.2	13.0
4	16.2	12.8	14.7
5	14.2	13.2	16.5
6	11.5	13.3	18.0
7	5.3	6.0	12.4
8	16.5	6.0	28.5
9	16.6	16.3	18.0
10	--	--	--
11	12.2	15.0	20.7
12	12.8	15.4	20.2
13	14.1	16.5	18.4
14	13.8	16.0	18.1
15	15.3	16.1	16.1
16	--	--	--
17	16.3	16.7	16.0
18	14.9	15.3	15.8
19	13.9	14.1	14.1
20	14.1	14.1	14.1
21	14.5	14.0	13.5
22	14.1	14.3	14.5
23	15.7	14.9	12.9

Table 4-6

Comparison of THF Soluble Resid Composition
H-Coal PDU Runs 5 and 8

<u>PDU Run</u>	<u>Period</u>	<u>Space Velocity</u>	<u>Wt % THF Soluble Resid^a</u>		
			<u>Oils</u>	<u>Asphaltenes</u>	<u>Preasphaltenes</u>
5	12-30	31	49.0	32.9	18.1
8	11-15	78	28.4	32.8	38.8
8	17-23	50	33.7	33.6	32.7

^a Average values, cf. text.

resid in PDU 5 is quite apparent, as is the improvement in resid quality during PDU 8 concurrent with the decrease in space velocity. The LCF method is apparently a sensitive indicator of recycle resid quality.

We believe that this high concentration of preasphaltenes in the recycled HO may have been responsible for or at least related to operability problems encountered particularly during the first stage of the run. On day 2, the unit was shut down by a plug in the slurry feed system. During period 5 a hydroclone failed, and an alternate hydroclone was put on line. On day 6 service was reestablished with the original hydroclone, but the underflow line to the vacuum still plugged. Attempts to restart the unit between periods 6 and 7 were hampered by a restriction in the internal recycle pump section. Later in the run both the catalyst addition and withdrawal systems became plugged.

All of these problems are consistent with the high concentration of preasphaltenes in the recycled resid. This in turn was no doubt aggravated by the swings in reactor temperature and hydrogen partial pressure which accompanied the various shutdowns and startups. These upsets no doubt greatly accelerated catalyst deactivation which would in turn increase the concentration of preasphaltenes in the process streams. Dropping the space velocity to the Intermediate mode seems to have ameliorated these difficulties although the period of Intermediate mode operation was short.

2. SESC Fractionation of the THF Soluble Resid

Normalized SESC data on the THF soluble HO resid from PDU Run 8 are given in Table 4-7. The yield of the least functional material (Fraction 1) decreased rapidly in the first few days of the run, with a corresponding increase in Fractions 6 and 7. The data show considerable scatter, outside the range of experimental uncertainty of the SESC method. The data look better during the middle of the run (days 11-15), and these data are probably more representative of recycle resid composition in the Fuel Oil mode.

Table 4-8 compares average SESC data during the four run segments of PDU Run 8 with the average results from PDU Run 5. The recycled resid from the Syncrude mode contains significantly less functional material. There is also a shift in the distribution, toward the less functional components, between operation in the Fuel Oil mode during days 11-15 and Intermediate mode operation (days 17-23). However, the change in composition is less obvious in the SESC data than in the LCF data reported above.

The comments made for the LCF analyses are equally pertinent here. The much greater concentration of functional material in the recycled resid in the Fuel Oil mode is a potential cause of the operability problems encountered in PDU Run 8.

3. Molecular Size Separation of the Soluble Resid

The molecular size distributions, by GPC, for the HO resids of PDU Run 8 are given in Table 4-9. The average molecular weight of the resid averaged 578 ± 24 amu as compared to 527 ± 12 amu during PDU Run 5. During the Intermediate mode segment of PDU 8 the average molecular weight was 576 ± 13 amu, not significantly less than during the Fuel Oil operation. These data are consistent with the LCF and SESC data, indicating a lighter resid in the Syncrude mode.

Table 4-7

SESC Fractionation of Hydroclone Overflow THF Soluble Resid
H-Coal PDU Run 8

Run Period	Wt % SESC Fraction, normalized						
	1	2	3	4	5	6	7
2	23.1	15.3	12.5	13.1	13.2	19.0	3.8
3	20.1	15.2	16.3	14.7	5.8	23.2	4.8
4	16.3	13.3	13.6	18.3	8.3	25.6	4.6
5	15.3	15.6	16.4	19.6	3.5	26.3	3.3
6	13.2	13.2	15.9	14.1	5.3	30.4	7.9
7	15.4	11.8	13.4	25.5	10.7	18.6	4.7
8	15.8	15.5	14.8	19.0	8.9	22.7	3.2
9	13.4	13.5	14.6	22.6	8.9	23.8	3.2
10	--	--	--	--	--	--	--
11	12.2	11.9	14.9	25.9	7.9	22.3	4.8
12	14.6	12.5	13.3	22.2	4.7	28.2	4.6
13	10.1	14.3	16.1	21.2	6.1	28.5	3.6
14	12.0	13.6	15.3	21.9	5.9	27.7	3.7
15	13.5	13.9	13.5	18.2	11.5	25.8	3.5
16	--	--	--	--	--	--	--
17	13.1	14.0	14.1	21.9	8.0	26.1	2.8
18	13.5	12.7	12.2	19.3	11.2	27.5	3.5
19	15.5	14.4	14.7	21.7	6.8	23.7	3.2
20	16.3	15.5	15.4	19.3	6.6	23.0	3.0
21	13.2	13.2	15.9	14.1	5.3	30.4	7.9
22	16.1	14.2	14.5	20.8	5.9	24.4	4.1
23	17.4	15.4	13.4	18.6	3.7	27.1	4.4

Table 4-8

Comparison of SESC Fractionation of THF Soluble Resid
H-Coal PDU Runs 5 and 8

Run	Average Wt % of SESC Fraction						
<u>Period</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
3-6	16.2	14.3	15.6	16.7	5.7	26.4	5.2
7-9	14.9	13.6	14.3	22.3	9.5	21.7	3.7
11-15	12.5	13.2	14.6	21.9	7.2	26.5	4.2
17-23	15.0	14.2	14.3	19.4	6.8	26.0	4.1
PDU Run 5 ^a	24.9	19.8	21.2	7.5	4.1	17.4	5.1

^a Average for days 12-30.

Table 4-9

Molecular Size Separation of Hydroclone Overflow THF Soluble Resid
H-Coal PDU Run 8

Run Period	Wt %					$\bar{M}_w^a$
	> 700 ⁺ amu	550 x 700 amu	400 x 550 amu	250 x 400 amu	< 250 ⁻ amu	
2	22.1	20.5	41.7	15.7	0.1	554
3	23.3	20.0	39.6	17.1	0.0	555
4	27.6	22.2	36.1	14.0	0.0	577
5	29.3	21.2	32.7	15.6	1.2	575
6	34.9	28.2	26.4	10.5	0.0	615
7	34.0	15.5	42.6	7.9	0.0	597
8	31.1	22.3	34.2	12.4	0.0	591
9	26.1	14.8	43.1	13.9	2.0	555
10	--	--	--	--	--	--
11	37.9	18.8	32.0	11.3	0.0	609
12	32.3	23.9	32.7	11.1	0.0	599
13	27.2	23.1	36.2	13.4	0.1	578
14	34.0	18.7	36.2	11.1	0.0	597
15	29.3	22.7	36.2	11.8	0.0	587
16	--	--	--	--	--	--
17	17.5	18.3	34.4	28.6	1.2	513
18	30.3	19.1	36.1	14.4	0.1	580
19	27.3	23.1	36.0	13.6	0.0	578
20	28.1	19.5	37.1	14.1	1.1	571
21	27.4	19.9	38.1	14.5	0.1	572
22	29.3	23.2	42.9	4.6	0.0	598
23	22.5	22.1	39.5	15.9	0.0	557

Avg. $\bar{M}_w = 578 \pm 24$ amu

^a Weight average molecular weight calculated assuming that the $\bar{M}_w$ of the 700⁺ amu component is 800 amu and that of the 250⁻ amu component is 250 amu.

C. ¹H-NMR ANALYSES OF SLURRY RECYCLE OIL COMPONENTS

1. Clean Oils Tank

In the report on PDU Run 5, the ¹H-NMR data proved to be very useful in establishing the quality of the recycle distillates as liquefaction media, and in determining the approach of the recycle oil to steady-state⁽¹⁾. Because of the planned and unplanned changes in the process conditions during PDU Run 8 we are unable to make any statistical statement concerning steady-state performance. For this reason we are content to report the normalized proton distributions, for comparison of the composition in the different modes of H-Coal operation, rather than converting the data to a recycle rate basis. The latter is necessary for determining the approach to steady-state.

Table 4-10 gives the proton distributions for the COT samples from PDU Run 8. The definitions of the different proton types were given in the first topical report⁽¹⁾. We note first that the samples on days 2, 7, 22 and 23 are much higher in condensed aromatics than during the remainder of the runs. (The HO distillates also show this, vide infra). This is evidence of makeup or startup oil in the samples. The condensed aromatics are also high on day 11, like day 7 a restart period. Eliminating data from these days, we get the average proton distributions for the fuel oil and intermediate mode periods shown in Table 4-11. For comparison, the average proton distribution for days 12-30 of PDU Run 5 is also shown. The proton distributions for the Intermediate and Syncrude operations are very similar, except that the COT samples from the Intermediate mode are higher in alkyl beta and gamma protons. The Fuel Oil mode produced a more aromatic recycle distillate. The change in proton distribution on going from the Fuel Oil to the Intermediate mode is significant. The increase in alkyl beta and gamma protons is indicative of a poorer solvent for the coal liquids.

The ratios of condensed-to-uncondensed aromatic protons and cyclic-to-alkyl aliphatic protons correlate with the hydrogen donor and physical solvent quality of the recycle distillates. These parameters are compared below for the three space velocities.

PDU Run	Period	Mode	Condensed Aromatics Uncondensed	Cyclic Alkyl Aliphatics
8	11-15	Fuel Oil	2.27	0.74
8	17-21	Intermediate	2.30	0.70
5	21-30	Syncrude	1.89	0.77

These data indicate that the average COT sample in the Fuel Oil mode is the best liquefaction solvent. The higher space velocity no doubt mitigates the over-hydrogenation of the distillate which was shown to occur in the Syncrude mode⁽¹⁾. All of these "average" distillates are good liquefaction media.

2. Hydroclone Overflow Distillate

The normalized proton distributions of the HO distillates (975°F) are given in Table 4-12. These show the same high concentrations of aromatic protons on days 2, 7, 11 and 23 as do the COT samples. Averaging the data from the remaining periods gives the results shown in Table 4-13, for the Fuel Oil and Intermediate modes. For comparison, the average proton distribution for days 12-30 of Run 5 are also shown. These data are similar to the NMR data on the COT samples

Table 4-10

Proton Distribution - Clean Oil Tank Samples
H-Coal PDU Run 8

Run Period	Wt % Total Hydrogen						
	Condensed Aromatics	Uncondensed Aromatics	Cyclic α	Alkyl α	Cyclic β	Alkyl β	γ
2	63.2	7.9	10.3	8.2	2.9	4.8	2.6
3	23.1	10.0	17.6	10.9	16.8	16.4	5.2
4	20.9	9.8	16.9	11.3	15.2	17.0	8.8
5	21.7	8.9	17.6	11.8	14.4	17.1	8.5
6	21.8	8.2	18.0	12.3	14.0	17.8	7.9
7	65.5	7.4	10.2	8.4	2.5	4.0	2.0
8	23.9	9.4	16.0	11.6	13.3	18.5	7.4
9	22.0	9.8	16.3	12.4	12.8	18.0	8.6
10	--	--	--	--	--	--	--
11	26.2	10.6	15.8	11.0	13.3	15.1	8.0
12	25.0	9.9	15.9	12.0	12.5	16.5	8.3
13	23.6	9.2	16.4	12.5	12.5	17.8	8.0
14	19.9	9.6	15.5	13.2	12.5	20.1	9.2
15	17.6	10.2	16.4	13.5	12.7	20.5	9.2
16	--	--	--	--	--	--	--
17	17.4	8.5	15.9	11.7	15.2	21.2	10.0
18	18.2	8.3	16.0	12.0	13.9	21.3	10.2
19	18.4	8.1	16.2	12.0	13.1	22.0	10.2
20	18.2	7.7	16.1	11.5	13.8	22.2	10.6
21	20.8	7.9	17.2	11.7	13.5	18.9	10.0
22	39.9	6.8	13.8	10.0	8.6	14.0	6.8
23	34.7	8.7	13.4	10.6	10.4	14.4	7.7
Start Up Oil	70.7	5.6	10.2	7.6	1.4	2.7	1.6

Table 4-11

Comparison of Proton Distributions -
Clean Oil Tank (COT) Sample
H-Coal PDU Runs 5 and 8

PDU Run	Space Velocity	Normalized Proton Distribution ^a						
		Condensed Aromatic	Uncondensed Aromatic	Cyclic α	Alkyl α	Cyclic β	Alkyl β	γ
5	31	19.6	10.5	16.5	12.5	13.9	17.7	9.3
8	78	22.2	9.6	16.6	12.9	13.6	17.7	8.1
8	50	18.6	8.1	16.3	11.8	13.9	21.1	10.2

^a Average values, cf. text.

Table 4-12

Proton Distribution - Hydroclone Overflow Distillate
H-Coal PDU Run 8

Run Period	Wt % Total Hydrogen						
	Condensed Aromatics	Uncondensed Aromatics	Cyclic α	Alkyl α	Cyclic β	Alkyl β	γ
2	33.5	8.6	17.1	8.7	14.1	11.9	6.0
3	27.2	8.9	17.6	10.3	13.9	14.5	7.6
4	25.6	8.4	18.7	11.0	13.9	15.1	7.4
5	24.9	8.3	18.4	11.8	13.6	15.6	7.5
6	24.5	8.6	18.5	12.1	12.9	16.1	7.7
7	31.9	7.6	17.8	8.9	13.6	13.5	6.6
8	29.6	8.1	17.8	11.4	11.9	14.6	6.6
9	26.8	9.1	18.1	12.2	11.8	15.2	6.7
10	--	--	--	--	--	--	--
11	31.1	8.4	17.0	10.9	12.0	14.1	6.5
12	28.6	9.0	16.7	11.8	11.4	14.3	7.2
13	27.3	10.2	16.4	12.8	10.9	15.3	7.2
14	23.7	11.0	16.2	13.2	11.1	16.7	8.2
15	23.2	11.2	16.7	13.6	11.1	16.3	7.8
16	--	--	--	--	--	--	--
17	24.6	9.3	17.2	11.7	12.0	17.3	7.9
18	21.4	8.6	16.4	12.1	12.5	19.4	9.6
19	19.4	8.6	15.8	11.7	12.8	21.2	10.4
20	20.4	8.2	16.5	11.8	12.9	20.2	10.0
21	22.4	8.3	16.7	11.8	12.3	19.1	9.4
22	21.8	8.8	16.3	11.7	12.9	19.0	9.4
23	30.5	8.9	16.7	11.0	11.7	14.1	7.1

Table 4-13

Comparison of Proton Distributions -
Hydroclone Overflow Distillate (525°C)
H-Coal PDU Runs 5 and 8

PDU Run	Space Velocity	Normalized Proton Distribution ^a						
		Condensed Aromatics	Uncondensed Aromatics	Cyclic α	Alkyl α	Cyclic β	Alkyl β	γ
5	31	26.7	11.1	17.3	12.2	11.9	13.5	7.3
8	78	26.6	9.2	17.5	11.9	12.2	15.3	7.3
8	50	21.6	8.6	16.5	11.8	12.5	19.4	9.5

^aAverage values, cf. text.

in that the proton distributions are not strongly dependent on the operating mode. There is a decrease in the aromatic protons on going from the Fuel Oil to the Intermediate mode, with a concurrent increase in the concentrations of alkyl beta and gamma protons.

The ratios of condensed-to-uncondensed aromatic protons and cyclic-to-alkyl aliphatic protons calculated from the average data in Table 4-13 are given below.

PDU Run	Period	Mode	Condensed Aromatics Uncondensed	Cyclic Aliphatics Alkyl
8	11-15	Fuel Oil	2.76	0.80
8	17-21	Intermediate	2.52	0.71
5	21-30	Syncrude	2.36	0.88

The cyclic/alkyl aliphatic ratio is substantially lower for the Intermediate mode than for either the Fuel Oil or Syncrude modes. It is very possible that this would not be the case if the entire run had been made in the Intermediate mode, that is, if it had lined out without the various operational difficulties at the beginning of the run.

While there are statistically significant differences among the recycle distillates at the various space velocities, they are small. It seems unlikely that these differences are great enough to have a major impact on process performance. It appears that material which is reduced into the distillate range is relatively constant in composition, regardless of the operating mode, and that the major differences occur in the composition of the resid, as was seen in Section 4-B.

3. Hydroclone Overflow THF Soluble Resid

Proton distributions of the HO resid samples are given in Table 4-14. These show little variation throughout the run, and are lower in aromatic protons than the recycled resid from the steady-state period of PDU Run 5. (Table 4-15). The major differences in chemical functionality which were seen in the liquid chromatographic separations (Section 4-B) are not apparent in the ¹H-NMR data. This is not surprising, since functional groups do not have a big impact on the proton distribution. This is because the number of protons associated with the functional group is small relative to the importance of the functionality in determining the chemistry of the molecule.

D. GC/MS Analyses of Recycle Distillates

Figure 1 is a total ion chromatogram of the HO distillate from period 21. HO distillates from the other periods are qualitatively similar. An example of a COT distillate from PDU 5 was given in the first topical report. The COT distillates have a greater concentration of lighter components, but show essentially the same components. Table 4-16 gives peak identifications corresponding to Figure 1. Uncertain assignments are given in parentheses.

As with the Run 5 samples, the PDU 8 recycle distillates are dominated by pyrene, methylphenanthrenes, phenanthrene and the cracking and isomerization products of the hydrophenanthrenes. The means used to make these

Table 4-14

Proton Distribution - Hydroclone Overflow THF Soluble Resid
H-Coal PDU Run 8

Run Period	Wt % Total Hydrogen			
	Aromatic	α	β	γ
2	37.0	33.4	23.8	5.8
3	41.0	32.6	21.3	5.1
4	40.4	33.0	21.6	5.0
5	40.2	33.5	21.3	5.0
6	39.7	34.2	21.3	4.9
7	33.0	36.2	24.8	6.0
8	42.1	32.9	20.2	4.9
9	42.7	32.3	20.5	4.5
10	--	--	--	--
11	40.2	32.5	22.1	5.2
12	43.7	30.2	21.0	5.1
13	44.9	32.0	19.0	4.1
14	44.2	32.0	19.4	4.4
15	47.3	29.8	18.0	4.9
16	--	--	--	--
17	41.2	32.9	21.1	4.9
18	43.3	31.4	20.3	5.0
19	40.6	32.7	21.5	5.2
20	42.3	31.8	20.9	5.0
21	43.3	32.8	19.4	4.5
22	40.3	32.6	21.6	5.4
23	42.8	32.7	20.0	4.4

Table 4-15

Comparison of Proton Distributions - HO THF Soluble Resids -
H-Coal PDU Runs 5 and 8

<u>PDU</u> <u>Run</u>	<u>Period</u>	<u>Space</u> <u>Velocity</u>	<u>Normalized Proton Distribution^a</u>			
			<u>Aromatic</u>	<u>α</u>	<u>β</u>	<u>γ</u>
5	12-30	31	46.5	30.2	18.5	4.8
8	11-15	78	42.0	32.4	20.7	4.9
8	17-23	50	44.1	31.3	19.9	4.7

^aAverage values, cf. text.

Table 4-16

Peak Identifications of Gas Chromatogram of
Hydroclone Overflow Distillate - Period 21 - PDU Run 8

1. benzofuran	69. (C ₂ -acenaphthene)
2. indan (internal standard)	70. tetrahydroanthracene
3. 1-methylindan	71. tetrahydrophenanthrene
4. 5-methylindan	72. (C ₃ -acenaphthene)
5. 4-methylindan	73. unknown
6. tetralin	74. phenanthrene
7. naphthalene	75. (methyl dihydrophenanthrene)
8. dimethylindan	76. (methyl dihydrophenanthrene)
9. dodecane	77. (C ₃ -acenaphthene)
10. 2-methyltetralin	78. (C ₃ -acenaphthene) and (methyl dihydrophenanthrene)
11. 1-methyltetralin	79. (C ₃ -acenaphthene)
12. ethylindan	80. octadecane
13. C ₂ -indan	81. (methyl dihydrophenanthrene)
14. 6-methyltetralin	82. phytane, i.e., 2,6,10,14-tetramethylhexadecane and C ₂ -tetrahydrophenanthrene)
15. C ₃ -indan	83. (C ₂ -tetrahydrophenanthrene)
16. 5-methyltetralin	84. unknown
17. 2-methylnaphthalene	85. (methyl tetrahydrophenanthrene)
18. 1-methylnaphthalene and tridecane	86. unknown
19. cyclohexylbenzene and C ₂ -tetralin	87. (methyl tetrahydrophenanthrene)
20. 1 or 2-ethyltetralin	88. methylphenanthrene
21. C ₃ -tetralin	89. methylphenanthrene
22. 5 or 6-ethyltetralin	90. (C ₂ -dihydrophenanthrene)
23. C ₃ -tetralin	91. nonadecane
24. biphenyl and tetrahydroacenaphthene	92. hexahdropyrene
25. C ₂ -tetralin	93. unknown
26. ethylnaphthalene	94. unknown
27. dimethylnaphthalene	95. 2-phenylnaphthalene
28. tetradecane	96. unknown
29. dimethylnaphthalene and methyl-cyclohexylbenzene	97. C ₂ -phenanthrene
30. methyltetrahydroacenaphthene or tetrahydrobenzindan	98. (C ₃ -tetrahydrophenanthrene)
31. dimethylnaphthalene	99. C ₂ -phenanthrene
32. n-propyltetralin	100. eicosane
33. C ₃ -naphthalene	101. (C ₂ -dihydrophenanthrene)
34. methyltetrahydroacenaphthene or tetrahydrobenzindan	102. unknown
35. methyltetrahydroacenaphthene or tetrahydrobenzindan	103. dihydropyrene and unknown
36. C ₄ -tetralin and unknown	104. unknown
37. acenaphthene and (methylbiphenyl)	105. fluoranthene
38. n-propylnaphthalene	106. unknown
39. C ₄ -tetralin	107. C ₃ -phenanthrene
40. isopropyl or methylethylnaphthalene	108. C ₃ -phenanthrene
41. pentadecane	109. unknown
42. C ₃ -naphthalene	110. C ₃ -phenanthrene
43. C ₄ -tetralin and (C ₂ -tetrahydroacenaphthene)	111. pyrene
44. methyl-n-propyl or sec-butylnaphthalene	112. heneicosane
45. n-butyltetralin	113. C ₃ -phenanthrene
46. tetrahydrobenzindan or methyltetrahydroacenaphthene	114. unknown
47. fluorene	115. methylpyrene or methylfluoranthene
48. benzindan or methylacenaphthene	116. unknown
49. n-butyl or isobutylnaphthalene	117. C ₃ -phenanthrene
50. benzindan or methylacenaphthene	118. unknown
51. benzindan or methylacenaphthene	119. methylpyrene or methylfluoranthene
52. hexadecane	120. methylpyrene or methylfluoranthene
53. (methylbenzindan)	121. docosane
54. (methylbenzindan)	122. methylpyrene or methylfluoranthene
55. methyl dibenzofuran	123. methylphenylnaphthalene
56. (methylbenzindan)	124. methylphenylnaphthalene
57. (methylbenzindan)	125. methylpyrene or methylfluoranthene
58. (C ₃ -acenaphthene)	126. methylpyrene or methylfluoranthene
59. dihydroanthracene	127. (C ₂ -phenylnaphthalene)
60. (C ₃ -acenaphthene)	128. tricosane
61. octahydroanthracene	129. C ₂ -pyrene or C ₂ -fluoranthene
62. dihydrophenanthrene	130. C ₂ -pyrene or C ₂ -fluoranthene
63. octahydrophenanthrene	131. (C ₂ -phenylnaphthalene)
64. (methylbenzindan)	132. C ₂ -pyrene or C ₂ -fluoranthene
65. methylfluorene	133. (C ₂ -phenylnaphthalene)
66. methyl-n-butylnaphthalene and unknown	134. unknown
67. heptadecane	135. tetrahydrochrysene or isomer
68. pristane, i.e., 2,6,10,14-tetramethylpentadecane and unknown	136. tetracosane
	137. chrysene or isomer
	138. pentacosane
	139. hexacosane
	140. heptacosane
	141. octacosane

Figure 4-1

TOTAL ION CURRENT CHROMATOGRAM OF
290°C/1 torr HYDROCLONE OVERFLOW

Period 21

PDU Run 8

identifications were detailed in the first topical report⁽¹⁾. Tables 4-17 and 4-18 list the cracking and isomerization products from the HO sample shown in Figure 1, along with the percentages of these components based on total ion abundances.

As in the first report⁽¹⁾, we have calculated the ratios of phenanthrene to selected n-alkyl naphthalenes as a measure of hydrogenation activity in the reactor. The alkylnaphthalenes used are peaks 7, 17, 18, 26, 38, 49 and 66, as identified in Table 4-16. The ratios for the COT and HO distillate samples are given in Table 4-19. The average values for PDU 8, discounting those samples which were indicated by the NMR data to contain make-up and start-up solvent, are also reported, along with the averages from PDU Run 5. The phenanthrene/alkylnaphthalenes ratio for the COT samples is the same for the PDU 5 and PDU 8 samples. The HO distillates from PDU 8 have a lower phenanthrene alkylnaphthalenes ratio than the PDU 5 samples, although the mean value for each run lies within one standard deviation of the mean of the other. The NMR data do show a higher aliphatic content in the HO distillate from PDU Run 8, consistent with these results. However, GC/MS data on the HO distillates from PDU Run 8 are not reliable enough to allow a definite conclusion.

In PDU Run 5 the phenanthrene/alkylnaphthalene ratio increased steadily during the run, from an initial value of around 0.15 to a final value near 0.30. In PDU 8 the ratio for the COT samples is relatively constant throughout the run, near 0.30 except for those periods (2, 7, 11, 22 and 23) during which make-up oil was apparently added. These data suggest that the catalyst activity declined to a steady-state level quite early in the run. This may have been the result of the high content of refractory resid used in the recycle stream at the Fuel Oil mode space velocity.

Table 4-17

Cracking Products of Hydrophenanthrenes
HO-88-21

<u>Peak #</u>	<u>Compound</u>	<u>Retention Time, min</u>	<u>% of Sample</u>
6	tetralin	8.3	0.06
7	naphthalene	8.9	0.08
10	2-methyltetralin	9.6	0.04
11	1-methyltetralin	10.1	0.01
14	6-methyltetralin	10.9	0.24
17	2-methylnaphthalene	11.6	0.38
18	1-methylnaphthalene	12.1	0.08
20	1 or 2-ethyltetralin	12.7	0.02
22	5 or 6-ethyltetralin	13.4	0.11
26	1 or 2-ethylnaphthalene	14.4	0.30
32	n-propyltetralin	16.1	0.12
33	isopropyl or methylethyl-naphthalene	16.3	0.06
38	n-propylnaphthalene	17.1	0.43
40	isopropyl or methylethyl-naphthalene	17.8	0.48
39	methylpropyl or sec-butyl-tetralin	17.6	0.20
44	methylpropyl or sec-butyl-naphthalene	18.9	0.10
45	n-butyltetralin	19.2	0.37
49	n-butyl-naphthalene	20.5	1.47
66	methylbutyl or (2-pentyl)-naphthalene	23.8	0.35

Table 4-18

Isomerization Products of Hydrophenanthrenes
HO-88-21

<u>Peak #</u>	<u>Compound</u>	<u>Retention Time</u>	<u>% of Sample</u>
24	biphenyl and tetrahydroace- naphthene (THA)	13.9	0.10
30	methyl-THA or tetrahydrobenzindan	15.8	0.10
34	methyl-THA or tetrahydrobenzindan	16.5	0.06
35	methyl-THA or tetrahydrobenzindan	16.7	0.18
37	acenaphthene and methylbiphenyl	17.1	0.53
46	tetrahydrobenzindan or methyl-THA	19.6	0.32
47	fluorene		
48	benzindan or methylacenaphthene	20.2	1.31
51	benzindan or methylacenaphthene	20.8	0.21
53	methylbenzindan or C ₂ -acenaphthene	21.3	0.10
54	methylbenzindan or C ₂ -acenaphthene	21.4	0.10
56	methylbenzindan or C ₂ -acenaphthene	21.8	0.30
57	methylbenzindan or C ₂ -acenaphthene	22.1	0.49
64	methylbenzindan or C ₂ -acenaphthene	23.4	0.89
65	methylfluorene	23.5	0.16
72	C ₃ -acenaphthene or C ₂ -benzindan	25.0	0.13
77	C ₃ -acenaphthene or C ₂ -benzindan	26.1	0.07
79	C ₃ -acenaphthene or C ₂ -benzindan	26.3	0.04

Table 4-19

Ratio of Phenanthrene to Alkyl naphthalenes
H-Coal PDU Run 8

<u>Run Period</u>	<u>Ratio to Phenanthrene to</u> <u>Alkyl naphthalenes, Total Ion Currents</u>	
	<u>COT</u>	<u>HO</u>
2	0.41	1.50
3	0.43	0.92
4	0.28	0.48
5	0.26	0.52
6	0.29	0.63
7	0.51	--
8	0.27	1.05
9	0.30	1.05
10	--	--
11	0.72	1.26
12	0.24	1.01
13	0.38	0.46
14	0.30	0.50
15	0.13	0.46
16	--	--
17	0.29	0.80
18	0.24	0.36
19	0.26	0.50
20	0.31	0.37
21	0.33	0.53
22	0.28	0.32
23	0.47	0.48

Section 5

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