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DEVELOPMENT OF A CORRELATION BETWEEN SLURRY OIL COMPOSITION AND PROCESS PERFORMANCE

Topical Report 1. Analyses of Slurry Recycle Oils from
H-Coal PDU Run 5

MASTER

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April 1980

Work Performed Under Contract No. AC05-79ET14503

Conoco Coal Development Company
Research Division
Library, Pennsylvania

U. S. DEPARTMENT OF ENERGY

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Topical Report 1

ANALYSES OF SLURRY RECYCLE OILS FROM
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ABSTRACT

Daily samples of the slurry recycle oils from the 30-day H-Coal PDU Run 5 (Syncrude mode, Illinois 6 coal) were analyzed by ^1H -NMR spectroscopy GC/MS, and liquid chromatographic techniques. The recycle oils composition in PDU Run 5 reached an initial steady-state at about day 12, but this was upset when the hydrogen partial pressure was increased on day 20. The recycle oil composition was again approaching a steady-state by the end of the run. The distillates increased in aromaticity during the first 12 days of the run, as catalyst activity declined. The more aromatic distillates are better liquefaction media. Therefore, the solvent quality of the recycle distillates improved as the run progressed. The recycle distillates boiling below phenanthrene consist largely of cracking and isomerization products of hydrophenanthrenes. The relative ratios of reactants and products may be useful in establishing catalyst activity during the run. The start-up solvent had little effect on the run, because it was rapidly replaced by coal-derived recycle oils.

The molecular weight distribution of the recycle resid (975°F^+ , THF soluble) was relatively unchanged during the run although the ratio of benzene solubles to insolubles first decreased as catalyst activity declined, then increased with the increased hydrogen partial pressure during the last ten days of the run.

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Section 1

INTRODUCTION

In the H-Coal process for the production of liquid fuels from coal, about two-thirds of the feed slurry is a process-derived recycle oil. This recycle stream consists of distillate and residual hydrocarbons, unreacted (solid) carbonaceous material, and coal minerals. The recycle slurry oil is chemically active in the liquefaction reactor, and therefore, its composition has a potentially important impact on process performance.

The object of this research is to apply a broad range of analytical tools to determine the composition of the recycle stream, in H-Coal PDU operation, and to relate that composition to process performance. An important aspect of this work is that the analytical methods employed produce a molecular characterization of the materials studies. Hydrogen distributions, (by ^1H -NMR spectroscopy), molecular size and chemical functionalities (by liquid chromatography), and identification of individual components (by GC/MS) are used to provide a detailed picture of recycle oil composition. These data are then used to determine:

- Changes in the slurry recycle stream during start-up.
- The manner in which the process reaches steady-state during start-up.
- The composition of the recycle stream during stable operation.
- The changes in recycle composition in response to planned changes in process variables.
- Changes in the recycle composition which cause or result from unplanned upsets in process operation.
- Changes in recycle composition as evidence of change in catalyst activity.
- Differences in recycle composition as a function of space velocity and feed coal.

Daily samples of the hydroclone overflow (HO) and the clean oil tank (COT) inventory, which comprise the recycle oil, were taken during the three PDU runs shown below:

<u>PDU Run</u>	<u>Coal Feed</u>	<u>Mode (Space Velocity)</u>
5	Illinois 6	Syncrude (31 lb/hr/ft ³)
8	Illinois 6	Fuel Oil + Intermediate (78, 65 and 50)
9	Kentucky 11	Syncrude (31)

PDU 5, a 30 day run, was completed in September, 1977. PDU 8, 23 days in duration, was made in July, 1979. PDU 9 comprised 30 days of operation in September, 1979. While recognizing that the age of the PDU 5 samples may affect the analytical results, it was desirable to use these samples for two reasons. First, they give a comparison between the same coal in two modes (PDU 5 vs. PDU 8) and two coals in the same mode (PDU 5 vs. PDU 9). Second, at the time this work was begun PDU 8 and PDU 9 were the only PDU runs scheduled. Therefore, the desired comparisons could only be obtained using the PDU 5 samples.

This report describes the results with the PDU 5 samples. A second topical report will be made of the PDU 8 results. The PDU 9 results will be included in the final comprehensive report.

Section 2

SUMMARY

A. DESCRIPTION OF PDU RUN 5

PDU Run 5 was made in the Syncrude mode (space velocity = 31 lb/hr/ft³) with Illinois #6 coal. Analyses of the coal and startup solvent - APO - are given in Tables 2-1 and 2-2, respectively.

The run was smooth, and demonstrated catalyst addition and withdrawal during the run. The principal operating anomaly was a low hydrogen partial pressure through the first twenty days of the run.

Product yields from PDU 5 are summarized in Table 2-3, along with the hydrogen partial pressure and hydrogen consumption. These data were taken from HRI's report of PDU Run 5⁽¹⁾. The net distillate (IBP x 975°F) yield, shows a decrease, presumably with declining catalyst activity, during the early stages of the run. After increasing the hydrogen partial pressure at day 21, the distillate yield increased during the last 10 days of the run. The yield structure was in reasonable agreement with projections and the pilot plant design basis.

B. RESULTS OF ANALYSES OF SLURRY RECYCLE OIL

The following conclusions are made based on the analyses performed.

- During the initial stages of operation the start-up solvent (APO) was rapidly replaced by coal-derived distillate. By day 3, the start-up solvent has no appreciable effect on the recycle distillate composition. This is important since it ensures that the samples taken accurately reflect what was occurring in the process at a given time.
- The concentration of aromatic protons in the recycle oil increased between day 3 and day 12 of the run following an initial decrease in aromaticity going from the start-up oil to day 3. This increase in aromaticity serves as a measure of the decline in hydrogenation activity, and presumably catalyst activity, as the recycle distillate approaches steady-state.
- The increased recycle rate of THF soluble resid (535°C⁺) during the run was accompanied by an increase in oils, asphaltenes and preasphaltenes (benzene insolubles) during the first 15 days of the run. After day 20, the recycle rate of preasphaltenes decreased, in apparent response to an increase in hydrogen partial pressure during the last 10 days of the run. The benzene soluble/insoluble ratio of the THF soluble resid during all stages of the run is high, relative to, for example, the same ratio for SRC. Reduction of the preasphaltenes

(i.e., benzene insoluble) content of the recycled resid is advantageous for catalyst activity.

- Separation of the THF soluble resid into functional group (SESC) categories shows that most of the increase in the recycle rate of resid during the run occurred in the less highly functional categories. These data also show an approach to steady-state recycle composition by about day 12 of this thirty-day run. The SESC data do not show as clear a response to the increased hydrogen partial pressure during the last 10 days of the runs as do the LCF data.
- The weight average molecular weight of the THF soluble resid was around 540 amu throughout the run. There was little variation in this molecular weight during the run.
- The ¹H-Nuclear Magnetic Resonance (NMR) data indicate that the quality of the recycle distillates, as liquefaction media, increased during the first 12 days of the run, then reached a steady-state. This increase in solvent quality can be attributed to a decline in catalyst activity during the run. The more active catalyst tended to overhydrogenate the distillates.
- The GC/MS data indicate that the chemistry of the recycle distillate is dominated by the cracking and isomerization of hydrogen donor hydroaromatics (particularly hydrophenanthrenes) to alkyl aromatics and cyclopenta-aromatics, respectively. The PDU Run 5 conditions (850°F, 1500-2000 psig H₂) are conducive to these reactions, which reduce the donatable hydrogen content of the recycle distillates. The natural decline in catalyst activity during the run would be expected to decrease hydrocracking and increase solvent quality, as the NMR data confirm. Data on the relative ratios of cracking reactants and products may be useful in establishing changes in catalyst activity during the runs.
- The composition of the slurry recycle oil, particularly as measured by solvent fractionation and NMR, was relatively unchanged during the last half of the run, except for the response to increased hydrogen partial pressure, noted above. This is evidence of an approach to steady-state operation during PDU Run 5.
- The replacement of the start-up solvent was sufficiently rapid, that it is unlikely that the nature of the start-up solvent can have a significant effect on process performance in the PDU unless it is such a poor physical solvent for the heavy resid that it leads to deposition of solids and coking.
- We do not believe that aging of the PDU 5 samples had a significant qualitative effect on our results. Comparison of the PDU 5 data with preliminary data from PDU 8 (Illinois 6 coal, Fuel Oil mode) indicates that the older PDU 5 samples were higher in quality, as would be expected for material made in the Syncrude mode.
- Future work, on samples from PDU Runs 8 and 9 will be directed toward establishing recycle composition as a function of feed coal and space

velocity. We will also be investigating the composition of the recycle distillates for evidence of the cracking and isomerization reactions of hydroaromatics higher in molecular weight than the hydrophenanthrenes.

Table 2-1

Analyses of Illinois 6 Coal, Burning Star Mine #2^a

Proximate Analysis	<u>Dry Basis, wt %</u>
Ash	10.66
Volatile Matter	38.34
Fixed Carbon	51.00
Ultimate Analyses	<u>Dry Basis, wt %</u>
Carbon	70.01
Hydrogen	5.01
Nitrogen	1.33
Sulfur (LECO)	3.54
Ash	10.66
Chlorine	0.06
Oxygen (diff)	9.39

^aAverages for coal fed to run periods (1-9), (10-17) and (18-30). Data taken from Reference 1.

Table 2-2

Analysis of APO^a

Elemental Analysis	<u>wt %</u>
Carbon	89.69
Hydrogen	8.05
Nitrogen	0.16
Sulfur	3.72
Oxygen (diff)	1.62
Atmospheric Distillation	
ASTM D1160, modified	<u>T, °C</u>
IBP	267
10 V %	311
30	334
50	357
70	377
90	410
FBP	471

^aFrom Reference 1.

Table 2-3

Product Yields (wt % Dry Coal) and Hydrogen Partial Pressure

H-Coal PDU Run 5

Nominal Run Conditions: Illinois 6 Coal, 850°F, SV = 31 lb/hr/ft³

Run Period	C ₁ x C ₆	IBP x 400°F	4CO x 975°F	IBP x 975°F	975°F Residual Oil		Hydrogen Partial Pressure	Hydrogen Consumption
					Toluene Soluble	Toluene Insoluble		
3	13.5	19.1	26.4	45.5	13.4	2.7	1525	5.8
4	12.9	17.4	28.5	45.9	14.2	4.8	1610	5.0
5	12.9	17.2	28.6	45.8	15.9	3.2	1670	5.5
6	13.5	16.9	27.6	44.4	13.9	4.5	1690	4.8
7	14.3	16.2	23.7	39.9	16.7	6.1	1710	5.4
8	13.1	15.8	25.8	41.6	15.9	6.4	1660	5.1
9	14.5	13.6	26.8	40.5	15.8	3.5	1540	5.1
10	15.4	14.1	24.4	38.6	14.6	9.4	1580	5.1
11	15.3	14.0	25.2	39.2	17.2	6.7	1510	5.0
12	14.6	14.4	23.5	37.9	17.9	6.7	1630	5.1
13	15.7	13.6	24.9	38.5	18.6	4.4	1450	5.3
14	16.4	13.2	25.8	39.0	19.3	4.9	1580	5.4
15	17.1	14.1	25.8	39.9	15.9	4.4	1480	4.8
16	16.2	15.0	24.5	39.5	17.7	5.2	1650	5.5
17	16.2	15.8	22.7	38.5	15.8	6.1	1680	5.0
18	17.0	14.7	24.3	38.9	17.1	4.6	1680	5.0
19	17.9	14.2	24.8	39.0	15.1	4.3	1570	4.9
20	16.8	14.3	25.7	39.9	15.7	5.3	1650	5.2
21	17.2	14.2	26.7	40.9	15.1	5.0	1730	5.3
22	15.7	14.4	26.9	41.3	16.6	3.6	1830	5.2
23	16.0	15.4	25.5	40.9	16.4	4.2	1820	5.0
24	16.8	14.8	27.3	42.1	15.5	4.7	1830	5.3
25	16.1	13.9	25.9	39.9	17.3	5.1	1890	5.1
26	15.1	13.4	26.4	39.8	19.1	4.6	1950	4.7
27	15.9	13.4	28.2	43.6	17.2	2.1	1840	5.4
28	15.3	15.6	29.0	44.5	16.5	4.4	1930	5.3
29	14.8	14.2	28.7	43.0	15.5	3.4	1920	4.9
30	15.3	13.1	30.4	43.5	16.2	3.6	1890	5.5

Section 3

EXPERIMENTAL

A. SAMPLE HANDLING AND PREPARATION

Samples were taken by HRI during days 3 through 30 of PDU Run 5 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 240°C pot and column temperature at 1 torr. A second cut (240 x 290°C, 1 torr) was then taken. 240°C and 290°C, 1 torr correspond to atmospheric boiling points of 470°C and 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⁽²⁾ 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⁽²⁾. 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⁽³⁾. 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^(4,5). 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 rps 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 three distillate fractions (COT, HO 240°C $^{-}$, 1 torr and HO 240 x 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 methyldene 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.

The proton distribution for the HO 290°C⁻, 1 torr samples was derived by weighted addition of the 240°C⁻, 1 torr and 240 x 290°C, 1 torr fractions. A hydrogen wt % factor was not taken into consideration. The resultant error was shown to be small by obtaining several spectra using both this method and back-mixing.

Integrations of the spectra of the HO THF soluble residue samples were performed by planimetry in triplicate. This mode 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 1,3,5-trimethylbenzene 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.

COT samples were analyzed as received. HO samples consisted of the 535°C⁻ distillate obtained by mixing both distillation cuts.

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 ~ 275 coal-related compounds. Typically there were between 125 and 175 GC peaks of which ~ 50 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 are, therefore, semi-quantitative.

Section 4

RESULTS AND DISCUSSION

A. RECYCLE COMPOSITION

The recycle slurry oil in the H-Coal PDU has two components: the hydroclone overflow (HO) and the clean oil tank inventory (COT). The COT consists of atmospheric still bottoms and vacuum overhead. The recycle rates of these three components, on a lb/lb solids basis, as reported by HRI⁽¹⁾ are given in Table 4-1. The recycle rate of COT components was reduced during the first nine days of the run, and the total slurry oil recycle rate was leveled off between 1.6 and 1.7 lb/lb coal at about that time. COT recycle rates were significantly higher on day 16 and 26. The recycle rate of HO was fairly constant throughout the run.

The recycle rate of distillate decreased during the run (Table 4-2 and Figure 4-1) because of a decrease in the COT recycle rate, and a decrease in the percentage of distillate in the hydroclone overflow (Table 4-3). The recycle rates of THF soluble resid, unconverted coal, and ash (Figures 4-1 and 4-2) all increased with the increasing concentration of these components in the HO, particularly during the early stages of the run.

B. LIQUID CHROMATOGRAPHIC SEPARATIONS OF THF SOLUBLE RESID

1. Liquid Column Fractionation

Table 4-1 gives the slurry recycle rates reported by HRI for PDU Run 5. Table 4-2 lists the recycle rates of distillate, THF soluble resid, unconverted coal and ash, based on the laboratory distillations done at CCDC. The increase in THF soluble resid in the hydroclone overflow and decrease in distillate recycle rate increased the relative resid content of the recycle oil during the run.

The LCF (solvent fractionation) data provide a measure of the composition of the THF soluble resid during the run. As Table 4-4 and Figure 4-3 show, the recycle rate of hexane and benzene solubles (oils and asphaltenes) tended to increase during the run. The recycle rate of preasphaltenes, increased during the first 15 days, then decreased, particularly after day 20. This is depicted in Figure 4-4 which shows the ratio of benzene solubles (oils + asphaltene) to benzene insolubles (preasphaltenes) in the THF soluble resid. Identifying this ratio with resid quality, the period up to day 10 may reflect decreasing catalyst activity with aging. The fairly level resid quality between days 10 and 20 represents apparent steady-state catalyst activity at the low hydrogen partial pressure during that stage of the run. Starting at day 20, the hydrogen partial pressure was raised to between 1850 and 1950 psig and the response of resid quality is seen in an increased ratio of benzene solubles to insolubles. The change in resid quality in response to P_{H_2} , especially during the latter stages of the run, is evidence of significant catalyst activity. The average catalyst age at the end of the run was 1100 lb coal/lb catalyst.

Table 4-1

Recycle Flows
H-Coal PDU Run 5

<u>Run Period</u>	<u>lb/lb Solids</u>			<u>Total</u>
	<u>Atmospheric Still Bottoms</u>	<u>Vacuum Still Overhead</u>	<u>Hydroclone Overflow</u>	
3	0.775	0.178	0.926	1.897
4	0.769	0.181	1.042	1.992
5	0.720	0.194	0.954	1.868
6	0.660	0.107	0.990	1.757
7	0.658	0.120	0.986	1.764
8	0.589	0.139	1.011	1.739
9	0.603	0.112	0.975	1.690
10	0.627	0.125	0.947	1.599
11	0.581	0.093	0.924	1.598
12	0.607	0.074	0.996	1.677
13	0.621	0.005	1.021	1.647
14	0.611	0.008	1.010	1.629
15	0.607	0.000	1.031	1.638
16	0.836	0.009	0.975	1.820
17	0.720	0.028	0.947	1.695
18	0.696	0.013	1.018	1.727
19	0.611	0.002	1.058	1.671
20	0.645	0.004	1.072	1.721
21	0.571	0.000	1.028	1.599
22	0.574	0.000	0.988	1.562
23	0.550	0.000	0.997	1.547
24	0.510	0.000	1.038	1.548
25	0.528	0.002	1.060	1.608
26	0.685	0.005	1.092	1.782
27	0.527	0.000	1.121	1.648
28	0.552	0.000	1.087	1.639
29	0.552	0.000	1.041	1.593
30	0.616	0.000	0.988	1.604

Table 4-2

Total Recycle Slurry Oil Composition

H-Coal PDU Run 5

<u>Run Period</u>	<u>lb/lb Solids</u>			
	<u>Distillate</u>	<u>THF Soluble Resid</u>	<u>Unconverted Coal</u>	<u>Ash</u>
3	1.462	0.319	0.031	0.056
4	1.510	0.368	0.039	0.067
5	1.392	0.359	0.040	0.068
6	1.191	0.425	0.050	0.084
7	1.225	0.405	0.047	0.078
8	1.193	0.405	0.048	0.079
9	1.132	0.411	0.057	0.083
10	1.153	0.424	0.048	0.073
11	1.059	0.398	0.055	0.080
12	1.105	0.446	0.051	0.069
13	1.092	0.418	0.056	0.079
14	1.074	0.423	0.054	0.075
15	1.000	0.496	0.055	0.084
16	1.272	0.436	0.044	0.064
17	1.169	0.390	0.047	0.074
18	1.123	0.467	0.055	0.078
19	1.075	0.437	0.070	0.086
20	1.129	0.443	0.061	0.086
21	0.985	0.455	0.061	0.091
22	1.005	0.418	0.052	0.086
23	0.996	0.407	0.058	0.084
24	0.936	0.467	0.054	0.087
25	0.987	0.463	0.059	0.086
26	1.158	0.476	0.057	0.086
27	1.010	0.470	0.063	0.102
28	1.012	0.467	0.058	0.097
29	0.938	0.471	0.056	0.105
30	0.996	0.448	0.052	0.103

Table 4-3

Distribution of Hydroclone Overflow Components
H-Coal PDU Run 5

Run Period	Wt % of Hydroclone Overflow			
	975°F ⁺		Unconverted	
	975°F ⁻	THF Soluble	Coal	Ash
3	55.0	34.4	3.4	6.1
4	53.7	35.3	3.7	6.4
5	50.1	37.6	4.2	7.1
6	42.8	42.9	5.0	8.5
7	45.3	41.1	4.8	7.9
8	46.0	40.1	4.7	7.8
9	42.8	42.2	5.8	8.5
10	42.3	44.8	5.1	7.7
11	41.7	43.1	5.9	8.7
12	42.6	44.8	5.1	6.9
13	45.6	40.9	5.5	7.7
14	45.0	41.9	5.3	7.4
15	38.1	48.1	5.3	8.1
16	43.8	44.7	4.5	6.6
17	45.5	41.2	5.0	7.8
18	40.7	45.9	5.4	7.7
19	43.7	41.3	6.6	8.1
20	44.8	41.3	5.7	8.0
21	40.3	44.3	5.9	8.9
22	43.6	42.3	5.3	8.7
23	44.7	40.8	5.8	8.4
24	41.0	45.0	5.2	8.4
25	42.3	43.7	5.6	8.1
26	42.9	43.6	5.2	7.9
27	43.1	41.9	5.6	9.1
28	42.3	43.0	5.3	8.9
29	39.0	45.2	5.4	10.1
30	38.5	45.3	5.3	10.4

Figure 4-1

SLURRY OIL RECYCLE RATES - PDU RUN 5

Figure 4-2

SLURRY OIL RECYCLE RATES - PDU RUN 5

The LCF data clearly show that the run progressed in three stages, as discussed by HRI⁽¹⁾. The first 10 days are marked by declining catalyst activity, followed by a steady-state period at low hydrogen partial pressure. Increasing the hydrogen pressure after day 20 increases the ratio of benzene solubles/insolubles to a new level which is higher than the original level with high catalyst activity but low hydrogen partial pressure.

The THF soluble HO resid in PDU Run 5 is a relatively high quality material. The percentage of preasphaltenes in SRC samples is frequently in the 25-35% range, which is considerably higher than the 15-20% which the recycled H-Coal resids average. Since the preasphaltenes are susceptible to regressive reactions which can lead to carbon deposition⁽⁶⁾, it is desirable to maintain a low preasphaltene content in the recycled resid. This is demonstrated in work reported by Mobil⁽⁷⁾ on the catalytic upgrading of short contact time and conventional SRC. Reduction of the preasphaltene content gave increased catalyst activities on the order of 50°F for the removal of sulfur and Conradson carbon residue.

2. SESC Fractionation of THF Soluble Resid

The THF soluble HO resid (535°C⁺) was separated into functional group categories, as described in the EXPERIMENTAL section, by the SESC method. The data show some scatter, possibly ascribable to the age and condition of the samples. The results are tabulated in Table 4-5 on a recycle rate (lb/lb coal) basis.

In Figure 4-5, the recycle rates of fractions 1 + 2, fractions 3 + 4 and fractions 5 + 6 + 7 are plotted vs. run period (day). Fractions 1 and 2 are non-functional or mildly functional material, examples of the latter being alcohols, thiols, ethers and non-basic nitrogen compounds. Fractions 3 and 4 consist of simple phenols and basic nitrogen compounds. Fractions 5, 6 and 7 contain material of increasingly complex functionality and increasing molecular weight. Grouping the fractions as in Figure 4-5 reduces somewhat the scatter in the data while maintaining a categorization by degree of functionality.

Figure 4-5 shows an increase in the recycle rate of the less functional material as the run progresses. The recycle rate of highly functional, high molecular weight material in fractions 5, 6 and 7 increases for the first 12 days of the run, then remains relatively constant for the remainder of the run. This is consistent with other data presented in this report which indicate the achievement of an initial steady-state recycle composition by about day 12. Unlike the LCF, the SESC results do not clearly show the effect of increased hydrogen partial pressure during the latter stages of the run. This is surprising, since we would expect the distribution of chemical functionalities to be sensitive to the hydrogen partial pressure. It is possible that aging of the samples has obscured chemical differences.

3. Molecular Weight Distributions of THF Soluble HO Resid

The molecular weight distributions calculated from GPC data for the THF soluble residue from PDU 5 are given in Table 4-6 on a recycle rate basis. There is an apparent increase in the recycle rates of all but the lightest fraction during the run, but this is only a reflection of the increasing recycle rate of THF soluble resid during the run.

Table 4-4

LCF Fractionation of HO THF Soluble Resid
 Recycle Rate, lb/lb Coal
 H-Coal PDU Run 5

Run Period	lb/lb Coal		
	Oils	Asphaltenes	Preasphaltenes
3	0.185	0.078	0.055
4	0.199	0.104	0.065
5	0.180	0.107	0.071
6	0.223	0.129	0.073
7	0.198	0.132	0.076
8	0.198	0.134	0.073
9	0.213	0.118	0.081
10	0.210	0.125	0.090
11	0.174	0.136	0.088
12	0.203	0.151	0.092
13	0.196	0.139	0.082
14	0.209	0.127	0.087
15	0.251	0.144	0.101
16	0.217	0.127	0.092
17	0.173	0.141	0.076
18	0.231	0.142	0.094
19	0.210	0.148	0.079
20	0.202	0.150	0.091
21	0.224	0.158	0.074
22	0.208	0.141	0.069
23	0.200	0.136	0.071
24	0.233	0.152	0.082
25	0.232	0.148	0.084
26	0.232	0.161	0.083
27	0.244	0.148	0.077
28	0.238	0.157	0.072
29	0.234	0.162	0.074
30	0.230	0.157	0.061

Figure 4-3

SOLUBILITY FRACTIONATION (LCF) OF H₀ 535°C+
THF SOLUBLES - PDU RUN 5

Figure 4-4

RATIO OF BENZENE SOLUBLES TO BENZENE INSOLUBLES
HO 535°C⁺, THF SOLUBLES - PDU RUN 5

Table 4-5

SESC Fractionation of HO THF Soluble Resid
 Recycle Rate, lb/lb Coal
 H-Coal PDU Run 5

Run Period	lb SESC Fraction/lb Coal						
	1	2	3	4	5	6	7
3	0.117	0.070	0.061	0.020	0.009	0.031	0.011
4	0.091	0.064	0.079	0.037	0.028	0.048	0.022
5	0.093	0.066	0.072	0.031	0.016	0.059	0.022
6	0.124	0.084	0.085	0.036	0.012	0.055	0.029
7	0.089	0.075	0.082	0.041	0.033	0.071	0.014
8	0.105	0.080	0.086	0.042	0.014	0.061	0.016
9	0.106	0.083	0.089	0.036	0.020	0.064	0.014
10	0.098	0.084	0.105	0.038	0.016	0.063	0.020
11	0.104	0.084	0.092	0.033	0.012	0.056	0.016
12	0.100	0.087	0.095	0.050	0.013	0.077	0.025
13	0.083	0.072	0.077	0.038	0.034	0.086	0.027
14	0.098	0.082	0.086	0.036	0.015	0.090	0.017
15	0.130	0.106	0.104	0.029	0.007	0.098	0.022
16	0.105	0.084	0.084	0.035	0.009	0.101	0.021
17	0.094	0.079	0.078	0.028	0.016	0.080	0.014
18	0.106	0.096	0.099	0.028	0.018	0.080	0.041
19	0.122	0.100	0.100	0.034	0.011	0.051	0.018
20	0.100	0.091	0.082	0.027	0.028	0.080	0.035
21	0.102	0.084	0.100	0.030	0.025	0.088	0.026
22	0.110	0.084	0.092	0.019	0.016	0.070	0.024
23	0.087	0.084	0.099	0.025	0.005	0.087	0.020
24	0.110	0.086	0.104	0.030	0.018	0.093	0.025
25	0.115	0.094	0.104	0.031	0.015	0.087	0.017
26	0.120	0.100	0.100	0.032	0.017	0.084	0.022
27	0.128	0.092	0.094	0.025	0.022	0.089	0.020
28	0.117	0.095	0.100	0.030	0.020	0.081	0.023
29	0.124	0.096	0.100	0.026	0.024	0.081	0.018
30	0.102	0.083	0.106	0.024	0.017	0.089	0.029

Figure 4-5

CHEMICAL FUNCTIONALITY SEPARATION (SESC) OF 535°C⁺
THF SOLUBLE HYDROCLONE OVERFLOW - PDU RUN 5

The normalized molecular weight distributions are given in Table 4-7. These show more clearly that there is no appreciable change in the molecular weight distribution beyond some decrease in the 250-400 amu component, with a corresponding increase in the higher molecular weight fractions, during the first few days. The GPC method, as used to obtain these data, does not have sufficient selectivity to reliably discern a molecular weight difference among the recycle residue samples from this PDU run.

We cannot calculate an exact molecular weight from the GPC data because of the high molecular weight material which is excluded on the GPC column (cf. Section 3-A-3). However, if we assume that the 700⁺ amu component has a weight average molecular weight of 800 amu, we calculate the weight average molecular weights given in Table 4-7. The weight average molecular weights of the THF soluble resid from days 3 through 30 average 527 amu with a standard deviation of 12 amu. This deviation is within experimental uncertainty. Obviously a choice other than 800 amu for the 700⁺ amu fraction would change the absolute values of the calculated molecular weights but would not change our conclusion that the GPC data show little variation throughout the run.

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

1. Clean Oils Tank

Table 4-8 gives the normalized proton distribution of the clean oils tank samples. The aromatic protons show a steady increase between days 3 and 12. This is accompanied by a decrease in the beta and gamma protons over the same period. Compared to the start-up solvent (APO), the condensed aromatics have decreased and uncondensed aromatics increased considerably by day 3. The beta and gamma protons are much higher in the day 3 COT sample than in the APO. These data indicate a rapid replacement of the startup solvent by process derived distillates. The increase in aromatics and decrease in paraffinic and naphthenic beta and gamma protons after day 3 reflects catalyst deactivation. Because of the variation in hydrogen partial pressure it appears that the proton distributions between days 20 and 30 deviate from steady-state values. As discussed further in Section 5, the data suggest that the proton distribution approached steady-state between days 12 and 20, then underwent variation in response to the change in hydrogen partial pressure.

The absolute values of the COT proton distribution over the last 10 days of the run are consistent with a high quality hydrogen donor solvent. The ratio of condensed to uncondensed aromatic protons (Table 4-9) averages 1.90. The ratio of cyclic to alkyl aliphatic protons average 0.77. This compares favorably with the corresponding ratios of 2.38 and 0.71 for a high quality SRC solvent, hydrogenated over a CoMo catalyst⁽⁹⁾. By contrast, the corresponding values for a low quality SRC distillate are 1.11 and 0.43, respectively.

It is interesting that both ratios (condensed-to-uncondensed aromatics and cyclic-to-alkyl aliphatics) increase as the run progresses. This implies an improvement in the quality of the COT material during the run. The NMR data indicate that, in the early stages of the run, the COT material is overhydrogenated by the highly active fresh catalyst, with respect to its hydrogen donor properties. This overhydrogenation has been reported for SRC-1 recycle distillates^(8,9). As the run progresses the catalyst activity declines. This produces a more aromatic recycle distillate with a lower paraffin and naphthene

Table 4-6

Recycle Rate of Molecular Weight Fractions
of HO THF Soluble Resid

H-Coal PDU Run 5

Run Period	250 ⁻ amu	250 x 400 amu	400 x 550 amu	550 x 700 amu	700 ⁺ amu
3	0.000	0.083	0.136	0.054	0.046
4	0.000	0.089	0.167	0.060	0.052
5	0.000	0.083	0.144	0.069	0.062
6	0.000	0.090	0.164	0.086	0.085
7	0.015	0.099	0.169	0.071	0.052
8	0.000	0.078	0.165	0.085	0.077
9	0.012	0.079	0.163	0.080	0.077
10	0.000	0.080	0.169	0.086	0.090
11	0.002	0.074	0.159	0.087	0.076
12	0.001	0.093	0.187	0.093	0.074
13	0.005	0.090	0.168	0.083	0.072
14	0.000	0.086	0.184	0.086	0.067
15	0.004	0.078	0.243	0.114	0.057
16	0.011	0.092	0.150	0.096	0.087
17	0.000	0.076	0.163	0.083	0.068
18	0.014	0.118	0.196	0.082	0.057
19	0.002	0.092	0.180	0.087	0.075
20	0.008	0.089	0.176	0.089	0.081
21	0.002	0.100	0.191	0.089	0.073
22	0.000	0.076	0.181	0.087	0.075
23	0.000	0.062	0.184	0.088	0.072
24	0.009	0.083	0.199	0.092	0.085
25	0.000	0.108	0.195	0.089	0.071
26	0.000	0.092	0.203	0.095	0.086
27	0.000	0.107	0.201	0.089	0.073
28	0.000	0.095	0.198	0.098	0.077
29	0.000	0.105	0.206	0.089	0.069
30	0.016	0.090	0.157	0.093	0.092

Table 4-7

Molecular Size Separation of HO THF Soluble Resid
H-Coal PDU Run 5

Run Period	Wt %					$\bar{M}_w^a$
	< 250 amu	250-400	400-550	550-700	> 700 amu	
3	0.0	25.9	42.6	17.0	14.5	509
4	0.0	24.3	45.3	16.2	14.2	509
5	0.0	23.2	40.2	19.2	17.3	525
6	0.0	21.2	38.5	20.3	20.0	539
7	3.6	24.4	41.7	17.4	12.9	498
8	0.1	19.2	40.8	20.9	19.1	540
9	3.0	19.1	39.7	19.5	18.7	530
10	0.0	18.9	39.8	20.3	21.1	546
11	0.4	18.5	40.0	21.9	19.2	542
12	0.2	20.8	41.8	20.8	16.5	529
13	1.1	21.5	40.3	19.8	17.3	526
14	0.0	20.4	43.4	20.3	15.9	527
15	0.8	15.8	49.1	23.0	11.4	522
16	2.6	21.0	34.4	22.1	20.0	536
17	0.0	19.6	41.9	21.2	17.4	534
18	2.9	25.3	42.0	17.6	12.2	497
19	0.5	21.1	41.3	20.0	17.1	528
20	1.8	20.2	39.8	20.0	18.3	531
21	0.5	21.9	42.0	19.6	16.0	522
22	0.0	18.2	43.2	20.8	17.9	538
23	0.0	15.2	45.3	21.7	17.8	543
24	1.9	17.7	42.6	19.8	18.1	533
25	0.0	23.4	42.1	19.2	15.4	519
26	0.0	19.4	42.6	19.9	18.1	535
27	0.0	22.7	42.8	19.0	15.5	520
28	0.0	20.3	42.4	20.9	16.4	529
29	0.0	22.4	43.7	19.0	14.7	517
30	3.6	20.2	35.0	20.7	20.5	534

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

Table 4-8

Proton Distribution - Clean Oil Tank Sample
H-Coal PDU Run 5

Run Period	Wt % Total Hydrogen						
	Condensed Aromatics	Uncondensed Aromatics	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
3	11.8	9.0	12.6	11.7	18.5	22.5	13.7
4	14.4	9.3	15.1	11.7	17.4	20.0	12.1
5	15.7	9.5	15.5	12.2	16.7	19.3	11.1
6	16.5	9.6	16.2	12.0	16.2	18.5	11.1
7	17.9	8.9	17.1	11.7	15.7	18.6	10.2
8	18.4	9.3	17.3	11.7	15.6	17.8	9.7
9	18.8	9.6	17.0	12.0	15.4	17.2	10.1
10	19.7	9.4	17.3	11.9	14.9	17.6	9.2
11	19.9	9.6	16.9	12.2	14.5	17.7	9.1
12	20.1	9.6	17.0	12.2	13.9	17.9	9.2
13	19.7	10.8	16.3	12.7	13.9	17.4	9.1
14	19.2	10.0	16.9	12.6	14.0	18.1	9.4
15	18.6	10.5	16.0	12.5	14.4	18.1	9.8
16	19.0	10.5	16.6	12.7	13.8	17.8	9.6
17	18.2	10.7	16.3	12.7	14.2	18.3	9.7
18	18.6	10.4	16.1	12.7	14.1	18.3	9.8
19	19.3	10.6	16.0	12.7	14.0	18.1	9.4
20	20.7	10.3	16.5	12.8	13.2	17.6	8.9
21	20.6	10.0	16.8	12.5	13.6	17.7	8.8
22	19.9	10.5	16.5	12.4	14.0	17.5	9.2
23	19.7	10.7	16.2	12.4	13.6	17.8	9.6
24	20.1	10.4	16.6	12.4	13.5	17.6	9.4
25	20.8	10.7	16.6	12.3	13.7	16.7	9.2
26	20.2	10.8	16.7	12.3	13.6	17.1	9.3
27	19.0	10.6	16.5	12.4	14.2	18.0	9.5
28	19.5	10.7	16.6	12.3	14.1	17.4	9.3
29	19.8	10.2	16.9	12.4	13.9	17.3	9.5
30	19.1	10.7	16.1	12.4	14.1	17.8	9.8
APO	39.9	5.1	13.3	19.4	4.6	11.5	6.2

Table 4-9

Ratios of Condensed to Uncondensed Aromatics
and Cyclic To Alkyl Aliphatics for COT and HO Distillates
H-Coal PDU Run 5

Run Period	Aromatics (Condensed/Uncondensed)		Aliphatics (Cyclic/Alkyl)	
	HO	COT	HO	COT
3	2.241	1.311	0.804	0.649
4	2.722	1.548	0.908	0.742
5	2.575	1.653	0.909	0.756
6	2.544	1.719	0.900	0.779
7	2.527	2.011	0.912	0.810
8	3.024	1.978	0.985	0.839
9	2.510	1.958	0.906	0.824
10	2.701	2.096	0.922	0.832
11	2.435	2.073	0.881	0.805
12	2.614	2.094	0.896	0.786
13	2.533	1.824	0.914	0.770
14	2.696	1.920	0.929	0.771
15	2.528	1.771	0.902	0.752
16	2.188	1.810	0.848	0.758
17	2.143	1.701	0.850	0.749
18	2.551	1.788	0.879	0.740
19	2.667	1.821	0.901	0.746
20	2.538	2.010	0.929	0.756
21	2.441	2.060	0.896	0.779
22	2.345	1.895	0.893	0.780
23	2.072	1.841	0.839	0.749
24	2.310	1.933	0.842	0.764
25	2.282	1.944	0.867	0.793
26	2.124	1.870	0.824	0.783
27	2.375	1.792	0.888	0.769
28	2.733	1.822	0.938	0.787
29	2.610	1.941	0.902	0.786
30	2.342	1.785	0.862	0.755

content and a higher concentration of hydroaromatics. This reaches a steady-state fairly soon (about day 12) and is not significantly altered by the increase in hydrogen partial pressure later in the run.

2. Hydroclone Overflow Distillate

¹H-NMR data on the HO distillate (Table 4-10) show much the same pattern as the COT samples. The aromatic protons increase between days 3 and 12, while the beta and gamma protons decrease during the same period. The comments made concerning the COT samples are equally applicable here.

3. Total Distillates

Normalized proton distributions for the total recycle distillates were calculated from the COT and HO data, and are given in Table 4-11. This calculation requires a knowledge of the percent hydrogen in each liquid and these values were estimated from data in the HRI report on Run 5⁽¹⁾. Because of this there is some uncertainty in the calculated results. However, the ¹H-NMR data on the individual samples indicate no large variations in the hydrogen percentages, and the calculated values are probably quite good.

These results confirm the approach to a steady-state proton distribution by about day 12 and response to P_{H₂} after day 20 (cf. Section 5-B). They also show the improvement in recycle solvent quality as the run progresses, as measured by the ratios of cyclic-to-alkyl aliphatics and condensed-to-uncondensed aromatics.

4. Hydroclone Overflow Resid

The NMR spectra of non-distillate samples are much more poorly resolved than the distillate samples. Therefore, we do not make the distinction between the condensed and uncondensed aromatics and cyclic and alkyl aliphatics. Nevertheless, the HO resid samples show the same general pattern seen with the distillates (Table 4-12). The aromatic protons increase during the initial stages of the run with a corresponding decrease in the beta and gamma protons.

We do not have an empirical relationship between resid composition and recycle quality. However, it has been demonstrated that non-volatile coal liquids can be excellent hydrogen transfer agents^(8,9). In principle we would expect that higher aromaticity and lower alkyl content would improve this hydrogen transfer property. That is, alkylated aromatics are more difficult to hydrogenate and make poorer hydrogen donors than non-alkylated aromatics.

5. ¹H-NMR of Total THF Soluble Recycle

The total recycle rates of the different hydrogen types were calculated from the data given above, and are given in Table 4-13 and Figure 4-6. This calculated hydrogen distribution summarizes the ¹H-NMR data on the individual slurry recycle oil components, and therefore, provides a useful set of parameters for comparison with process performance, as discussed in Section 5.

Table 4-10

Proton Distribution - Hydroclone Overflow Distillate
H-Coal PDU Run 5

Run Period	Wt % Total Hydrogen						
	Condensed Aromatics	Uncondensed Aromatics	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
3	19.5	8.7	16.1	11.5	15.8	17.1	11.1
4	21.5	7.9	18.3	11.4	15.3	16.7	8.9
5	22.4	8.7	18.1	11.6	14.7	15.9	8.6
6	22.9	9.0	17.8	11.5	14.5	15.8	8.6
7	23.5	9.3	18.1	11.7	13.9	14.9	8.5
8	25.4	8.4	18.9	11.3	14.0	14.4	7.7
9	25.1	10.0	17.8	11.7	13.0	14.2	8.1
10	26.2	9.7	18.3	11.7	12.5	14.3	7.4
11	26.3	10.8	17.4	12.3	12.1	13.7	7.5
12	26.4	10.1	17.8	12.1	12.2	14.1	7.3
13	27.1	10.7	17.7	12.1	12.0	13.3	7.1
14	27.5	10.2	18.2	11.9	11.8	13.4	7.0
15	27.3	10.8	17.5	12.2	11.8	13.3	7.0
16	24.5	11.2	17.2	12.3	12.3	14.4	8.1
17	25.5	11.9	16.9	12.3	11.9	13.6	8.0
18	27.3	10.7	17.4	12.2	11.6	13.4	7.4
19	28.0	10.5	17.7	12.1	11.4	13.5	6.7
20	26.9	10.6	18.1	12.1	12.0	13.3	7.0
21	27.1	11.1	17.4	12.2	11.8	13.4	7.0
22	26.5	11.3	17.4	12.0	11.9	13.4	7.4
23	25.9	12.5	16.5	12.4	11.6	13.3	7.8
24	26.8	11.6	16.4	12.8	11.8	13.4	7.3
25	26.7	11.7	16.9	12.1	11.7	13.4	7.5
26	25.7	12.1	16.3	12.6	11.8	13.8	7.7
27	26.6	11.2	17.2	11.9	12.1	13.6	7.5
28	27.6	10.1	18.1	11.9	12.1	13.2	7.1
29	27.4	10.5	17.4	12.0	12.1	13.5	7.2
30	27.4	11.7	16.7	12.2	11.5	13.0	7.5

Table 4-11

Proton Distribution - Total Distillates
H-Coal PDU Run 5

Run Period	Wt % Total Hydrogen						
	Condensed Aromatics	Uncondensed Aromatics	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
3	14.5	8.9	13.8	11.6	17.6	20.6	12.8
4	17.0	8.8	16.3	11.6	16.6	18.8	10.9
5	18.0	9.2	16.4	12.0	16.0	18.1	10.2
6	18.8	9.4	16.8	11.8	15.6	17.5	10.2
7	19.9	9.0	17.5	11.7	15.0	17.3	9.6
8	21.1	8.9	17.9	11.5	15.0	16.5	8.9
9	21.1	9.7	17.3	11.9	14.5	16.1	9.4
10	22.0	9.5	17.6	11.8	14.1	16.5	8.6
11	22.2	10.0	17.1	12.2	13.6	16.2	8.5
12	22.5	9.8	17.3	12.2	13.2	16.4	8.5
13	22.9	10.8	16.9	12.4	13.1	15.7	8.2
14	22.7	10.1	17.5	12.3	13.1	16.1	8.4
15	22.0	10.6	16.6	12.4	13.4	16.2	8.7
16	20.8	10.7	16.8	12.6	13.3	16.7	9.1
17	20.9	11.1	16.5	12.6	13.4	16.6	9.1
18	21.8	10.5	16.6	12.5	13.2	16.5	8.9
19	23.0	10.6	16.7	12.4	12.9	16.1	8.2
20	23.3	10.4	17.2	12.5	12.7	15.8	8.1
21	23.3	10.5	17.1	12.4	12.8	15.9	8.0
22	22.7	10.8	16.9	12.2	13.1	15.7	8.4
23	22.5	11.5	16.3	12.4	12.7	15.8	8.8
24	23.1	10.9	16.5	12.6	12.7	15.7	8.4
25	23.5	11.2	16.7	12.2	12.8	15.2	8.4
26	22.4	11.3	16.5	12.4	12.9	15.8	8.7
27	22.6	10.9	16.8	12.2	13.2	15.9	8.5
28	23.2	10.4	17.3	12.1	13.2	15.5	8.3
29	23.0	10.3	17.1	12.2	13.1	15.7	8.5
30	22.3	11.1	16.3	12.3	13.1	16.0	8.9

Table 4-12

Proton Distribution - HO THF Soluble Resid
H-Coal PDU Run 5

<u>Run Period</u>	<u>Wt % Total Hydrogen</u>			
	<u>Aromatic</u>	<u>Alpha</u>	<u>Beta</u>	<u>Gamma</u>
3	40.5	31.0	22.4	6.0
4	40.5	31.6	22.2	5.7
5	41.8	30.0	22.0	6.3
6	43.1	30.0	20.9	6.0
7	43.5	30.5	20.5	5.5
8	43.6	31.5	19.9	5.0
9	45.9	29.1	19.7	5.3
10	43.3	30.2	21.0	5.5
11	47.0	29.8	18.2	5.0
12	45.8	30.0	19.2	5.0
13	47.1	29.6	18.7	4.6
14	46.1	30.8	18.6	4.5
15	45.6	29.1	19.7	5.5
16	45.3	31.0	19.3	4.3
17	46.1	29.8	18.9	5.2
18	47.2	30.8	17.7	4.3
19	49.6	29.9	16.4	4.1
20	47.6	30.3	17.8	4.3
21	45.8	30.0	18.9	5.3
22	48.5	30.2	17.2	4.2
23	46.9	30.8	17.9	4.4
24	47.8	29.9	17.8	4.6
25	46.1	29.9	18.9	5.1
26	45.9	30.3	18.6	5.1
27	45.6	30.2	18.9	5.3
28	45.5	30.4	19.2	4.9
29	46.6	30.4	18.5	4.5
30	46.2	29.5	19.0	5.3

Figure 4-6

^1H -NMR OF TOTAL THF SOLUBLES IN THE RECYCLE SLURRY OIL - PDU RUN 5

Table 4-13

Proton Distribution of Total THF Solubles
(COT + HO Distillate + THF Soluble Resid), lb/lb Coal

H-Coal PDU Run 5

<u>Run Period</u>	<u>Aromatic</u>	<u>Alpha</u>	<u>Beta</u>	<u>Gamma</u>
3	0.0349	0.0359	0.0504	0.0166
4	0.0398	0.0408	0.0487	0.0149
5	0.0391	0.0384	0.0438	0.0131
6	0.0372	0.0349	0.0375	0.0115
7	0.0384	0.0360	0.0373	0.0109
8	0.0387	0.0357	0.0354	0.0099
9	0.0386	0.0336	0.0331	0.0100
10	0.0395	0.0349	0.0340	0.0095
11	0.0379	0.0319	0.0302	0.0086
12	0.0400	0.0339	0.0317	0.0090
13	0.0402	0.0328	0.0300	0.0085
14	0.0389	0.0331	0.0301	0.0085
15	0.0385	0.0314	0.0297	0.0087
16	0.0435	0.0381	0.0362	0.0106
17	0.0404	0.0345	0.0333	0.0100
18	0.0413	0.0345	0.0321	0.0094
19	0.0408	0.0326	0.0296	0.0083
20	0.0422	0.0345	0.0307	0.0086
21	0.0381	0.0310	0.0297	0.0078
22	0.0381	0.0306	0.0277	0.0079
23	0.0375	0.0300	0.0272	0.0082
24	0.0376	0.0296	0.0263	0.0076
25	0.0387	0.0304	0.0271	0.0080
26	0.0434	0.0352	0.0321	0.0096
27	0.0386	0.0313	0.0288	0.0084
28	0.0388	0.0318	0.0286	0.0081
29	0.0375	0.0306	0.0274	0.0079
30	0.0380	0.0305	0.0286	0.0086

Table 4-14

GC/MS Analysis of PDU Run 5 Start-Up Solvent

	<u>No. of Isomers Detected</u>	<u>% of Sample^a</u>
Methyl Fluorene	2	2.1
Dibenzothiophene	1	0.6
Phenanthrene/Anthracene	2	11.4/0.4
Methyl Dihydrophenanthrene	4	3.2
Methyl Dibenzothiophene	2	2.0
Methyl Phenanthrene	5	21.9
C ₂ -Dihydrophenanthrene	2	1.1
C ₂ -Dibenzothiophene	3	2.3
C ₂ -Phenanthrene	6	22.2
C ₃ -Dibenzothiophene	3	1.9
C ₃ -Phenanthrene	8	8.0
Pyrene	1	4.7
Methyl Pyrene	3	2.9
C ₂ -Pyrene	2	0.8
C ₄ -Phenanthrene	3	0.8
C ₃ -Pyrene	1	0.3
Chrysene	1	0.2
n-Alkanes	4	1.5

^a% total ion abundance.

D. GC/MS ANALYSES OF RECYCLE DISTILLATES

1. Analysis of APO

The start-up solvent for PDU Run 5 was APO. The composition of this material as determined by GC/MS, is given in Table 4-14. The major components are phenanthrene and the alkyl phenanthrenes. We have made no attempt to identify individual isomers, the observed number of which is listed for each component. It is interesting that a series of dibenzothiophene homologs is present, out to C₃. Four normal alkanes (C₂₂H₄₆ to C₂₅H₅₂) are also detected. Other n-alkanes are presumably present, but were not resolved.

The APO has very little donatable hydrogen. Only a few dihydrophenanthrene homologs were found. This is consistent with the NMR data (Table 4-8) which show a very low concentration of cyclic beta hydrogen. As a result, the ratio of cyclic-to-alkyl aliphatics is low, 0.48.

The high ratio of cyclic alpha to cyclic beta protons suggests the presence of methylene bridges, as in dihydrophenanthrene, fluorene, diphenyl methane, etc., as opposed to naphthenes or hydroaromatics like tetrahydrophenanthrene. The GC/MS data confirm this.

Compared to anthracene oils we have analyzed, APO has a high concentration of alkyl aromatics. For example, the anthracene oil used as a start-up solvent for PDU Run 8 consists of a few major components (Table 4-15). The non-alkylated hydrocarbons make up over 60% of the anthracene oil, as opposed to less than 20% of the APO. The APO also has a higher initial boiling point than the anthracene oil.

Because of the rapid replacement of the start-up solvent by coal-derived distillates (cf. Section 4-C, and below) it is unlikely that the choice of start-up solvent would have a major effect on process performance. The only exception would be if the start-up solvent were too poor a physical solvent for the coal liquids to keep them in solution during initial operation. This could lead to deposition of material on the catalyst and consequent catalyst fouling. This does not appear to have occurred in PDU Run 5. In any event continuous catalyst replacement would mitigate this effect.

2. Qualitative Analysis of Distillate Samples

Figure 4-7 is the gas chromatogram of the COT sample from run period 17. The identities of the individual components are given in Table 4-16. Identifications were based on retention times and standard mass spectra when possible. For those components for which standard spectra were not available, the mass spectra were used to infer identifications. Because many of the aromatic hydrocarbons in the sample give, or would be expected to give, similar mass spectra, some of the identifications are uncertain. These are noted as such in Table 4-16.

The gas chromatogram in Figure 4-7 is representative of those for all of the COT and HO distillate samples from Run 82. Peak intensities varied during the run, but the same components were detected for each sample. The HO distillates had a higher concentration of higher boiling components, but the gas chromatograms were grossly similar to those of the COT samples.

Table 4-15

GC/MS Analysis of PDU Run 8 Start-Up Oil
(Allied 24CB Anthracene Oil)

<u>Component</u>	<u>No. of Isomers Detected</u>	<u>% of Sample^a</u>
Naphthalene	1	16.8
Quinoline	1	2.4
Methylquinoline	1	0.3
Methylnaphthalene	2	22.0
C ₂ -Naphthalene	6	4.8
Biphenyl	1	4.2
Acenaphthene	1	9.9
Methylacenaphthene	1	0.5
Dibenzofuran	1	5.8
Fluorene	1	6.0
Methylbiphenyl	2	1.1
Methyldibenzofuran	2	1.6
Dibenzothiophene	1	1.0
Phenanthrene/Anthracene	2	9.8/0.9
Methylphenanthrene	3	1.2
Cyclopenta (d,e,f) Phenanthrene	1	1.3
Dihdropyrene	1	0.4
Fluoranthene	1	3.7
Pyrene	1	2.2

^a% total ion abundance.

Table 4-16

**Peak Identifications of Gas Chromatogram
of Clean Oil Tank Sample - Period 17 - PDU Run 5**

1. C ₈ -cycloalkane	58. n-propylnaphthalene	114. methylphenanthrene
2. xylene	59. C ₄ -tetralin	115. methylphenanthrene
3. unknown cycloalkane	60. isopropyl or methylethynaphthalene	116. (C ₂ -dihydrophenanthrene)
4. C ₉ -cycloalkane	61. dibenzofuran	117. n-C ₁₉ -alkane
5. 1,3,5-trimethylbenzene (internal standard)	62. n-C ₁₅ -alkane	118. hexahydopyrene
6. C ₃ -benzene	63. (tetrahydrobenzindan) or (methyl-tetrahydroacenaphthene)	119. unknown
7. n-C ₁₀ -alkane (impurity from standard)	64. unknown	120. unknown
8. unknown	65. C ₄ -tetralin	121. 2-phenylnaphthalene
9. indan	66. methylpropyl or sec-butyl naphthalene	122. unknown
10. C ₄ -benzene	67. unknown	123. C ₂ -phenanthrene
11. decalin	68. n-butyltetralin	124. C ₂ -phenanthrene and unknown
12. éfésol	69. C ₄ -naphthalene and (tetrahydrobenz-indan) or (methyltetrahydroacenaphthene)	125. C ₂ -phenanthrene
13. 1- or 2-methylindan	70. fluorene	126. n-C ₂₀ -alkane
14. n-C ₁₁ -alkane	71. unknown	127. dihydropyrene
15. methyldecalin	72. (benzindan) or (methylacenaphthene)	128. fluoranthene
16. 5-methylindan	73. n-butyl or iso-butyl naphthalene	129. C ₃ -phenanthrene
17. xylene	74. (benzindan) or (methylacenaphthene)	130. methylphenylnaphthalene
18. 4-methylindan	75. (benzindan) or (methylacenaphthene)	131. unknown
19. tetralin	76. (tetrahydromethylbenzindan) or (C ₂ -tetrahydroacenaphthene)	132. pyrene
20. unknown	77. n-C ₁₆ -alkane	133. n-C ₂₁ -alkane
21. naphthalene	78. (methylbenzindan) or (C ₂ -acenaphthene)	134. unknown
22. dimethylindan	79. (methylbenzindan) or (C ₂ -acenaphthene)	135. methylphenylnaphthalene
23. dimethylindan	80. unknown	136. methylpyrene or fluoranthene
24. n-C ₁₂ -alkane	81. (methylbenzindan) or (C ₂ -acenaphthene)	137. C ₃ -phenanthrene
25. 2-methyltetralin	82. (methylbenzindan) or (C ₂ -acenaphthene)	138. unknown
26. 1-methyltetralin	83. (C ₃ -acenaphthene) or (C ₂ -benzindan)	139. methylpyrene or fluoranthene
27. ethylindan	84. dihydroanthracene	140. n-C ₂₂ -alkane
28. C ₂ -indan	85. unknown	141. methylpyrene or fluoranthene
29. C ₃ -phenol	86. dihydrophenanthrene	142. unknown
30. 6-methyltetralin	87. octahydrophenanthrene	143. unknown
31. C ₃ -indan	88. methylfluorene	144. methylphenylnaphthalene
32. unknown	89. (methylbenzindan) or (C ₂ -acenaphthene)	145. unknown
33. unknown	90. methylfluorene	146. n-C ₂₃ -alkane
34. 5-methyltetralin	91. methyl-n-butyl naphthalene	147. C ₂ -pyrene or fluoranthene
35. 2-methylnaphthalene	92. n-C ₁₇ -alkane	148. unknown
36. unknown	93. unknown	149. unknown
37. 1-methylnaphthalene	94. pristane, i.e., 2,6,10,14-tetramethyl-pentadecane	150. unknown
38. cyclohexylbenzene and C ₂ -tetralin	95. tetrahydroanthracene	151. (tetrahydrochrysene or isomer)
39. 1- or 2-ethyltetralin	96. tetrahydrophenanthrene	152. n-C ₂₄ -alkane
40. C ₂ -tetralin and unknown phenol	97. (C ₃ -acenaphthene) or (C ₂ -benzindan)	153. unknown
41. 5- or 6-ethyltetralin	98. phenanthrene	154. unknown
42. C ₃ -tetralin	99. (methyl-dihydrophenanthrene)	155. unknown
43. biphenyl and C ₂ -tetralin	100. (methyl-dihydrophenanthrene)	156. unknown
44. tetrahydroacenaphthene	101. (methyl-tetrahydrophenanthrene)	157. unknown
45. ethylnaphthalene	102. (methyl-tetrahydrophenanthrene)	158. unknown
46. dimethylnaphthalene	103. C ₆ -naphthalene and unknown	159. n-C ₂₅ -alkane
47. n-C ₁₄ -alkane	104. C ₆ -naphthalene and (methyl-dihydrophenanthrene)	160. unknown
48. dimethylnaphthalene	105. (methyl-dihydrophenanthrene)	161. unknown
49. methylcyclohexylbenzene	106. n-C ₁₈ -alkane	162. (methylchrysene or isomer)
50. C ₃ -tetralin and unknown	107. (methyl-dihydrophenanthrene) and unknown	163. n-C ₂₆ -alkane
51. dimethylnaphthalene and (methyl-tetrahydroacenaphthene)	108. phenyltetralin	164. n-C ₂₇ -alkane
52. (tetrahydroacenaphthene)	109. dihydropyrene	165. n-C ₂₈ -alkane
53. n-propyltetralin	110. unknown	
54. C ₃ -naphthalene	111. (methyl-tetrahydrophenanthrene)	
55. C ₃ -tetralin	112. (methyl-tetrahydrophenanthrene)	
56. (methyl-tetrahydroacenaphthene)	113. (methyl-tetrahydrophenanthrene)	
57. acenaphthene and (methylbiphenyl)		

TOTAL ION CHROMATOGRAM
COT SAMPLE, DAY 17 - PDU RUN 5

The composition of the H-Coal recycle distillates is dominated by phenanthrene and compounds which are logical hydrocracking and hydro-isomerization products of phenanthrene. Since essentially no anthracene is seen in the recycle distillates we have taken the expedient of referring to phenanthrene and anthracene-based homologs as "phenanthrenes". However, in some instances the corresponding anthracene based and phenanthrene-based homologs are indistinguishable. In one instance, (peaks 95 and 96) we see both the tetrahydrophenanthrene and tetrahydroanthracene. The mass spectra are essentially identical, but differences in relative retention time indicate two different compounds.

3. Phenanthrene Hydrocracking

One of the largest peaks in Figure 4-7 is labeled (73, 74) and contains primarily a C₄-naphthalene. A small amount of a second component is also present. These two components are occasionally resolved in some chromatograms. Only one other C₄-naphthalene is observed, a relatively minor peak (#66). A substantial C₄-tetralin peak is also observed (#68). Both the C₄-naphthalene and C₄ tetralin give mass spectra which have M-43 base peaks, where M is the molecular weight of the parent molecule. This behavior is consistent with butyl substitutions on the aromatic rings. These data would suggest that hydrogenated phenanthrenes are readily cracked to the corresponding alkyl naphthalene and tetralin (i.e., sym-octahydrophenanthrene to butyltetralin and tetrahydrophenanthrene to butylnaphthalene).

This facile cracking of the hydrophenanthrenes is confirmed by the presence of the other n-alkyl tetralins and naphthalenes, spanning the range from methyl to butyl. A C₅-naphthalene (peak 91) is also seen. Its mass spectrum is consistent with a methyl butyl substitution. Data on the alkyl tetralins and naphthalenes are summarized in Table 4-17. All of the methyl tetralins and naphthalenes were detected. 5-m-tetralin appears as a weak leading shoulder on the 2-m-naphthalene peak and is not listed. Two features are apparent: the preference for alkyl substitution in the aromatic ring of the tetralin molecule, and the preference for substitution at the β position as in 6-m-tetralin and 2-m-naphthalene. The ethyl tetralins also show the preference for substitution on the aromatic ring. The mass spectra and retention times of the 5- and 6-ethyl tetralins are too similar to allow a distinction between these two isomers on the basis of the available data.

Only a few dimethyl naphthalenes and tetralins are observed, (e.g., peaks 40, 42, 46, 48, 51) and these are relatively minor components.

These data indicate that the predominant mechanism of phenanthrene hydrocracking is the opening of a saturated end ring, as in tetrahydrophenanthrene or sym-octahydrophenanthrene. The other possible cracking mechanism for phenanthrenes and anthracene involves hydrogenation (to the dihydro-) and opening of the middle ring to form alkylated biphenyls. A small amount of biphenyl is observed, coeluting with tetrahydroacenaphthene (peaks 43 + 44). No methyl biphenyls are observed. Several peaks (72, 74, 75) give mass spectra which are consistent with the spectra of methyl biphenyls, but they elute much too late to be identified as methyl biphenyls. A more plausible identification of these components is given below.

Table 4-17

Cracking Products of Hydrophenanthrenes
COT-82-17

<u>Peak #</u>	<u>Compound</u>	<u>% of Sample</u>	<u>Retention Time, (min)</u>
19	Tetralin	0.60	8.9
21	Naphthalene	0.41	9.4
25	2-Methyltetralin	0.33	10.2
26	1-Methyltetralin	0.11	10.4
30	6-Methyltetralin	0.92	11.5
35	2-Methylnaphthalene	1.29	12.3
37	1-Methylnaphthalene	0.26	12.7
39	1 or 2-Ethyltetralin	0.09	13.4
41	5 or 6-Ethyltetralin	0.42	14.1
45	1 or 2-Ethylnaphthalene	0.69	15.2
53	n-Propyltetralin	0.40	16.9
54	Isopropyl or Methylethylnaphthalene	0.05	17.0
58	n-Propylnaphthalene	0.62	18.1
60	Isopropyl or Methylethylnaphthalene	0.48	18.5
59	Methylpropyl or sec-Butyltetralin	0.23	18.4
66	Methylpropyl or sec-Butylnaphthalene	0.19	19.7
68	n-Butyltetralin	0.59	20.1
73	n-Butylnaphthalene	1.31	21.3
91	Methylbutyl or (2-pentyl) Naphthalene	0.45	24.6

These results are consistent with the report by Haynes, et al., on the hydrogenation mechanisms of phenanthrene⁽¹⁰⁾. They found substantial yields of butylnaphthalenes and tetralins for the hydrogenation of phenanthrene over a CoMo catalyst at 2000 psig H₂. The yields of butylnaphthalene and butyl-tetralin have maxima near 850°F, which was the average reactor temperature in PDU Run 5. Haynes also found low yields of biphenyl homologs indicating that opening of the central ring was not an important mechanism in phenanthrene hydrocracking at the conditions studied.

4. Hydroisomerization of Phenanthrene

In a manner similar to the isomerization of tetralin to methyl indan, hydrophenanthrenes can rearrange to form a potentially wide variety of cyclopenta-aromatic compounds. Cronauer, et al. have discussed some aspects of this question⁽¹¹⁾. Table 4-18 lists compounds which we believe are isomerization products of hydrophenanthrenes and hydroanthracenes. Examples of several possible isomerization routes are given in Figure 4-8. The most probable ring openings involve bond cleavage at an aromatic ring, because of stabilization of the resultant radical in the ring. The aliphatic portion can rearrange to form a secondary radical which is more stable than the primary radical. Recombination produces the methylcyclopenta rings. Figure 8 is not comprehensive. Tetrahydroanthracene can produce either of two methylbenzindans; tetrahydrophenanthrene can produce three methylbenzindan isomers, which have the methyl group in the saturated 5-member ring. Sym-octahydroanthracene or phenanthrene can undergo Reactions C and D to produce the respective methyltetrahydrobenzindans. A sym-octahydroanthracene and phenanthrene can, in principle, undergo reactions analogous to A and B to form the respective hexahydrofluorenes. Sym-octahydro molecules can undergo rearrangement of both end rings to form dicyclopentabenzene. Further, the isomerization products can be reduced to remove the methyl or, as in Reaction E, ethyl group. Note also that stabilization by hydrogen additions of the radicals formed will produce n-alkyl naphthalenes and tetralins, and that the tetralins produced (from sym-octahydrophenanthrenes and anthracenes) will have the alkyl substituents in the aromatic ring.

The listing of potential cyclopenta-aromatic isomers in Table 4-18 includes all potential candidates detected which would not be positively identified as other isomers.

The number of isomers detected of each type are listed below:

	No. of Isomers Detected
Tetrahydroacenaphthene (THA)	1
Methyl THA or Tetrahydrobenzindan (THBI)	4
Acenaphthene	1
Fluorene	1
Methylfluorene	1
Benzindan or Methylacenaphthene	2
Methylbenzindan or C ₂ -Acenaphthene	5
C ₂ -Benzindan or C ₃ -Acenaphthene	3

It is possible that other isomers exist, but they must be relatively minor components, and were not resolved.

Table 4-18

Isomerization Products of Hydrophenanthrenes
COT-82-17

<u>Peak #</u>	<u>Compound</u>	<u>% of Sample</u>	<u>Retention Time, (min)</u>
43	Biphenyl	0.18	14.6
44	Tetrahydroacenaphthene	0.31	14.7
51	Methyltetrahydroacenaphthene	0.32	16.5
56	Methyltetrahydroacenaphthene or Tetrahydro-benzindan	0.27	17.4
57	Acenaphthene and Methylbiphenyl	0.64	17.8
69	Tetrahydrobenzindan or Methyltetrahydro-acenaphthene	0.35	20.4
70	Fluorene	0.59	20.8
72	Benzindan or Methylacenaphthene	1.47	21.1
75	Benzindan or Methylacenaphthene	0.19	21.6
78	Methylbenzindan or C ₂ -Acenaphthene	0.09	22.2
79	Methylbenzindan or C ₂ -Acenaphthene	0.22	22.3
81	Methylbenzindan or C ₂ -Acenaphthene	0.27	22.6
82	Methylbenzindan or C ₂ -Acenaphthene	0.48	23.0
89	Methylbenzindan or C ₂ -Acenaphthene	0.84	24.4
90	Methylfluorene	0.84	24.5
97	C ₃ -Acenaphthene or C ₂ -Benzindan	0.23	26.1
101	C ₃ -Acenaphthene or C ₂ -Benzindan	0.12	26.9

Figure 4-8

POSSIBLE ISOMERIZATION REACTIONS OF HYDROPHENANTHRENES

We prefer the identification of the benzindan homologs as such, rather than as alkyl acenaphthenes, for a number of reasons:

- The mechanism which produces benzindans and hydrobenzindans is analogous to the known route for conversion of tetralin to methyl indans.
- The mass spectra of the supposed benzindans are very similar (although at higher mass) to the analogous indan spectra.
- The observed number of benzindan and methylbenzindan isomers agrees with the theoretical number possible with methyl substitution on the cyclopenta ring. This is the substitution which the isomerizations of Figure 4-8 would be expected to produce.
- There is one strong benzindan (peak 72) and one weak one (peak 75), corresponding to isomerization of tetrahydrophenanthrene and tetrahydrophenanthracene, respectively. These are three strong methylbenzindan peaks (81, 82 and 89) and two weak ones (78 and 79). This also agrees with the expected number of isomers and relative intensities.

A strong methylfluorene (peak 90) is observed, corresponding to reaction B, Figure 4-8.

These results are suggestive rather than conclusive. We do not intend a treatise on the isomerization and cracking reactions of hydrophenanthrenes. Instead we draw attention to a body of evidence which suggests that the majority of the components in H-Coal distillates, which boil below phenanthrene (340°C) are directly attributable to cracking and isomerization of hydrophenanthrenes. Phenanthrene itself is a major component on the recycle distillate for PDU Run 5, and it must be coal-derived. The turnover rate of distillate is sufficiently high, as indicated by the disappearance of the start-up oil by day 3, to preclude the possibility that it is simply a residual component of the start-up solvent. We also know⁽¹⁰⁾ that phenanthrene is readily hydrogenated over a CoMo catalyst, at conditions similar to those prevalent in PDU Run 5, to produce hydrophenanthrenes and, ultimately, alkyl tetralin and naphthalene.

The inference which we draw from these data is that much of the chemistry of H-Coal recycle distillate can be deduced from hydrogenation, cracking and isomerization mechanisms of the type described. The large number of phenanthrene-derived hydrocarbons may reflect the production of phenanthrene from higher molecular weight hydroaromatics, such as pyrene (via dihydropyrene) which are prominent components in the H-Coal recycle distillates. We will be exploring these possibilities in future work.

5. Hydrogen Donor Properties of H-Coal Distillates

In regard to the quality of H-Coal distillates as recycle solvents for coal liquefaction, these data indicate that process conditions are not conducive to a high concentration of hydroaromatic hydrogen donor molecules in the solvent. The concentrations of the hydrophenanthrenes and tetralins are relatively small, although the tetrahydrobenzindans, tetrahydroacenaphthenes and

alkyl/tetralins are probably active donors. The predominance of the cracked and isomerized products indicates high kinetic rates for these reactions, which reduce the donor hydrogen content of the distillate. Presumably, similar reaction can occur for higher molecular weight hydroaromatics and we will attempt to establish this in future work. It is interesting to note that some hydroaromatics, like dihydroanthracene, do not have facile isomerization routes and these may be important hydrogen donors.

To better establish the hydrogen donor properties of the H-Coal distillation, we used COT and HO distillate samples from days 3 and 28 to extract Indiana V coal at 750°F, 30 min, 2/1 solvent/coal, and measured conversion to THF solubles as an indication of donor hydrogen concentration. The use of this method was previously described⁽⁹⁾. The results are shown below:

Solvent	Conversion to THF Solubles, wt % MAF Coal	
	Day 3	Day 28
COT	69.8	80.6
HO Distillate	80.6	81.4

The COT results clearly show the effect of overhydrogenation during the early stages of the run, as determined from the NMR data. The conversion values for the samples taken on day 28 are also in agreement with the conclusion drawn for the NMR data, that the H-Coal distillates are relatively high quality hydrogen donors, compared to SRC solvents. Hydrogenation of these distillates at milder conditions (e.g., 700°F) would produce much better hydrogen donor solvents.

6. Phenanthrene/Alkyl Naphthalene Ratio as a Measure of Catalyst Activity

The fact that many prominent components of the H-Coal distillates can be identified as cracking products of phenanthrene, suggests the use of the ratio of phenanthrene to the n-alkyl naphthalenes as a measure of catalyst activity. These ratios were calculated from the GC/MS data for the COT and HO distillate samples, and combined to give a value for the total recycle distillate (Table 4-19). The alkylnaphthalenes are identified in Table 4-16 as peaks #21, 35, 37, 45, 60, 69 and 91.

The results show a rapid increase in the phenanthrene/alkyl naphthalene ratio during the first seven or eight days of the run, but with a more gradual increase throughout the run. This can be seen in Figure 4-9. The results are consistent with a steady but declining rate of catalyst deactivation throughout the run. This interpretation is somewhat compromised by the increase in hydrogen partial pressure during the last 10 days of the run. This may have increased the rate of production of phenanthrene from higher aromatics, thus increasing the phenanthrene/alkyl naphthalene ratio. We intend to further explore this area in the data from PDU Run 9, which operated smoothly for 30 days without the wide variation in hydrogen partial pressure experienced in PDU 5. Nevertheless, while the exact interpretation may be in doubt, these data indicate a more subtle long-term variation in recycle composition than is apparent from the other analytical techniques.

The other experimental measurements discussed above, particularly the ¹H-NMR and LCF data, do not show this substantial and constant variation as the

run progressed. The NMR and LCF data show a reasonable approach to steady-state by the middle of the run, with some response to the change in hydrogen partial pressure. The GC/MS data are able to indicate more subtle changes in recycle composition, which may signal longer term variations in process performance than are apparent from the less selective analytical methods.

Table 4-19

Phenanthrene to Alkyl Naphthalenes Ratio
H-Coal PDU Run 5

<u>Run Period</u>	<u>COT</u>	<u>HO</u>	<u>Total Distillate</u>
3	0.17	0.38	0.24
4	0.18	0.37	0.25
5	0.19	0.50	0.30
6	0.21	0.43	0.29
7	0.23	0.82	0.45
8	0.27	0.68	0.43
9	0.28	0.70	0.43
10	0.28	0.64	0.41
11	0.26	0.74	0.43
12	0.26	0.78	0.46
13	0.26	0.58	0.40
14	0.24	0.44	0.32
15	0.25	0.93	0.52
16	0.24	0.87	0.45
17	0.31	0.88	0.52
18	0.25	0.96	0.51
19	0.25	0.68	0.43
20	0.31	0.78	0.51
21	0.21	0.76	0.44
22	0.28	0.73	0.47
23	0.28	0.85	0.54
24	0.31	1.02	0.63
25	0.45	1.01	0.71
26	0.39	0.71	0.52
27	0.32	0.61	0.46
28	0.34	0.94	0.61
29	0.41	1.02	0.67
30	0.32	0.97	0.57

Figure 4-9
RATIO OF PHENANTHRENE TO ALKYLNAPHTHALENES,
TOTAL DISTILLATE - PDU RUN 5

Section 5

ESTIMATION OF APPROACH TO STEADY-STATE

A. METHOD OF ESTIMATION OF STEADY-STATE PERFORMANCE

One object of this work is to use the recycle slurry oil composition data to provide information on the approach of the H-Coal process to steady-state operation. The principal assumption is that, if the recycle slurry oil composition and rate are constant, then one criterion of steady-state operation is met. Unplanned variations in coal feed or process conditions (other than declining catalyst activity) are not predictable. Therefore, given constant coal feed and process conditions, a constant recycle composition is a necessary condition for steady-state operation.

Strictly speaking, one can never determine that the process is at steady-state. The strongest statement that can be made is that, for a given period of time, no variations in a measured variable occur which exceed the experimental uncertainty of that variable. The limiting factor is the length of the time period over which a given variable can be measured. Obviously, the longer the run, the greater the confidence that a true steady-state has been reached.

Application of this method of determining an approach to steady-state requires measurement of the average deviation in a measured quantity for a given time period, and estimating the experimental uncertainty in that measurement. A difficulty arises, because the experimental uncertainty is a composite of the uncertainties of the analytical method and uncertainties introduced by sample acquisition and subsequent handling. As described below, we have taken the approach of estimating the experimental uncertainty by making a linear approximation to the variable for sequential trial periods during the run, and calculating the average deviation between the observed and (linear) calculated values. We also used an analogous approach, but with an exponential approximation. The linear and exponential methods gave equivalent results. Since the linear approximation is somewhat easier to apply, we have used it throughout.

In mathematical terms we have a sequence of experimental measurements, A_{ij} ($i = 1 \rightarrow N$), and ($K-N$) trial periods of duration K , ending on day j . Then the mean value of the variable in question for the period ending on day j is

$$M_j = \sum_{i=1}^K \frac{A_{ij}}{K} \quad (2)$$

We calculate a linear approximation to the period ending on day j , and represent the calculated values for each day in the period as B_{ij} . The deviation between the least square line and the observed variables, which serves as an upper limit on the experimental uncertainty (E), averaged over the ($N - K$) trial periods is

$$E = \left(\frac{1}{N - K} \right) \sum_{j=K}^N \sum_{i=1}^K \frac{(A_{ij} - B_{ij})}{K} \quad (3)$$

For each trial period ending on day j , the average deviation between the observed variables and the mean for that period is given by

$$D_j = \frac{1}{K} \sum_{i=1}^K |M_j - A_{ij}| \quad (4)$$

If $D_j > E$, the average deviation in trial period exceeds the experimental uncertainty in the measured variable, and the system is not at steady-state. If $D_j \leq E$ the deviation in the data is within experimental uncertainty, a situation we cannot distinguish from steady-state.

Selection of the trial period length for the calculation was not found to be critical. A shorter trial period reduces both the calculated experimental uncertainty and the average deviation in the measured variable. We selected ten days as the length of the trial period on the basis of the statement in the HRI report⁽¹⁾ of PDU 5 that the run reached catalyst steady-state in ten days, and that this confirmed the predictions of previous bench-scale work.

The experimental uncertainties calculated by this method for the slurry oil composition data are given in Table 5-1. The proton distributions of the total THF soluble recycle (on a recycle rate basis) show a relative deviation averaging around 4%. This corresponds to an absolute deviation near 1%. The proton distribution of the total distillate has a calculated experimental uncertainty averaging 2% relative, or about 0.3% absolute. The deviation for the NMR data on total THF solubles includes variations in the recycle rates of the individual components, and is, therefore, a larger number. The experimental uncertainty in the normalized NMR of the total distillates is close to the experimental uncertainty of the analytical method.

The average deviations of the LCF, SESC and GPC data were calculated using the recycle rate data. The relative deviations for the LCF data average around 6%, corresponding to an absolute error of 2%. The GPC data show a similar behavior. The estimated experimental error in the SESC data is considerably greater. This is particularly true for the more functional fractions. In what follows it will be seen that the value of an experimental variable as an estimator of steady-state performance is directly related to its uncertainty.

B. ¹H-NMR DATA AS A MEASURE OF STEADY-STATE RECYCLE COMPOSITION

Figure 5-1 compares average deviations with experimental uncertainty for H-NMR data on the total THF solubles (COT + HO distillate + HO THF soluble resid, cf. Section 4-C-5). The horizontal line is the calculated experimental uncertainty in Figures 5-1 thru 5-8. The data are on a recycle rate basis. The variations in the data all show an approach to steady-state by the 10 day period ending on about day 17 of the run. The mid-point of this period (day 12) is in reasonable agreement with the assumption of steady-state in ten days made by HRI⁽¹⁾.

Table 5-1

Estimated Experimental Uncertainties as Percentage
of Measured Variables - Slurry Recycle Oil Components
H-Coal PDU Run 5

<u>Variable</u>	<u>Estimated Experimental Uncertainty</u>
Aromatic Protons - Total THF Solubles - 1b/1b Solids	2.9%
Alpha	4.0
Beta	4.9
Gamma	5.8
Condensed Aromatic Protons - Total Distillate - Normalized	2.7
Uncondensed Aromatic	2.7
Cyclic Alpha	1.7
Alkyl Alpha	0.8
Cyclic Beta	1.7
Alkyl Beta	1.6
Gamma	3.0
LCF Fraction, 1b/1b Solids	
Oils	6.1
Asphaltenes	5.1
Preasphaltenes	7.3
SESC Fraction, 1b/1b Solids	
1	8.3
2	7.3
3	7.4
4	11.8
5	31.9
6	11.0
/	16.0
Molecular Weight (GPC) Fractions, 1b/1b Solids	
700 amu ⁺	9.7
550 x 700	5.8
400 x 550	6.7
250 x 400	7.9

Figure 5-1

DETERMINATION OF STEADY-STATE FROM PROTON DISTRIBUTION
OF TOTAL THF SOLUBLE RECYCLE (RECYCLE RATE BASIS) PDU RUN 5

Figure 5-2A

DETERMINATION OF STEADY-STATE USING THE NORMALIZED PROTON
DISTRIBUTION OF THE TOTAL RECYCLE DISTILLATE - PDU RUN 5

Figure 5-2B

DETERMINATION OF STEADY-STATE USING THE NORMALIZED PROTON
DISTRIBUTION OF THE TOTAL RECYCLE DISTILLATE - PDU RUN 5

Figure 5-3
 DETERMINATION OF STEADY-STATE USING LCF DISTRIBUTION
 (RECYCLE RATE BASIS) OF THF SOLUBLE RESID - PDU RUN 5

Last Day of 10 Day Period

Figure 5-4

DETERMINATION OF STEADY-STATE USING THE RATIO OF BENZENE
SOLUBLES TO BENZENE INSOLUBLES OF THF SOLUBLE RESID - PDU RUN 5

Figure 5-5
 DETERMINATION OF STEADY-STATE USING SESC DATA
 (RECYCLE RATE BASIS) FROM PDU RUN 5

Figure 5-6

DETERMINATION OF STEADY-STATE USING GPC DISTRIBUTION
(RECYCLE RATE BASIS) PDU RUN 5

Figure 5-7

DETERMINATION OF STEADY-STATE USING THE RATIO
OF PHENANTHRENE TO ALKYLNAPHTHALENES - PDU RUN 5

Figure 5-8
DETERMINATION OF STEADY-STATE USING PRODUCT
DISTRIBUTIONS FROM PDU RUN 5 (WT % MAF COAL)

Last Day of 10 Day Period

Figures 5-2A,B, which considers the total distillate proton distribution, again on a recycle rate basis, is in good agreement with the assertion that a steady-state had been approached between the 10th and 15th days of the run. Note that each point plotted reflects the behavior of the variable during that day and the preceding nine.

After day 20, the data in Figures 5-1 and 5-2A and B consistently show a departure from steady-state performance, in response to the increased hydrogen partial pressure during that stage of the run. This response is fairly short-lived, and the average deviations in the data are within experimental uncertainty by the end of the run for most of the measured quantities.

C. SOLVENT FRACTIONATION OF THF SOLUBLE RESID BY LCF

Figure 5-3 shows the relationship between average deviation and experimental uncertainty for the recycle rates of oils, asphaltenes and preasphaltenes during PDU Run 5. The oils recycle rate appears to approach steady-state in the ten day period ending on day 27, although the shape of the curve is unusual. The variations in the asphaltenes recycle rate are near the experimental uncertainty from about day 15 to the end of the run. The preasphaltenes, as discussed in Section 5-B-1, approach a steady-state toward the middle of the run, then decrease in response to the increased hydrogen partial pressure after day 20. They also appear to be approaching a new steady state by the end of the run.

Figure 5-4 shows the data treatment applied to the ratio of benzene solubles to benzene insolubles in the THF soluble resid. These data clearly show the approach to steady-state in the middle of the run, and subsequent departure in response to P_{H_2} .

D. SESC FRACTIONATION OF THE THF SOLUBLE RESID

The treatment of the SESC data (Figure 5-5) shows the result of a large experimental uncertainty on the estimation of an approach to steady-state. The variations fluctuate around the experimental uncertainties for most of the run, indicating little if any clear trend. The heavier fractions (3 + 4 and 5 + 6 + 7) do indicate an approach to steady-state during the 10 day period ending on about day 28. Fractions 1 + 2 are close to the experimental uncertainty. While these results do not contradict the assumptions of steady state performance drawn from the NMR and LCF data, our results do not seem to have sufficient precision to make the SESC method useful as a measure of steady-state performance.

E. MOLECULAR WEIGHT FRACTIONATION OF THF SOLUBLE RESID BY GPC

The GPC results (Figure 5-6) show substantial periods of stable performance for the 400⁺ amu material beginning at the period ending on day 25. The recycle rate of 250 x 400 amu material shows greater variation. This may be an experimental artifact, caused by the laboratory distillation of the H₀ sample to produce the resid. Failure to achieve a precise cut-point would have its greatest effect on the lower molecular weight components. This may also explain the erratic behavior of the oils, in the LCF analysis, and fractions (1 + 2) in the SESC.

F. PHENANTHRENE/ALKYL NAPHTHALENE RATIO

The results of the treatment of the phenanthrene/alkyl naphthalene data (Section 4-D-6) are given in Figure 5-7. This ratio increases rapidly for the first seven days of the run, then levels off, and increases further toward the end of the run. These results may indicate a long-term variation in hydrogenation activity, but one which may not have a significant effect on the more important parameters of process performance, such as distillate and resid yields. Since phenanthrene is a small molecule relative to the bulk of the coal-derived distillates and resid, it may have portions of the catalyst surface available to it, from which the large molecules are rapidly excluded by pore blockage, during the initial stages of the run. Thus, we see a slower catalyst deactivation rate for phenanthrene hydrogenation, than for that of the larger coal-derived molecules in the heavy distillate and resid. The feed stock must be specified before catalyst activity can be assessed.

G. APPROACH TO STEADY-STATE OF PRODUCT YIELDS FROM PDU RUN 5

Figure 5-8 shows the variations in yields of 975°F distillate, C₁ x C₆ gases and residual oil from PDU Run 5, and the calculated experimental uncertainties. The distillate yield shows an approach to steady-state during the period ending on day 18, and an increase with the increased hydrogen partial pressure. The resid yield also makes a reasonable approach to steady-state during the last half of the run. These results are in reasonable agreement with the conclusions made by HRI in their report of PDU Run 5.

Section 6

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