315
4-27-81

(2)

Dr. 2614

DOE/PC/30027-4

NTIS-25
BINS-227

FOSSIL ENERGY

RECYCLE SLURRY OIL CHARACTERIZATION

Quarterly Report No. 1 for Period October 1—December 31, 1980

By
F. P. Burke
R. A. Winschel

MASTER

January 1981

Work Performed Under Contract No. AC22-80PC30027

Conoco Coal Development Company
Library, Pennsylvania

U. S. DEPARTMENT OF ENERGY

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Printed Copy A02
Microfiche A01

DOE/PC/30027-4
Distribution Category UC-90d

RECYCLE SLURRY OIL CHARACTERIZATION

Quarterly Report No. 1

Period: October 1 through December 31, 1980

Prepared by

F. P. Burke
R. A. Winschel

Conoco Coal Development Company
Research Division
Library, Pennsylvania 15129

January, 1981

Prepared for the
United States Department of Energy
Under Contract No. DE-AC22-80PC30027

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Section 1

INTRODUCTION

This is the first quarterly report under the subject contract reporting the results of analyses of recycle slurry oils in direct liquefaction processing. This work is similar in scope and intent to that recently completed under Contract DE-AC05-79ET-14503, "Development of the Correlation Between Slurry Oil Composition and Process Performance". That contract was devoted to the analyses of slurry recycle oils from the H-Coal process development unit operated by HRI at Trenton, New Jersey. In the current contract we expect that the majority of samples will come from the two-stage liquefaction bench scale unit operated by Lummus at New Brunswick, New Jersey. The Lummus unit consists of a short contact time coal liquefaction, followed by Lummus solvent deashing of the short residence time product. The deashed coal liquids are then upgraded in a Lummus-Cities Service LC-fining unit. The Lummus work is being conducted under DOE Contract DE-AC02-79ET-14804. DOE will also provide samples from other sources for analysis under this contract. The work is divided into three tasks as described below:

Task 1 Analytical Evaluation

Under this task CCDC will review the operational flow schemes, existing analytical plans, and required analytical data resulting from operations of the Lummus two-stage liquefaction bench scale unit. CCDC will then develop an analytical plan for the conduct of analytical characterization on recycle slurry oils and other process oils based upon the need for a thorough process characterization. The evaluation plan will identify sampling requirements, sample gathering techniques, sampling containers, and shipment procedures. This task has been completed.

Task 2 Analytical Characterization

Samples received from the two-stage liquefaction process development unit or other samples specified by DOE will be subjected to a series of analytical characterization tests. The procedures for analytical testing are based upon the work conducted under Contract DE-AC05-79ET-14503. The following characterization methods will be employed for some or all of the samples as deemed appropriate.

1. Distillation to quantitatively determine the distillate and resid fractions.

2. Tetrahydrofuran (THF) extraction, as appropriate, of the resid fraction to quantitatively determine the soluble residue, unconverted coal, and ash.

3. Combustion, as appropriate, of the THF insoluble residue to determine the unconverted coal and ash.

4. Microautoclave extractions at 2/1 slurry oil/coal, 30 min, and 750°F, termed the "Equilibrium" (EQ) run, to provide a relative measure of the total hydrogen donor content of the slurry oil, and at 8/1 solvent/coal, and 10 min, termed the "Kinetic" (KIN) run, to measure the kinetic activity of the hydrogen donors, based upon THF solubles.

5. Proton nuclear magnetic resonance analysis of recycle slurry oils, process oils, and appropriate boiling range fractions thereof to determine the proton distribution (total, aromatic, aliphatic) and thus the donatable hydrogen.

6. Gas chromatographic/mass spectrometric (GC/MS) analysis of oil fractions to determine molecular composition.

7. Liquid chromatographic (LC) analyses, as appropriate, of the THF soluble residues to fractionate the sample by solubility class (LCF), chemical functionality (SESC), and molecular size (GPC).

8. ^{19}F-nuclear magnetic resonance of fluorinated derivatives of distillate samples to measure the concentration of functional (-OH, -SH, -NH) components. These data will provide information on catalyst aging and selectivity.

9. Reverse phase liquid chromatography (RPLC) of distillate samples to separate functional components and hydrocarbons of different degrees of alkylation.

We foresee the possibility that during the two-year duration of this project analytical methods other than those listed above may be deemed desirable. A limited number of new analytical methods may be employed during the course of this contract, if time and money allow.

Task 3 Data Interpretation and Reporting

Our intention in this work is not simply to provide analytical data, but to utilize the measurements of recycle slurry and process oil characteristics to provide assistance to DOE and to the personnel involved in DOE funded liquefaction projects for evaluating the relationship between coal liquid properties and process performance. Areas of process performance to be investigated include but are not limited to the following:

1. Changes in the slurry recycle and process oil stream compositions during start-up.

2. The manner in which the process reaches steady state operation during start-up.

3. The composition of the recycle and process oil streams during stable operation.

4. The changes in recycle oil composition in response to planned variations in process variables.
5. Changes in recycle oil compositions which cause or result from unplanned upsets in process operation.
6. Differences in recycle and process oil compositions as a function of process operating conditions.
7. Differences in recycle and process oil compositions as a function of process feed materials.

Section 2

SUMMARY

Task 1

The sampling points and sample frequency necessary to perform the desired analytical characterization of the Lummus two-stage liquefaction bench scale unit have been identified in discussions with the Lummus project personnel. It was decided that four routine samples should be taken:

1. Paste solvent composed of deashed first-stage product from the LC-finer feed tank and flashed LC-finer product. A new batch of paste solvent is mixed every one to two days. We will receive a 200 g sample from each new batch. This sample should be essentially solids free but may in fact contain solids because the deashing unit is sometimes bypassed. Occasionally we will receive two samples from the same batch so that we may determine experimental uncertainties caused by sampling.

2. Flashed first-stage product containing distillate, soluble resid, unconverted coal and ash. We will receive a 200 g sample for each new batch of solvent.

3. Second-stage feed composed of deashed first-stage product. This sample may also contain solids as mentioned above. Each batch has a 40 hour inventory. We will receive a 200 g sample of each batch.

4. Second stage product. This sample may also contain solids. We will receive one 200 g sample each day of operation. Less frequent samples may be taken if specific needs arise.

Other samples will be taken from the unit as agreed by DOE, Lummus and CCDC to address specific questions that may arise.

Task 2

We have received 10 samples from the Lummus two-stage liquefaction unit. These 10 samples have been distilled, and the distillate fractions analyzed by proton NMR. 35 clean oil tank (COT) samples from H-Coal PDU Run 10 have also been analyzed by ^{1}H-NMR. The data thus far obtained are not sufficient to allow more than qualitative conclusions.

Section 3

EXPERIMENTAL

Descriptions are given below of all the analytical techniques which we propose to use in this work. It is recognized that modifications may be made in these techniques, some may be deleted from, and others added to the analytical scheme. Previous work has indicated that ^{1}H-NMR, LCF and ^{19}F-derivatization are among the most useful analytical techniques. The microautoclave method provides a good empirical measure of coal liquefaction solvent quality. These are expected to be the most commonly used characterization methods.

A. SAMPLE HANDLING AND PREPARATION

Ten samples of two-stage liquefaction materials, were shipped to CCDC from Lummus. In addition, samples of the hydroclone overflow (HO) and clean oil tank (COT) were taken by HRI during days 4 through 40 of PDU Run 10 and shipped to CCDC. The samples were shipped in one-pint metal containers, blanketed with argon. Samples were stored at ambient temperatures until analysis. The Lummus samples were identified, and the rationale for their selection was given in Section 2 of this report. Although the distillate portion of the HO "overlaps" to some extent the boiling range of the COT, these two streams can change composition independently. For example, the COT consists of atmospheric still bottoms and vacuum overhead which are themselves independently variable. Therefore, to obtain an assessment of the composition of the <u>total</u> recycle distillate, it was not adequate to analyze only one of the distillate recycle streams.

Clean oil tank samples are analyzed by ^{1}H-NMR, GC, GC/MS, ^{19}F-derivatization and microautoclave extraction without any further treatment.

Hydroclone overflow samples are distilled in a 1" x 3' jacket heated Vigreaux 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 will be analyzed by ^{1}H-NMR, GC and GC/MS. Some samples will also be analyzed by ^{19}F-derivatization and microautoclave extraction. The 535°C residue is ground using a mortar and pestle and a 5 gram sample pressure filtered with freshly distilled tetrahydrofuran (THF) through Whatman No. 42 paper at ambient temperature. The filter cake is washed with THF until the filtrate is colorless. The solids are 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 is removed from the filtrate by rotary vacuum evaporation. The resultant THF soluble HO resid is analyzed by SESC, LCF, GPC, and ^{1}H-NMR. These experimental techniques are described below.

The Lummus samples are treated in the same manner as the HO samples, except that the distillation endpoint is 270°C head, 320°C pot, 5 torr.

B. LIQUID CHROMATOGRAPHIC SEPARATIONS

The THF soluble resid fractions are characterized by three separation procedures. LCF (liquid column fractionation) separates primarily by solubility. 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. An ultra-violet 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. A small amount of column effluent is 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.

Upon leaving the evaporator oven, the coated wire passes into a heated (800°C) quartz tube, where the deposited sample is quantitatively burned in an air stream. The resultant CO_2 passes into a molecular entrainer, where H_2 is mixed with the stream. This mixture is carried into a Ni catalyst chamber. The CO_2 is quantitatively reduced to CH_4, to which the FID responds.

Because detector response is dependent upon the 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. 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(1) 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 50 g/l in THF. Peak areas were measured with an LDC computing integrator in the digitize mode. Response factors were applied to the peak areas to obtain weight percentages of the three fractions.

The LCF method is not expected to reproduce the more conventional Soxhlet methods. However, it is rapid, reproducible, and of acceptable analytical precision(1). Its rapidity (∿ 20 min) makes it much more suitable for process monitoring than the Soxhlet methods which have turnaround times 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% w/w H_2O added). The SESC procedure used in this project is a modified version of the method developed by Farcasiu(2). Seven solvents are used in the sequence, which, along with the compounds eluted in each fraction, is listed below:

Fraction	Solvent	Flow Time, min	Content
1	85/15 Hexane/Benzene	17	Saturates + aromatics
2	Chloroform	19	Polar aromatics, furans, thio-Phenes, non-basic N
3	90/10 Chloroform/Diethyl Ether	17	Monophenols
4	97/3 Diethyl Ether/Ethanol	17	Basic nitrogen heterocyclics
5	Methanol	10	Highly functional material, >10% w/w heteroatoms
6	Tetrahydrofuran	14	Increasing functionality and increasing molecular weight
7	Pyridine		

Solvent mixture ratios are given as volume percent. 3% ethanol is added to solvent 4, diethyl ether, to deactivate 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). Because of deactivation and residual adsorption, the column must be repacked with fresh silica gel for each run. Sample size is 100 μℓ and sample concentration is 40 g/l.

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 size distributions(3,4). A polymer, usually polystyrene or similar inert material, with a specified degree of crosslinking, is the stationary phase. Depending on their 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 oligiomers 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 oligiomer 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 versus molecular weight, which, when fitted to the distribution curve produced by GPC on the same sample, allows an empirical relationship between elution time and molecular weight to be established. This takes the form:

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

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 (daltons). Above this weight was the exclusion peak and a small fraction of the distribution ($\sim$ 15%). The remainder of the distribution was arbitrarily divided into 4 cuts, 700 → 550 amu, 550 → 400 amu, 400 → 250 amu, and < 250 amu.

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

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

^{1}H-NMR spectra were recorded on a Varian EM-360L 60 MHz instrument. Homogenized distillate samples are dissolved in chloroform-d, to make a $\sim$ 12% v/v solution, then filtered. Homogenized THF soluble residue samples are dissolved in pyridine-d_5 to $\sim$ 190 g/l then filtered. An internal tetramethylsilane (TMS) reference is used to lock the RF field. Samples are spun at $\sim$ 50 rps in 5 mm OD precision sample tubes. Spectra are scanned from 10.5 to 0 ppm over 5 min at 0.05 mG RF power.

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

Integrations for the distillate fractions are performed in duplicate on the instrument using a sweep rate of 1 min. The integrations are divided into seven regions corresponding to seven proton types.

Chemical Shift (TMS), ppm	Proton Type	Description
10.5 → 7.15	Condensed Aromatics	Proton attached to a condensed aromatic ring.
7.15 → 4.7	Uncondensed Aromatics and Hydroxyl	Proton attached to an uncondensed aromatic ring or to oxygen
4.7 → 2.5	Cyclic Alpha	Proton on naphthenic carbon adjacent to fused aromatic ring of naphthenoaromatic.
2.5 → 2.0	Alkyl Alpha	Methyl or non-cyclic methylene or methylidene 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 THF soluble residue samples are performed by planimetry in triplicate. This method makes it possible to subtract the effects of pyridine peaks and any residual THF. The integrations are divided into four regions corresponding to four proton types as previously described.

Chemical Shift (TMS)	Proton Type
10.5 → 4.7 ppm	Aromatics and Hydroxyl
4.7 → 2.0 ppm	Alpha
2.0 → 1.0 ppm	Beta
1.0 → 0.5 ppm	Gamma

D. GC and GC/MS

Some distillate samples will be analyzed by gas chromatography using a Perkin-Elmer 900 gas chromatograph equipped with a flame ionization detector (FID) and a 50 m x 0.2 mm methyl silicone fluid fused silica WCOT column from Hewlett-Packard. Data are handled with a Perkin-Elmer Sigma 10 data system. No internal standards are used. 0.5 μℓ of an 80% v/v solution of sample in THF is injected into a 300°C injection port with a 100 to 1 split for 1 minute.

The temperature program runs from 70-270°C at 4°/min. Initial temperature is held for 6 minutes. The column head pressure is 46 psig using a carrier gas of helium. The FID peak areas were used for quantitation assuming a response factor of unity for all components.

Selected samples will also be analyzed by GC/MS for qualitative information utilizing a Hewlett-Packard 5992 gas chromatograph/mass spectrometer (GC/MS) with a capillary interface. The same column used for GC is used for GC/MS. We inject 0.01 μℓ of a 4% v/v solution of sample in THF. Samples are injected according to the splitless method of Grob and Grob(5,6) at a column temperature of 50°C, permitting elution of the THF and cold entrapment of the sample at the column head. At 3 min after injection, the injection port is flushed for 15 secs. After 4.5 min the oven temperature is brought rapidly to 100°C then programmed to 270°C at 4°/min. The helium carrier gas is 99.9999 mole % pure and has a head pressure of 58 psig resulting in a flow of 2.2 ml/min at 100°C column temperature.

The mass spectrum of each GC peak and that of its background is stored on flexible disc. Each background spectrum is subtracted from its corresponding peak spectrum and the background subtracted mass spectrum of each GC peak was searched against our library of 300 coal-related compounds. Typically, there were between 150 and 200 GC peaks detected for an H-Coal distillate of which ca. 60 matched our library spectra. Identifications of those peaks which do 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 total, assuming uniform response. These data are semi-quantitative.

E. ^{19}F-NMR OF TRIFLUOROACETYLATED DISTILLATE SAMPLES

Selected samples will be analyzed as follows by a modified version of a method developed by Sleevi, Glass and Dorn(7,8). Trifluoroacetyl derivatives of each COT sample and selected HO distillate samples are prepared by reaction with trifluoroacetyl chloride (TFACl). A sample mixture is prepared by quantitatively dissolving ∿ 20% w/w α,α,α-trifluoroacetophenone in the sample as an internal quantitative standard. The reaction mixture is prepared by taking ∿ 0.28 g sample mixture and ∿ 0.02 g 2,6-lutidine as catalyst, diluting to 1 ml with chloroform and cooling to ∿ -23°C in a carbon tetrachloride/dry ice bath. Gaseous TFACl (b.pt. -18°C) is bubbled into the reaction mixture until there is a 0.4 ml volume increase from the condensed gas. The reaction is allowed to proceed at temperature for 10 min. The mixture is then removed from the bath and allowed to warm at room temperature. The unreacted TFACl is removed by bubbling N_2 through the mixture.

^{19}F-NMR spectra of the derivatized samples are recorded on a Varian EM-360L 60 MHz instrument. An internal shift reference of 1,2-difluorotetrachlorethane (FDTCE) is added to the filtered reaction mixture. Samples are spun at ∿ 50 rps in 5 mm OD precision sample tubes. Spectra are scanned from 0 to -10 ppm (DFTCE = 0) over 5 min at 0.05 mG RF power with the field locked on the shift reference. Triplicate integrations are run at scan speeds of 2 min.

Derivatized phenols resonate between -7 and -8 ppm(7,8). The number of equivalents of derivative per gram of sample is calculated from the weight ratio and area ratio of the internal quantitative standard and the sample.

F. MICROAUTOCLAVE EXTRACTIONS

Selected distillate samples are used as extraction solvents in microautoclave experiments. The experimental procedure was developed as part of a CCDC project for the Electric Power Research Institute(9). The results obtained in this study are internally consistent but do not necessarily correspond to the EPRI work because the "standard" coal sample may not have retained its integrity with time.

Microautoclave extractions are conducted using a 30 ml stainless steel pipe bomb, shaken vertically in a fluidized sandbath at 1000 strokes per minute. The stroke length is one inch. The microautoclave contains a 1/4" stainless steel ball for mixing. The microautoclave and sandbath apparatus are shown in Figures 3-1 and 3-2.

The sequence of steps in a typical run is as follows. After loading a standard feed charge (e.g., 5 gm Indiana V coal and 10 gm solvent) the microautoclave is threaded into the connecting rod and the motor switched on. The counterweights are then released to raise the sandbath and immerse the microautoclave. As the autoclave nears the prescribed run temperature, small doses of cold sand are added to the bath to hold the autoclave at the desired temperature. For a 15 gm sample, the heat-up time is 120 seconds to temperatures of 750 to 850°F. Heat-up curves are shown in Figure 3-3.

At the end of the prescribed residence time, the sandbath is lowered and covered with a trancite lid. An empty container is placed under the microautoclave and quickly filled with cold water to quench the autoclave contents to ambient temperature in about 30 seconds. Upon completion of the run, the contents are washed from the bomb with tetrahydrofuran (THF) and filtered under 5-10 psig N_2 through Whatman #42 filter paper. The filter cake is then dried and weighed to determine the combined weight of ash and unconverted coal. Conversions are calculated from the filter cake weight and the known proximate analysis of the coal.

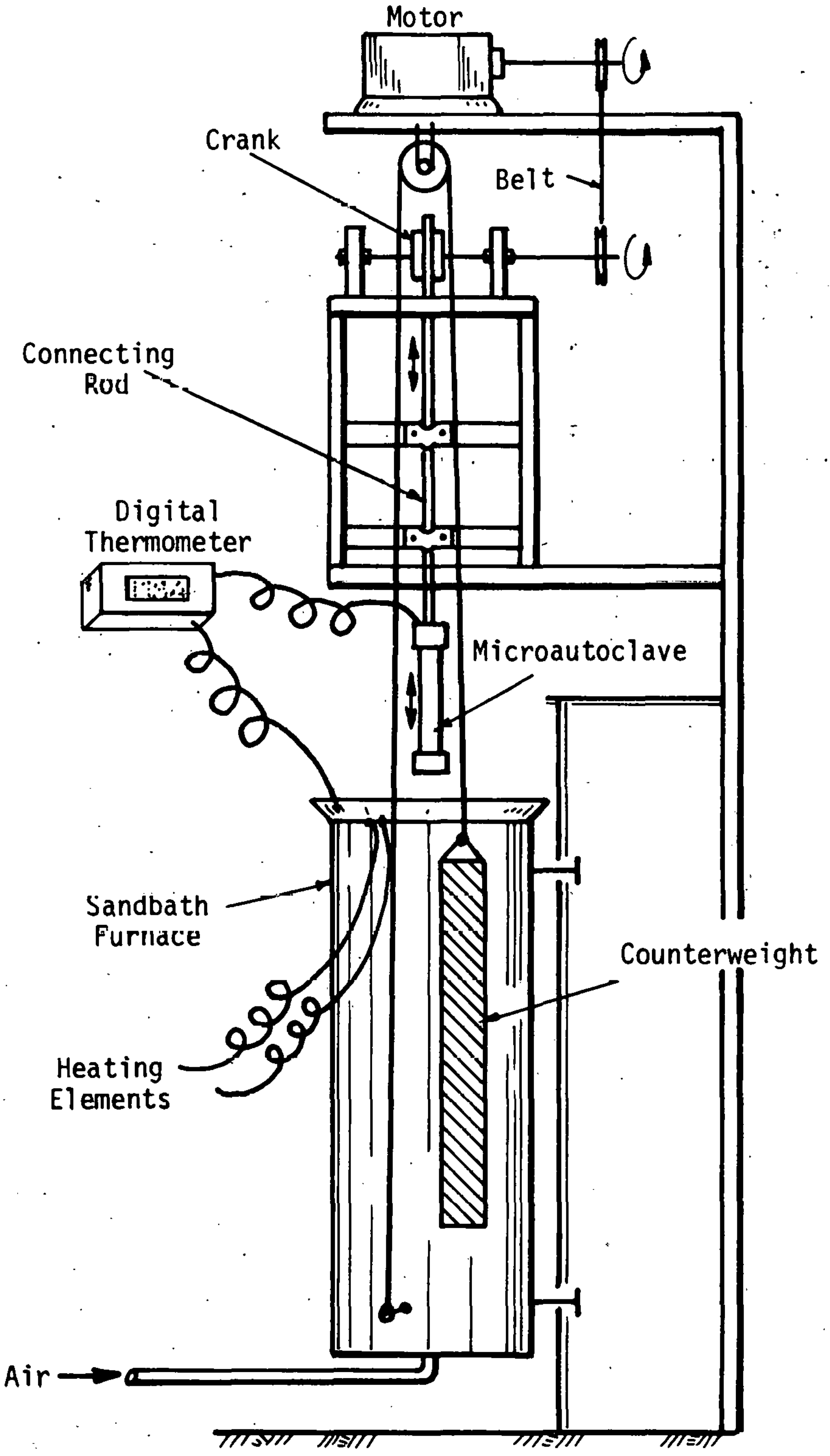
$$\text{Conversion} = \frac{\text{MF Coal - THF Insolubles}}{\text{MAF Coal (Oxidized Ash Basis)}} \times 100\%$$

G. REVERSE PHASE LIQUID CHROMATOGRAPHY (RPLC)

Reverse phase differs from adsorption chromatography (such as SESC) in that the column is packed with a non-polar bonded phase. The packing is prepared by treating silica gel with a chlorosilanated C-18 straight chain hydrocarbon. The chlorosilane reacts with free -OH on the silica, permanently bonding the C-18 chain to the silica surface and producing a bonded hydrocarbon packing. When a sample is introduced to the column, the least polar materials are most strongly retained (alkanes, highly alkylated aromatics)

Figure 3-1

MICROAUTOCLAVE UNIT



Sandbath Dimensions: Length = 31", I.D. = 6", O.D. = 9"

Figure 3-2

Design Details of the 30 ml Microautoclave

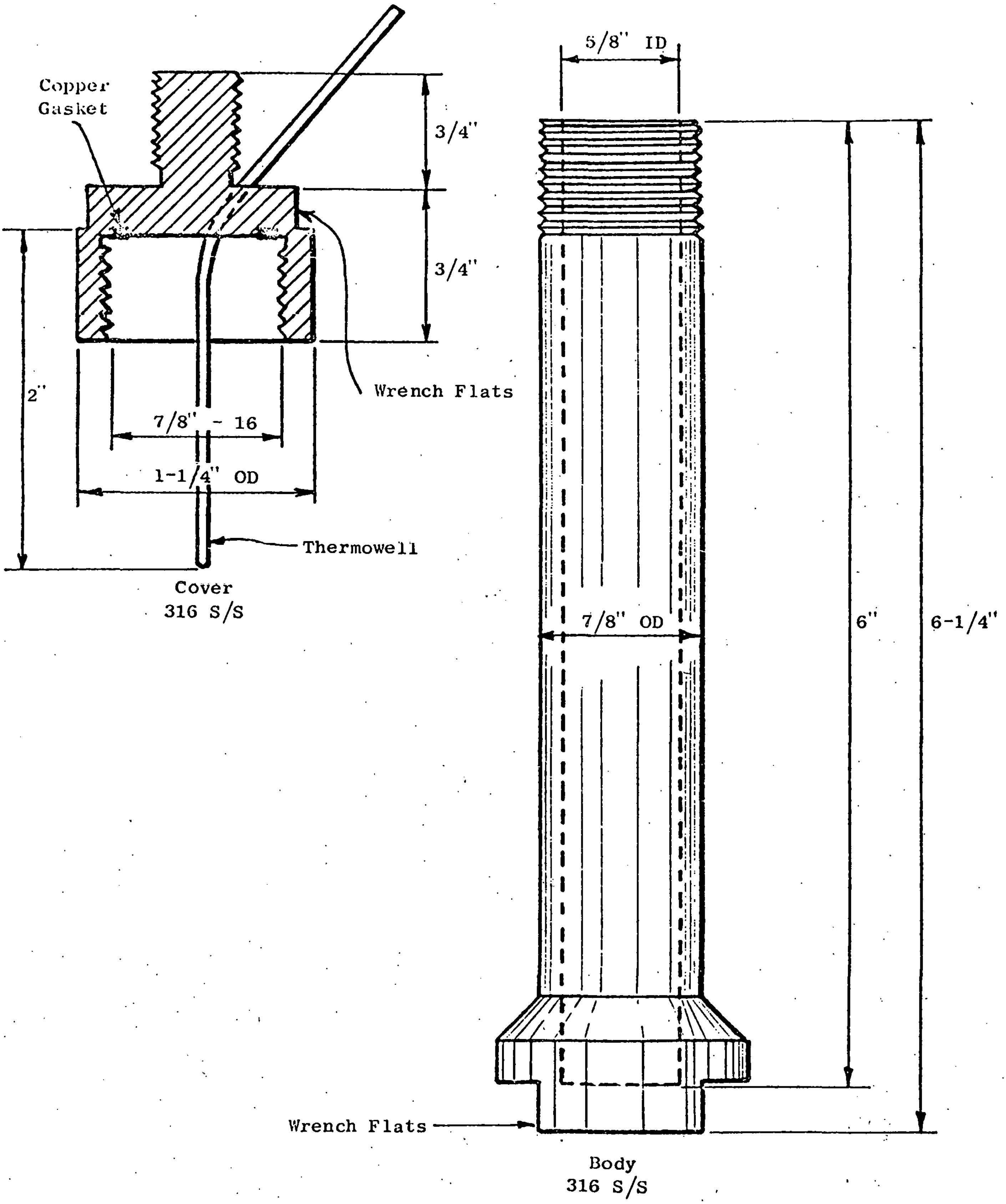
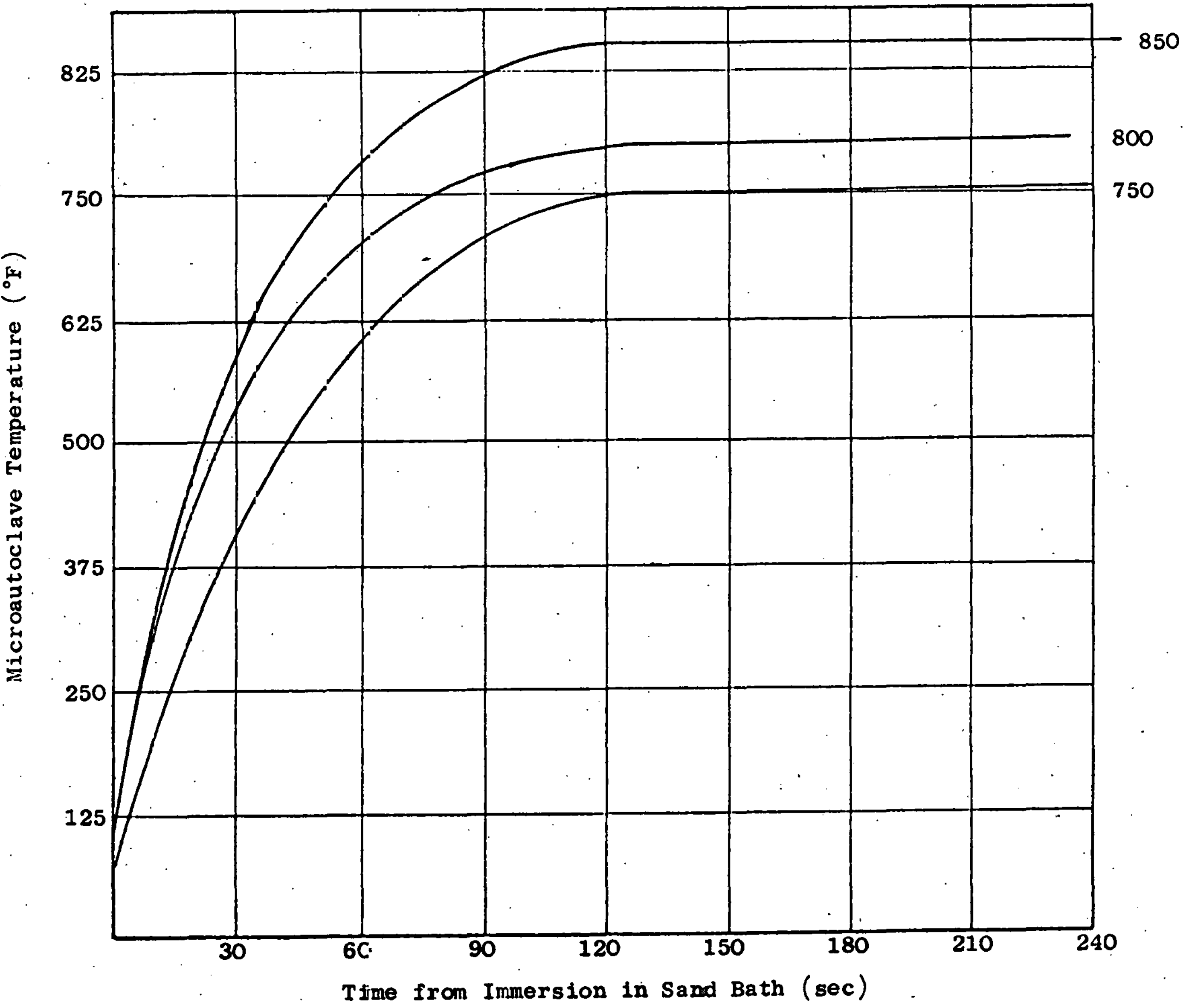


Figure 3-3

Microautoclave Heat-Up Curves



and the most polar components are eluted first. The polarity of the solvent (MeOH: H_2O) is decreased to elute less polar compounds by decreasing the percentage of water in the mixture. The polarity can be changed gradually or in discrete step changes. We have chosen the latter because, although a continuous gradient increases separation and resolution, a stepwise program brings out various classes of compounds as fractions, which can be quantified.

A Pye-Unicam LCM2 moving wire flame ionization detector (FID) is used. It has a quantitative response to the carbon content of the sample. The components of the individual fractions are identified by GC/MS. The solvent system is methanol/water, varied from 60/40 v/v MeOH/H_2O to 100% MeOH, followed by a THF flush. Run time is approximately two hours.

The chromatograph used is an Altex/Beckman 332 Gradient LC system with an Altex 5 μ C-18 Ultrasphere ODS 25 cm x 4.6 mm ID column and a 20 μℓ loop injector. Sample concentration is 250 g/l on analytical runs, and 500 g/l on prep runs for GC/MS identification. The flow rate is 1 ml/min and a two minute gradient is programmed for each step change in solvent strength.

RPLC Program

Time, min	% MeOH in H_2O
0	60.0
15	67.5
29	70.0
45	82.5
57	83.7
77	87.5
96	92.5
110	100.0
127	THF Flush

Section 4

RESULTS AND DISCUSSION

Task 2 Analytical Characterization

A. H-Coal PDU Run 10

We received seventy H-Coal PDU Run 10 samples from HRI. Of these, the thirty-four clean oil tank (COT) samples have been analyzed by ^{1}H-NMR. The proton distributions are listed in Table 1. We did not receive samples from those days for which no data are listed. For the first 15 days of PDU Run 10, the COT inventory increased in condensed aromatic proton concentration and decreased in cyclic beta proton concentration. This is similar to the manner in which the COT developed in PDU Runs 5 and 9(10). Following day 15, the concentration of condensed aromatics increased from 15.7 to 18.9% then decreased over the rest of the run to 11.4%. The other six proton classifications also changed in a complex manner after day 15. The period of PDU Run 10 following day 15 was operated at lower space velocity (25 vs. 31 lb/hr/ft^3) and lower slurry oil to solids ratio (1.5 vs. 1.75) than the first fifteen days(11). We expect to better understand these data when the detailed report of H-Coal PDU Run 10 is available.

The ^{1}H-NMR spectra of PDU Run 10 COT samples differ from those of PDU Runs 5, 8 and 9 in that the paraffinic -CH peak is very intense. PDU Run 10 was made with Wyodak subbituminous coal while Runs 5 and 8 were made with Illinois 6 and Run 9 with Kentucky 11, both bituminous coals. PDU Runs 5, 9 and 10 were operated in the Syncrude mode. PDU Runs 8 was run in the Fuel Oil and Intermediate modes.

The measured proton distributions (Table 4-1) show that PDU Run 10 COT samples are less aromatic and more paraffinic than COT samples from PDU Runs 5 and 9. Average values from these three Syncrude runs are given in Table 4-2. Based on these data we would expect the COT material from PDU Run 10 to be a poorer liquefaction medium than the PDU Run 5 or 9 material. Future work will further resolve these distinctions.

B. Lummus Two-Stage Liquefaction

We received ten samples from Lummus' two-stage liquefaction (TSL) unit. Each sample was distilled to a 270°C/5 torr cut point (pot temperature = 320°C). We are in the process of determining the percent THF solubles, insoluble organic matter (unconverted coal) and ash along with C, H, N and S content of the distillates. Distillation data are given in Table 4-3. The sum of the percent distillate plus resid equals the material balance of the distillation, which ranged from 97.7 to 99.6%. The unaccounted material is column hold-up.

The distillations went smoothly except for the short contact time (SCT) feeds, i.e., samples #3, 8 and 9. During the distillation of the samples, at approximately 270°C pot temperature, gas formed and carried distillate

Table 4-1

Proton Distribution of Clean Oil Tank Samples
H-Coal PDU Run 10

Run Day	Condensed Aromatics	Uncondensed Aromatics	Cyclic α	Alkyl α	Cyclic β	Alkyl β	γ
4	9.3	9.5	13.4	11.4	16.8	26.2	13.5
5	10.0	9.3	13.3	11.4	16.0	26.7	13.4
6	11.1	9.4	13.3	11.5	14.8	26.7	13.2
7	11.5	8.8	13.1	11.3	14.4	27.9	13.1
8	12.1	8.9	13.0	11.5	13.6	28.2	12.8
9	11.6	9.1	12.7	11.4	13.6	28.3	13.2
10	12.4	8.7	12.5	11.4	13.3	28.8	12.9
11							
12	12.1	8.9	12.3	11.5	13.7	27.9	13.7
13							
14	12.8	8.3	13.0	10.9	13.7	28.9	12.5
15							
16	15.7	9.0	13.2	9.5	16.1	24.3	12.2
17	16.8	8.3	13.1	9.8	13.6	26.2	12.2
18	16.5	7.9	13.2	9.8	13.8	26.6	12.1
19	18.6	8.3	13.9	9.9	14.4	24.2	10.8
20	18.9	8.0	14.1	10.2	14.1	24.0	10.6
21	15.8	8.1	13.2	10.5	13.6	27.1	11.7
22	14.1	7.9	12.7	10.3	13.8	28.2	13.1
23	16.5	7.7	12.9	10.4	13.4	27.4	11.8
24	16.6	7.3	13.7	10.5	13.5	27.2	11.2
25	14.5	8.3	13.0	11.0	12.7	28.5	12.1
26	14.4	8.0	12.5	10.7	13.4	28.6	12.4
27	14.8	7.2	14.0	10.7	14.0	27.8	11.5
28	14.6	8.4	12.4	10.9	12.5	28.4	12.8
29	14.1	7.5	13.1	10.7	13.4	28.9	12.4
30	13.2	7.9	12.6	10.6	13.1	29.8	12.8
31	13.7	7.6	13.0	10.6	13.4	29.1	12.6
32[1]	13.8	7.6	13.4	10.5	13.8	28.8	12.1
32	13.8	7.8	13.1	10.6	13.3	29.4	11.9
33	13.7	7.6	13.0	10.7	13.4	29.3	12.2
34	13.7	7.8	12.7	10.7	13.4	29.6	12.2
35	13.9	7.1	13.1	10.6	13.6	29.9	11.8
36	12.8	7.6	12.8	10.6	14.0	29.6	12.6
37	12.1	7.8	13.3	10.7	14.6	29.2	12.3
38							
39	11.1	6.9	11.6	10.1	13.8	31.8	14.8
40	11.4	7.7	11.3	10.4	12.9	31.7	14.7

[1] This sample taken at 5:00 a.m., all others at 10:00 or 10:30 a.m.

Table 4-2

Average Proton Distributions by ^{1}H-NMR: COT Samples

PDU				Aromatics		Alpha		Beta		
Run	Coal	Mode	Catalyst	Condensed	Uncondensed	Cyclic	Alkyl	Cyclic	Alkyl	Gamma
5	Illinois 6	Syncrude	Cyanamid HDS-1442A	19.6	10.5	16.5	12.5	13.9	17.7	9.3
9	Kentucky 11	"	"	19.4	9.7	16.8	12.3	14.5	18.0	9.4
10	Wyodak	"	Amocat 1A	13.4	8.1	13.2	10.6	13.8	28.5	12.4

through the condenser into the cold trap. Much of this material condensed in the vacuum lines further down stream. We subsequently found out that these samples contained feed coal, as opposed to being the recycle pasting solvent. Future samples will not contain the coal.

The ten samples can be divided into five groups corresponding to feed and product for a given reactor at a given date. In all cases, the product contained more distillate than the feed. Generally, the increase was moderate (about 5%). An exception is the sample pair 5 and 6 where the increase was 20%.

Proton distributions of the distillates, determined by ^{1}H-NMR, are given in Table 4-4. The LC-finer (LCF) product distillates differ from the feed distillates mainly in having a lower concentration of condensed aromatic protons and a correspondingly higher concentration of beta and gamma protons. This is a consequence of ring hydrogenation followed by hydrocracking. The two LCF feed distillate samples have considerably different proton distributions but the two product distillates are nearly identical. This is also true of the distillation data for these samples.

In all cases, the SCT product distillates have a higher concentration of condensed aromatic protons and a lower concentration of cyclic alpha and beta protons than the corresponding feed distillate. However, the fact that the SCT-F samples contained the feed coal makes any conclusions unreliable.

Table 4-3

Distillation Data
Lummus TSL Samples

Sample No.	Sample I.D.	320°C$^-$/5 torr Distillate, %	Resid, %	Material Balance
2	3LCF6-43F11080	50.1	49.1	99.2
1	3LCF6-43P11080	55.1	44.5	99.6
3	SCT12-6F11080	42.0	55.6	97.7
4	SCT12-6HO11080	45.6	53.0	98.6
5	3LCF6-64F11180	28.5	70.0	98.5
6	3LCF6-64P11180	49.4	50.1	99.5
8	SCT13-5F11180	34.3	65.0	99.3
7	SCT13-5HO11180	41.7	57.8	99.6
9	SCT14-1F11280	37.0	61.2	98.2
10	SCT14-1HO11280	41.0	58.6	99.6

Table 4-4

Distillate Proton Distributions
Lummus TSL Samples

Sample No.	Distillate Sample	Condensed Aromatics	Uncondensed Aromatics	Cyclic α	Alkyl α	Cyclic β	Alkyl β	γ
1	3LCF6-43P11080	14.2	7.3	15.4	8.7	24.1	18.6	11.7
2	3LCF6-43F11080	26.4	7.6	16.5	9.1	18.6	13.7	8.2
3	SCT12-6F11080	15.7	7.5	15.6	8.8	23.5	18.0	11.0
4	SCT12-6HO11080	21.8	7.5	14.6	8.6	19.8	16.9	10.7
5	3LCF6-64F11180	35.7	6.5	15.6	7.6	14.9	12.4	7.3
6	3LCF6-64P11180	14.5	6.4	15.4	8.1	23.6	19.7	12.4
7	SCT13-5HO11180	29.2	8.2	14.8	9.5	15.8	13.8	8.6
8	SCT13-5F11180	22.8	7.7	18.2	10.3	19.7	13.8	7.5
9	SCT14-1F11280	25.2	6.6	16.3	10.0	18.9	14.7	8.3
10	SCT14-1HO11280	28.9	8.3	14.4	10.2	14.9	14.3	9.0

Section 5

REFERENCES

1. Burke, F. P., Winschel, R. A., and Wooton, D. L., Fuel 58, 539 (1979).

2. Farcasiu, M., Fuel, 56, 9 (1977).

3. Coleman, W. M., Wooton, D. L., Dorn, H. C. and Taylor, L. T., J. Chrom., 123, 419 (1976).

4. Coleman, W. M., Wooton, D. L., Dorn, H. C. and Taylor, L. T., Anal. Chem., 49, 533 (1977).

5. Grob, K. and Grob, K., Jr., J. Chrom., 94, 53 (1974).

6. Grob, K. and Grob, G., J. Chromatogr. Sci., 7, 584 (1969).

7. Sleevi, P. L., Glass, T. C., Dorn, H. C., Analytical Chemistry, 51 (7), 1531 (1971).

8. Dorn, H. C., Sleevi, P. L., Koller, K. and Glass, T. C., ACS Div. of Fuel Chemistry Preprints, 24, (2), 301 (1979).

9. Kleinpeter, J. A., Burke, F. P., Dudt, P. J. and Jones, D. C., "Process Development for Improved SRC Options: Short Residence Time Studies," EPRI Project 1134-1, Final Report, EPRI AP-1425, June 1980.

10. Burke, F. P., Winschel, R. A. and Pochapsky, T. C., "Development of a Correlation Between Slurry Oil Composition and Process Performance," Final Report, DOE Contract No. DE-AC05-79ET14503, November 1980.

11. Hydrocarbon Research Incorporated, Phase III Laboratory Support for H-Coal Project, Monthly Progress Report No. 61, October 1980.

☆U.S. GOVERNMENT PRINTING OFFICE: 1980-740-145/1123