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A Characterization and Evaluation of Coal Liquefaction Process Streams

Quarterly Technical Progress Report
October 1 through December 31, 1994

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EXECUTIVE SUMMARY

HRI RUN POC-2

Analytical characterizations were completed by CONSOL on 65 process oil samples from representative periods of HRI Run POC-2 in which coal, coal/plastics, and coal/rubber were the feedstocks. These analyses provide information on the chemical transformation of these feedstocks and their distribution in product and recycle streams. The characteristics of the products and process streams were found to be dependent on both feedstock changes and operating conditions. Several unusual process oil characteristics were observed when wastes were coprocessed with coal, especially during the coal/plastic operation. Several major conclusions follow.

- Analyses indicate that first-stage reactor temperature in Run POC-2 was a dominant run variable. An increase in reactor temperature after period 21 of the run is associated with an increase in the aromaticity of virtually every process stream and with an increase in phenolic -OH of several process streams. Space velocity also was increased after period 21; however, the aromaticity of most streams did not return to the values observed in Periods 21 and earlier when the space velocity was reduced again in coal/waste periods 43 and 45. The phenolic -OH content of most streams decreased in the coal/waste periods, which may indicate that space velocity affected phenolic -OH concentration more than it affected aromaticity.

- High make-up oil rates were used during the waste/coal periods. The plant was not in solvent balance and results from the coal/waste periods do not reflect steady-state operation at those conditions. It appears that the higher-boiling "tail" in the naphtha stabilizer bottoms (NSB) samples from coal/waste periods 43 and 45 may be attributed, in part, to contributions from the high make-up oil use.

- Significant amounts of ethylbenzene and cumene (isopropyl benzene) components are present in the naphtha stabilizer bottoms (NSB) product from coal/plastics operation; these appear to be products from the liquefaction of the polystyrene. Unreacted or partially reacted polyethylene was found in product streams. Polystyrene appears to be a more reactive feedstock than polyethylene for coal/plastics liquefaction.

- The insoluble organic material (IOM) from the coal/plastics period 43 has unusual characteristics. This may be a result of the unusual solubility characteristics of liquefied plastics, especially polyethylene. Heavy THF-insoluble wax found in the deashed oil (DAO) seems to be unreacted or partially reacted polyethylene.

- Coal conversions were calculated by the ash balance method for various process streams. For samples taken sequentially through the process during period 43 (the coal/plastics period), there is an apparent increase in conversion, followed by a decrease in conversion.

- The feed conversion to THF solubles increased from 57% based on analysis of the second-stage product sample (reactor liquid flash vessel bottoms, RLFVB) to 97% based on analysis of the ROSE feed sample (vacuum still bottoms, VSB), and then decreased to 77% based on analysis of the ROSE bottoms sample. HRI saw parallel behavior in the conversion to quinoline solubles. These results suggest that, in order to better understand the conversion behavior of plastics, it may be useful to obtain the molecular weight distributions of the polyethylene and its intermediate products.

- The NSB sample from coal/plastics operation contained about 14 mg/kg of sediment not found in other samples. This material appears to be primarily elemental sulfur, but it also may contain oxygenated hydrocarbons. The stability of the coal/plastics product oil toward sediment formation should be investigated further.

- In general, distillate streams were quite low in phenolic -OH concentration (<≈0.10 meq/g). Although low phenolic -OH concentrations have typically been observed in HRI product liquids from bench unit runs, even streams as heavy as the vacuum still overhead (VSOH) were observed here to be quite low in phenolic -OH concentration (≈0.10 meq/g). No phenolic -OH was detected in the lighter distillates (NSBs and atmospheric still bottoms, ASBs), in agreement with HRI's findings that the product oil was consistently low in heteroatom content.

- Bypassing the K-3 hydrotreater in periods 33 and 44 had a slight effect to no effect on aromaticity, paraffinicity, and phenolic -OH concentration of the O-5 reactor overhead stream samples, relative to comparison periods 36 and 45.

ANALYSIS OF HRI RUN POC-1 OIL/WATER SEPARATOR SAMPLE

CONSOL analyzed a sample of the oil phase of the oil/water separator from HRI Run POC-1 for total phenols and types of phenols. The sample was extracted with caustic to concentrate the phenolics, and the neutralized extract was analyzed by gas chromatography/mass spectrometry to identify and provide semi-quantitative information on the phenolic compounds present. Approximately 1 wt % of the sample is comprised of phenolic compounds. Fifty-one individual chromatographic peaks were tentatively identified as phenolic compounds, including phenols with from zero to five carbon substituents.

COAL CALIBRATION

Chemical analyses and microautoclave tests were performed to monitor the oxidation and measure the reactivity of the standard coal (Old Ben Mine No. 1) which has been used for the last six years to determine solvent quality of process oils analyzed in this and previous DOE contracts. Because there was a large change in coal chemical properties and poor reactivity was found, a new sample of Old Ben Mine No. 1 coal was obtained from Ziegler Coal Co. The reactivity of this new coal is equivalent to the old batch as it was received in 1988, although the sulfate sulfur content is three times higher in the new sample.

UNIVERSITY OF DELAWARE

The University of Delaware has begun its experimental program to explore the reactivity of coal liquefaction resids. The Delaware quarterly technical report is appended to this document.

TECHNOLOGY TRANSFER

Two papers were prepared for the 209th Annual Meeting of the American Chemical Society in Anaheim, CA, in April: "Characterization of Coal/Waste Coprocessing Samples From HRI Run POC-2" by G. A. Robbins, R. A. Winschel and F. P. Burke will appear in the Symposium on Coprocessing of Coal and Waste Materials and "The Role of Recycle Oil In Direct Coal Liquefaction Process Development" by F. P. Burke will appear as an invited paper in the Storch Award Symposium. The papers appear in Appendices 5 and 6, respectively.

Section 2
INTRODUCTION

This is the Technical Progress Report for the second quarter of activities under DOE Contract No. DE-AC22-94PC93054. It covers the period October 1 through December 31, 1994.

CONTRACT OVERVIEW

The objectives of this project are to support the DOE direct coal liquefaction process development program and to improve the useful application of analytical chemistry to direct coal liquefaction process development. This project will build on work performed in DOE Contract No. DE-AC22-89PC89883. Independent analyses by well-established methods will be obtained of samples produced in direct coal liquefaction processes under evaluation by DOE. Additionally, analytical instruments and techniques which are currently underutilized for the purpose of examining coal-derived samples will be evaluated. The data obtained from this study will be used to help guide current process development and to develop an improved data base on coal and coal liquids properties. A sample bank will be established and maintained for use in this project and will be available for use by other researchers. The reactivity of the non-distillable resids toward hydrocracking at liquefaction conditions (i.e., resid reactivity) will be examined. From the literature and data experimentally obtained, a mathematical kinetic model of resid conversion will be constructed. It is anticipated that such a model will provide insights useful for improving process performance and thus the economics of direct coal liquefaction.

CONTRACT ACTIVITIES THIS QUARTER

- Analyses were completed on 65 process samples from representative periods of HRI Run POC-2 in which coal, coal/plastics, and coal/rubber were the feedstocks. The analytical results reported here provide information on the chemical transformation of these feedstocks and their distribution in product and recycle streams. The characteristics of the products and process streams were dependent on both feedstock changes and operating conditions. Several unusual process oil characteristics were observed when wastes were coprocessed with coal, especially during the coal/plastic operation. Implications of these results for future coal/waste liquefaction development and analytical characterization of the materials are discussed.

- A request was made to HRI for samples from the coal/plastics co-liquefaction bench Run CMSL-8, which was conducted during this reporting period. The sample request is included as Appendix 1 of this report. DOE asked CONSOL to act as a clearinghouse for samples from HRI Run CMSL-8. HRI will supply sufficient sample to us for further distribution to other research groups, e.g., the Consortium for Fossil Fuel Liquefaction Science.

- A sample of the oil phase of the oil/water separator from HRI Run POC-1 was analyzed to determine the types and concentrations of phenolic compounds present, at HRI's request. The sample was extracted with caustic to concentrate the phenolics and the neutralized extract was analyzed by gas chromatography/mass spectrometry.

- Chemical analyses and microautoclave tests were performed to monitor the oxidation and measure the reactivity of the standard coal (Old Ben Mine No. 1) which has been used for the last six years to determine solvent quality of process oils analyzed in this and previous DOE contracts. Because there was a large change in coal chemical properties and poor reactivity was found, a new sample of Old Ben Mine No. 1 coal was obtained from Ziegler Coal Co. The reactivity of this new coal is equivalent to the old batch as it was received in 1988, although the sulfate sulfur content is three times higher in the new sample.

- Substantial progress was made in the subcontract with the University of Delaware this quarter. A conference call was held with Delaware to discuss the goals of the program and methods to achieve those goals (see Appendix 3). Subsequently, we visited Delaware to set up the experimental program (see Appendix 3). Additional items sent to Delaware were the following:

    1. letter describing candidate samples for the resid reactivity studies to be conducted by Delaware.
    2. Available analytical data for the candidate samples.

3. A composite Wilsonville Run 258 V131B resid was made from individual run period resid samples and combined with the previously made composite to produce approximately 2100 g of sample; 1200 g were sent to Delaware.

4. An information package on Wilsonville Run 258.

5. A drawing of our pressure filter apparatus.

6. The experimental procedures used by CONSOL and HRI for resid determination by TGA.

7. Two Wilsonville 850 °F$^-$ distillate samples (V131B composites from Runs 261 and 262, 250 g each); descriptions of the samples and analytical data also were provided.

8. Gram-size samples of seven pure organic compounds with boiling points close to 850 °F were shipped to Delaware for use in TGA calibration.

9. A package of information describing Wilsonville 259G (including mass balances, temperatures, gas treat rates, flow diagram, etc.) was assembled and sent to Delaware.

- Four 240 g batches of oil-saturated Shell 324 catalyst (presulfided for Wilsonville Run 260) were stripped of oil by Soxhlet extraction under N_2 with THF. They are being stored under N_2 prior to being ground, packaged and sent to Delaware. Two Wilsonville resids (V131B and V1067 from Run 262) were composited from individual run period samples for use by Delaware. All Wilsonville resid samples chosen for the Delaware subcontract were submitted for proximate and ultimate analyses. The University of Delaware's quarterly technical report is appended.

- Elemental analyses of six samples from the University of Pittsburgh were reported to Pitt. Three of the samples are lignocellulosic waste materials and three are the pentane-soluble oil products from the liquefaction of wastes. The samples were generated under a Consortium for Fossil Fuel Liquefaction Sciences (CFFLS) Contract No. UKRF-4-26973-93-200 (DOE Reference Number 5-36479).

- Two papers were prepared for the 209th Annual Meeting of the American Chemical Society in Anaheim, California, in April: "Characterization of Coal/Waste Coprocessing Samples From HRI Run POC-2" by G. A. Robbins, R. A. Winschel and F. P. Burke will appear in the Symposium on Coprocessing of

Coal and Waste Materials, and "The Role of Recycle Oil In Direct Coal Liquefaction Process Development" by F. P. Burke will appear as an invited paper in the Storch Award Symposium. The papers appear in Appendices 5 and 6, respectively.

ACTIVITIES IN PROGRESS

- The status of analytical physicochemical methods for application of direct coal liquefaction, with emphasis on resid reactivity, is being assessed.

- An analytical plan was formulated with Burns and Roe Services Corp. to characterize the net product from HRI Run POC-2. Cost quotes were requested to obtain the necessary tests and analyses.

- Ten coal and process oil samples from the Exxon bench unit were received for characterization.

Section 3

RESULTS AND DISCUSSION

HRI RUN POC-2

Introduction and Run Background

In July 1994, HRI completed nine days of coal/waste coprocessing during the DOE Proof-of-Concept direct liquefaction Run POC-2.[2-5] Several key accomplishments of the HRI run were: Black Thunder Mine subbituminous coal was processed without deposition problems such as were encountered at the Wilsonville pilot plant; an in-line hydrotreater was operated to produce high-quality distillate low in heteroatom content; an overall material balance of 99.6% was achieved; and the plant successfully converted fifteen tons of plastic and waste tires into premium fuels with high conversion and a lower hydrogen requirement than during coal-only operation. A diagram of the plant[6] as configured for HRI Run POC-2 is shown in Figure 1. CONSOL analyzed 65 samples collected throughout the run; sample points are shown in Figure 1. Run conditions and yields for coal and coal/waste operating periods are shown in Tables 1-3. The main variables were feedstocks, reactor temperatures, space velocity, recycle type (ashy or solids-free), and solvent/feed ratio. The periods were relatively constant in severity, according to HRI's severity index.[2] Feed characteristics and analyses reported by HRI are given in Tables 4-7.

During 45 days of operation from June 1 through July 28, 1994, 350 tons of Black Thunder mine subbituminous coal and 15 tons of plastics and scrap tire rubber were processed. Other conditions were as follows: the Ni/Mo supported catalysts used were Akzo AO-60 in ebullated-bed reactors K-1 and K-2, and Criterion 411 in fixed-bed reactor K-3 (the in-line hydrotreater); space velocities were 20-40 lb MF coal/h/ft^3 reactor (per stage K-1 and K-2); K-1/K-2/K-3 reactor temperatures were 750-810 °F/815-837 °F/675-720 °F (399-432 °C/435-447 °C/357-387 °C); the ROSE-SR unit was used for solids separation (the vacuum tower was used for start-up); and the operation mode was for 700 °F$^+$ (371 °C$^+$) extinction, with ashy recycle used during the coal periods, and solids-free recycle during coal/waste periods. A dispersed Mo additive was used during Condition 5. For the waste/coal periods, the waste was pre-dissolved with recycle solvent in a separate vessel. This mixture then was transferred to the slurry mix tank, where coal was added. For this reason, waste feedstock components were present in the recycle oil during the waste/coal periods.

Sample Description and Experimental Details

CONSOL analyzed 65 process stream samples from Run POC-2. A summary of the analytical scheme for these samples is given in Table 8. Sample points, SP-xx, given in the table correspond to those shown in Figure 1. In the following discussion, the abbreviations shown in Table 8 will be used, e.g., NSB for naphtha stabilizer bottoms, DAO for deashed oil. Most samples were received in 1-quart or 1-gallon cans; some of the NSB product oils were received in 1-quart glass bottles. Also received from Run POC-2, but not analyzed, were several catalyst withdrawal samples from reactors K-1 and K-2.

The period 44 HTR bypass sample 0-5 was obtained from PETC. It consisted of two phases. The lower phase was water and contained only minor amounts of hydrocarbon. Therefore, analyses of the water layer are omitted from the analytical data tables, and the results reported for the 0-5 period 44 sample are only from the upper phase.

Experimental details about most of the analytical methods used have been provided elsewhere.[7,8] GC/MS analyses were done with a DB-5 column, 30 m x 0.25 mm, 0.25 μm film thickness. GC conditions were: 5 min at 10 °C; 2 °C/min to 100 °C, 4 °C/min to 320 °C, up to 20 min at 320 °C. The injection port was held at 300 °C. The carrier gas was He at 20 psig. One percent solution of make-up oil sample in tetrahydrofuran, or neat NSB samples were injected in the splitless mode. The mass spectrometer was scanned from 33 to 300 amu. Peak identifications were based on searches of the Wiley/NBS mass spectral library and retention times.

Analytical Objectives

One objective was to determine the fates of the various waste feedstocks processed. Information is desired on the relative convertability of the feedstocks, the product streams to which the feedstocks are converted (bottoms vs. distillate), interactions of feedstocks, and their effects on product quality. In order to address these objectives, property characteristics reflecting feedstock differences must be distinguished from those caused by the choice of other process conditions. In this case, important process conditions included: 1) ashy vs. ash-free recycle, 2) high make-up oil use in waste coprocessing periods, 3) high solvent/feed ratios in waste coprocessing periods, 4) ROSE-SR operations, and other factors, such as reactor temperature, space velocity, and catalyst age. Other performance issues of interest in HRI Run POC-2 include achievement of steady state, unit performance (such as the ROSE deasher), retrograde reactions, and product stability issues.

Comparison Period Conditions

Properties of process samples from HRI work-up periods representing coal operation (periods 21, 34, and 36; Conditions 2B, 4C, and 5, respectively), coal/plastics operation (period 43, Condition 6), and coal/rubber operation (period 45, Condition 7) were compared. The conditions for periods being compared were relatively constant in severity (5.16-5.25), as determined by HRI's severity index computed from time, temperature, and space velocity.[2,3] Conditions 4C and 5 were equivalent for most operating conditions, but 150 ppm Mo additive was used in condition 5. The differences between Conditions 7 and 6 were 70/30 coal/rubber feed in Condition 7 and 75/25 coal/plastics feed in Condition 6. Conditions 6 and 7 differed from Condition 2B in having higher K-1 and K-3 temperatures; higher catalyst addition rate in reactors K-1 and K-2; solids-free vs. ashy recycle; 2.0 vs. 1.2 recycle/feed ratio; and coal/waste vs. coal feed. Conditions 6 and 7 differed from Conditions 4C and 5 in having lower space velocity; no Mo additive in condition 6 or 7; solids-free vs. ashy recycle; 2.0 vs. 1.2 recycle/feed ratio; and coal/waste vs. coal feed.

Feedstock Analyses

The Black Thunder Mine feed coal samples from several periods were analyzed (Table 9). Oxidation indices were measured by diffuse reflectance FTIR[9,10] in duplicate on three samples of the Run POC-2 feed coal. The samples gave values of 3.34 ±0.11, 3.32 ±0.07, and 3.11 ±0.04, respectively, from Periods 15, 21, and 36 (coal-only feed periods). Previous oxidation index results with two Wilsonville Black Thunder Mine coal samples from Run 262 were 4.48 ±0.02 for a pile sample and 3.90 ±0.51 for a tote bin sample.[11] The somewhat lower values obtained for the HRI feeds indicate that there is no evidence of coal oxidation.

Table 10 shows the analyses of the waste feed samples. The polyethylene terephthalate has a high oxygen content, making it a less-desirable feed because of the expected high hydrogen consumption to produce water. In contrast with HRI's analyses of the polyethylene (Table 6), CONSOL's analyses (Table 10) do not show any significant concentration of sulfur.

Table 11 shows major and trace elemental composition of ashes from selected samples. The samples were analyzed for Mo and Ni to look for evidence of possible catalyst attrition in periods 36, 43, and 45. Samples from period 45 were analyzed for Zn to determine the fate of the rubber ash. The results of these analyses are discussed in a later section.

Overall Run Results, Including Coal-Only Periods

Aromaticities of many process streams increased significantly after Period 21, beginning in periods 34 or 36, as shown in Figures 2-4 and Tables 14-16 (including the coal/waste periods). In most cases, they did not decrease to the levels of period 21 after the space velocity was reduced after period 36. Since there was a step increase in reactor K-1 temperature to 810 °F after period 21, it appears that it is the dominant cause. Furthermore, such an effect of reactor temperature on oil aromaticity is commonly observed. Although space velocity also increased after period 21, aromaticities generally did not decrease to as great an extent when the space velocity was decreased for periods 43 and 45. Increased temperature favors cracking over hydrogenation can increase aromaticity by: 1) increasing coal conversion, thus increasing the amount of solubilized, but not upgraded, resid; and 2) by increased cracking of aliphatic materials, including alkyl side chains.

Phenolic -OH concentration in most process streams also increased after period 21 (Figures 5 and 6, Table 17), but it generally returned to a lower value in periods 43 and 45, in which the space velocity was lower and wastes were coliquefied with coal. Typically, the increases were ≈0.05 meq/g for distillates, and ≈0.10 meq/g or higher for resid streams. Affected streams include: the CONSOL-generated 850°F distillate and resid fractions of 0-43 (recycle oil) and 0-46 (RLFVB); and the THF-solubles from the VSB, ROSE bottoms, and DAO. It appears that perhaps phenolic -OH is more sensitive to space velocity than is aromaticity.

Notably, no phenols were detected in the NSB and ASB stream samples. This is consistent with HRI's observation that the product oil was very low in heteroatoms.

The donor solvent quality of the O-43 recycle oil (Table 18, measured by microautoclave test) was generally good, ranging from about 75 to about 86% conversion. The highest value of 86% occurred during coal/plastics period 43, in which feed plastic was present in the recycle oil. The 850 °F^+ fraction generally improved the solvent quality of the 850 °F^- fraction by 5 to 10% (absolute) conversion, except in the rubber period. The RLFVB whole oils had good donor solvent qualities in about the same range (74 to 87%), except that periods 21 and 43 gave poor values of 61 and 67%, respectively. In many of the periods, the donor quality of the RLFVB was equivalent to or higher than that of the corresponding recycle oil. Addition of Mo in period 36 relative to period 34 resulted in a 7% increase in RLFVB whole oil solvent quality. The start-up/make-up solvent had an excellent donor solvent quality of about 89%, but the COT P-3 oils tended to be low in solvent quality, ranging from 62 to 74% conversion.

Although HRI observed an improvement in coal conversion and hydrogen consumption when a dispersed Mo precursor (Molyvan 822) was used in period 36 relative to period 34 (Table 1), we observed minor or no impact on oil characteristics (Tables 12-14 and 15-18), other than an increase in RLFVB donor quality (5% for the distillate and 7% for the whole oil).

Only small increases in phenolic -OH concentration (from not detected to 0.07 meq/g), and proton aromaticity (from 8% to 11%) were observed in the O-5 reactor overhead stream when the K-3 hydrotreater was bypassed in period 44, relative to its use in period 45. No differences were evident in the K-3 bypass period 33 relative to K-3 use in period 36.

Duplicate VSB samples were received from period 21 (Table 12); however, their determined IOM and ash contents do not agree well (Table 12), and they differed slightly in phenolic -OH concentration (Table 17), but the NMR spectra of the two samples were quite similar (Table 14). We do not know if sampling or analysis is the source of the discrepancy.

Characteristics of Coal/Waste Samples

The conditions in periods 21 and 34-36 generally bracket the conditions used during co-liquefaction of coal and wastes. Therefore, it would be expected that the characteristics of period 43 and 45 samples would be intermediate between the period 21 and period 34-36. We will address those period 43 and 45 results which appear to be exceptional.

A comparison of 0-43 recycle oil samples is limited because of the presence of premixed plastics or rubber in the samples from those periods in which plastics or rubber were added upstream of the slurry mix tank. The presence of the waste feed components may be responsible for distinctive proton distributions (Table 14) in periods 43 and 45.

Various period 43 and 45 samples have different IOM and ash contents than the coal periods (Table 12). In these cases, IOM is always high, and ash is always low, except in the case of the DAO from period 45, in which the ash content was relatively high. HTI observed ash carryover during period 45.[3] The 850 °F$^-$ distillate content of the period 43 and 45 RLFVB samples was unusually high (Table 12). In several instances, the concentrations of oils, asphaltenes, and preasphaltenes in the period 43 and 45 samples were unusual (Table 13). A good example is the high preasphaltene concentration in the period 43 and 45 DAO samples. Undoubtedly, solids-free recycle operation in periods 43 and 45 played a role in some of these differences. Besides the feedstocks, other conditions, such as ROSE operating conditions, could also affect the characteristics of DAO and ROSE bottoms samples (see also the later section on "ROSE-SR Performance").

Plastics and Rubber Product Oils

Gas chromatography/mass spectrometry (GC/MS) total ion chromatograms are shown in Figure 7 for NSB product oils and the make-up oil. The make-up oil was used to supplement recycle when there was insufficient process-derived solvent. The NSBs contain paraffins with carbon numbers ranging up to about 24 (tetracosane, boiling point 736 °F); this generally is consistent with the expected boiling point of these products. The product from the coal/plastics and coal/rubber periods had more material boiling in the range 600-750 °F, in agreement with HRI's distillation data.[2] The make-up oil has a higher boiling point distribution than the NSBs, although the boiling points of the two overlap. The make-up oil may contribute to some of the higher boiling components seen in the NSBs from the coal/plastics and coal/rubber periods. Distillation, hydrogenation, and hydrocracking are all routes by which this higher-boiling make-up material may find its way into the NSB boiling range. Make-up oil comprised 27 wt % of the period 43 recycle stream composition and 43 wt % of the period 45 recycle stream composition, compared with none during the coal period 36 (Table 3). The contribution of make-up oil was greater because of the higher solvent/feed ratio (≈2.3) in the waste/coal periods than in the coal period (1.3). Thus, the higher-boiling material seen in the coprocessing period NSBs seems to be attributable to plant operating conditions, and not specifically to the feedstocks used. Since the plant was not in solvent balance during the coal/waste periods, sample and yield data may not represent plant operation at steady-state conditions.

Unusual Materials from Plastics Period

Significant amounts of ethylbenzene (EB) and cumene (isopropyl benzene, (IPB)) components were found in the NSB only from the plastics period, as determined by GC/MS (Figure 7, see marked peaks at retention times 16.77 and 21.85 minutes). Proton NMR confirms this (Figure 8), since distinctive peaks from ethylbenzene or diethylbenzene are present only in the spectrum of the plastics period NSB product. These components are believed to be products from the liquefaction of the polystyrene. Thus, the presence of these components is attributable to the feedstock. It was estimated by integration of the GC/MS total ion chromatogram and independently by integration of the ^{1}H-NMR spectrum that these two components comprise 10.5 wt % of the period 43 product oil. This constitutes a yield of 7.7 wt % MAF from polystyrene, which is 10.7 wt % of the MAF feed. Expressed another way, 72% of the feed polystyrene is found as ethylbenzene and cumene products. Ethylbenzene and cumene comprised 0.5 wt % of the period 36 NSB product, and 1.8 wt % of the period 45 NSB, based on GC/MS analysis.

The DAO from the plastics period was extracted with THF and found to contain insolubles. This insoluble material is gray in color, waxy in appearance, and melts below 100 °C. Diffuse reflectance FTIR (Figure 9) indicates that the material contains methylene and methyl aliphatic groups, with essentially no aromatics or heteroatomics. Except for a more intense methyl C-H stretch peak, the DAO insolubles spectrum is very similar to that of a polyethylene film sample

(Figure 9). The sharp doublets around 1470 and 720 cm^{-1} are excellent matches with polyethylene. The peak at ≈720 cm^{-1} is indicative of long-chain paraffins. The elemental composition of the DAO insolubles is similar to that of the polyethylene feed, and they are almost identical in H/C ratio (Table 10). Since this is apparently non-distillable wax, much heavier than waxes observed with coal alone,[12] we believe that this material results from polyethylene liquefaction. In fact, the evidence strongly suggests that this material is unreacted or partially reacted polyethylene.

Unusual IOM Characteristics in Plastics Period

An increase in IOM across the ROSE unit was reported by HRI[2] (quinoline solubility basis) and confirmed in CONSOL data (THF solubility basis, Table 19). The coal conversion determined by CONSOL by the ash-balance method (Table 19) was 57.5% based on the RLFVB sample, 96.8% based on the VSB sample, and 77.3% based on the ROSE bottoms sample (sequential points through the process). At face value, these data suggest that coal conversion increased across the vacuum still and that retrograde reactions occurred across the ROSE-SR unit in the plastics/coal period. However, it appears likely that these results reflect unusual solubility characteristics of liquefied plastics, especially polyethylene. In addition to the increased IOM in the ROSE bottoms, a significant amount of the waxy IOM is recycled in the DAO. As shown above, this IOM material is polyethylene or a derivative of it. The presence of this material in the DAO may result from unusual phase behavior or instability. A relatively high preasphaltene concentration in the period 43 DAO coincides with the presence of IOM in this stream (Table 19). The solubility of the IOM component in the RLFVB stream seems to be different than in the VSB stream.

These results suggest that in studying plastics liquefaction, it may be useful to obtain the molecular weight distributions of the plastic and its intermediate products. This would provide information to better understand the conversion behavior of the plastics.

There was no evidence that polystyrene did not convert completely, but there seem to be problems associated with polyethylene liquefaction (waxy DAO insolubles) The high oxygen content of polyethylene terephthalate would appear to make it less desirable as a feedstock, though we have no evidence that it manifested problems. It appears that polystyrene would be the preferred feedstock, based on this test. Liquefaction of the plastic feedstocks separately from each other would help resolve some issues.

ROSE-SR Performance

ROSE bottoms samples from the periods 15, 21, 43, and 45 were less aromatic and less phenolic than corresponding samples from periods 34 and 36 (Table 20). These properties are consistent with the lower organic rejection during periods 34 and 36, during which HRI changed the deashing solvent to operate the ROSE unit differently. However, the space velocity was also highest in periods 34 and 36, confounding it with the ROSE operating conditions. These results illustrate that it is not necessary to invoke feed differences, per se, to account for these differences in ROSE bottoms properties in periods 43 and 45.

The unusual IOM characteristics during coal/plastics operation in period 43 became particularly evident in ROSE feed and product samples. Perhaps processing in the ROSE unit caused a component soluble in the VSB sample to become insoluble, analyzed as high IOM in both ROSE products (the DAO and the bottoms).

The ROSE bottoms sample in period 43 appeared to contain some separate lumps of dull and shiny components. Since the ROSE unit can produce material ranging in consistency and appearance (e.g., "gummy", "powdery"), this could represent variation within a sampling period. On the other hand, it could be evidence of different phases. No attempt was made to characterize these materials individually.

Product Oil Sediment in Plastics Period

The NSB from the plastic/coal period contained about 14 ppm (mg/kg) of sediment not present in other samples from this run, or in product oil samples from prior Wilsonville pilot plant runs or from HRI bench-scale runs. A portion of the sediment is slightly soluble in THF or pyridine. A sample of sediment was obtained for characterization by filtration of the NSB through a silver membrane filter, followed by a hexane wash and vacuum drying. The filter deposit was characterized in-situ by diffuse reflectance FTIR and SEM/EDX. FTIR (Figure 10) indicated a primarily aliphatic material with a hydrogen-containing functional group (such as O-H); some aromatic and some carbonyl seem also to be present.

SEM/EDX (Figure 11) showed the deposit to consist primarily of sulfur, with smaller amounts of carbon and oxygen also evident. The collective evidence suggests that the bulk of the sample is elemental sulfur, which has little infrared activity and limited solubility in common solvents.

Major and Trace Ash Elemental Analyses from Coal/Waste Samples

In several operating periods of Run POC-2, HRI found a significant amount of fines in the catalyst withdrawal samples from the reactors, especially from the second-stage reactor K-2. Excessive fines are an indication of an unusual amount of catalyst degradation through attrition. We analyzed several process stream samples from periods 43, and 45 for Mo and Ni to look for evidence of possible catalyst attrition and a sample from period 36 for comparison.

The feed coal ash from period 36 contains 0.01 wt % or less of these elements (Table 11). The feed rubber ash likewise contains no more than 0.01 wt % Mo or Ni. Since there is almost no Ni or Mo in the feeds, any elevated concentrations of Mo or Ni in the stream samples must represent attrited catalyst, or some other source of Ni and Mo. The AO-60 catalyst used during Run POC-2 is assumed to contain 2.5 wt % Ni and 8.0 wt % Mo, based on analyses of Amocat 1C catalyst,[19] which is equivalent to Akzo EXP-AO-60. To simplify the calculations and reduce variability, we used the sum of wt % Ni and Mo to estimate the amount of attrited catalyst. The catalyst contains 10.5 wt % Ni + Mo and the process stream samples range in Ni + Mo from 0.07 to 0.35 wt % in the ash (Table 11). The lowest value of 0.07 wt % was obtained after subtracting the contribution of Mo in the dispersed catalyst, which was added as Molyvan L in period 36 (Table 11, note c).

Concentrations of Ni and Mo were elevated (0.07 to 0.35 wt % Ni + Mo in ash, Table 11) in samples from periods 36, 43, and 45, in which the feeds had concentrations of Ni+Mo of about 0.01 wt % in the ash. If the plant were at steady state, these concentrations would represent attrited catalyst of 0.6 lb/ton MF feed (coal plus waste) in Period 36, 1.3 lb/ton in period 43, and 3.4 lb/ton in period 45 (based on the ROSE bottoms sample analyses). However, during periods 43 and 45, the plant was not operating at steady state, and so these estimates may not accurately reflect the degree of catalyst attrition. As an indication of the transitory nature of this portion of the run, note that the concentration of Zn in the ROSE bottoms sample ash from period 43 is slightly elevated (0.05 wt %, Table 11), but there is little Zn present in the feed coal (0.01 wt % of ash, Table 11). This elevated concentration of Zn in the period 43 sample may reflect carryover of rubber ash from periods 37 and 38 when coal/rubber liquefaction was first attempted.

Perhaps because of the transitory nature of this portion of Run POC-2, some inconsistencies exist in the period 45 VSB, ROSE bottoms, and DAO (ROSE overheads) data. The ash content (SO_3-free) of the DAO stream is equivalent to that of the ROSE feed stream (i.e., the VSB stream) at 4.3 %, but the ROSE bottoms stream has a higher ash content of 14.2 % (Table 11). This could only happen if the ROSE bottoms had a miniscule flow rate, which is not the case. Therefore, one or more of the stream analyses is based on a bad sample, or other analytical error which is misrepresenting the ash content.

Samples from period 45 were analyzed for Zn to determine the fate of the rubber ash (Table 11), since Zn is a major component of the rubber ash. The stream with the highest ash Zn concentration downstream of liquefaction is the DAO stream. This suggests that a fair amount of rubber may be recycled in the DAO stream, although the exact selectivity for rubber and coal components is not known. As discussed above, the inconsistencies in the ash concentration in the VSB, ROSE bottoms, and ROSE overheads (DAO) stream samples from period 45 casts some doubt on the validity of these stream samples and analyses.

ANALYSIS OF HRI RUN POC-1 OIL/WATER SEPARATOR SAMPLE

Introduction and Summary

At the request of Mr. A. G. Comolli and Mr. S. Mikhail of HRI,[13] CONSOL analyzed a sample of the oil phase of the oil/water separator from Run POC-1 for total phenols and types of phenols. The sample was extracted with caustic to concentrate the phenolics and the neutralized extract was analyzed by gas chromatography/mass spectrometry to identify and provide semi-quantitative information on the phenolic compounds present. Approximately 1 wt% of the sample is comprised of phenolic compounds. Fifty-one individual chromatographic peaks were tentatively identified as phenolic compounds, including phenols with from zero to five carbon substituents.

Discussion

The sample was identified as "260-14-44B, 0-45, filtered", which indicates that it was a filtered sample originally taken from the oil/water separator during period 44B of Run POC-1. The material was a light-brown, low-viscosity oil that was somewhat turbid and that left a thin, brown deposit on the walls of the glass jar in which it was stored. Centrifugation of the sample produced a very minor amount of a powdery, distinctly red solid that was insoluble in THF. CONSOL's analytical approach was 1) to obtain a ^{1}H-NMR spectrum and a GC/MS analysis of the original sample and to determine its phenolic -OH concentration by FTIR, 2) to quantitatively extract the phenolics with caustic, and 3) to analyze the extract and raffinate by ^{1}H-NMR, FTIR and GC/MS (extract only).

The original sample has a proton aromaticity of 7.5% and a phenolic -OH concentration of 0.10 meq/g (Table 21); this phenolic -OH concentration is not particularly high relative to other light coal liquids from the HRI CTSL process that we have analyzed.[18] GC/MS analysis showed components with boiling points ranging from toluene (111 °C) to n-nonacosane (441 °C), but the bulk of intensity was provided by materials that eluted before naphthalene (bp 218 °C).

Caustic extraction of the original sample gave an extract yield of 1.1 wt% and a raffinate yield of 98.0 wt% for a total mass balance of 99.1 wt% (Table 22). As might be expected, the raffinate gave a ^{1}H-NMR spectrum very similar to the original sample (its aromaticity of 7.5% is identical) and its phenolic -OH concentration was below detection limits (Table 21).

On the other hand, the caustic extract has a very different NMR spectrum that is characteristic of cresylics; it has a very high aromaticity of 36.2% (Table 21). The caustic extract has a measured phenolic -OH concentration of 6.25 meq/g. This compares to the calculated phenolic -OH concentrations of the following pure compounds (in meq/g): xylenol, 8.2; C_3-phenol, 7.3; and C_4-phenol, 6.7; and indicates that the caustic extract is indeed highly concentrated phenolics. GC/MS analysis of the caustic extract resulted in the separation of 51 peaks that were identified, some tentatively, as substituted phenols with from zero to five carbon substituents (Table 23). Those phenol peaks represent 80% of the area of the total ion chromatogram; thus, we estimate that approximately 80 wt% of the caustic extract is phenolic compounds. Most of the non-phenolic compounds identified were substituted benzenes.

Experimental

Proton nuclear magnetic resonance analyses and phenolic -OH determinations were made using CONSOL's standard procedures.[7,8] The NMR distributions are area percentages, normalized after omitting the area of the hydroxyl peak. Omitting the hydroxyl peak is inconsequential for most samples; however, since the caustic washed fraction has such an intense hydroxyl peak, this omission does affect its reported proton distribution. Phenolic -OH concentrations are determined from the -OH peak located between about 3270 and 3335 cm^{-1}.

GC/MS analyses were done with a DB-5 (5% diphenyl:94% dimethyl:1% vinyl polysiloxane) capillary column, 30 m x 0.25 mm, 0.25 μm film thickness. The GC conditions used for the analysis of the caustic extract were: 5 min at 10 °C then 2 °C/min to 200 °C then 4 °C/min to 320 °C; injection port 300 °C; He carrier gas at 20 psig. 10 nL of 1% solutions of samples in tetrahydrofuran were injected in the splitless mode. The mass spectrometer was scanned from 33 to 300 amu. Peak identifications were based on searches of the Wiley/NBS mass spectral library, CONSOL's library of coal-derived compounds, and retention times.

The sample was caustic washed as follows. Sample (100.03 g) was contacted three times with 30 mL of 6 wt% NaOH solution and then twice with 20 mL of deionized water in a separatory funnel, leaving 97.98 g of caustic raffinate. The combined aqueous phase was acidified with concentrated HCl, then contacted three times with 30 mL of methylene chloride in a separatory funnel. The combined organic phase was stripped of solvent in a rotary evaporator, leaving 1.12 g of caustic extract.

CALIBRATION AND ANALYSIS OF STANDARD COAL

Routine microautoclave solvent quality assays are made with a single standard coal: Old Ben No. 1 Mine, Indiana V seam. The previous batch of coal was received in November 1988. In April 1990, this coal batch was found to be rapidly deteriorating and it was repacked for long-term storage in air-tight, N_2-purged plastic bags in batches of 500 g.[14]

Generally, it has been found that oxidation results in a decrease in liquefaction yields.[15,16] In order to determine the relative decline in performance of the standard coal, batch microautoclave tests were periodically made using this coal and solvents containing varying ratios of tetralin and 1-methylnaphthalene. The results of the most recent tests on a sample of coal opened in August 1994, and tests made in January 1993 are given in Table 25 along with the results of tests made on the as-received sample. The coal conversions obtained with the most recent tests (8/94) indicate that the coal has deteriorated significantly.

Chemical analyses of the recently opened (8/94) plastic bag of this coal sample showed the coal to be deteriorated (Table 24). This is apparent by comparison of the analyses of this batch and the analyses of the as-received coal (November 1988), the analyses made upon resealing the coal in April 1990, and the analyses made one, two, and three years later in March 1991, March 1992, and January 1993. The degree of deterioration of the coal sample via weathering is indicated by an increase in sulfate sulfur and an increase in total and organic oxygen content.[17] Pyritic sulfur is known to slowly convert to sulfate; this and a loss of calorific value often are the only perceptible changes in the chemical analysis of the coal sample. The analyses given in Table 24 show that the recently opened (8/94) batch of coal has a higher sulfate sulfur content than the batch tested in January 1993.

Consequently, a five gallon sample of Old Ben Mine No. 1 coal was requested and received from Ziegler Coal Co. This sample was air-dried to about 7% moisture, divided into two 10 lb batches and stored in tri-layer bags. One bag of coal was ground to pass 100 mesh and subdivided into 150 g batches and sealed in tri-layer bags. Analysis of this new batch of Old Ben Mine No. 1 is given in Table 24. Results of Kinetic and Modified-Equilibrium microautoclave solvent quality tests for this new coal batch are given in Table 25. This sample has a higher Btu content than the old sample as it was received in 1988. The sulfate content of this new sample is about four times greater than the previous sample when it was new; however, solvent quality tests indicate that this new sample is as reactive as the old sample when it was received in 1988.

Section 4

EXPERIMENTAL

Experimental details are described, where appropriate, in the Discussion section of this report. Details of the other analytical techniques used in this work were reported previously.[7,8]

Section 5

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TABLE 1A

OPERATING SUMMARY AND PROCESS PERFORMANCE[2,3]
HRI Run POC-2

Process Conditions (a)	L/O	1B	2B	4C	5**
Period(s)	4,12	14-15	20-21	33-34	35-36
Recycle Type	Ashy	Ashy	Ashy	Ashy	Ashy
Space Velocity, kg/hr/m^3	308.50	305.00	458.00	608.30	614.50
K-1:					
Temperature, °C	399.30	399.50	413.00	431.20	432.20
Cat Replacement Rate, kg/tonne MF Coal	0.10	0.10	0.45	0.75	0.75
Cat Age, kg MF Coal/kg Cat	720.00	936.00	1042.00	1040.00	1026.00
K-2:					
Temp., °C	434.00	435.00	444.00	447.20	443.50
Cat Replacement Rate, kg/tonne MF Coal	0.16	0.16	0.90	1.25	1.25
Cat Age, kg MF Coal/kg Cat	6.26	702.00	721.00	618.00	626.00
Flow Rates					
Coal Feed, kg/hr	69.35	67.75	102.00	137.05	138.40
Oil Streams to SMT					
0-43 Recycle to SMT, kg/hr	51.08	53.00	43.85	65.85	67.85
Make-up Oil, kg/hr	0.00	7.75	0.00	20.20	0.00
ASB (through COT) to SMT, kg/hr	31.50	27.30	87.53	95.90	108.85
Solvent/Coal Ratio, kg/hr	1.19	1.30	1.30	1.30	1.30
Material & Ash Balances					
Liquefaction Section Recovery, wt %	102.10	101.55	100.30	99.05	100.10
Overall Material Recovery, wt %	101.85	100.60	97.80	97.00	99.35
Normalization Factor	0.99	0.99	0.99	1.01	1.00
Ash Balance, wt %	95.00	102.65	106.53	107.70	103.70
Normalized Yields, wt % MAF Coal*					
H_2S	0.48	0.84	0.47	0.74	0.56
NH_3	1.22	1.09	0.94	1.13	1.03
H_2O	19.44	18.11	19.08	21.45	19.26
COx	1.24	0.24	0.44	1.13	1.16
C_1-C_3	9.46	8.13	9.43	9.68	10.11
C_4-C_6	4.41	4.12	4.40	3.04	4.50
IBP-177 °C	12.65	12.36	14.93	15.37	18.28
177-288 °C	21.61	22.17	23.57	26.72	24.91
288-343 °C	17.65	19.76	11.07	10.36	1.32
343-524 °C	8.66	7.78	7.85	1.08	8.42
524 °C$^+$ (Solids-free)	3.00	3.58	8.46	7.63	11.67
524 °C$^+$ (Tol. Insols)	0.22	0.22	0.24	0.34	0.34
Unconverted Coal	8.85	10.33	7.40	8.22	6.51
Process Performance*					
Chemical H_2-Consumption, wt % MAF	7.72	8.60	8.26	6.86	8.05
Coal Conversion, wt % MAF	91.15	89.65	92.60	91.80	93.50
524 °C$^+$ Conversion, wt % MAF	87.95	85.85	83.90	83.85	81.50
Denitrogenation, wt %	86.50	82.50	87.70	85.70	86.25
C_4-343 °C Net Distillates, wt % MAF	55.40	58.35	53.95	55.50	49.00
C_4-524 °C Distillates, wt % MAF	64.05	66.10	61.80	56.60	57.45
C_1-C_3 Selectivity, kg/kg of C_4-524 °C (x 100)	14.65	12.25	15.25	17.10	17.60
H_2 Efficiency, kg of C_4-524 °C/kg H_2	8.30	7.70	7.50	8.30	7.15
Deasher Performance					
Organic Rejection, wt % MAF	24.15	24.35	22.00	12.70	13.80
Energy Rejection, %	23.05	23.10	21.00	11.95	13.60
Deasher Coal Conversion, wt % MAF	88.25	89.80	91.50	89.80	90.90
Deasher Rejection of 524 °C$^-$ Material, wt % MAF	5.10	3.70	3.00	1.70	1.85

NOTE: Elemental analyses of all the work-up periods are not yet available to accurately evaluate the H_2 consumption.
*Based on Liquefaction Section: 0-13 Bottoms
**Molyvan-822 was a moly-additive used in Condition 5 at 150 ppm Mo relative to coal

(a) ROSE-SR used for solids separation in all reported periods.

TABLE 1B

OPERATING SUMMARY AND PROCESS PERFORMANCE[2,3]
HRI Run POC-2

Process Conditions (a)	5	6	6	7
Period(s)	35-36	42	43	45
Recycle Type	Ashy	Solids-Free	Solids-Free	Solids-Free
Feed, wt %***				
Coal	100.00	68.00	70.00	74
Plastics (42, 43)and Rubber (45)	0.00	32.00	30.00	26
HDPE	n/a	19	15	n/a
PS	n/a	13	10	n/a
PET	n/a	0	5	n/a
Ground Rubber	n/a	n/a	n/a	26
Space Velocity, kg/hr/m^3	614.50	379.00	433.60	398.40
K-1: Temperature, °C	432.20	428.30	431.10	430.00
Cat Replacement Rate, kg/tonne MF Feed	0.75	0.45	0.45	0.00
Cat Age, kg MF Feed/kg Cat	1026.00	1044.00	1056.00	1072.00
K-2: Temp., °C	443.50	442.80	443.80	442.80
Cat Replacement Rate, kg/tonne MF Feed	1.25	0.90	0.90	0.00
Cat Age, kg MF Feed/kg Cat	626.00	632.00	641.00	660.00
Flow Rates				
Coal Feed, kg/hr	138.40	60.00	68.80	66.40
Plastics/Rubber	0.00	28.24	29.50	23.30
Oil Streams to SMT				
0-43 Recycle to SMT, kg/hr	67.85	103.50	64.88	71.56
Make-up Oil, kg/hr	0.00	40.00	58.53	93.52
ASB (through COT) to SMT, kg/hr	108.85	55.67	96.20	54.49
Solvent/Coal Ratio, kg/kg	1.30	2.26	2.24	2.45
Material & Ash Balances				
Liquefaction Section Recovery, wt %	100.10	97.10	97.70	99.70
Overall Material Recovery, wt %	99.35	97.80	100.30	98.80
Normalization Factor	1.00	1.03	1.02	1.00
Ash Balance, wt %	103.70	118.99	108.90	116.44
Normalized Yields, wt % MAF Feed*				
H_2S	0.56	1.61	1.25	2.25
NH_3	1.03	0.68	0.63	0.86
H_2O	19.26	14.72	16.56	16.30
COx	1.16	0.49	0.99	0.85
C_1-C_3	10.11	14.39	10.28	11.94
C_4-C_6	4.50	7.77	4.17	6.61
IBP-177 °C	18.28	27.81	22.04	22.05
177-288 °C	24.91	39.31	31.08	40.16
288-343 °C	1.32	15.39	15.94	24.27
343-524 °C	8.42	-22.62	-3.73	-26.92
524 °C$^+$	12.01	-0.42	0.10	3.79
Unconverted Coal	6.51	7.20	7.20	5.32
Process Performance*				
Chemical H_2-Consumption, wt % MAF	8.05	6.34	6.50	7.47
Total Feed Conversion, wt % MAF	93.50	92.80	92.80	94.68
524 °C$^+$ Conversion, wt % MAF	81.50	93.20	92.70	90.90
Denitrogenation, wt %	86.25	77.40	78.00	74.60
C_4-343 °C Net Distillates, wt % MAF	49.00	90.30	73.20	93.10
C_4-524 °C Distillates, wt % MAF	57.50	67.70	69.50	66.20
C_1-C_3 Selectivity, kg/kg of C_4-524 °C (x 100)	17.60	21.30	14.80	18.00
H_2 Efficiency, kg of C_4-524 °C/kg H_2	7.16	10.70	10.70	8.90
Deasher Performance				
Organic Rejection, wt % MAF	13.80	29.50	25.60	28.50
Energy Rejection, %	13.60	28.30	25.70	29.00
Deasher Coal Conversion, wt % MAF	90.90	79.00	85.50	85.50
Deasher Rejection of 524 °C$^-$ Material, wt % MAF	1.850	5.30	4.80	3.60

*Based on Liquefaction Section: 0-13 Bottoms

**Molyvan-822 was a moly-additive used in Condition 5 at 150 ppm Mo relative to coal

***Fresh Feed is a combination of coal and plastics or coal and crumb rubber for Periods 42, 43, and 45

(a) ROSE-SR used for solids separation in all reported periods.

TABLE 2

GAS MAKE DURING COAL/WASTE CO-LIQUEFACTION
HRI RUN POC-2

Period	**33-36**	**41**	**42**	**43**	**44**	**45**
Coal Concentration, wt %	100	69.3	66.0	67.5	81.9	72.0
C_1-C_3 Gases, % MAF Feed	9.89	10.86	12.85	9.59	13.74	11.48
From Coal		6.85	6.53	6.68	8.10	7.12
From Waste Material		4.01	6.33	2.92	5.64	4.36
% Waste Feed		13.1	18.6	9.0	31.1	15.6
C_4-C_6 Gases, % MAF Feed	3.77	5.23	6.61	3.66	8.62	6.04
From Coal		2.61	2.49	2.54	3.09	2.71
From Waste Material		2.62	4.13	1.11	5.54	3.32
% Waste Feed		8.5	12.1	3.4	30.6	11.9

Source: References 2 and 3

TABLE 3

RECYCLE STREAM COMPOSITION, wt %
HRI RUN POC-2

Period	5	15	21	34	36	39	40	41	42	43	44	45
Make-up Oil	34.63	6.14	0	7.66	0	11.27	29.14	15.73	19.79	26.84	25.21	42.84
0-13 Btm	0	27.83	21.04	15.30	15.75	1.19	0	0	0	0	0	0
ASB	14.93	22.34	69.30	54.07	62.68	52.04	31.81	31.53	27.56	43.94	36.28	24.96
VSOH	27.19	32.07	7.30	11.46	9.41	24.40	24.95	42.69	41.13	15.85	28.90	13.51
DAO	23.26	11.63	2.36	11.51	12.16	11.10	14.10	10.06	11.52	13.37	9.61	18.69

Source: References 2 and 3

TABLE 4

HRI ANALYSES OF HYDROTREATED START-UP OIL
HRI No. L-814

ASTM D-1160 Distillation

Vol. %	° F
IBP	588
3	650
5%	664
10	706
20	742
30	769
40	798
50	819
60	840
62	850
70	873
80	944
84	975

Distribution, wt %

IBP-850 °F	58.99
850-975 °F	22.18
975 °F$^+$	18.36
Loss	0.47

Elemental Analysis, wt %

Carbon	88.47
Hydrogen	10.54
Nitrogen	0.83
Sulfur	0.11
Oxygen (diff.)	0.05
H/C Ratio (atomic)	1.43

NOTE: Oil is from petroleum catalytic cracker cycle oil; start-up oil also is used for solvent make-up when recycle inventory is insufficient.

Source: References 2 and 3

TABLE 5

HRI ANALYSIS OF BLACK THUNDER MINE FEED COAL
HRI RUN POC-2

Proximate Analysis, wt % **(Empire Coke Lab)**		
Moisture	10.28	10.85
Volatile Matter, dry	39.46	43.17
Fixed Carbon, dry	52.40	50.16
Ash, dry	8.14	6.67
Sulfur, dry	0.47	0.40

Ultimate Analysis, wt % **(Commercial Testing and Engrg Co.)**	
Moisture	7.89
Carbon	64.59
Hydrogen	4.71
Nitrogen	0.91
Sulfur	0.32
Ash	5.70
Oxygen, diff.	15.88
	100.00

Forms of Sulfur, wt %, dry	
Pyritic	0.05
Sulfate	0.01
Organic, diff.	0.29
Total	0.35

Mineral Analysis, wt % **Ignited**	
SiO_2	29.52
Al_2O_3	16.08
TiO_2	1.41
Fe_2O_3	5.25
CaO	23.98
MgO	4.87
K_2O	0.33
Na_2O	1.46
SO_3	14.41
P_2O_5	1.03
SrO	0.31
BaO	0.48
Mn_3O_4	0.07
Undetermined	0.80
	100.00

Source: References 2 and 3

TABLE 6

HRI ANALYSIS OF PLASTIC FEEDSTOCKS
HRI RUN POC-2

Analysis Type	PS (a)	HDPE (b)	PET (c)
Solubility Test, wt %			
Cyclohexane Insol	0.29	100	100
CI Ash	0.02	0	0.04
Quinoline Insol	0.24	100	100
QI Ash	0.04	0.04	0
Sulfur, wt %	0.006	0.46	0.006

(a) PS - Polystyrene
(b) HDPE - High density polyethylene
(c) PET - Polyethylene terephalate

Source: References 2 and 3

TABLE 7

HRI ANALYSIS OF USED RUBBER TIRE FEEDSTOCK
HRI RUN POC-2

Supplier:	Baker Rubber Inc.
Code:	Granulite WRF-30
Lot No.:	9509
Feature:	Ground rubber; steel and fiber-free

Baker Test Results		HRI Analysis	
<u>Composition</u>, dry wt %		<u>TGA Analysis</u>, dry wt %	
Acetone Extraction	11.9	Extender	10.44
RHC (Residual Hydrocarbon)	46.5	Polymer	53.80
Carbon Black	36.6	Carbon Black	30.67
Ash	5.0	Ash	5.09
Moisture, wt %	0.39	Moisture, wt %	0.61
		<u>Elemental Analysis, wt %, as is</u>	
		Carbon	82.94
		Hydrogen	7.12
		Nitrogen	0.29
		Sulfur	1.88
		Oxygen, by diff.	2.71
		Ash	5.06

Source: References 2 and 3

TABLE 8

OVERVIEW OF CONSOL ANALYSES OF SAMPLES FROM HRI RUN POC-2

Sample Description	Periods	Technique	Information Sought (Refer to Key)	Note
ATMOSPHERIC STILL BOTTOMS (ASB) N-2 BTMS SP-4	5, 15, 21, 36, 43, 45	^{1}H-NMR	A	
		FTIR in THF Sol'n	B	
VACUUM STILL BOTTOMS (VSB) N-3 BTMS SP-6	15, 21, 36, 43, 45	THF Extraction, Ash	E	1
		THF Extract: ^{1}H-NMR	A	
		THF Extract: FTIR in THF Sol'n	B	
		THF Extract: Solvent Fractionation (O,A,P)	F	
VACUUM STILL OVERHEADS (VSOH) N-3 OVRHDS SP-5	15, 21, 36, 43, 45	^{1}H-NMR	A	
		FTIR in THF Sol'n	B	
NAPHTHA STABILIZER BOTTOMS (NSB) N-5 BTMS SP-3	15, 21, 36, 43, 45	^{1}H-NMR	A	
		FTIR in THF Sol'n	B	
		GC-MS	C	
		(Period 43) Filtration; FTIR, SEM/EDX, elemental analysis of sediment	D	
REACTOR OVERHEAD SEPARATOR O-5 OIL SP-19	15, 33, 36, 43, 44, 45	^{1}H-NMR	A	2
		FTIR in THF Sol'n	B	

Sample Description	Periods	Technique	Information Sought (Refer to Key)	Note
RECYCLE OIL 0-43 OIL SP-11	5, 15, 34, 36, 43, 45	Microautoclave Test with Standard Coal	G	1
		^{1}H-NMR	A, H	
		850°F Distillation	I	
		Distillate: ^{1}H-NMR	A, H	
		Distillate: FTIR in THF Sol'n	B	
		Distillate: Microautoclave Test with Standard Coal	G	
		Resid: THF Extraction, Ash	E	
		Resid THF Extract: ^{1}H-NMR	A, H	
		Resid THF Extract: FTIR in THF Sol'n	B	
		Resid THF Extract: Solvent Fractionation (O,A,P)	F	
REACTOR LIQUID FLASH VESSEL BOTTOMS (RLFVB) 0-46 MATERIAL SP-9	5, 15, 21, 34, 36, 43, 45	Microautoclave Test with Standard Coal	G	3
		^{1}H-NMR	A, H	
		850°F Distillation	I	
		Distillate: ^{1}H-NMR	A, H	
		Distillate: FTIR in THF Sol'n	B	
		Distillate: Microautoclave Test with Standard Coal	G	
		Resid: THF Extraction, Ash	E	
		Resid THF Extract: ^{1}H-NMR	A, H	
		Resid THF Extract: FTIR in THF Sol'n	B	
		Resid THF Extract: Solvent Fractionation (O,A,P)	F	

Sample Description	Periods	Technique	Information Sought (Refer to Key)	Note
0-63 ROSE BTMS SP-27A/B	15, 21, 34, 36, 43, 45	THF Extraction, Ash	E	1, 3
		THF Extract: ^{1}H-NMR	A	
		THF Extract: FTIR in THF Sol'n	B	
		THF Extract: Solvent Fractionation (O,A,P)	F	
DE-ASHED OIL (DAO) 0-65 DAO SP-25	15, 21, 34, 36, 43, 45	^{1}H-NMR	A	1, 4
		FTIR in THF Sol'n	B	
		Solvent Fractionation (O,A,P)	F	
		THF Extraction, Ash (Some Periods)	E	
CLEAN OIL TANK (COT) P-3 OIL SP-24	21, 36, 43, 45	^{1}H-NMR	A	
		FTIR in THF Sol'n	B	
		GC-MS	C	
MAKE-UP OIL (M/U) TANK 4 OIL SP-28	1	^{1}H-NMR	A	
		FTIR in THF Sol'n	B	
		GC-MS	C	
		Microautoclave Test with Standard Coal	G	
P-2 COAL SP-16	15, 21, 36	Proximate and Ultimate, S Forms, Cl, Btu Content, Ash Elementals	J	
		Oxidation Index by FTIR	K	
OTHER FEEDS: POLYETHYLENE, POLYSTYRENE, POLYETHYLENE TEREPHTHALATE, RUBBER	43, 45	C, H, N, S, Ash Content; Ash Elementals + Zn, Mo, Ni in Rubber	J	3

KEY TO INFORMATION SOUGHT:

A. Hydrogen distribution (7 classes), aromaticity (degree of hydrogenation), paraffinicity
B. Phenolic -OH content; limited structural information
C. Composition; carbon numbers of paraffins
D. Identity and origin of sediment
E. Resid, ash and IOM content; coal conversion; resid conversion
F. Resid composition
G. Donor solvent quality
H. Hydrogen donors
I. Distillate content
J. Feed Characteristics
K. Evidence of Coal Oxidation

NOTES:

1. To address fate of rubber ash, selected Period 45 samples were analyzed for major ash elements and Zn.
2. Periods 33 and 44 are K-3 HTR reactor bypass periods.
3. To address catalyst attrition, selected Period 36, 43, and 45 samples were analyzed for major ash elements, Mo, and Ni.
4. Period 43 DAO THF-insolubles were analyzed for elemental content and by FTIR for identification of non-distillable waxy material.

TABLE 9

ANALYSIS OF FEED COAL SAMPLES
HRI Run POC-2

HRI Sample No. and Run Period	Results				
	LO-6375, P-2 Coal, Period 15	LO-6415, P-2 Coal, Period 21		LO-6416, P-2 Coal, Period 36 (a)	
Oxidation Index by FTIR	3.34 ±0.11	3.32 ±0.07		3.11 ±0.04	
Aliquot No.	Aliquot 1	Aliquot 1	Aliquot 2	Aliquot 1	Aliquot 2
Moisture Content, wt % as determined	10.90	11.33	11.32	11.95	11.91
Volatile Matter, wt % dry basis	47.52	46.52	-	47.18	-
Ash Content, wt % dry basis	6.10	6.33	6.36	6.32	6.27
Ultimate Analysis, wt % dry basis					
Carbon	70.69	70.25	70.14	70.32	69.96
Hydrogen	5.05	4.75	4.73	5.07	4.66
Sulfur	0.44	0.45	0.43	0.44	0.45
Nitrogen	0.94	0.91	0.98	0.89	0.97
Chlorine	<0.001	<0.01	0.014	<0.01	<0.01
Oxygen (by difference)	16.78	17.31	17.35	16.96	17.69
Sulfur, Total	0.44	0.45	0.43	0.44	0.45
Sulfur, Pyritic	0.07	0.06	0.06	0.07	0.06
Sulfur, Sulfate	0.01	0.02	0.01	0.02	0.01
Sulfur, Organic (by difference)	0.36	0.37	0.36	0.35	0.38
Elemental, wt % of Ash					
Na_2O	1.20	1.17	1.44	1.26	1.29
K_2O	0.31	0.40	0.45	0.35	0.37
CaO	21.87	21.51	21.64	21.74	20.30
MgO	4.05	3.98	4.56	4.50	4.30
Fe_2O_3	6.11	5.48	5.24	5.71	5.21
TiO_2	1.09	1.08	1.21	1.21	1.17
P_2O_5	0.89	0.89	1.06	0.84	0.92
SiO_2	29.97	31.47	31.28	31.20	29.01
Al_2O_3	15.39	15.92	16.00	15.36	14.67
SO_3	17.95	16.75	15.27	16.47	20.72
Unaccounted	1.17	1.35	1.85	1.36	2.04
Calorific Value, Btu/lb dry basis	12,729	12,639	12,648	12,694	12,636

Analyses performed by CONSOL R&D.

(a) Trace element analyses for Aliquot 2 of this coal are given in Table 11.

TABLE 10

ELEMENTAL ANALYSES OF SELECTED SAMPLES
HRI Run POC-2

Sample Type	HDPE Feed	PS Feed	PET Feed	THF Insolubles from DAO	Rubber Feed
Period	43	43	43	43	45
Sample No.	LO-6459	LO-6458	LO-6460	-	LO-6461
Ash, wt % As-Determined	0.02*	<0.01*	0.03*	0.20*	4.94* (4.64**)
Ultimate Analysis, wt % As-Determined					
Carbon	85.73	91.91	63.19	80.83	83.44
Hydrogen	14.40	7.30	4.06	13.18	6.45
Nitrogen	0.07	0.13	0.06	0.04	0.42
Sulfur	0.01	0.01	<0.01	0.02	1.74
Oxygen (by difference)	-0.23*	0.65*	32.66*	5.73*	3.01* (3.31**)
H/C Ratio by Weight	0.168	0.079	0.064	0.163	0.077
H/C Atomic Ratio	2.00	0.94	0.76	1.94	0.92

Note: Analyses performed by CONSOL R&D, samples were assumed to be free of moisture

* SO_3-containing ash basis
** SO_3-free ash basis

TABLE 11

MAJOR AND TRACE ASH ELEMENTAL ANALYSES OF SELECTED SAMPLES
HRI RUN POC-2

Sample	Feed Coal (a)	ROSE Bottoms	0-46 RLFVB	ROSE Bottoms
Period	36	36	43	43
Sample No., LO-	6416	6408	6404	6409
Analysis, wt % As Determined				
Ash, Including SO_3	6.27	25.51	3.22	13.41
Ash, SO_3-Free	4.97	24.09	2.97	12.47
Elemental, wt % of Ash (Not Corrected for SO_3)				
Mo, wt % of Ash	0.00	0.29(c) (0.05)	0.09	0.15
Ni, wt % of Ash	0.01	0.02	0.03	0.04
Zn, wt % of Ash	0.01	0.01	0.07	0.05
Na_2O	1.29	1.53	1.57	1.65
K_2O	0.37	0.52	0.40	0.47
CaO	20.30	24.12	24.06	23.12
MgO	4.30	5.11	5.01	4.83
Fe_2O_3	5.21	5.65	5.72	6.07
TiO_2	1.17	1.42	1.40	1.37
P_2O_5	0.92	1.21	1.12	1.18
SiO_2	29.01	33.14	32.16	33.25
Al_2O_3	14.67	18.19	16.96	17.69
SO_3	20.72	5.57	7.88	7.03
Unaccounted (b)	2.01	3.06	3.45	2.99

Analyses performed by CONSOL R&D.

(a) Aliquot 2 as reported in Table 9.
(b) Mo, Ni, and Zn were accounted as MoO_3, Ni_2O_3, and ZnO.
(c) An amount of Mo of 0.24 wt % of ash was provided by the dispersed catalyst added as 150 ppm Mo on an MF coal basis. The value shown in parentheses is without the dispersed catalyst contribution.

TABLE 11 (Continued)

MAJOR AND TRACE ASH ELEMENTAL ANALYSES OF SELECTED SAMPLES
HRI RUN POC-2

Sample	Feed Rubber (c)	O-43 Recycle Oil	VSB	ROSE Bottoms	DAO
Period	45	45	45	45	45
Sample No., LO-	6461	6398	6394	6410	6464
Ultimate Analysis, wt % Dry					
Ash, Including SO_3	4.74	0.94	4.65	15.46	4.87
Ash, SO_3-Free	4.55	0.87	4.33	14.19	4.34
Mo, wt % of Ash	0.01	0.07	0.11	0.28	0.26
Ni, wt % of Ash	0.01	0.05	0.04	0.07	0.07
Zn, wt % of Ash	30.37	24.33	0.06	1.57	4.54
Elemental, wt % of Ash					
Na_2O	0.92	1.13	1.69	1.50	1.29
K_2O	0.91	0.81	0.42	0.43	0.53
CaO	4.72	7.24	24.31	20.57	18.03
MgO	1.52	1.95	5.07	4.37	3.82
Fe_2O_3	2.73	3.50	5.86	5.63	4.77
TiO_2	5.88	4.42	1.43	1.46	1.66
P_2O_5	0.83	0.91	1.17	1.12	1.00
SiO_2	24.23	26.12	32.26	33.83	30.95
Al_2O_3	9.06	10.78	17.69	18.52	16.24
SO_3	4.10	7.10	6.98	8.19	10.93
Unaccounted (b)	45.10	36.04	3.12	4.38	10.78

Analyses performed by CONSOL R&D.

(b) Mo, Ni, and Zn were accounted as MoO_3, Ni_2O_3, and ZnO.

(c) Ash values differ from those shown in Table 10, because a different sample and ashing method were used.

TABLE 12

COMPONENT DISTRIBUTION OF SOLIDS-CONTAINING SAMPLES
HRI RUN POC-2

Sample			HRI LO-	wt % of Sample			
Type	Period	Condition		850 °F$^-$ Dist	THF-Sol Resid	IOM	Ash
O-43 Recycle Oil	5B	1A*	6371	71.0	27.0	0.6	0.3
	15A	1B	6372	63.2	32.0	2.5	1.3
	34B	4C	6395	60.4	32.4	3.4	2.5
	36B	5	6396	56.4	35.8	3.7	2.8
	43B	6	6455	64.7	10.4	23.7	0.01
	45B	7	6398	61.7	29.6	6.9	0.9
O-46 RLFVB	5B	1A*	6377	46.4	32.5	12.7	8.0
	15A	1B	6378	46.9	34.0	11.4	7.0
	21B	2B	6402	39.8	29.4	16.3	14.3
	34B	4C	6403	48.8	31.4	10.8	9.0
	36B	5	6457	43.1	36.8	10.7	8.6
	43B	6	6404	50.4	24.9	20.6	3.2
	45B	7	6405	55.8	29.7	10.4	3.9
O-63 ROSE BTMS	15A	1B	6376	-	24.9**	50.9	24.2
	21A/B	2B	6406	-	51.4**	27.0	21.6
	34B	4C	6407	-	41.9**	34.9	23.2
	36B	5	6408	-	43.3**	31.2	25.5
	43B	6	6409	-	40.4**	46.2	13.4
	45B	7	6410	-	36.4**	48.1	15.5
N-3 BTMS VSB	15B	1B	6502	-	62.7**	23.3	14.0
	21B	2B	6441	-	55.9**	24.3	19.8
	21B	2B	6454	-	58.4**	14.0	27.6
	36B	5	6442	-	68.3**	18.1	13.6
	43B	6	6507	-	63.0**	12.1	24.9
	45B	7	6394	-	63.7**	31.7	4.6
O-65 DAO	15A	1B	6379	-	99.43**	0.56	0.01
	21B	2B	6503	-	95.97**	2.91	1.12
	34B	4C	6417	-	99.56**	0.31	0.13
	36B	5	6418	-	99.98**	0.02	<0.01
	43B	6	6463	-	89.88**	10.10	0.02
	45B	7	6464	-	81.01**	14.12	4.87

*Not a balance period
**By difference

TABLE 13

SOLUBILITY FRACTIONATION OF SAMPLES
HRI RUN POC-2

Sample			HRI LO-	wt % of THF-Soluble Sample (a)		
Type	Period	Condition		Oils	Asphaltenes	Preasphaltenes
O-43 Recycle Oil	5B	1A*	6371	90.5	4.6	5.0
	15A	1B	6372	86.2	7.3	6.5
	34B	4C	6395	82.4	12.2	5.4
	36B	5	6396	79.0	13.4	7.7
	43B	6	6455	76.2	21.0	2.8
	45B	7	6398	78.1	20.5	1.4
O-46 RLFVB	5B	1A*	6377	83.3	15.5	1.2
	15A	1B	6378	79.9	12.4	7.7
	21B	2B	6402	75.5	18.4	6.1
	34B	4C	6403	76.1	20.0	3.9
	36B	5	6457	74.6	21.8	3.7
	43B	6	6404	70.5	19.6	9.8
	45B	7	6405	78.7	14.2	7.1
O-65 DAO	15A	1B	6379	93.8	5.5	0.7
	21B	2B	6503	91.7	7.0	1.4
	34B	4C	6417	91.1	8.6	0.3
	36B	5	6418	94.1	5.8	0.1
	43B	6	6463	83.9	5.0	11.1
	45B	7	6464	81.1	10.9	8.0
O-63 ROSE BTMS	15A	1B	6376	56.4	28.8	14.7
	21A/B	2B	6406	72.9	18.8	8.3
	34B	4C	6407	63.7	23.5	12.7
	36B	5	6408	65.5	25.9	8.5
	43B	6	6409	69.4	22.0	8.7
	45B	7	6410	67.3	23.1	9.3
N-3 BTMS VSB	15B	1B	6502	83.6	13.1	3.2
	21B	2B	6441	75.6	20.5	3.9
	21B	2B	6454	78.7	18.6	2.8
	36B	5	6442	76.7	20.7	2.7
	43B	6	6507	85.8	13.2	1.0
	45B	7	6394	83.2	15.1	1.8

(a) For 0-43 and 0-46 samples, the analysis was performed on the THF-soluble component of the 850 °F$^+$ fraction. For the other samples, the analysis was performed on the THF-soluble component of the entire sample.

*Not a balance period

TABLE 14

PROTON DISTRIBUTION OF SOLIDS-CONTAINING SAMPLES
HRI RUN POC-2

Sample			HRI LO-	Proton Distribution, %						
Type	Period	Cond		Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
O-43 Recycle Oil	5B	1A*	6371	9.0	3.9	13.2	9.1	18.0	29.5	17.3
	15A	1B	6372	7.9	4.2	11.9	7.8	17.9	31.2	19.2
	34B	4C	6395	14.7	5.1	13.6	8.6	14.9	28.4	14.7
	36B	5	6396	13.3	5.3	13.2	8.6	15.4	29.4	14.8
	43B	6	6455	11.3	6.0	10.8	9.8	14.9	29.3	17.9
	45B	7	6398	14.2	5.2	12.7	11.1	14.5	26.5	15.8
O-46 RLFVB	5B	1A*	6377	10.0	4.6	13.6	8.4	16.6	29.1	17.7
	15A	1B	6378	9.7	4.8	12.0	8.1	16.8	31.3	17.2
	21B	2B	6402	11.2	4.2	12.4	6.6	16.8	32.4	16.5
	34B	4C	6403	15.8	4.9	15.7	8.6	15.6	26.5	12.8
	36B	5	6457	17.4	5.1	16.2	8.6	15.0	26.8	10.9
	43B	6	6404	15.6	5.6	14.0	9.5	15.6	29.5	10.2
	45B	7	6405	15.7	4.3	14.1	9.3	14.7	27.8	14.1
O-63 ROSE BTMS	15A	1B	6376	24.3	5.2	16.7	8.2	15.3	18.0	12.3
	21A/B	2B	6406	20.1	3.6	16.0	8.1	15.6	23.8	12.8
	34B	4C	6407	34.1	5.8	19.9	10.0	12.5	11.2	6.6
	36B	5	6408	34.1	6.1	20.5	9.7	12.5	10.7	6.3
	43B	6	6409	28.3	4.8	18.6	9.7	13.7	15.1	9.7
	45B	7	6410	28.7	4.8	18.2	9.3	14.6	15.2	9.3
N-3 BTMS VSB	15B	1B	6502	13.6	4.9	14.1	8.1	15.2	30.0	14.1
	21B	2B	6441	16.4	5.4	15.5	8.1	15.0	27.2	12.3
	21B	2B	6454	15.4	6.2	15.0	7.8	14.7	27.7	13.3
	36B	5	6442	19.9	7.6	16.2	9.9	13.6	22.1	10.8
	43B	6	6507	16.4	6.6	13.0	8.6	13.3	28.1	13.9
	45B	7	6394	16.6	5.4	13.9	9.4	14.0	27.9	12.8
O-65 DAO	15A	1B	6379	10.8	4.2	13.6	8.2	16.0	32.2	14.9
	21B	2B	6503	11.6	4.0	12.9	7.0	15.7	34.3	14.5
	34B	4C	6417	16.7	6.5	14.6	9.4	13.4	26.5	13.0
	36B	5	6418	16.7	7.1	14.8	9.6	13.2	26.2	12.4
	43B	6	6463	15.1	4.6	13.7	9.1	13.6	30.3	13.5
	45B	7	6464	18.2	4.3	14.6	9.6	14.3	26.0	13.0

*Not a balance period

TABLE 15

PROTON DISTRIBUTION OF SOLIDS-FREE SAMPLES
HRI RUN POC-2

Sample			HRI LO-	Proton Distribution, %						
Type	Period	Cond		Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
Tank 4 M/U Oil	1B	L/O-1	6380	15.9	7.1	14.6	14.6	12.2	21.4	14.1
P-3 COT Oil	21B	2B	6456	2.0	2.8	6.7	5.0	20.9	39.8	22.7
	36B	5	6399	5.7	4.8	10.6	7.6	19.1	34.2	17.9
	43B	6	6400	6.0	4.2	10.0	7.3	18.9	33.7	20.0
	45B	7	6401	6.2	4.8	10.3	8.0	17.8	33.2	19.7
N-5 Btms NSB	15B	1B	6451	0.7	2.6	3.9	4.3	24.5	34.9	29.2
	21B	2B	6384	0.7	3.1	4.4	4.8	23.5	35.6	27.9
	36B	5	6385	0.7	3.5	4.9	5.7	24.3	33.8	27.2
	43B	6	6386	2.6	6.3	6.1	6.1	21.6	32.7	24.7
	45B	7	6387	1.8	4.7	5.9	6.3	21.4	33.4	26.5
N-2 Btms ASB	5B	1A*	6368	2.0	3.3	8.6	6.3	21.9	36.6	21.4
	15A	1B	6369	1.4	1.9	7.1	6.2	22.8	38.0	22.6
	21B	2B	6452	1.9	2.6	6.4	5.2	20.7	39.9	23.3
	36B	5	6388	3.8	4.3	10.3	7.1	20.4	35.1	18.9
	43B	6	6389	3.9	3.8	8.3	6.5	20.0	35.1	22.5
	45B	7	6390	4.3	4.7	9.7	8.0	19.3	34.0	19.9
N-3 OVHDS VSOH	15A	1B	6370	6.4	3.2	11.1	7.7	19.3	34.1	18.0
	21B	2B	6453	7.0	3.7	9.1	6.2	17.4	37.5	19.2
	36B	5	6391	10.8	4.6	12.9	7.9	16.9	32.4	14.4
	43B	6	6397	11.9	4.8	11.6	8.6	15.8	30.4	17.0
	45B	7	6392	12.5	5.0	12.1	9.6	15.8	29.4	15.6
O-5 Htr Prod	15A	1B	6498	1.9	3.0	6.0	5.2	24.0	35.1	24.9
	36B	5	6499	2.8	4.5	8.3	5.1	20.9	35.9	22.5
	43B	6	6500	4.1	6.0	7.8	6.5	19.8	34.1	21.7
	45B	7	6501	3.2	4.7	7.1	7.4	20.2	33.9	23.4
O-5 Htr Bypass	33B	4C	6453	3.4	4.4	7.0	6.3	20.1	35.4	23.4
	44B	**	-	6.0	4.7	8.4	7.7	18.8	32.7	21.7

*Not a balance period
**Condition number not identified

TABLE 16

PROTON DISTRIBUTION OF FRACTIONATED SAMPLES
HRI RUN POC-2

Sample				Proton Distribution, %						
Type	Period	Cond	HRI LO-	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
850 °F$^-$ Distillates										
O-43 Recycle Oil	5B	1A*	6371	7.7	4.8	11.1	9.0	18.0	29.7	19.7
	15A	1B	6372	6.2	3.7	8.9	7.1	17.9	34.2	22.1
	34B	4C	6395	11.6	4.4	11.6	8.7	15.7	31.4	16.6
	36B	5	6396	9.5	5.6	9.7	7.5	15.3	32.9	19.5
	43B	6	6355	10.5	4.7	10.7	8.6	15.4	31.5	18.7
	45B	7	6398	11.2	5.8	9.1	10.2	13.9	30.3	19.6
O-46 RLFVB	5B	1A*	6377	8.3	4.3	10.7	8.1	17.6	31.7	19.2
	15A	1B	6378	7.9	4.4	10.3	7.4	17.6	32.8	19.7
	21B	2B	6402	6.9	4.3	9.0	6.0	18.3	36.9	18.7
	34B	4C	6403	12.5	4.7	12.7	8.2	15.5	31.5	14.8
	36B	5	6457	11.9	4.9	12.0	7.4	15.3	32.8	15.7
	43B	6	6404	12.3	4.8	10.9	8.4	15.3	30.8	17.5
	45B	7	6405	13.1	5.1	11.6	8.9	14.3	30.4	16.7
850 °F$^+$ Resid										
O-43 Recycle Oil	5B	1A*	6371	10.4	4.0	11.3	7.9	15.2	32.6	18.5
	15A	1B	6372	10.4	4.3	11.6	7.4	15.3	33.8	17.2
	34B	4C	6395	21.4	4.5	17.7	9.0	14.3	22.6	10.3
	36B	5	6396	20.4	5.9	17.7	9.4	13.7	23.1	9.7
	43B	6	6455	19.0	8.2	15.0	8.4	13.5	24.3	11.7
	45B	7	6498	16.3	7.0	12.0	12.9	20.0	21.4	10.3
O-46 RLFVB	5B	1A*	6377	14.0	4.7	14.1	8.2	15.8	28.4	14.8
	15A	1B	6378	13.6	4.9	14.6	8.1	15.1	29.1	14.6
	21B	2B	6402	19.6	6.0	16.7	8.4	14.6	23.3	11.4
	34B	4C	6403	23.5	6.0	19.2	9.8	13.8	19.4	8.3
	36B	5	6457	28.1	4.1	19.7	9.2	13.7	16.6	8.7
	43B	6	6404	19.8	7.6	15.0	8.8	13.1	24.6	11.1
	45B	7	6405	21.0	4.2	15.7	8.7	13.7	25.7	10.9

*Not a balance period

TABLE 17

PHENOLIC -OH CONCENTRATION BY FTIR - HRI RUN POC-2

Sample			HRI LO-	Phenolic -OH Concentrations, meq/g					
Type	Period	Cond		Whole Conc	Whole Pk, cm^{-1}	Dist Conc	Dist Pk, cm^{-1}	Resid Conc	Resid Pk, cm^{-1}
O-43 Recycle Oil	5B	1A*	6371			0.08	3317	0.14	3310
	15A	1B	6372			0.07	3317	0.16	3309
	34B	4C	6395			0.12	3311	0.30	3301
	36B	5	6396			0.11	3314	0.35	3300
	43B	6	6455			0.06	3311	0.12	3307
	45B	7	6398			0.08	3312	0.13	3305
O-46 RLFVB	5B	1A*	6377			0.09	3318	0.23	3307
	15A	1B	6378			0.08	3315	0.24	3305
	21B	2B	6402			0.08	3316	0.29	3297
	34B	4C	6403			0.12	3310	0.37	3298
	36B	5	6457			0.13	3312	0.45	3296
	43B	6	6404			0.07	3311	0.28	3298
	45B	7	6405			0.09	3310	0.23	3301
O-63 ROSE Btms	15A	1B	6376					0.29 (a)	3306 (a)
	21B	2B	6406					0.28	3299
	34B	4C	6407					0.44	3295
	36B	5	6408					0.55	3295
	43B	6	6409					0.23	3301
	45B	7	6410					0.24	3298
N-3 Btms VSB	15A	1B	6502					0.20	3303
N-3 Btms VSB (TS)	21B	2B	6441					0.27	3298
N-3 Btms VSB (TS)	21B	2B	6454					0.22	3300
N-3 Btms VSB (TS)	36B	5	6442					0.36	3300
N-3 Btms VSB (TS)	43B	6	6507					0.16	3307
N-3 Btms VSB (TS)	45B	7	6394					0.17	3303
Solids-Free									
Tank 4 M/U Oil	1B	L/O-1	6380	0.12	3307				
P-3 COT Oil	21B	2B	6456	ND	ND				
P-3 COT Oil	36B	5	6399	0.05	3325				
P-3 COT Oil	43B	6	6400	0.02	3324				
P-3 COT Oil	45B	7	6401	0.02	3325				
N-5 Btms NSB	15A	1B	6451	ND	ND				
	21B	2B	6384	ND	ND				
	36B	5	6385	ND	ND				
	43B	6	6386	ND	ND				
	45B	7	6387	ND	ND				
N-2 Btms ASB	5B	1A*	6368	ND	ND				
	15A	1B	6369	ND	ND				
	21B	2B	6452	ND	ND				
	36B	5	6388	ND	ND				
	43B	6	6389	ND	ND				
	45B	7	6390	ND	ND				
N-3 OVHDS VSOH	15A	1B	6370	0.07	3316				
	21B	2B	6453	0.09	3316				
	36B	5	6391	0.12	3314				
	43B	6	6397	0.07	3312				
	45B	7	6392	0.07	3312				
O-65 DAO	15A	1B	6379	0.18	3309				
O-65 DAO (TS)	21B	2B	6503					0.14	3308
O-65 DAO	34B	4C	6417	0.29	3305				
O-65 DAO	36B	5	6418	0.24	3303				
O-65 DAO (TS)	43B	6	6463					0.13	3306
O-65 DAO (TS)	45B	7	6464					0.15	3304
O-5 Htr Prod	15A	1B	6498	ND	ND				
	36B	5	6499	ND	ND				
	43B	6	6500	ND	ND				
	45B	7	6501	ND	ND				
O-5 Htr Bypass	33B	4C	6462	ND	ND				
	44B	**	-	0.07	3320				

O-65 DAO periods 15A, 34B, 36B Analysis performed on sample as received; O-65 DAO periods 21B, 43B, 45B analysis performed on THF-soluble resid.

*Not a balance period

**Condition number not identified

(a) Unknown interfering peak at ~3400 cm^{-1} was present.

TABLE 18

MICROAUTOCLAVE TEST RESULTS
HRI RUN POC-2

Sample			HRI LO-	Coal Conversion, wt % MAF (a)	
Type	Period	Cond		Dist	Whole
0-43 Recycle Oil	5B	1A*	6371	74.2	79.1
	15A	1B	6372	70.8	74.7
	34B	4C	6395	73.0	80.7
	36B	5	6396	69.6	81.0
	43B	6	6455	76.7	86.2
	45B	7	6398	77.7	75.5
0-46 RLFVB	5B	1A*	6377	76.0	86.7
	15A	1B	6378	74.6	84.8
	21B	2B	6402	67.4	60.9
	34B	4C	6403	78.8	74.0
	36B	5	6457	74.2	80.6
	43B	6	6404	77.7	67.0
	45B	7	6405	82.7	79.3
Tk No. 4 Oil	1B	L/O-1	6380	x	88.6
P-3 Oil	21B	2B	6456	x	62.4
P-3 Oil	36B	5	6399	x	66.8
P-3 Oil	43B	6	6400	x	69.8
P-3 Oil	45B	7	6401	x	74.1

*Not a balance period
(a) Modified equilibrium test, 9 g solvent, 6 g coal, 30 min, 750 °F

TABLE 19

DATA INDICATING UNUSUAL IOM CHARACTERISTICS IN COAL/PLASTICS PERIOD

		Coal Conversion, wt %			Component of Soluble Resid, wt %		Resid Proton Distribution, %	
Period	Sample	HRI (a)	CONSOL (b,c)	Phenolic -OH in Soluble Resid, meq/g	Asph.	Preasph.	Aromatic (d)	Paraffinic (e)
15 Coal	Recycle Oil	—	87.3	0.16	7.3	6.5	12.1	50.4
	RLFVB	89.7	89.3	0.24	12.4	7.7	14.5	48.5
	VSB	—	—	0.20	13.1	3.2	18.5	44.1
	ROSE Btms	89.8	86.1	0.29	28.8	14.7	29.5	30.3
	DAO	—	—	0.14	5.5	0.7	15.0	47.1
21 Coal	RLFVB	92.6	92.5	0.27	18.4	6.1	15.4	48.9
	VSB (LO-6441/	—	91.9/	0.22/	20.5/	3.9/	21.8/	39.5/
	LO-6454)		96.7	0.27	18.6	2.8	21.6	41.0
	ROSE Btms	91.5	91.8	0.28	18.8	8.3	23.7	36.6
	DAO	—	—	0.14	7.0	1.4	15.6	48.8
34, 36 Coal	Recycle Oil	—	91.3	0.35	13.4	7.7	18.6	44.2
			(91.0*)	(0.30*)	(12.2*)	(5.4*)	(19.8*)	(43.1*)
	RLFVB	93.5	—	0.45	21.8	3.7	22.5	37.7
		(91.8*)			(20.0*)	(3.9*)	(20.7*)	(39.3*)
	VSB	—	91.2	0.36	20.7	2.7	27.5	32.9
	ROSE Btms	90.9	91.9	0.55	25.9	8.5	40.2	17.0
		(89.8*)	(90.1*)	(0.44*)	(23.5*)	(12.7*)	(39.9*)	(17.8*)
	DAO	—	—	0.24	5.8	0.1	23.8	38.6
				(0.29*)	(8.6*)	(0.3*)	(23.2*)	(39.5*)
43 Coal/Plastics	Recycle Oil	—	—	0.12	21.0	2.8	17.3	47.2
	RLFVB	92.8	57.5	0.28	19.6	9.8	21.2	39.7
	VSB	—	96.8	0.16	13.2	1.0	23.0	42.0
	ROSE Btms	85.5	77.3	0.23	22.0	8.7	33.1	24.8
	DAO	—	—	0.13	5.0	11.1	19.7	43.8

*From Period 34 (Condition 4C), at same conditions except that no Mo additive was used.

(a) Conversion based on quinoline solubility.
(b) Conversion based on tetrahydrofuran (THF) solubility.
(c) MAF % Conversion = [(100 - ash% in dry feed) - (sample % IOM)*(ash% in dry feed)/(sample % ash)]*100/(100 - ash% in dry feed); plastics ash content was assumed to be 0%.
(d) Condensed aromatic plus uncondensed aromatic protons.
(e) Alkyl beta plus gamma protons.

TABLE 20

ROSE-SR BOTTOMS SAMPLE DATA
HRI RUN POC-2

Period	HRI OR*	Proton Distribution, %							Phenolic -OH, meq/g
		Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma	
15	24.4	24.3	5.2	16.7	8.2	15.3	18.0	12.3	0.29
21	22.0	20.1	3.6	16.0	8.1	15.6	23.8	12.8	0.28
34	12.7	34.1	5.8	19.9	10.0	12.5	11.2	6.6	0.44
36	13.8	34.1	6.1	20.5	9.7	12.5	10.7	6.3	0.55
43	25.6	28.3	4.8	18.6	9.7	13.7	15.1	9.7	0.23
45	28.5	28.7	4.8	18.2	9.3	14.6	15.2	9.3	0.24

*Organic rejection in ROSE-SR as wt % feed (coal + waste)

TABLE 21

^{1}H-NMR ANALYSES AND PHENOLIC -OH DETERMINATIONS
HRI Run POC-1 Sample

	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma	Phenolic -OH Conc. meq/g
Original Sample	3.3	4.2	8.1	7.2	21.6	33.4	22.1	0.10 (b)
Caustic Raffinate	3.1	4.4	5.0	6.9	23.2	34.9	22.5	N.D.
Caustic Extract (a)	2.5	33.7	10.5	20.6	9.3	15.2	8.2	6.25

(a) Strong -OH peak disregarded prior to normalization of ^{1}H-NMR spectrum.
(b) Includes a contribution from amines.

TABLE 22

CAUSTIC EXTRACTION YIELDS
HRI Run POC-1 Sample

	wt %
Caustic Extract	1.1
Caustic Raffinate	98.0
Total Recovery	99.1

TABLE 23

GC/MS ANALYSIS OF CAUSTIC EXTRACT
HRI Run POC-1 Sample

Tentative Identification	No. of Peaks	Total Ion Chromatogram Area %
phenol	1	6.13
o-cresol	1	7.22
m/p-cresol	2	12.81
2,6-xylenol	1	1.22
other xylenols	4	8.96
o-ethyl phenol	1	3.11
m/p-ethyl phenol	2	10.42
o-n-propyl phenol	1	1.88
m/p-n-propyl phenol	2	3.23
other C_3-phenols	12	10.53
o-n-butyl phenol	1	2.21
other C_4-phenols	16	9.00
indanol	1	1.66
C_5-phenols?	4	0.98
C_2-indanols?	2	0.75
TOTAL	51	80.11

TABLE 24

ANALYSIS OF OLD BEN NO. 1 MINE, INDIANA V COAL

	Sample Date						
	11/88 (a)	4/90 (b)	3/91 (c)	3/92 (c)	1/93 (c)	8/94 (c)	10/94 (d)
Moisture, wt % as determined	8.67	8.24	7.69	7.09	6.96	6.65	7.38
Proximate, wt % dry basis							
Volatile Matter	41.24	41.17	41.29	41.62	40.97	N/A	N/A
Fixed Carbon	49.53	49.69	49.65	49.43	50.02	N/A	N/A
Oxidized Ash	9.23	9.14	9.06	8.95	9.01	8.86	9.84
Ultimate, wt % dry basis							
Carbon	71.35	71.91	71.11	71.22	72.03	71.19	71.86
Hydrogen	5.04	4.98	4.99	5.00	4.98	4.89	5.11
Nitrogen	1.43	1.49	1.38	1.44	1.54	1.48	1.37
Oxygen (diff.)	9.03	8.70	9.57	9.61	8.70	9.45	7.65
Sulfur, Total	3.87	3.78	3.85	3.73	3.74	3.66	4.17
Pyritic	1.59	1.04	1.15	1.08	1.13	0.89	1.77
Sulfate	0.10	0.57	0.66	0.63	0.70	0.84	0.37
Organic (diff.)	2.18	2.17	2.04	2.02	1.91	1.91	2.03
Chlorine	0.05	N/A	0.04	0.05	N/A	0.05	<0.01
Oxidized Ash	9.23	9.14	9.06	8.95	9.01	8.86	9.84
Elemental, wt % oxidized ash							
Na_2O	0.44		0.55		0.52	0.53	0.50
K_2O	2.12		2.21		2.20	2.09	2.59
CaO	4.78		4.86		4.90	4.51	4.24
MgO	0.81		0.83		0.86	0.81	1.02
Fe_2O_3	26.94		27.32		27.56	28.08	26.88
TiO_2	0.89		0.92		0.92	0.88	0.93
P_2O_5	0.18		0.18		0.14	0.15	0.10
SiO_2	39.57		39.44		40.06	40.42	39.83
Al_2O_3	18.82		19.17		18.75	18.02	17.59
SO_3	3.12		3.30		2.89	3.30	4.20
Unaccounted	2.33		1.22		1.20	1.21	2.12
Calorific Value, dry (HHV), Btu/lb	13154	12799	12788	12745	12908	13834	14287

(a) As-received sample, 11/88, sample #89680

(b) Sample stored in plastic bucket

(c) Sample stored (from 4/90) in heat-sealed, nitrogen-purged, plastic bag.

(d) As-received sample, 8/94, sample #131-1621-33

TABLE 25

MICROAUTOCLAVE TEST MATRIX AND CONVERSIONS
Old Ben No. 1 Mine, Indiana V Coal

	Solvent		Test Date			
Test	Tetralin, wt %	1-Methyl-Naphthalene wt %	12/88 (a)	1/93 (a)	8/94 (a)	10/94 (b)
KIN	0	100	63.2	-	50.6	62.4
KIN	5	95	72.4	62.8 (c)	57.1	70.7
KIN	10	90	74.6	-	62.1	74.6
KIN	25	75	76.5	73.6	68.6	77.5
KIN	50	50	77.8	76.1	72.8	78.9
KIN	100	0	72.3	71.3	71.5	75.8
EQ	0	100	56.6	-	-	-
EQ	5	95	68.2	58.2 (c)	-	-
EQ	10	90	74.0	-	-	-
EQ	25	75	83.4	76.0	-	-
EQ	50	50	82.5	81.2	-	-
EQ	100	0	87.0	84.2	-	-
MOD-EQ	0	100	58.0	-	43.7	58.2
MOD-EQ	5	95	63.9	56.4	-	65.1
MOD-EQ	10	90	69.3	-	-	71.9
MOD-EQ	25	75	80.9	72.9	-	82.4
MOD-EQ	50	50	86.8	81.5	-	88.9
MOD-EQ	100	0	90.9	85.4	-	89.9

KIN = Kinetic Test: 12g solvent, 1.5g coal, 10 min, 750°F
EQ = Equilibrium Test: 10g solvent, 5g coal, 30 min, 750°F
MOD-EQ = Modified Equilibrium Test, 9g solvent, 6g coal, 30 min, 750°F
S.D. is ~1.2 for each test

(a) batch received 11/88 (Sample #89680)
(b) batch received 8/94 (Sample #131-1621-33)
(c) this value is an average of two test results

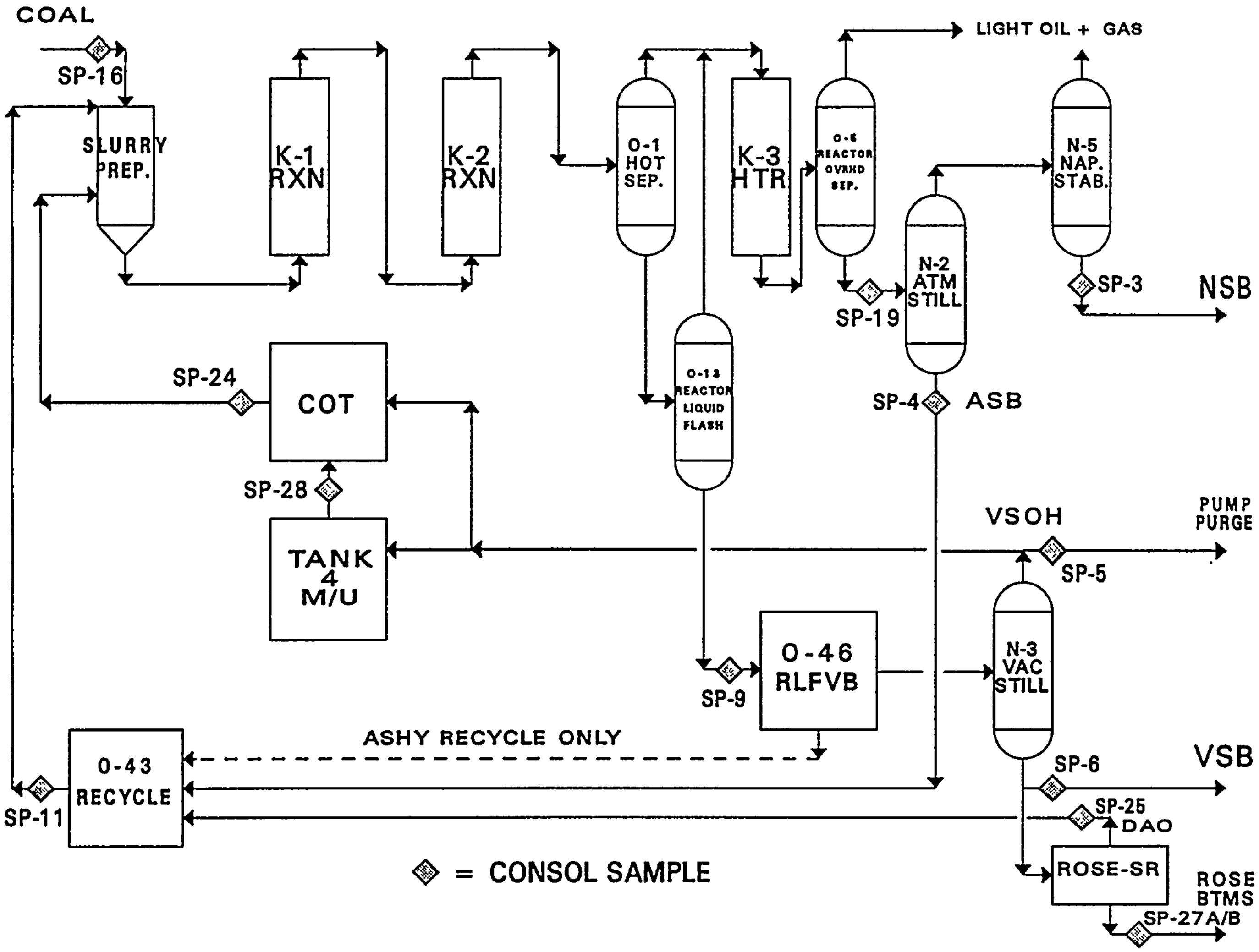


Figure 1. HRI Proof-of-Concept Plant as Configured for Run POC-2.

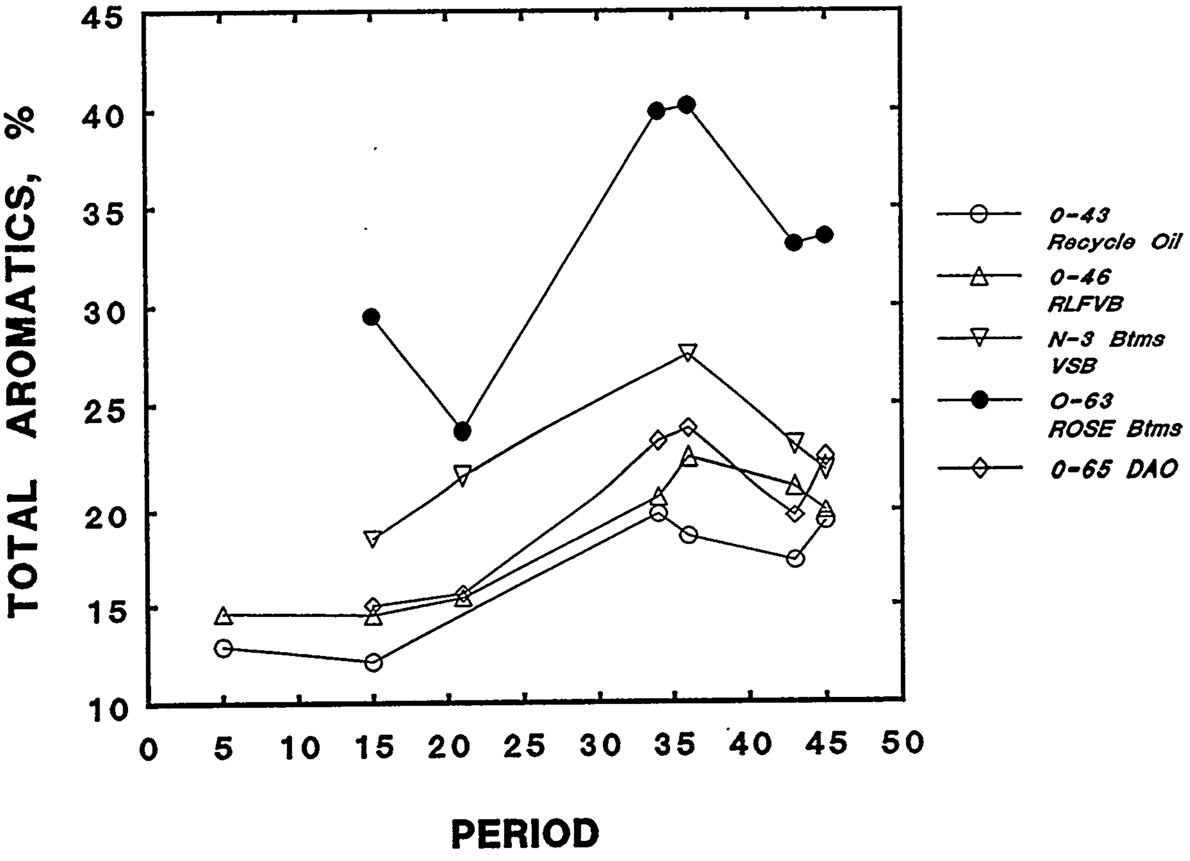


Figure 2. Aromaticities of Solids-Containing Streams.

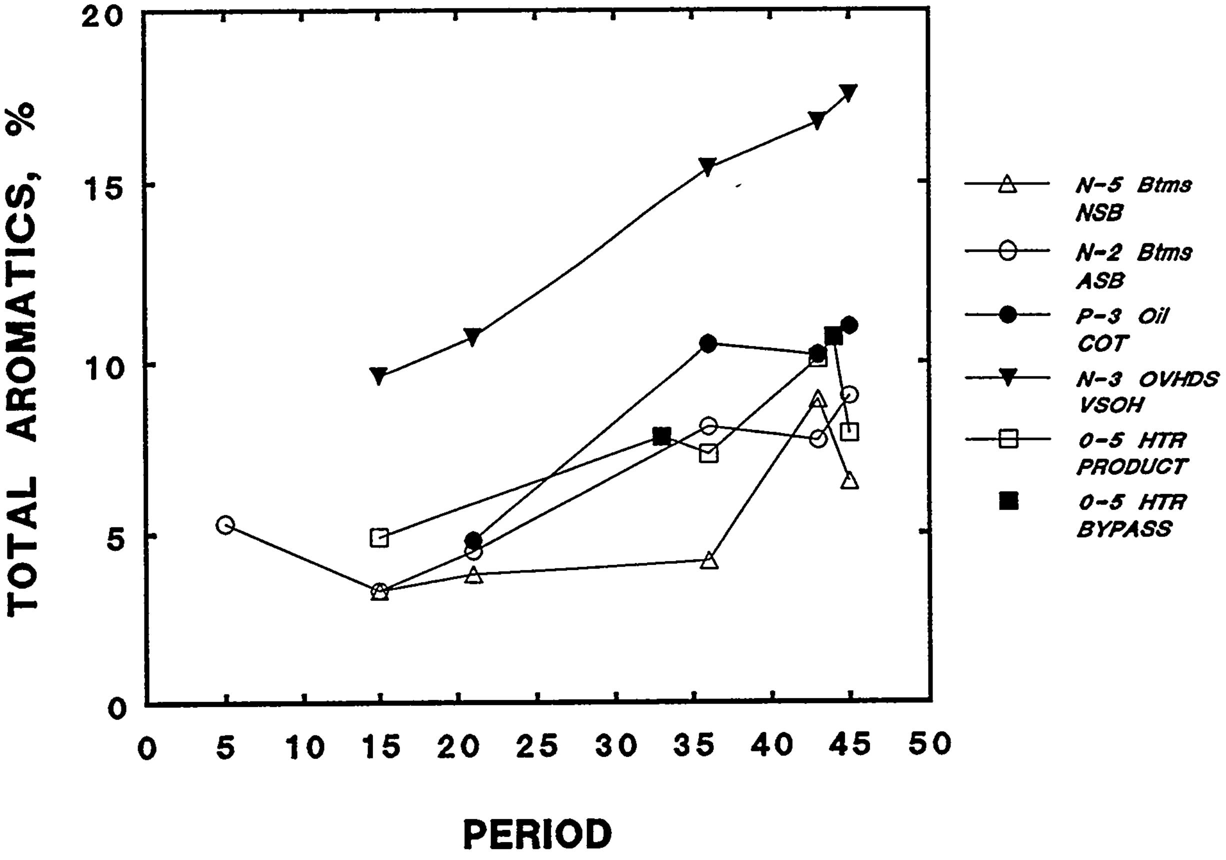


Figure 3. Aromaticities of Solids-Free Streams.

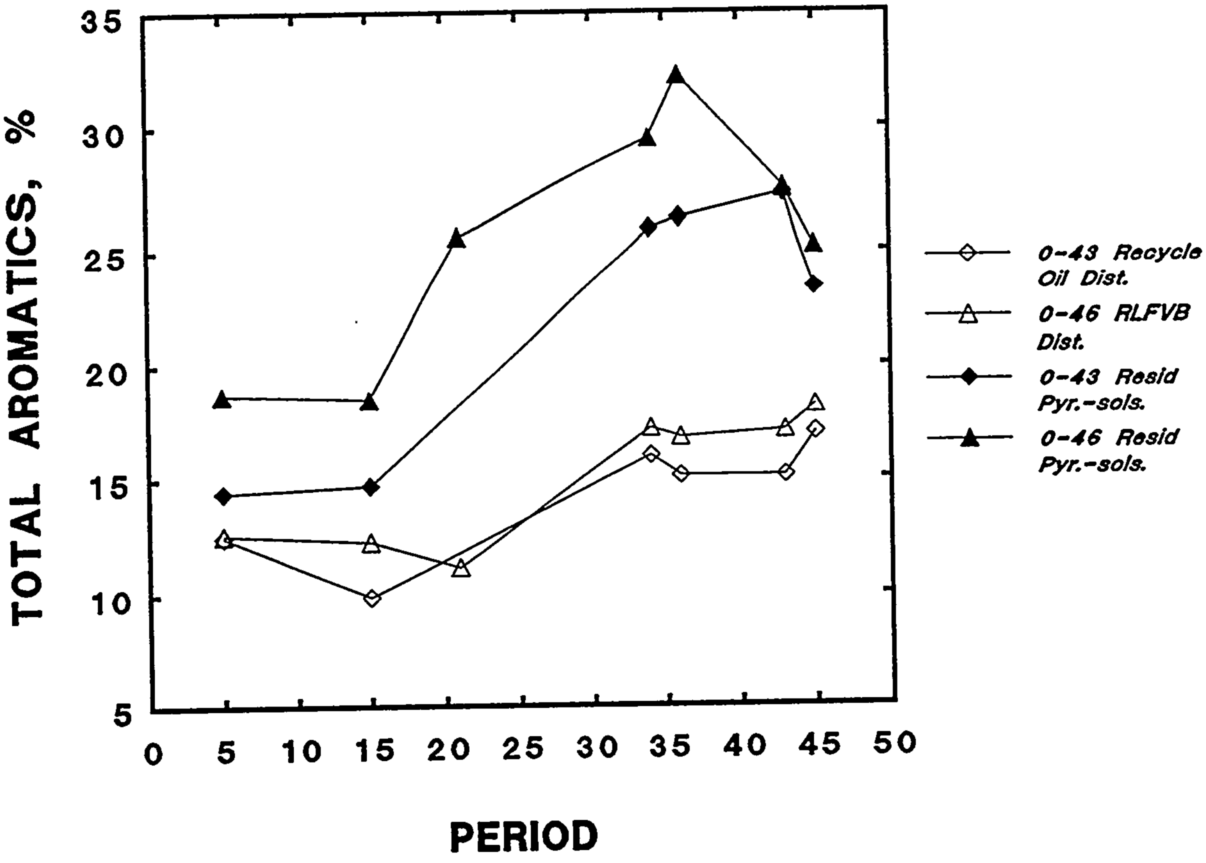


Figure 4. Aromaticities of Solids-Containing Stream Fractions.
(850 °F Distillate and Resid)

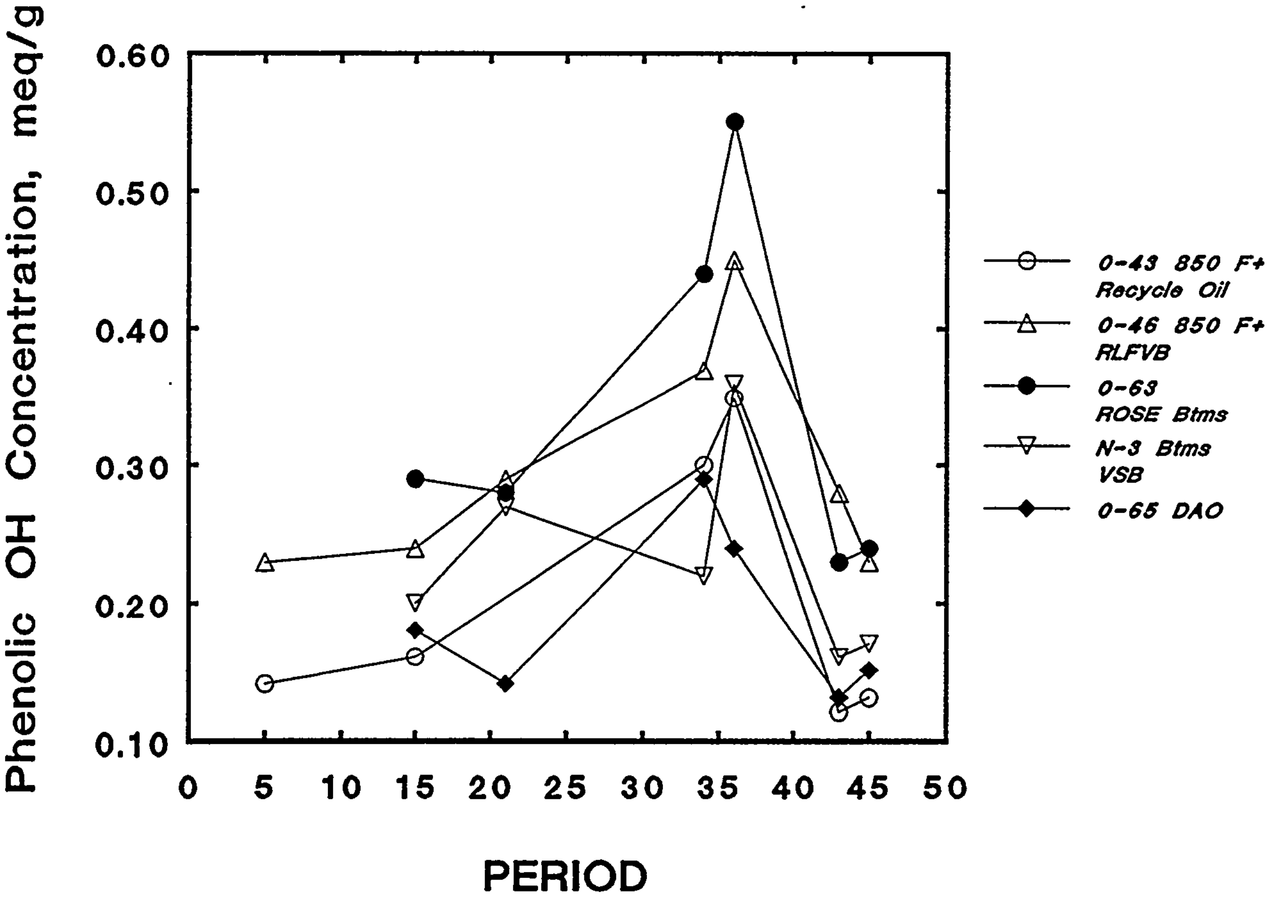


Figure 5. Phenolic -OH Concentrations of Resid Samples.

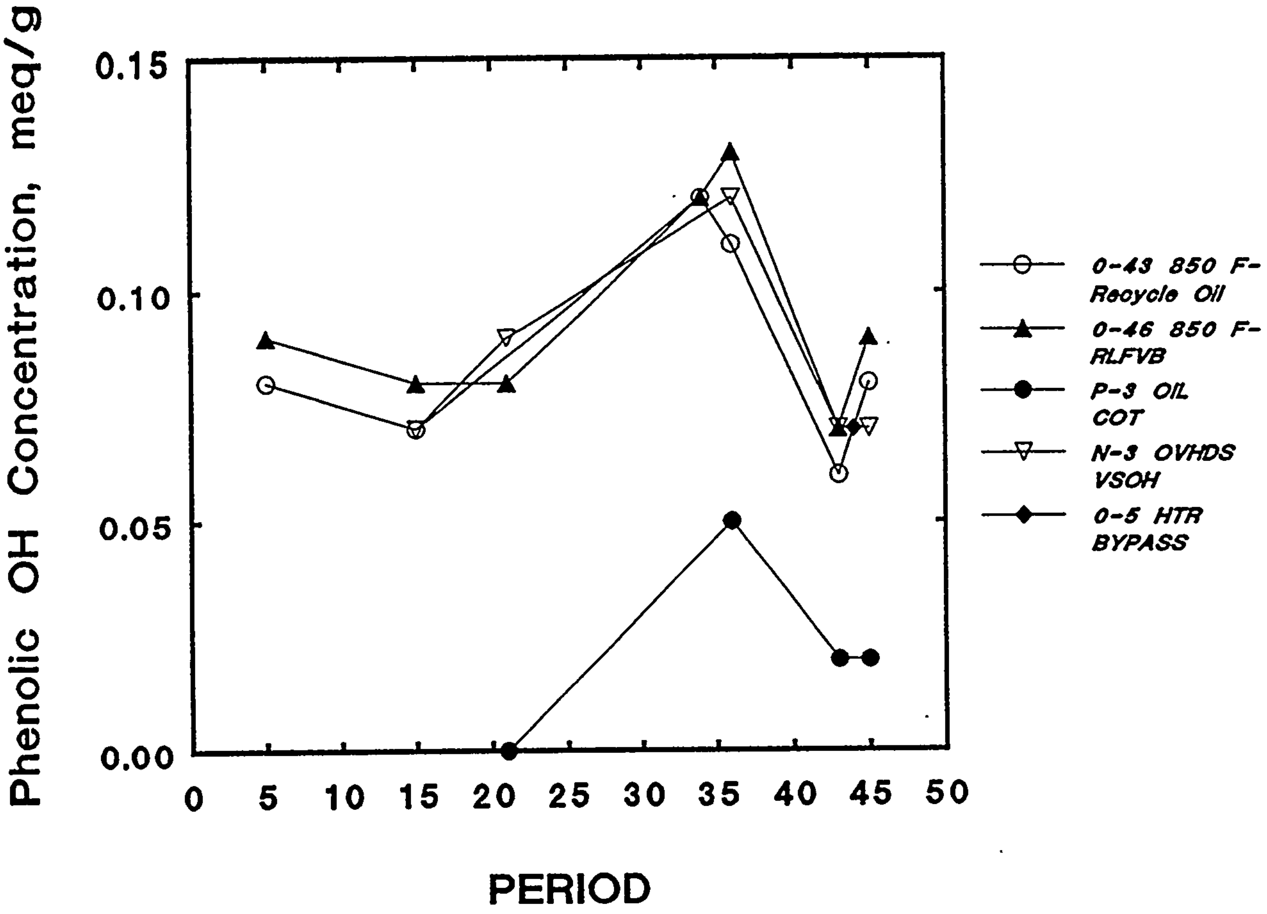


Figure 6. Phenolic -OH Concentrations of Distillate Samples.

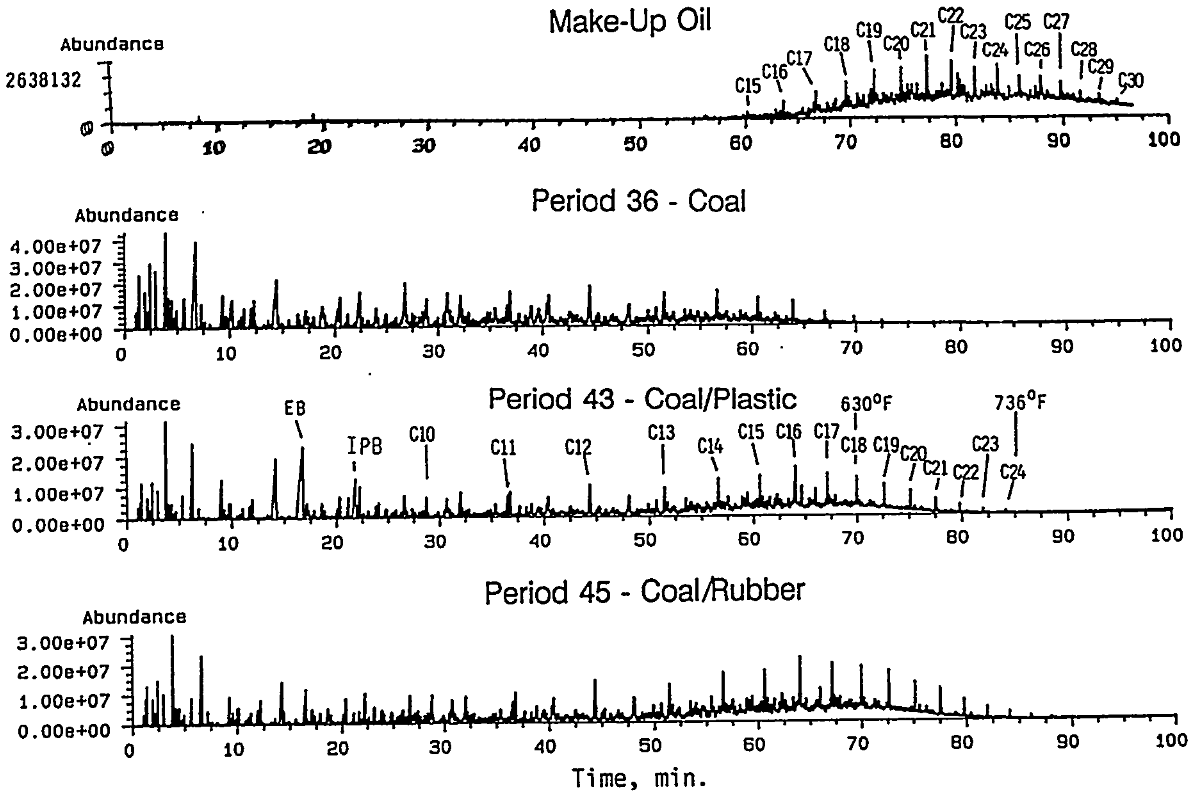
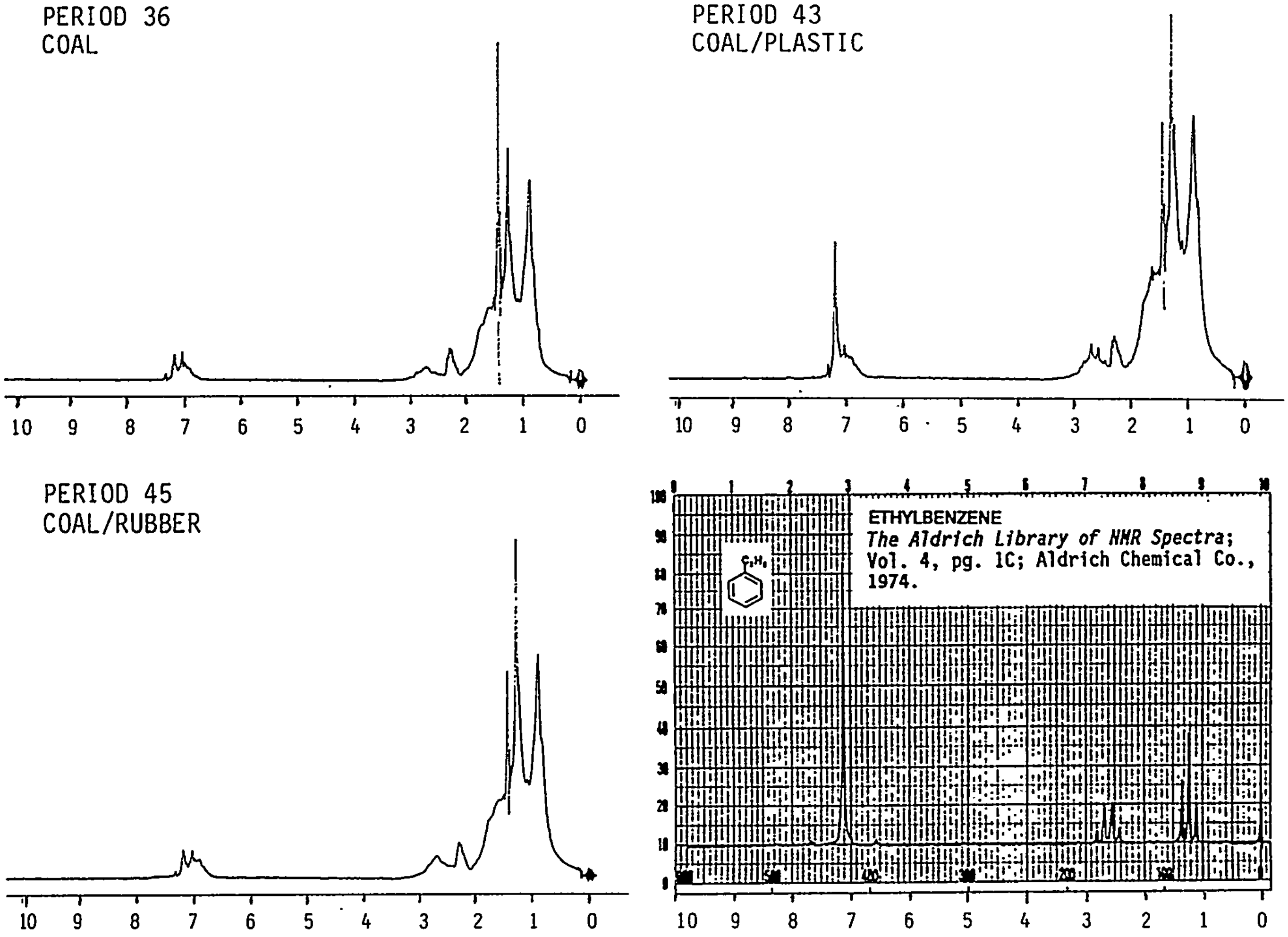


Figure 7. GC/MS Total Ion Chromatograms of Waste/Coal NSB Samples.



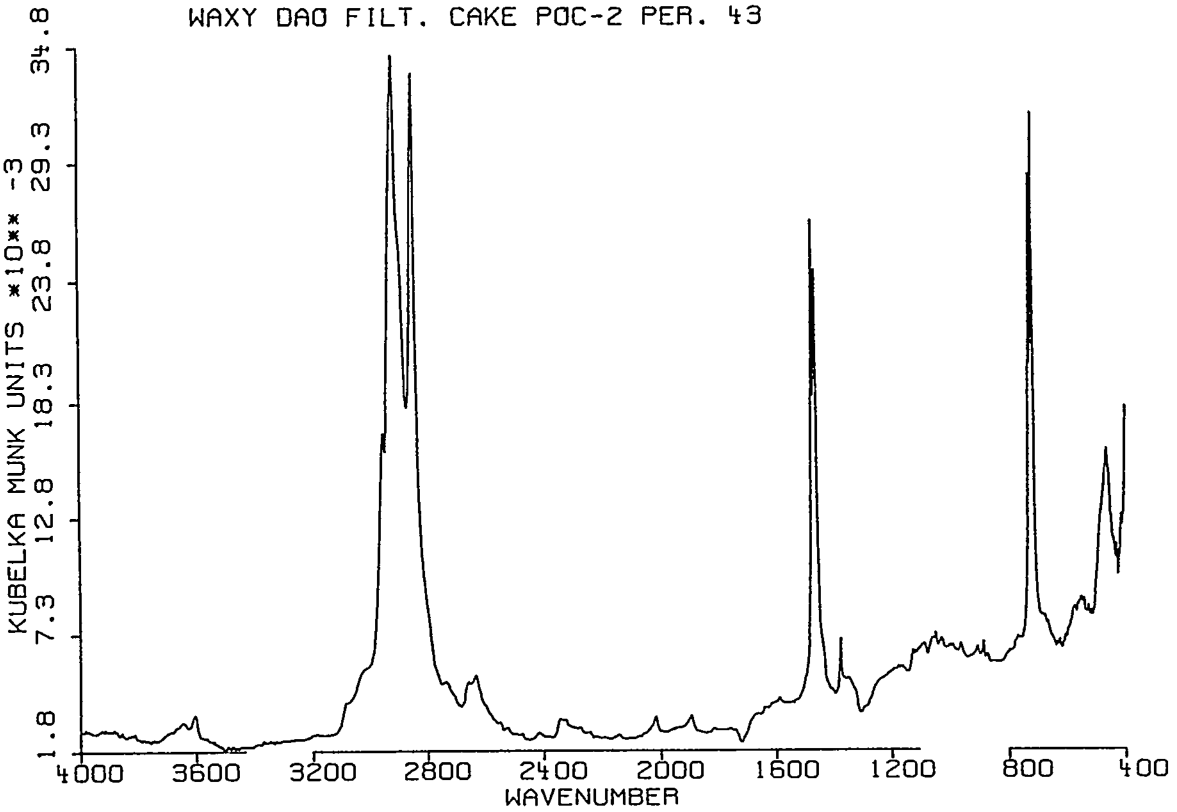
PERIOD 36
COAL

PERIOD 43
COAL/PLASTIC

PERIOD 45
COAL/RUBBER

ETHYLBENZENE
The Aldrich Library of NMR Spectra; Vol. 4, pg. 1C; Aldrich Chemical Co., 1974.

Figure 8. NMR Spectra of Waste/Coal NSB Samples and Ethylbenzene Reference.



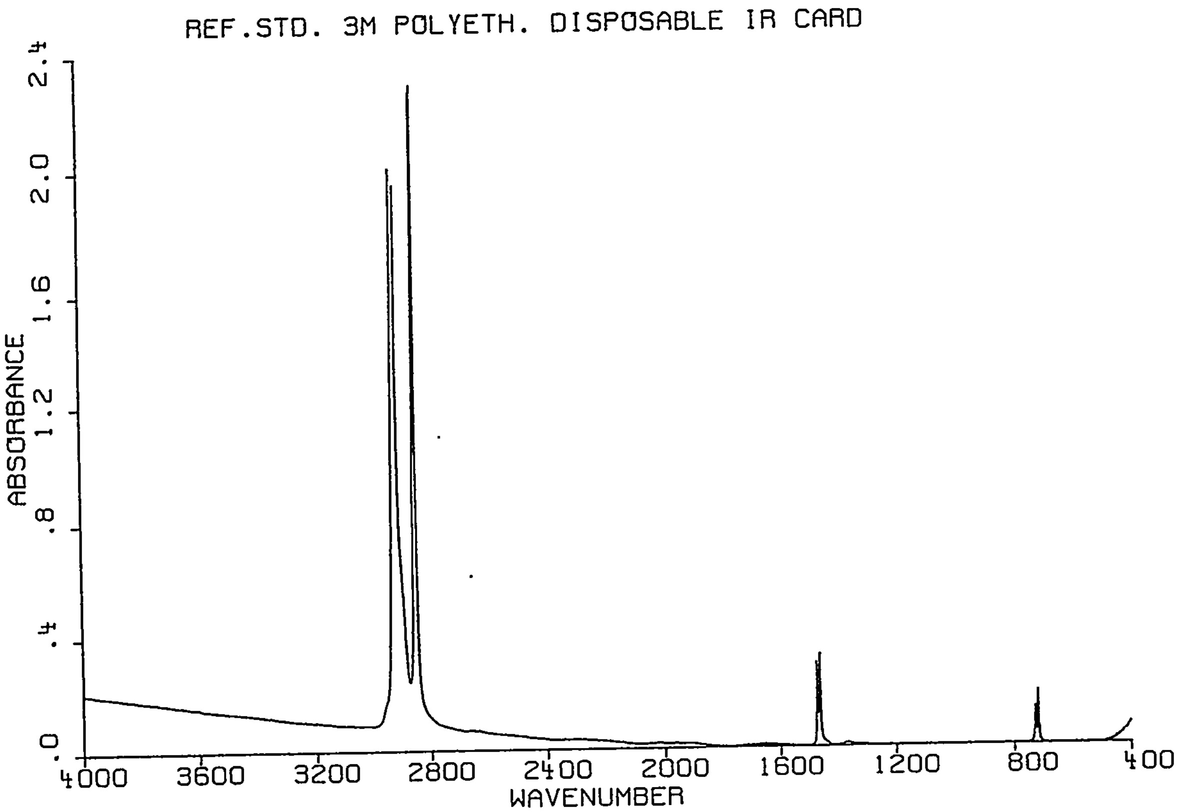


Figure 9. FTIR Spectra of Period 43 Waxy DAO Insolubles and Reference Polyethylene.

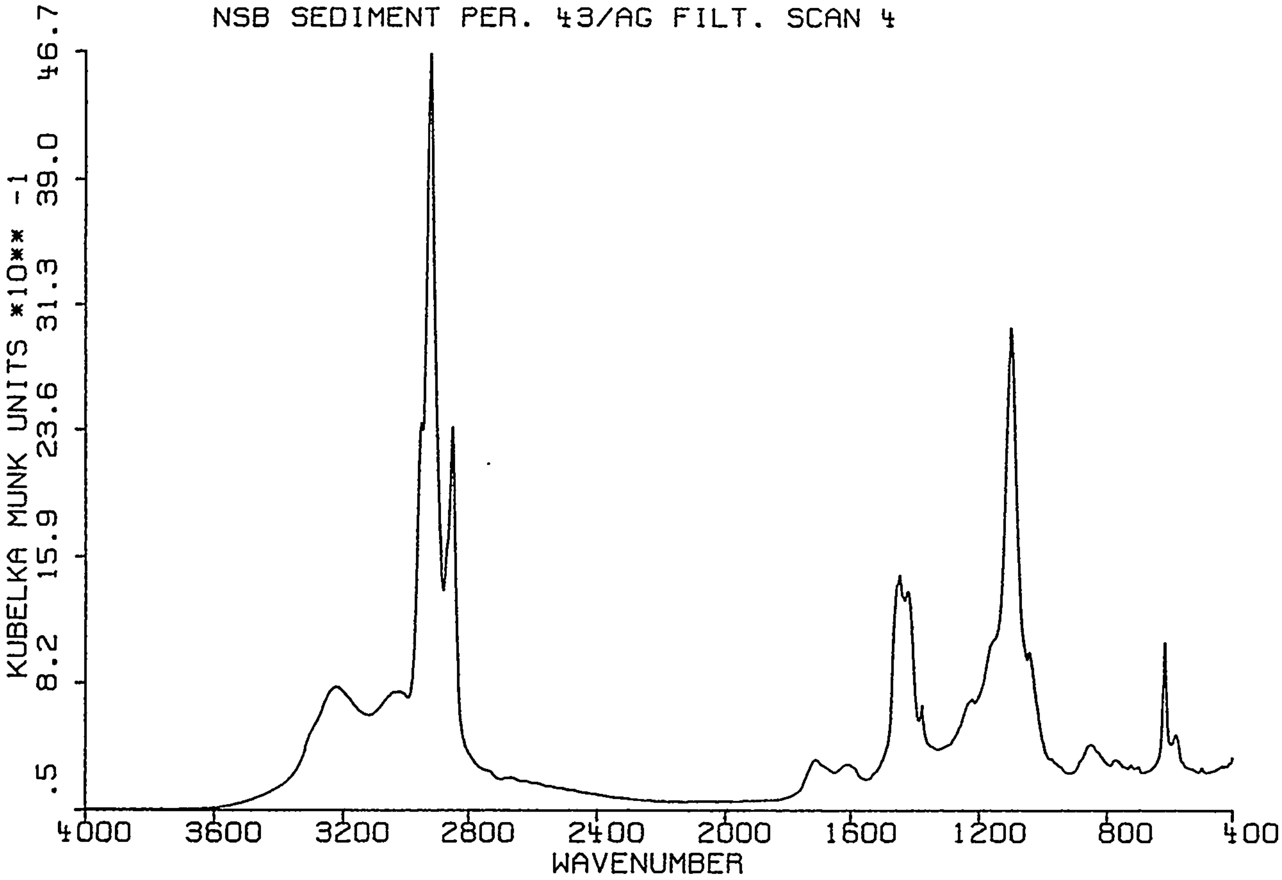


Figure 10. FTIR Spectrum of Period 43 NSB Sediment.

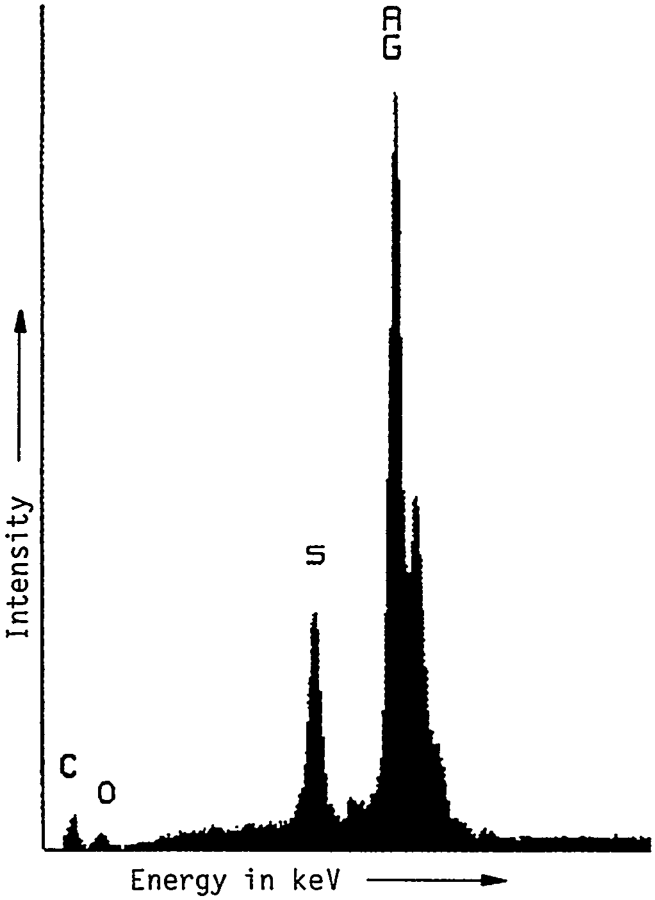


Figure 11. EDX Spectrum of Period 43 NSB Sediment.

APPENDIX 1

HRI RUN CMSL-8 SAMPLE REQUEST

CONSOL Inc.
Research & Development
4000 Brownsville Road
Library, PA 15129-9566
412-854-6600
FAX: 412-854-6613
412-854-6748

October 27, 1994

Dr. V. Pradhan
HRI, Inc.
100 Overlook Center, Suite 400
Princeton, NJ 08540

Dear Vivek:

We are requesting samples from Run CMSL-8 as follows. We would like to receive from each run condition: (1) 100 g of separator overhead (SOH) and 100 g of atmospheric still overhead (ASOH) or 100 g of SOH/ASOH blended in the correct product ratio; (2) 150 g of start-up/make-up oil; (3) 200 g of pressure-filter liquid (PFL); (4) 150 g of pressure-filter cake (PFC); and (5) 200 g of interstage sample (first-stage product). If you cannot provide these quantities, we can work with smaller quantities.

Although Runs CMSL-6 and CMSL-7 have already been completed and the sample quantities may be limited, we are interested in a similar sample set from these runs. We would appreciate any of these samples that you can provide.

Please let us know of any problem fulfilling this request. Thank you for your assistance.

Sincerely,

Gary

G. A. Robbins
Sr. Research Chemist

/ls

cc: A. G. Comolli - HRI
M. A. Nowak - PETC
E. B. Klunder - PETC
F. P. Burke
R. A. Winschel
S. D. Brandes

Addendum to Run CMSL-8 Sample Request

The sample request was verbally modified on 11/9/94 to add 200 g of continuous atmospheric still (CAS) bottoms per balance period.

APPENDIX 2

UNIVERSITY OF DELAWARE QUARTERLY TECHNICAL REPORT

THE KINETICS OF COAL LIQUEFACTION DISTILLATION RESID CONVERSION

Quarterly Report
9/16/94 - 12/15/94

Michael T. Klein
Principal Investigator

William H. Calkins
Co-Principal Investigator

He Huang
Postdoctoral Fellow

and

Shaojie Wang
Visiting Scientist

Center for Catalytic Science and Technology
Department of Chemical Engineering
University of Delaware
Newark, Delaware 19716

Subcontract from CONSOL under DOE Contract DE-AC22-94PC93054

EXECUTIVE SUMMARY

The objectives of the subcontract are to use the Short Contact Time Batch Reactor (SCTBR) developed in this laboratory, and such analytical methods as thermogravimetric analysis (TGA), gas chromatography (GC), gas chromatography/mass spectrometry (GC/MS) and other characterization methods to:

1. Develop and verify an experimental protocol for measuring <u>relative</u> coal resid reactivity to break down into lower boiling products using tetralin solvent and a standardized catalyst and coal liquefaction conditions;

2. To study the conversion kinetics of these resids with and without catalysts and in the presence of different solvents (including actual recycle process solvents). This will include determination of reaction order, reaction rate constants, activation energies and pre-exponential factors to obtain a better understanding of the conversion reactions and to enable the application of this kinetic information to actual liquefaction processes;

3. To measure the conversion reactivities of a number of resids using the protocol referred to in objective 1) to correlate <u>reactive reactivity</u> with chemical structure and physical properties of the resids; and

4. To use the above-determined mechanistic and kinetic information and structure correlations to derive a mathematical reaction model of the resid conversion process.

A meeting was held on November 14, 1994, with F. P. Burke, R. A. Winschel, and S. D. Brandes of CONSOL and He Huang, Shaojie Wang and W. H. Calkins of the University of Delaware at the U. of D. campus. The goals and objectives of the program were discussed.

The development of a suitable method for evaluation of resid convertibility will be based upon the previous work at Delaware on the same topic. However, this method now has to be made more quantitative and firmed up by further experimental work. To this end, CONSOL has supplied 1200 grams of a "typical" resid which will be used for this purpose. Its analytical data also was made available.

As a working hypothesis, the following definition of resid conversion was agreed to:

$$X\ (\text{wt}\ \%) = S \times \frac{A_T}{A_{total}}$$

where S is the resid soluble fraction determined by ash balance (wt %) using a TGA method, A_T is the area of the DTG curve of the liquid fraction up to an 850 °F equivalent, excluding the tetralin material, and A_{total} is the total area of the liquid DTG curve from the tetralin completion temperature to the end.

To prove the feasibility of defining resid conversion (X) using TGA requires that the TGA apparatus be calibrated with compounds of known boiling point (or range) to define the 850 °F equivalent point. We have designed special quartz pans for the TGA instrument with three sizes of orifices. We will attempt to calibrate the instrument using model compounds and mixtures. When these special quartz pans for TGA are received from the glass blower at the University of Delaware, we will run compounds of known high boiling points (some of them were supplied by CONSOL), some mixtures of known simulated distillation analysis as well as some resids already converted in the previous project.[1] Some modification may be needed in the design of the TGA pans when we have the preliminary tests completed.

The Delaware group will continue to search for an apparatus such as that used by Frank Schweighardt for determination of the GC pattern of a liquid sample, while at the same time measuring the weight of material not volatilized into the GC.

A diagram of a pressure filter has been received from CONSOL and will be considered as a means of speeding up the filtration and washing process.

Two samples of coal liquefaction recycle solvent were received from CONSOL.

Our visiting scholar Shaojie Wang has now arrived from China and is getting familiar with the project, the equipment, and instrumentation involved in the Coal Liquefaction Resid Conversion Project.[2] He has been learning to run the SCTBR reactor. Some modifications have also been made in both the TGA unit and SCTBR reactor system to make them easier and safer to operate.

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1. Subcontract from CONSOL under DOE Contract DE-AC22-89PC89883
2. DOE Contract No. DE-FG22-93PC93205

APPENDIX 3

UNIVERSITY OF DELAWARE CONFERENCE CALL RECORD

RECORD OF CONFERENCE CALL

October 14, 1994

Re: University of Delaware Subcontract from CONSOL Under DOE Contract DE-AC22-94PC93054

Participants: University of Delaware
W. H. Calkins
H. Huang

CONSOL
F. P. Burke
R. A. Winschel
S. D. Brandes

A copy of the agenda prepared by CONSOL is attached.

Delaware's visiting professor will arrive some time after November 1. Frank Burke suggested that CONSOL visit the University of Delaware at that time to discuss project plans in more detail.

Goals and Objectives (Agenda Item 1)

An overview of the goals and objectives of the program was discussed. The development of an empirical method for the evaluation of resid conversion will build on work done in Delaware's previous subcontract from CONSOL in which the STBR system was used to convert resids to soluble products.

The highest priorities of the Phase 1 program will be Items 1.a. and 1.b. We hope to make some progress on 1.c. It is expected that most of the modeling work (Item 1.d) will be deferred pending funding of Phase 2. However, it would be very valuable to make at least some initial progress on the correlations and modeling work to help justify funding of the Phase 2 work to DOE.

Resid Conversion Definition (Agenda Item 2)

It was agreed that the definition of "resid conversion", and the means of measuring it are key to the success of this research. To be consistent with process development data, resid conversion was operationally defined to be a change of the resid boiling above 850 °F to materials boiling below 850 °F. In the absence of retrograde reactions, resid conversion is defined as the disappearance of material boiling above 850 °F. The main focus of Phase 1 of the subcontract is not on characterization of the products. However, characterization data will be necessary in correlation and modeling.

Experimental Details (Agenda Item 3)

Experimental details were discussed (Items 3.a.1.-3.a.3.). It will require a large amount of experimental work to obtain the kinetic parameters, and retrograde reactions may make the reaction orders very hard to determine. However, at the planned experimental conditions, CONSOL expects little retrogressive reaction. In the previous experiments at temperatures of 420-435 °C, very little conversion (based on tetralin solubility) was obtained. However, conversions were expected to be low because we are simulating only one pass of a recycling system. In actuality, near-30% conversions (even though they were not based on distillation of the resid reaction products, but instead were based on solubility) were what is expected in one pass of a two-stage liquefaction unit with bottoms recycle.

Delaware believes that in order to do a good job on developing kinetic parameters, a large number of runs with a few resid samples should be made. However, for correlating kinetics with resid properties, many different resids should be investigated.

Delaware would like to receive all 14 samples designated in the letter of Sue Brandes to Bill Calkins on October 5, 1994, and would like one large (1.5 kg) sample to start with. They propose to develop procedures and to test this one sample under all conditions. It may be possible in the testing of this large sample also to try a different catalyst sample. They will then react and work-up two to four different samples with a narrower set of conditions. They requested about 500 g of these samples. Finally, they propose to investigate the reactivity of the remaining ten to twelve samples with a narrower set of conditions; 50-100 g of these samples will be sufficient. To decide on reaction conditions, Delaware proposed to scan the H_2 pressure and concentration ratios with the large sample to optimize resid conversion. They intend to include longer times and higher temperatures than those which were used in their previous subcontract to improve conversions.

The question of whether one catalyst should be used throughout all the runs was discussed (Item 3.a.4.). It was agreed that a single catalyst sample should be sufficient. Because thermal runs have such low yields, only one run will be made for each resid without catalyst; all other runs will be made with catalyst present. The catalyst:resid ratio will be held constant for all catalytic runs. The use of a dispersed vs. supported catalyst was discussed. There are advantages to each. The use of a dispersed catalyst would simplify the work-up procedures and it is presumed make it easier to obtain good kinetic values. Delaware suggested using ammonia tetrathiomolybdate (ATTM) or moly naphthenate (MoNaph), or Molyvan L. However, most dispersed catalysts (including these three) are hydrogenation catalysts but not good cracking catalysts. Additionally, there would be no easy way, under the conditions of the STBR system, to sulfide the dispersed catalyst in situ. Simulation of a "real life" liquefaction system would be better with a supported catalyst. It was decided that CONSOL would make the decision as to which catalyst to use and send Delaware sufficient catalyst for the entire subcontract.

The "real" solvent samples are of interest to Delaware (Item 3.6.). Delaware was offered the two 850 °F- samples as were proposed in CONSOL's October 5 letter, or a resid-containing whole oil. Delaware prefers the distillate so that they can add it back to the resid in the ratios that they will choose.

Additional analytical methods may be used by Delaware (Item 3.c.). Delaware acknowledged that the gases made in the conversion reaction will be lost. They will use the ash content of the soluble and insoluble portions of the product to adjust for incomplete mass balance. In an effort to analyze the low boiling products of the soluble material Bill would like to use a heatable pre-injection system for GC. This equipment currently is not available. Information describing such a system (by F. Schweighardt) was offered to Delaware. Bill described a TG-gas chromatograph (GC) system which they were trying to procure for the university Chemistry Department, which they also may use in this program.

Delaware will make provisions to retain samples of solid and soluble products from all runs (Item 3.c.). CONSOL may request some of these for additional analyses.

Data Analysis - Resid Conversion Measurement (Agenda Item 4)

The method to measure 850 °F^+ conversion was discussed. In Delaware's previous work, the resid was reacted and the recovered products of reaction were extracted with methylene chloride. The filtrate was stripped of methylene chloride and analyzed by thermogravimetric analysis (TGA). The filter cake was dried and it, too, was analyzed by TGA. Ash balances were used to adjust for incomplete product recoveries. Based on the definition of resid conversion under the present subcontract (given above), Delaware will determine conversion by simulating distillation of the reaction products using a thermogravimeric analyzer (TGA). Delaware proposes to use the product of the area under the differential TG (DTG) curve and the percent of material that solubilizes in the reacting solvent (tetralin) and methylene chloride to derive a relative value for conversion of different resids. This method assumes that the filter cake contains no products of the reaction, as defined above. Delaware will verify the assumption that the solids from the filtration contain no converted material. Depending on how the TGA analysis is conducted, the unreacted feed resid may produce some volatile matter. If so, the conversion calculations will need to take this into consideration. The TGA program to be used by Delaware may be one similar to HRI's 950 °F^+ resid conversion method that was adapted by CONSOL for DuPont TGA equipment. The HRI and CONSOL procedures will be sent to Delaware.

Action Items

Five items were left for further action.

- CONSOL will select a single large sample (1.5 kg), based on availability and relevance to the project.
- CONSOL will select and supply catalyst for the experimental program.
- Delaware will further determine and validate the method for determining resid conversion.
- CONSOL will send the HRI and CONSOL TGA protocols for determining resid contents to Delaware.
- CONSOL will send information describing a pre-injection-pyrolysis/GC system to Delaware.

AGENDA

University of Delaware
Conference Call, 10/14/94

1. Goals and Objectives of the Program
    a. develop an empirical method for the evaluation of resid conversion
    b. develop simple kinetic parameters to define resid reactivity based on a series of experiments
    c. correlate chemical and physical characteristics of resids with resid reactivity
    d. develop mathematical kinetic and mechanistic models

2. Define "Resid Conversion"

3. Experimental Details
    a. Samples
        1. number of resid samples
        2. quantity of each resid sample
        3. is one resid sample in large quantity required
        4. is one catalyst sample sufficient
        5. what quantity of catalyst is required
        6. solvent samples
        7. sample information will accompany samples

    b. STBR Experiments
        1. conditions (time, temperature, H_2 pressure, solvent:resid ratio, catalyst)
        2. recovery

    c. Work-up of Reaction Products
        1. TGA method
        2. GC, GC/MS
        3. additional analyses
        4. return of a portion of products to CONSOL

4. Data Analysis
    a. Relative Resid Reactivity Measurement

    b. Kinetic Data
        1. determination of reaction order
        2. determination of reaction rate constants
        3. determination of activation energies and pre-exponential factors

    c. Correlation of Relative Reactivity with Chemical Structure and Physical Properties of Resids

    d. Derivation of Reaction Model Based on Kinetics and Structural Information

APPENDIX 4

UNIVERSITY OF DELAWARE TRIP REPORT

Trip Report:	University of Delaware
Date of Visit:	January 17, 1995
Address:	Department of Chemical Engineering Colburn Laboratory University of Delaware Newark, DE 19716-3110
Principal Contact:	Dr. W. H. Calkins Phone: 302-831-2213

Attendees:

<u>University of Delaware</u>
Mike Klein
Bill Calkins
He Huang
Shaojie Wang
Keyu Huang

<u>CONSOL</u>
Frank Burke
Dick Winschel
Susan Brandes

DISCUSSION

Subject: University of Delaware subcontract from CONSOL under DOE Contract DE-AC22-94PC93054

Bill Calkins hosted our visit to the University of Delaware on January 17, 1995. The purpose of our visit was to discuss the expansion of the program that Delaware is conducting to study direct coal liquefaction resid reactivity. The expanded program will include Task 1.4.2 of the subject contract. This task includes the construction of a mathematical kinetic model.

Frank Burke informed Delaware that the expanded program provides an additional \$67,000 (approximate) for completion of Task 1.4.2. by Delaware. It also provides funds for subcontracting with other organizations to provide special analyses. Suggestions for what analyses would be useful were solicited from Delaware. They believe that ^{1}H-NMR and ^{13}C-NMR (especially the type of analyses provided by Ron Pugmire of the University of Utah) will be very useful. Molecular weight determinations are considered useful, but their reliability is viewed with some concern, regardless of whether the method is vapor phase osmometry (VPO) or field ionization mass spectrometry (FIMS). Bill Calkins believes that size exclusion chromatography (SEC) (or gel permeation chromatography (GPC)) is a preferable method for determination of molecular weight ranges.

He Huang made a presentation of the work completed to date on using the TGA apparatus to obtain a simulated distillation. During our previous discussion (November 14, 1994), he indicated that one reason TGA is a poor method to simulate distillation is because, depending on the geometry of the TGA pan, mass transport rates can change as the sample volatilizes. He proposed to design and construct TGA pans made from quartz that have a cavity and a small circular opening in the top. The appropriate size of the opening will depend on gas flow rate, pressure, volatility, and heating rate. This design, he believes, will eliminate the variable mass-transfer rate of the liquid going into the gas phase. At this meeting we were shown three 'closed' vessels which were made by drawing quartz tubing. The closed vessels are generally cylindrical in shape, approximately 1 cm high, with concave tops and bottoms internally. In the top of the closed vessel a circular hole was made. Each of the three 'pans' has a different diameter opening of 0.615 mm, 0.974 mm, or 1.538 mm. These openings can be reproduced within a tolerance of ±0.005 mm.

Using these pans, experiments were made initially with water (because of the large quantity of available data on the behavior of water). The experimental data gave a reproducible straight line relation of ln rate loss vs 1/T which shows a parallel relationship to literature data of ln p_{vap} vs. 1/T. The relationship between vapor pressure and rate of weight loss was found to be good. Data plotted as ln (rate of weight loss) vs. 1/T also produced a reproducible straight line (with an $r^2 = 0.99$). The heat of vaporization could be calculated from the Clausius-Clapeyron relationship ($\Delta H^{vap} = -R[d(\ln p^{sat})/d(1/t)]$); however, this was not yet done. A simple model was proposed: rate = $kp_{vap}(T)$ (or $kp_{vap}(T)^n$); where rate = $f(p_{vap}(T)$, T, molecular properties). Data from the TGA of a set of model compounds (water, tetralin, pyrene, and others) with known boiling points were fitted to these curves. Data fitted straight lines up to temperatures of about 380 °C. No pyrolysis was evident up to about 400 °C. Initial work was done at constant heating rates (1 °/min, 2 °/min, and 5 °/min). At higher heating rates (5 °/min), a temperature lag (constant for that heating rate) was apparent. This was corrected for each data point in the temperature range used. Each model compound studied under the same conditions gave highly reproducible results. It was concluded that under these conditions the rate of weight loss was a function of only p_{vap}.

From this work, an equation to calculate resid conversion from STBR runs and TGA analysis was proposed:

$$\text{Conversion} = S \times \frac{W_{T_o} - W_{tet}}{W_o - W_{tet}}$$

where:
W_{To} = the amount of material which boils below T_o (the temperature of interest, e.g., 850 °F)
W_o = the weight of material charged to the TGA pan
W_{tet} = the weight of the tetralin used as a solvent (obtained from GC analyses)
S = solubility

In order to determine W_{To}, three methods were considered. To obtain a boiling point from a simple ramping run would be very difficult (if not impossible). Rate-constant runs could be used where the rate of weight loss would be held constant at that rate which corresponds to the boiling point, but this, in practice, would be difficult to control. The third method is something Delaware is calling the "Jump and Iso-track" (JIT) method. In this method W_{To} is determined by a rate-decay curve. The experiment is run at some fixed temperature. To obtain better control of the experiment, the thermocouple positioned to measure the sample temperature (not the one near the TGA pan) was used to control temperature. A decay rate curve is obtained and examined. An equivalent temperature to W_{To} is determined by calibration with model compounds of known boiling points. The method is constrained by keeping the unknown samples below pyrolysis temperatures. This can be achieved by lowering the temperature of the TGA experiment and taking advantage of the finding that the rate of weight loss under these conditions is a function of the vapor pressure (which is a function only of temperature). Pressure also can be reduced which also allows operation at lower temperature.

The sweep-gas flow rate was examined and found to be a factor. Higher gas flow rates (100 mL/min) are considered preferable so that vaporized material is rapidly carried away from the TGA balance.

Bill proposed to use the TGA experiment for further analyses. He believes that the rate of weight loss can be held constant (corresponding to a certain boiling point, for example 850 °F) and directly transfer the effluent from the TGA into a gas chromatograph to examine the volatile materials.

Mike Klein reviewed the University's lumped kinetic modeling/network construction (Delplot) work that was done on petroleum asphaltenes (as an example of what information the computerized system provides; mainly kinetic rate constants, activation energies, etc.). Mike cautioned that this method provides kinetic information, but no structural information. He referred to these methods as 'data analysis' and assured us that given enough rate data, his group could produce kinetic information with these techniques with the computer programs in place in the chemical engineering department.

In order to get a molecular model and the same kinetic information, a structural model can be "built" using a Monte Carlo technique. In this technique, structures are built based on the probability distribution that they can exist. These structures then are "reacted" based on the probability that they can undergo certain molecular scission and combination reactions. The system at the completion of reaction is neutral; all reactions end in termination steps. The properties of the 'reacted' system then are checked against measured properties of the materials being modeled. An iterative procedure is used to cause the computer simulated model to conform to the experimental data. Some experimental data is not useful at this time, because no (good) correlations exist to relate the measured value with molecular structure. Where good correlations are available, the experimental data can be used. Examples of experimental methods previously used to provide data in this modeling work are solubility class separations such as saturates, aromatics, naphthenes, aliphatics (SARA), high resolution mass spectrometry, ^{1}H- and ^{13}C-NMR spectroscopy, elemental analyses, high performance liquid chromatography, and vapor phase osmometry (for molecular weight determination).

Conversion and characterization data on samples of interest can be incorporated into the model as it is being constructed. Experiments performed in systems other than Delaware's STBR, such as in microautoclaves, can provide data useful in the refinement of the model. Characterization data on products of reaction of coal liquefaction resids which would be useful for the modeling work include elemental analysis, ^{1}H- and ^{13}C-NMR analyses, molecular weight analyses, and SARA(-like) separations, and the same analyses on the solubility fractions as would be performed on the whole product.

Analytical data compiled by CONSOL on many coal liquefaction resid samples (not necessarily just those that Delaware will be analyzing) will be helpful in constructing the model. CONSOL will compile as much of this information as possible and send it to Delaware. Most of the data will come from the previous contract and the Participants Program from that contract. Data on some samples will include analyses by field ionization mass spectrometry (FIMS), ^{13}C-NMR, ^{1}H-NMR, solubility separation, electron spin resonance (ESR) spectroscopy, and Fourier transform infrared spectroscopy (FTIR).

Follow-up

The following items will be acted on by CONSOL.

- CONSOL will modify the subcontract with the University of Delaware to authorize work on Phase 2.
- A set of analytical data for coal liquefaction resids samples will be compiled by CONSOL and sent to Delaware for use in constructing the kinetic model.

- The computer software format that is appropriate for delivery of the final kinetic model will be determined by CONSOL on consultation with the DOE. This information will be transmitted to Delaware.
- CONSOL agreed to perform elemental analyses of STBR products for Delaware. It is expected that 3 to 7 samples per week may be sent by Delaware.
- Further discussion with Delaware will be scheduled to specify the final form of the kinetic model.

APPENDIX 5

CHARACTERIZATION OF COAL/WASTE COPROCESSING SAMPLES FROM HRI RUN POC-2

G. A. Robbins, R. A. Winschel, F. P. Burke

Prepared for presentation
ACS Spring National Meeting
Anaheim, CA

April 2-7, 1995

Conference paper removed
for separate processing.

APPENDIX 6

THE ROLE OF RECYCLE OIL IN DIRECT COAL LIQUEFACTION PROCESS DEVELOPMENT

F. P. Burke

Prepared for presentation
ACS Spring National Meeting
Anaheim, CA

April 2-7, 1995

Conference paper
removed for separate
processing.