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**Coal Liquefaction Process Streams
Characterization and Evaluation,**

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**Quarterly Technical Progress Report
October 1 through December 31, 1992**

S. D. Brandes, R. A. Winschel
F. P. Burke, and G. A. Robbins

October 1993

CONSOL Inc.
Research & Development
4000 Brownsville Road
Library, PA 15129

Under Contract to:

United States Department of Energy
Contract No. DE-AC22-89PC89883

U.S. DOE Patent Clearance was provided by
Chicago Operations Office on 9/14/93.

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**COAL LIQUEFACTION PROCESS STREAMS CHARACTERIZATION AND EVALUATION
QUARTERLY TECHNICAL PROGRESS REPORT, OCTOBER 1 THROUGH DECEMBER 31, 1992**

This is the thirteenth Quarterly Technical Progress Report under DOE Contract DE-AC22-89PC89883. Major topics reported are:

- Analyses were performed on three coals and eleven process oils from HRI, Inc. process development unit Run 260-03. Run 260-03 was the first process development unit test of Black Thunder Mine subbituminous coal. Significant operating problems were encountered. Sample properties are discussed in context to the operational problems.
- A summary of the status of the Participants Program is given.
- Summaries of the final reports produced by the University of Chicago, the University of Utah, Iowa State University, and the University of Kentucky under the Participants Program, are presented.

Section 1

INTRODUCTION

This is the Technical Progress Report for the thirteenth quarter of activities under DOE Contract No. DE-AC22-89PC89883. It covers the period October 1 through December 31, 1992.

OVERVIEW

The Research and Development Department of CONSOL Inc. (CONSOL) is conducting a program to characterize process and product streams from direct coal liquefaction process development projects sponsored by the Department of Energy. In this program, CONSOL obtains samples from current process development activities in coal liquefaction and coal-oil coprocessing, and characterizes them using established analytical techniques. In addition, selected samples are characterized by other analytical techniques to evaluate their potential for aiding process development. These analyses and interpretation of the results in relation to process operations are provided by the subcontractor.

CONTRACT OBJECTIVES

CONSOL is conducting a program to characterize process and product streams from direct coal liquefaction process development projects. The program has two main objectives. The first of these is to support ongoing DOE-sponsored coal liquefaction process development efforts. This is being accomplished by the application of a variety of standard testing techniques to appropriate process samples. The interpretation of the data so obtained aids plant operations and planning. The second objective is to obtain and provide appropriate direct coal liquefaction process-derived samples for the evaluation of novel analytical methods. The criteria used for evaluation of techniques or methods includes the usefulness of the method to monitor the liquefaction process and to obtain specific chemical information. Methods which show promise for providing useful information for coal liquefaction process development may be utilized in conjunction with the first objective of this program.

CONTRACT ACTIVITIES - THIS PERIOD

Contract activities for this quarter are listed below.

- Analyses were performed on three coal samples and eleven process oil samples from HRI, Inc. Catalytic Two-Stage Liquefaction (CTSL) Run 260-03. Run 260-03 was the first process development unit test of the CTSL process with subbituminous coal (Black Thunder Mine). Significant operating problems were encountered. Sample properties are discussed in context of the operational problems. Sample properties are compared to the properties of samples from HRI bench unit Run CC-1 (also known as 227-55) and Wilsonville Run 262, which also were operated with Black Thunder Mine subbituminous coal as the feed.
- Substantial progress was made in the Participants Program this quarter. A summary of activities in the Participants Program is presented. All remaining Phase II final reports were received. Evaluations were written for four of the five reports received this reporting period. The CONSOL evaluations and the executive summaries excerpted from those reports are found in this quarterly report. Phase III was initiated.
- Work in progress, but not yet completed this quarter, includes the following:
 1. Analysis of oils from Wilsonville Run 263 is under way.
 2. A literature search concerning analytical methods for coal liquids is being conducted.
 3. Process oil samples were received for analysis from HRI CTSL Runs CC-15 and CC-16. Analyses will begin next quarter.

Section 2

EXECUTIVE SUMMARY

HRI RUN 260-03

In support of DOE-sponsored coal liquefaction process development efforts, CONSOL analyzed process oils and feed coals from HRI Run 260-03. This was the first HRI process development unit test of Black Thunder Mine subbituminous coal. During this run, HRI experienced a number of operating problems.

The major findings of this study are summarized here. Detailed results are presented and discussed later in this report.

- Process samples were examined to determine if there was an excessive amount of waxy or grease-like components in the filter samples which could have caused the filtration problems experienced during the run. Sample properties, as determined here, support the idea that there is a high concentration of waxes in the Run 260-03 samples. The paraffinicity of the samples increased as the run progressed. A sample of material obtained from the process line down-stream of the filter was found to have similar properties as the filter cake sample taken at the same time. It is, therefore, concluded that this sample is process-derived (i.e., not an extraneous contaminant).
- As determined by batch microautoclave tests, the process-derived recycle solvents declined in solvent quality as the PDU run progressed. In general, Run 260-03 recycle oils were found to be quite waxy and paraffinic, and to become increasingly so as the run progressed. The recycle solvents from periods 11 and 14 contained 21% and 32% n-paraffins, respectively. The increasing paraffinicity of the solvents as the run progressed is believed to be responsible for the reduction in solvent quality. Filtrate samples also were found to contain about 50 wt % wax. It was found that the Run 260-03 filtrate samples are poorer solvents than the PFLs produced in bench unit Run CC-1. The Run 260-03 filtrates also became more paraffinic and declined in solvent quality as the run progressed. Naphtha stabilizer bottoms samples were found to contain,

predominantly, long-chain alkanes, naphthenes, and substituted tetralins.

- The Wyodak-Anderson (Black Thunder Mine) subbituminous coal used in Run 260-03 was found to be contaminated with high volatile bituminous coal (3-5 vol %) and isotropic coke (~0.1 vol %). These contaminants are presumed to have been introduced when the coal was ground. The properties of the coal fed to the PDU, including elemental composition and oxidation index, did not change significantly over the length of the run.
- In summary, the oils produced in Run 260-03 are highly hydrogenated and paraffinic, and are poor donor solvents.

PARTICIPANTS PROGRAM

The following items were accomplished in the Participants Program.

Phase II

Final reports were issued for subcontracts with West Virginia University, Lehigh University, and Vander Sande Associates.

CONSOL evaluations were written for subcontracts with the University of Chicago, the University of Utah, Iowa State University, and the University of Kentucky. They appear later in this report, along with the respective executive summaries from the subcontractors' final reports.

A revised draft final report was received from the University of Pittsburgh. With the exception of the University of Pittsburgh report, all Phase II reports have now been issued.

Phase III

A Participants Program Phase III was initiated. Letters soliciting information about the potential new application of three analytical techniques (or methods) were sent to Dr. I. Wender, the University of Pittsburgh, Dr. L. Pfefferle, Yale University, and Dr. P. Hatcher, The Pennsylvania State University. Both Dr. Wender and Dr. Hatcher responded with proposals for work under Phase III of the Participants Program. Two organizations (SRI International and the

University of Utah), which participated in previous phases of the Participants Program, were invited to participate in Phase III.

Quotes were obtained for the application of petroleum inspection tests to coal liquids from National Institute for Petroleum and Energy Research and from Alberta Research Council. An estimate for the same work was obtained from Conoco, Inc.

Section 3

RESULTS AND DISCUSSION

HRI RUN 260-03

Introduction

Eleven process-derived samples and four coal samples were obtained for analysis from Hydrocarbon Research, Inc. (HRI) from their process development unit (PDU) Run 260-03. This run was operated with Wyodak and Anderson seam subbituminous coal (Black Thunder Mine). During the run, HRI experienced operating problems including catalyst carry-over, deposition in the process lines, and plugging of the filters. The samples were chosen from periods which represent the end of the two operating segments (periods in which operating problems occurred), in addition to periods in which excessive wax in the filter cake was noted. The process samples were obtained from five different locations in the plant. These samples are start-up (S/U) solvent and process-derived recycle solvent (which, in the case of the two samples analyzed, contain some S/U solvent), filter cake, filtrate, naphtha stabilizer bottoms (NSB), and deposit material obtained from the process line connecting the filter and the filter cake storage drum. Several questions will be addressed concerning the nature of these samples, as well as how the nature of the samples taken at the same location changed during the run. HRI has designated Run CC-1 (also known as Run 227-55) as the previous run which can most closely be compared to Run 260-03. CONSOL's analyses of Run CC-1 samples were reported previously.¹ Run CC-1 was a bench unit operation, whereas Run 260-03 was carried out in the PDU. However, some comments addressing the similarities and differences in the analyses of the process streams from the two runs will be made.

Run 260-03²⁻⁴

This run was made in the HRI process development unit (PDU), which is diagrammed in Figure 1. Due to operating problems, Run 260-03 was divided into two segments. The first segment consisted of Periods 1 and 2, which were carried out in November 1991. At the conclusion of Period 2, the run was shut down for equipment modifications. The second segment of the run consisted of Periods 3 through 13; it was started in June 1992. Shutdown occurred on July 19, 1992 (Period 14A). The shutdown was ordered because of catalyst carry-over in the second-stage reactor. Temperatures of reactors 1 and 2 for the entire run can

be seen in Figure 2. The catalyst used in both reactors during the run was Criterion 317 (Ni/Mo/Al, 1/16" extrudate). The initial batch of catalyst was equilibrated for 8-10 days, then catalyst addition/withdrawal operations were started and continued for the remainder of the run. The run was operated with Wyodak and Anderson seam subbituminous coal (Black Thunder Mine) prepared by Empire Coke Co.

Coal conversion in Run 260-03 was reported by HRI to be lower than expected on the basis of results with the same coal in the bench unit. Run CC-1 had coal conversions ranging from 87.2% (Period 1) to 92.3% (Period 4).¹ Coal conversion at the end of Run 260-03 was only 78.1%.⁴

Sample Description²⁻⁴

All samples were obtained from HRI, Inc. and are associated with Run 260-03. Numbers given in parentheses starting with the designation 'LO' refer to the HRI sample number. The samples are described in Table 1.

Samples of feed coal (Wyodak and Anderson seam subbituminous coal, Black Thunder Mine) were received from HRI from the first (Period 1, LO-6038)) and last period (Period 14A, LO-6095) of the run. Analyses of these samples can be found in Table 3. For comparison, another sample (LO-6096) of Black Thunder Mine coal prepared for HRI at the same location (Empire Coke Co.) also was analyzed. HRI noted that this sample showed more liquefaction activity in batch tests than the feed coal to Run 260-03. Its analysis is also given in Table 3. One additional coal sample (LO-6039) was analyzed and was found to be a bituminous coal sample which was sampled by HRI in error. Sample LO-6039 will not be further discussed.

Start up solvent (LO-6040) was obtained from the Wilsonville Advanced Two-Stage Direct Coal Liquefaction Facility in Wilsonville, Alabama. The solvent is a composite of topped distillate process solvents generated from Wilsonville Runs 262 and 263 and is, consequently, a mixture of solvents which were derived from subbituminous coal. The sample analyzed is a sub-sample, obtained on July 29, 1992, of an aliquot of the topped solvent taken before the start of Run 260-03 in November 1991. Two process-derived recycle solvents also were analyzed. These samples (LO-6041 and LO-6042) are mixtures of the topped Wilsonville solvent plus excess process solvent generated during the HRI PDU run.

The proportions of start-up solvent to process-generated oils in these samples are not available. These three samples were taken from solvent holding tank 4 (not shown in Figure 1).

The two naphtha stabilizer bottoms samples were obtained from Periods 2 (LO-6043) and 13 (LO-6044). They represent the end of the two operational segments; they were obtained from unit N-5 (Figure 1).

Three filter cake samples were analyzed. Samples were taken from drum D-8 (Figure 1). They were obtained from Periods 10 (LO-6047), 12 (LO-6048), and 13 (LO-6049). HRI observed excessive 'waxy' or 'greasy' material associated with the filter cakes collected after Periods 10 and 13. There was no washing of the filter cake in the beginning of the run. However, because of the presence of the observed 'waxy' material, washing of the filter cake was initiated in Period 10B and continued through to the end of the run.

The filtrate samples taken from the filtrate holding tank (labeled O-48 in Figure 1) were obtained from Period 2 (LO-6045) and Period 13 (LO-6046). The filtrate sample taken from Period 13 contains an unknown quantity of the light coal-derived vacuum overhead oil used to wash the filter cake.

One additional sample (LO-6097), taken at the end of the run (Period 14A), was supplied by HRI. It is a 'greasy' material taken from the process line downstream of the PDU leaf filter through which the filter cake is withdrawn. Filtration rates had fallen very rapidly immediately before the end of the run, and it was speculated that the presence of this material, which had accumulated on the filter cake, was responsible.

Experimental

The fifteen coal and process-derived samples were analyzed by the following procedures, as appropriate: solubility separation, distillation, nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, microautoclave solvent quality assay, gas chromatography/mass spectrometry (GC/MS), gas chromatography/flame ionization detection (GC/FID), proximate analysis, elemental analysis, and petrographic analysis. See Table 2 for analyses performed on each sample. Most experimental procedures used to

analyze the samples have been published elsewhere.⁵⁻⁷ The oxidation index was determined by a Fourier transform infrared spectroscopic method.⁸ Petrographic methods are ASTM D-2796, D-2797, D-2798, and D-2799.

GC/FID experiments were performed on a Perkin Elmer 2000 instrument using an SPB5, 30 m column, 0.25 mm ID, 0.25 μ m thickness. The temperature program used was 50 °C for 4 min, 4 °C/min to 300 °C, and 10 min hold at 300 °C. Dewaxing studies were performed on selected samples. Two methods were used. The procedure for the first method (Method A) was based on that described in Reference 14; 30 mL of acetone was added to approximately 10 g of process solvent. The mixture was warmed to assure homogeneity. The mixture was then cooled to -35 °C in an acetone/dry ice bath. The cooled sample was filtered through Whatman 42 filter paper and washed with cold acetone. The filtrate was dried of acetone by rotary evaporation and vacuum drying at 78 °C. The filter cake (wax) was washed from the filter paper with freshly distilled THF; the THF was driven off by rotary evaporation. The wax fraction was re-dissolved in hexane and passed through pre-conditioned (1 hr, 400 °F) alumina; column dimensions: 0.5 m x 2.5 cm. The second method (Method B) entails mixing the process solvent with hexane, warming to ensure good mixing, and passing the mixture through one or two columns of alumina using hexane as eluent. Wax yields are presented as weight percent of whole oil, unless specified otherwise. Values presented for the gas chromatographic method (Method C) were determined by integrating the chromatogram of the wax, obtained by one of the two methods described above, and calculating the percent of straight chain (normal) paraffins in the wax. The same compounds were identified and integrated in the chromatogram of the corresponding whole oil from which the wax was derived. A ratio of these two values is reported as "wax as percent of whole oil".

High-volatile bituminous coal and coke contaminants found in the subbituminous feed coal and filter cake samples were determined by a point-count method. The reflectance of high-volatile bituminous coal and coke is significantly different than that of the subbituminous coal. This difference is used to distinguish the contaminants in the coal samples. Five hundred to one thousand total points were examined on the surface of a polished pellet of material. The contaminants are counted separately and are reported as a volume percent of the sample.

Results and Discussion

Coal Samples

The coal samples were analyzed by proximate, elemental, and petrographic analyses (Table 3). For comparison, the analysis of the coal fed during HRI Run CC-1¹ is also given in Table 3. In addition to the other analyses, the oxidation index for each sample was obtained using an FTIR method.⁸ Except for the initial moisture content, the coals fed in Run CC-1 and Period 1 of Run 260-03 have similar proximate and elemental analyses. It also is apparent that there was no substantial difference in the chemical composition of the two samples of coal fed to the PDU during the run. Both the oxidation index obtained by FTIR, and the sulfate content are essentially the same for the two samples. There was a small decrease in the volatile matter (VM) content of the coal fed in period 14A (from 46.5% to 43.5%, dry); however, the coal sampled in Period 14A has the same VM content as the coal used in HRI Run CC-1, a run in which no operational problems were encountered. Since the coals from periods 1 and 14 are so similar, it is considered unlikely that the coal fed during Run 260-03 deteriorated enough over the length of the run to cause the operational problems encountered. The third sample of coal (LO-6096) prepared at the same location (the Empire Coke Co.), which was included for comparison, is similar to the two samples obtained during Run 260-03 except that it differs significantly in the total sulfur content (0.90% vs 0.42 and 0.50%). The elevated sulfate value of this sample indicates that some of its pyrite has oxidized, and thus may not be a good comparison for the coal fed during Run 260-03.

The petrographic data for the coals are given in Table 3. It was found that the two coal samples from Run 260-03 (LO-6038 and LO-6095) and the comparison sample (LO-6096) are contaminated with 3-5 vol% of medium- and high-volatile bituminous coal and about 0.1 vol% anisotropic coke. The contaminants were observed in the microscopic examination of the sample as material having higher reflectance than the subbituminous Black Thunder coal which comprises 95-97 vol% of the samples examined. The contaminants were quantified by counting 500 to 1000 points and calculating the percentage of points that had the higher reflectance. The vitrinite types of the contaminants were determined separately and are reported in Table 3, normalized to 100%. The mean maximum reflectance (R_o) values for the contaminants are also reported in Table 3. They are significantly higher than those of subbituminous coal. The petrographic analyses of the three coal samples

associated with Run 260-03 are different from the analysis of the coal used in Run CC-1. The CC-1 coal analysis shows a lower vitrinite content and a lower mean maximum reflectance value (0.36% vs 0.43-0.48%).

Process Samples

The process-derived samples were analyzed with a number of different techniques (Table 2). In order to facilitate the discussion of the results, the data for each type of sample will be compared among the samples obtained at the same sampling location, in the chronological order in which the samples were produced. A comparison to the samples taken during HRI Run CC-1 and Wilsonville Run 262 also will be made.

Start-up solvent (LO-6040) and recycle process solvents (LO-6041 and LO-6042) show changes in properties as the run progressed. In the solvent quality assay, the start-up solvent gave conversion of our standard Old Ben Mine coal⁹ of 70.3 wt % (Table 5). The process recycle solvent obtained from Period 11 (LO-6041) gave a coal conversion of 59.6 wt %, and the process solvent obtained at the end of the run, Period 13 (LO-6042) yielded only 56.8 wt % conversion. The initial start-up solvent contained 2.6 wt % 850 °F⁺ distillation resid, and the recycle materials contain 5.5 and 5.4 wt % resid (Table 4). This small increase in resid content cannot account for the substantial decrease in solvent quality (Table 5) as the run progressed. The phenolic -OH content of the three solvents decreased from 0.35 meq/g for the start-up solvent to 0.18 and 0.10 meq/g for the solvents from Period 11 and 13, respectively (Table 6). This is contrary to what might be expected for the decreasing solvent quality as the run progressed. Examination of the proton NMR data (Table 6) shows that the aromatic proton content of the three samples declined with time as the run progressed. The large increase in alkyl β and γ protons indicates an enrichment of aliphatic components in the process streams, which may result in the decline in solvent quality of the samples as the run progressed. The start-up solvent and the recycle solvents were subjected to at least one of the two dewaxing procedures, and the oils and waxes were examined by GC/FID. The results are presented in Table 11. The GC data indicate that the total contents of the recycle oils are within two standard deviations ($2\sigma = 5.6$) of triplicate values obtained with one of these samples (LO-6042) and are thus considered relatively unchanged from Period 11 to 13; however, the percent of straight chain paraffins

in the whole oil increased from Period 11 to 13. The NMR data, which indicate an increased aliphatic nature for the samples, is supported by the GC/FID data. The increased aliphatic content seems to provide the best explanation for the decline of solvent quality in the recycle solvents.

The GC/MS total ion chromatograms of the distillable portion of the start-up solvent, and the naphtha stabilizer bottoms, and the distillable portion of the filtrate from Period 2, can be seen in Figure 3. It appears that there is a bimodal distribution of the peaks in the chromatogram of the start-up solvent. In the GC/MS chromatogram of the recycle process solvent obtained in Period 13 (Figure 4), this bimodality has disappeared. This may be due, in part, to the start-up oil being derived from a mixture of process-derived coal liquids.³

The aromatic proton content of the start-up solvent is greater than that of the recycle oils (Table 6). This is supported by the dewaxing experiments. The wax contents (by GC analysis) of the start-up solvent and the two recycle solvents were determined to be about the same (about 55% for the start-up solvent and 53% and 49% for the recycle solvents) (Table 11). However, the percent of straight chain paraffins in the start-up solvent is much lower than that found in the two recycle solvents (13% vs 21% and 29%).

The naphtha stabilizer bottoms samples (LO-6043 and LO-6044) were obtained from Periods 2 and 13. GC/MS analyses of the two samples are reproduced in Figures 5 and 6. The most prominent peaks are alkanes and substituted tetralins (Tables 7 and 8). There are differences discernable between these two samples. Primarily, the sample obtained in Period 13 has a higher boiling component (longer retention time). The prominent peaks at the longer retention times in the Period 13 sample are straight chain alkanes (n-paraffins). The proton NMR analyses of these materials (Table 6) indicate that these materials are paraffinic. A prominent signal at 1.4 ppm in the NMR spectra of the samples was determined to be cyclohexane.

The two filtrate samples (LO-6045 and LO-6046) were obtained from Periods 2 and 13, respectively. There is significantly more 850 °F+ distillation resid in the filtrate sample obtained in Period 13 than in that obtained from Period 2 (Table 4). The Period 13 sample contains 14.5 wt % resid (average of two

determinations) vs 5.2 wt % resid in the sample taken during Period 2. The proton NMR data (Table 6) indicate that the sample taken during the later period is slightly more saturated (6.9% vs 7.3% total aromatics), and the shift is to more paraffinic structures (39.4% vs 35.0% alkyl β) and less donor hydrogen (26.5% vs 29.4% cyclic α and cyclic β). Dewaxing data (Table 11) support these findings. The filtrate sample from Period 13 contains more straight chain paraffins (21.1% vs 39.9%) and more total wax (56.4% vs 48.7%) than the sample obtained from Period 2. The shift to more paraffinic content and lower donor content, and the increased resid content, may be responsible for the shift to poorer solvent quality (55.1 wt % vs 62.2 wt % by microautoclave assay, Table 5). A comparison of the chromatograms for the distillable portion of these two filtrate samples (Figure 7) shows that there is a shift to higher concentrations of components with longer retention times in the the sample from Period 13 (LO-6046). This is consistent with the increased resid content. The prominent peak at a retention time of 45.18 min in the Period 13 sample is identified as a non-donor 3,3a,4-cyclohexapyrene, a mononaphthenic pyrene of molecular weight 242 daltons, superimposed on a C-26 n-paraffin. This species has been identified in a number of coal-derived products.¹⁰

Three filter cake samples (LO-6047, LO-6048, and LO-6049) and a sample of material (LO-6097) which had accumulated in the process line through which the filter cake is withdrawn, were analyzed for solubility properties (Table 9). There is a small variation in the ash content of the samples; however, the THF-solubilities of all four samples on an ash-free basis are essentially equivalent. The proton distributions and phenolic -OH contents of the THF soluble portions of the four samples (Table 6) are very similar. The phenolic -OH concentrations of the samples are very low. This is consistent with the low aromaticities and high paraffinities. The phenolic -OH concentrations and peak locations are more typical of distillates than resids. The THF-soluble extracts from these four filter cakes are less aromatic (Table 10B) and less phenolic (Table 10D) than virtually all the 850 °F⁺ fractions and most of the 850 °F⁻ fractions from the filter liquids CONSOL has analyzed from HRI Bench Runs CC-1¹, CC-2,5,6, and CC-8.¹¹ The wax content of the THF solubles of one of the filter cakes (LO-6048) was found to be 37 wt %. It appears that the wax content of the filter cakes from Run 260-03 is responsible for the low filtration rates encountered during during the run.

Although all the filter cake materials have relatively high concentrations of n-paraffins, a comparison of the GC chromatograms of the THF-soluble portions of the four samples (Figure 8) reveals that these materials are not equivalent. The most striking difference is the preponderance of lower boiling (shorter retention time) material in the deposit material found in the process line after the filter (LO-6097). It is to be noted, however, that the filter cakes in Run 260-03, after Period 10, were washed with light vacuum overhead oil. The wash oil contacted the deposit sample in situ. It is presumed that the low boiling components evident in the gas chromatogram are a result of the presence of wash oil remaining in the sample. The prominent peak at a retention time of 45.2 min in each of the GCs of the THF-soluble portion of the filter cakes and the sample found in the line after the filter is attributed to the mononaphthenic pyrene (which was discussed previously) superimposed on the C₂₆ n-paraffin.

Comparison of Process Oils from HRI Run 260-03, HRI Run CC-1 and Wilsonville Run 262

The best process-oil comparison of Runs 260-03 and CC-1 can be made between the pressure-filter liquids (PFLs) of Run CC-1 and the recycle oils and filtrates of Run 260-03 (Tables 10A-D). In comparison to the pressure filter liquid (PFL) samples of Run CC-1¹, the solvent quality of the Run 260-03 filtrates is lower. Conversion of the standard Old Ben Mine coal with Run CC-1 samples ranged from 75.2 wt % to 86.0 wt % compared to the 53.4 wt % and 60.8 wt % for the Run 260-03 filtrate samples (Table 10A). The Run 260-03 oils contain substantially less 850 °F+ resid than the Run CC-1 oils. This indicates that less resid was recycled in Run 260-03, either because resid conversion was greater or because more resid was rejected by the filtration system. Several factors indicate that the latter explanation is correct: coal conversion was quite low at the end of Run 260-03 (more resid would be entrained by the reject), and filtration problems were experienced; there was a need to wash the filter cake beginning in period 10. The proton distributions of the CC-1 PFL samples are two to three times more aromatic than the Run 260-03 samples (11.1% to 22.2% vs 6.9% and 7.3%) (Table 10B). In part, these higher aromaticity values result from the higher resid content of the Run CC-1 PFLs (21.9% to 39.9% vs 5.2% and 14.5%) (Table 10C). However, even Run 260-03 whole oils (resid containing) are less aromatic than the 850 °F⁻ distillate fractions of the Run CC-1 PFLs. In fact, the Run 260-03 oils are more paraffinic than any process-generated liquefaction

recycle oils analyzed in our laboratory; only those oils produced in Wilsonville Run 262 are comparable. Run 262 also was made with Black Thunder Mine coal, and it was the only Wilsonville ITSL run, to our knowledge, in which wax deposition led to operating problems.¹² It also should be noted that the Run 260-03 oils contain a lower concentration of phenolics than the Run CC-1 oils. As was discussed above, one result of these differences in composition is that the Run 260-03 oils are substantially poorer donor solvents than the Run CC-1 oils.

In summary, the Run 260-03 oils are highly hydrogenated, highly paraffinic, and poor donor solvents. To some extent, these oil properties reflect the sub-bituminous feed coal; this coal produces more paraffins upon liquefaction than do typical bituminous coals. However, the waxy nature of the Run 260-03 oils relative to the Run CC-1 oils and the Wilsonville Run 262 oils, which were produced from the same coal, indicates that processing must also play a role in the production of wax in the oils. It would appear that Run 260-03 was operated such that hydrogenation was promoted, at the expense of cracking. Because of the apparently lower cracking rate, the paraffins (which are relatively less reactive to hydrocracking than naphthenoaromatics and multi-ring and two-ring naphthenes¹³) became concentrated in the recycle oil stream to a greater extent than in past HRI experience. The increasingly paraffinic nature of the oils as Run 260-03 progressed is consistent with this hypothesis.

PARTICIPANTS PROGRAM STATUS

Phase II

The final reports from Lehigh University, West Virginia University, and Vander Sande Associates were issued.

CONSOL evaluations were written for subcontracts with the University of Chicago, the University of Utah, Iowa State University, and the University of Kentucky. They appear later in this report, along with the respective executive summaries from the subcontractors' final reports. These reports were issued. This closes out eight of the nine Phase II subcontracts.

A revised draft final report was received from the University of Pittsburgh. The researchers at Pitt were able to solubilize the resid samples in their sample set in tetrahydrofuran and still obtain Raman spectra. This obviated the need to cast the samples as films, and spin the film under the laser light to prevent localized heating, as was detailed in the Statement of Work. The draft final report was reviewed with researchers at Pitt. It was revised by Pitt and resubmitted. The CONSOL evaluation of the report was drafted and the report was sent to DOE for review.

A set of solids-free coal liquid resids was sent to the University of Kentucky to allow them to follow-up on their Phase II subcontract. Solids (mostly pyrrhotite) in the original samples examined by Kentucky interfered with the speciation of the organic sulfur by the XANES technique. The follow-up work is not being done under contract; however, Kentucky will share their findings with us.

Phase III

Phase III was initiated. Letters soliciting information about potential, new applications of three analytical techniques (or methods) were sent to Dr. I. Wender, the University of Pittsburgh, Dr. L. Pfefferle, Yale University, and Dr. P. Hatcher, The Pennsylvania State University. Both Dr. Wender and Dr. Hatcher responded with proposals for work under Phase III of the Participants Program. Dr. Wender's work concerns catalytic dehydrogenation studies to assess hydrogen donor activity and reactivity, and Dr. Hatcher's studies utilize a novel two-dimensional high performance liquid chromatograph coupled to a high resolu-

tion mass spectrometer. Negotiations with these two parties will continue in the next quarter of the contract.

Two organizations (SRI International and the University of Utah) who participated in previous phases of the Participants Program were invited to participate in Phase III. SRI International successfully used the technique of field ionization mass spectrometry to examine direct coal liquefaction-derived 850 °F⁺ distillation resid samples in Phase I. The University of Utah, in Phase II of the program, analyzed resids by ¹³C NMR and derived a set of structural parameters. It tentatively is planned to utilize both techniques on the same samples to obtain a more complete picture of the properties of process derived materials. The samples will be obtained from the HRI, Inc. bench unit. Contract negotiations will begin next quarter.

We plan to subcontract in Phase III for petroleum inspection tests on two or three coal liquids. Cost quotes for the work were obtained from National Institute for Petroleum and Energy Research and from Alberta Research Council. A cost estimate was obtained from Conoco Inc.

CONSOL EVALUATION AND EXECUTIVE SUMMARY OF FINAL REPORT FROM THE UNIVERSITY OF CHICAGO

Introduction

Under subcontract from CONSOL Inc. (U.S. DOE Contract No. DE-AC22-89PC89883), the University of Chicago speciated and quantified the oxygen functional groups in coal-derived resids. Hydroxyl functional groups in the resids were selectively derivatized by phase-transfer methylation. In order to characterize and quantify the ether groups in the resids, single-electron transfer reactions were used to cleave certain ether groups to produce phenols, which then were derivatized by phase-transfer methylation. The methylated products of reaction were evaluated by ¹³C-NMR. The executive summary authored by the University of Chicago researchers is presented here. The following assessment briefly highlights the major findings of the project, and evaluates the potential of the method for application to coal derived materials. These results will be incorporated by CONSOL into a general overview of the application of novel analytical techniques to coal derived materials at the conclusion of this contract.

Summary

This study demonstrated the feasibility of using phase-transfer methylation reactions for the derivatization of hydroxyl functionalities and single-electron transfer reactions to cleave ether groups in distillation resid materials derived from direct coal liquefaction. ^{13}C -NMR was used to analyze the reaction products. It was demonstrated that the techniques can be used to speciate and quantify about half of the oxygen in resids. The remaining half of the oxygen is presumed to be present as unreactive ethers, probably dibenzofurans. Hydroxyl concentrations were determined on five resid samples and ether cleavage reactions were conducted on three of those five. Further development of this general analytical strategy as a process development tool is justified based on these results.

Program Description

This report describes the work performed at the University of Chicago under a subcontract from CONSOL Inc., Research and Development. CONSOL's prime contract to the U.S. Department of Energy (Contract No. DE-AC22-89PC89883, "Coal Liquefaction Process Streams Characterization and Evaluation") established a program for the analysis of direct coal liquefaction derived materials. The program involves a number of participating organizations whose analytical expertise is being applied to these materials. This Participants Program has two main objectives. The broad objective is to improve our understanding of fundamental coal liquefaction chemistry to facilitate process improvement and new process development. The specific approach to achieving this objective is to provide a bridge between direct coal liquefaction process development and analytical chemistry by demonstrating the application of various advanced analytical methods to coal liquefaction materials. The methodologies (or techniques) of interest are those which are novel in their application for the support of coal liquefaction and those which have not been fully demonstrated in this application. CONSOL is providing well-documented samples from different direct coal liquefaction production facilities to the program participants. The participants are required to interpret their analytical data in context to the processing conditions under which the samples were generated. The methodology employed is then evaluated for its usefulness in analyzing direct coal liquefaction derived materials.

Participant's Methodology

The University of Chicago speciated and quantified the hydroxyl and ether functional groups in the pyridine-soluble portion of 850 °F distillation resids. This was accomplished by: 1) derivatization of the hydroxyl groups in five pyridine-soluble resids by phase-transfer methylation, and 2) ether cleavage reactions of three of the five resids with Lewis acids and single-electron transfer reagents followed by methylation, and 3) quantitation of the reaction products by ^{13}C -NMR spectroscopy. The pyridine-soluble resids are solids at room temperature. The original process samples, from which the pyridine-soluble resids were generated, were produced at the Wilsonville pilot plant. The samples are composites of samples taken over long periods of single runs at Wilsonville. Two major processing parameters were varied among the Wilsonville runs: feed coal and reactor configuration (thermal/catalytic vs catalytic/catalytic). Samples were taken from two locations: between the first- and second-stage reactors, and after the second-stage reactor. These samples are expected to represent different extents of coal liquefaction. The experimental procedures for phase-transfer methylation, Lewis acid and single-electron transfer ether cleavage reactions, and ^{13}C -NMR spectroscopy are included in the full report (DOE/PC 89883-64).

Participant's Major Findings

The following principal observations for the derivatization of the hydroxyl groups in the pyridine-soluble portion of coal liquefaction resids, and the ether cleavage and subsequent methylation of the product phenols, were reported by the University of Chicago. An expanded discussion can be found on pages 7-14 in DOE/PC 89883-64.

Derivatization of the hydroxyl groups in the pyridine-soluble resids was accomplished by reaction with a phase-transfer base (tetrabutylammonium hydroxide) and subsequent methylation of the product oxyanions with $^{13}\text{CH}_3\text{I}$. The number and kind of hydroxyl groups present in the samples were determined by ^{13}C -NMR. Three types of hydroxyl groups were found to be present: hindered phenols, unhindered phenols, and carboxylic acids. It was concluded that the carboxylic acids are not native to the samples, but arise in the preparation and handling of the pyridine-soluble resids and by reaction with atmospheric CO_2 during the derivatization procedure. The ratio of hindered to unhindered phenols was about 1:2.

The quantitative analysis of total hydroxyl concentration agreed reasonably well with phenolic -OH concentration values obtained by the Fourier transform infrared (FTIR) method used by CONSOL.

Ether cleavage was accomplished in three ways: 1) with boron tribromide (BBr_3), a Lewis acid, 2) with potassium-naphthalene in tetrahydrofuran, and 3) with lithium in dioxane (the last two are different single-electron transfer reagents). The BBr_3 reaction proved unsuccessful; this Lewis acid apparently catalyzes degradative condensation reactions in the resid as well as the desired ether cleavage reactions. The apparent condensation reactions resulted in a reduction in the number of derivatizable hydroxyl groups in the Lewis acid treated sample (relative to the initial pyridine-soluble resid sample). The first of the two single-electron transfer reagents (potassium-naphthalene) increased the number of derivatizable hydroxyl groups in two of three pyridine-soluble resids reacted, indicating that some ethers were cleaved. Use of the second single-electron transfer reagent (lithium in dioxane) was unsuccessful in increasing the number of derivatizable hydroxyl groups; it is presumed, therefore, that no ethers were cleaved.

It was proposed by the University of Chicago on the basis of their findings and the assumption that the quantity of total oxygen in the resids (which is determined by difference) is correct, that approximately 40% of the total oxygen (determined by difference) in the pyridine-soluble resids is phenolic. Another 0 to 10% was found to be cleavable ethers. The remaining 50% of the oxygen, it was speculated, exists in the resids as non-cleavable (via single-electron transfer reaction) ethers, such as dibenzofurans or dinaphthofurans, or possibly, dialkyl ethers.

CONSOL Evaluation

The phase transfer methylation technique was employed successfully to derivatize the available hydroxyl species in the pyridine-soluble resid samples. The total quantity of phenolic -OH determined by this method agrees reasonably well with the value obtained by FTIR, with the exception of two samples in which solubility in chloroform (the NMR solvent) was poor. In addition to measuring the total hydroxyl content, the derivatization/NMR method provides classification of the hydroxyl groups into hindered, nonhindered and carboxylic acid classes.

Indications are that the carboxylic acids are an artifact both of sample preparation and handling for methylation experiments, and probable incorporation through oxidative processes before receipt by the University of Chicago.

Although not optimized for coal-derived resid samples, the use of single-electron transfer reagents for selective cleavage of ether groups in the pyridine-soluble resids was demonstrated. The use of two different reagents, one which was effective and the other which was not, illustrates the need for a more detailed study with this type of reagents, 1) to find the optimum reagent system for use with coal-derived materials for the cleavage and subsequent analysis of the ethers, and 2) to better understand the fundamental chemistry which occurs when coal-derived materials are reacted with these reagents.

Each phase-transfer methylation experiment requires approximately five days per sample (two days for a duplicate reaction, two days for work-up, and one day for NMR data acquisition). Ether cleavage reactions require an additional five days for sample preparation, reaction and work-up. The reagents, which are commercially available, cost approximately \$20.00 for each phase transfer methylation reaction and about \$50.00 for each single-electron transfer reaction followed by phase transfer methylation. The ^{13}C -NMR spectrometer used in this study costs approximately \$350,000, and the ^1H -NMR spectrometer costs approximately \$150,000.

Further Development

The use of potassium-naphthalene as a single-electron transfer reagent to induce ether cleavage met with success in this limited study. Many different alkali metals, electron shuttling agents and solvent combinations could be applied to the study of fossil fuels. The optimum combination must be determined empirically. It is recommended that a study be undertaken to determine the most effective combination for ether cleavage in coal-derived materials.

The Lewis acid (BBr_3) used in this study proved to be ineffective because of its promotion of degradative condensation reactions as well as ether cleavage. It is recommended that additional studies be made with BBr_3 and other Lewis acids to determine if milder reaction conditions could promote the ether cleavage reactions over the condensation reactions.

Because the determination of the relative proportion of oxygen functional groups ultimately lies in relying on the value obtained for the total oxygen in the samples, it is recommended that total oxygen content be determined in a more rigorous manner than by difference.

The original resids used in this work were obtained by pyridine extraction of distillation resids. The ^{13}C -NMR analysis of the reaction products was conducted in chloroform solution. Although the methylated products are expected to be more soluble than the original resids, chloroform may not completely solubilize the entire product. Therefore, it is recommended that pyridine or some other good coal-liquid solvent be employed as the NMR solvent in future work.

Participant's Statement of Work

Oxygen is the the principal heteroatom in most coal liquids. Though it often is inferred to be important in coal liquefaction chemistry, its chemical form in coal liquids is ill-defined. The derivatization of hydroxyl oxygen (phenolic, alcoholic, and carboxylic) with ^{13}C labeled methyl iodide, followed by ^{13}C -NMR results, in the case of petroleum-derived resids, in clearly distinguishable and quantifiable signals in the NMR. Selective cleavage of etheric bonds followed by derivatization with ^{13}C methyl groups and identification of the derivatized species by ^{13}C -NMR has been demonstrated with model compounds. These techniques can be used to quantitatively speciate oxygen; however, they have not been demonstrated with process-derived coal liquids, or investigated for their ability to answer questions pertaining to the chemistry of coal conversion. As such, they fit well within the scope of the participants program.

The derivatization of the hydroxyl oxygen, and cleavage and derivatization of the etheric oxygen, followed by subsequent characterization by ^{13}C -NMR of a sample set of six samples will allow a demonstration of the value of these techniques for the examination of the oxygen compounds in coal liquefaction-derived resids. Samples will be derivatized with ^{13}C labeled reagents and analyzed via ^{13}C -NMR to yield a total hydroxyl oxygen value for each of the six samples. Three of the samples will be selectively cleaved at ether linkages utilizing two different methods. In the one method, the ethers will be cleaved by forming anion radicals with an electron transfer reagent. This reagent will cleave heterocyclic and non-heterocyclic ethers. The cleavage products will be marked with labeled

reagents. NMR spectra of the starting material, alkylated starting material, and the alkylated product of the ether-cleaved material will allow for quantitation of the oxygen-containing species in the pyridine-soluble resid samples. The second method entails cleavage of the ether groups in the starting pyridine-soluble resid sample with a boron trihalide reagent to be chosen by the research group at the University of Chicago. This reagent will cleave non-heterocyclic ethers but not heterocyclic ethers. The treated sample then will be alkylated with a ^{13}C labeled reagent and analyzed by ^{13}C NMR. Comparison of the NMR spectra of the starting material, the alkylated starting material and the alkylated cleaved materials produced by both methods will allow for quantitative speciation of the oxygen-containing compounds in the pyridine-soluble resid samples.

Six samples will be supplied by CONSOL to the University of Chicago. These samples have been selected so that the utility of the method described above for the measurement of the forms of oxygen can be assessed in application with pyridine-soluble coal liquefaction resids. The samples will be supplied to the University of Chicago with the following information, as available: elemental analyses, phenolic -OH concentration by FTIR, calorific value, hydrogen classes by ^1H -NMR, and the full history of the sample (plant, process conditions, age, and storage conditions). The six samples are the pyridine-soluble portion of the 850 °F distillation residual materials. Sample size will be at least 10 g. The six pyridine-soluble resid samples will be brittle pitch-like materials that will be supplied as approximately minus 60 mesh powder.

University of Chicago Executive Summary

The broad objectives of this program are to identify and evaluate promising analytical techniques that will be useful in coal liquefaction process development and to demonstrate their direct application to coal liquefaction resids. For our phase of the work, there were two subtasks: first, to characterize and quantify the hydroxylic groups that exist in a selected group of resids that were derived from the liquefaction of coal and, second, to study new chemical methods of cleaving ether linkages in these resids and to characterize and quantify these ether groups.

The first task was accomplished by reacting the resids with a phase-transfer base, tetrabutylammonium hydroxide (E1), and subsequently methylating the

oxyanions formed with $^{13}\text{CH}_3\text{I}$ (E2). The number and types of hydroxylic groups were determined by

qualitative and quantitative analyses of the carbon NMR spectra of the methylated products.

The carbon NMR spectra of the methylated samples indicated that the hydroxylic groups found in the resids could be subdivided into hindered phenols, unhindered phenols and carboxylic acids. For reasons that are explained thoroughly in the discussion, it is our conclusion that the carboxylic acids are not really native to the resids. Rather, these compounds were incorporated into the samples before they were received in Chicago through oxidative processes during handling and storage. Further, we showed that the concentrations of these compounds are increased in side reactions between carbanions and adventitious carbon dioxide. Accordingly, these substances are not significant to the main thrust of this study. The phenolic content of the six resids that we studied ranged from about 0.5 meq/g to slightly more than 1 meq/g of the resid; approximately two-thirds of the phenols are of the unhindered type and about a third are of the hindered type.

The quantities of phenolic hydroxyl groups determined from the carbon NMR spectroscopy of the methylated samples agree quite well with IR spectroscopic data for four of the six resid samples. The remaining discrepancies may be attributed to three sources. First there are some problems in obtaining homogeneous solutions of the samples. Second, whereas the IR values were obtained from the THF solutions of the resids, our samples were the pyridine-soluble portions of the resids. Third, the IR data require the assumption of an average extinction coefficient, while NMR results are based on direct observations. Time limitations of the research contract did not allow us to study this point.

The second task was accomplished by applying three chemical methods of effecting ether cleavage reactions to the resids, and subsequently phase-transfer methylating the treated samples with $^{13}\text{CH}_3\text{I}$ to determine the extent of cleavage.

In the first method, resid samples were treated with boron tribromide, a Lewis acid which is commonly used to cleave alkyl aryl ethers (especially methyl aryl ethers) and dialkyl ethers. The samples were subsequently methylated with $^{13}\text{CH}_3\text{I}$, and the extent of methylation was determined by carbon NMR spectroscopy. Treatment of the resid samples with the Lewis acid gave partly insoluble products. This was accompanied by a substantial decrease in the concentrations of phenolic hydroxyl groups, together with a change in the relative proportion of hindered and unhindered phenolic hydroxyl groups. Clearly, boron tribromide catalyzes degradative condensation reactions and ether cleavage reactions. The degradative condensation reactions apparently occur more rapidly than any ether cleavage reactions. Thus, this method does not appear to be generally suitable for investigations of ether functional groups in resids.

The second method consisted of reacting the resid samples with potassium-naphthalene, a single electron transfer reagent, in dry THF. The samples were subsequently phase-transfer methylated with $^{13}\text{CH}_3\text{I}$ and their carbon NMR were obtained and analyzed quantitatively. This second method noticeably increased the phenolic hydroxylic groups of two of the three samples and the ratio of hindered to unhindered

CONSOL 05

Hindered Phenols (meq/g)		Hindered Phenols (meq/g)
0.17		0.28
Unhindered Phenols (meq/g)	$\xrightarrow{\text{SET ether cleavage}}$	Unhindered Phenols (meq/g)
0.37		0.42

phenolic hydroxylic groups by a modest amount. In contrast to the reactions with the Lewis acid, this single electron transfer reagent preserved the chemical integrity of the samples. From these results, it is our conclusion that single electron transfer still offers the best possibilities of characterizing and quantifying the etheric groups in resids.

The third method was carried out by refluxing a particular resid sample with lithium in dry dioxane, another single electron transfer reaction. The reaction did not increase the quantity of phenolic groups and the relative proportion of hindered-to-unhindered phenolic groups remained practically unchanged.

The Illinois 6 coal (Burning Star) from which three of the resid samples were derived has around 10% oxygen (determined by difference), about 6 meq/g. Several lines of evidence suggest that about half of these oxygen atoms occur in phenolic compounds. The other half are thought to be mainly ethers. The resids that were derived from this coal contain much less oxygen than the original coal, about 2.4 meq/g. The new results and the IR data indicate that approximately 0.5 to 1 meq/g occur in phenolic hydroxyl groups, a large decrease from the raw coal. The ether cleavage reactions indicate that about 0.2 meq/g of the remaining 1.4 to 1.9 meq/g oxygen occur in ethers that are susceptible to single electron transfer reagents. Uncertainties about the meaning of the by-difference analytical data for oxygen render any further discussion highly speculative. But if we adopt that view that the by-difference oxygen content is accurate, about half of the atoms in the resid have been speciated with confidence. Assuming the proportion of the different kinds of organic oxygen compounds are similar in the coals and the resids, it can be inferred that the remaining oxygen atoms must be in the form of single electron transfer reagent-resistant ethers. Since it has been well-established that alkyl aryl ethers and benzyl aryl ethers are readily cleaved by potassium/naphthalene, we conclude that 1.2 to 1.7 meq/g of oxygen are present in the form of refractory ethers, presumably of the dibenzofuran/dinaphthofuran or the dialkyl type.

CONSOL EVALUATION AND EXECUTIVE SUMMARY OF FINAL REPORT FROM THE UNIVERSITY OF UTAH

Introduction

Under subcontract from CONSOL Inc. (U.S. DOE Contract No. DE-AC22-89PC89883), the University of Utah studied the use of solid-state cross-polarization/magic angle spinning (CP/MAS) ^{13}C -nuclear magnetic resonance (^{13}C -NMR) spectroscopy to provide data from which a set of carbon structural parameters and molecular structural descriptors can be derived for the characterization of coal liquefaction resids. The executive summary authored by the University of Utah is presented here. The following assessment briefly highlights the major findings of the project, and

evaluates the potential of the method for application to coal-derived materials. These results will be incorporated by CONSOL into a general overview of the application of novel analytical techniques to coal-derived materials at the conclusion of this contract.

Summary

This study demonstrated the feasibility of using CP/MAS ^{13}C -NMR spectroscopy for the chemical structural examination of distillation resid materials derived from direct coal liquefaction. A set of twelve carbon skeletal-structure parameters and eight molecular structural descriptors were derived from the NMR data. The technique was used previously to determine these parameters for coal and char, and in the construction of a coal pyrolysis model. The method was applied successfully to the tetrahydrofuran (THF)-soluble portion of eleven 850 °F⁺ distillation resids and one 850 °F⁺ distillation resid which contained ash and insoluble organic material (IOM). The results of this study demonstrate that this analytical method can provide data for construction of a model of direct coal liquefaction. Its further development and use is justified based on these results.

Program Description

This report describes the work performed at the University of Utah under a subcontract from CONSOL Inc., Research and Development. CONSOL's prime contract to the U.S. Department of Energy (Contract No. DE-AC22-89PC89883, "Coal Liquefaction Process Streams Characterization and Evaluation") established a program for the analysis of direct coal liquefaction derived materials. The program involves a number of participating organizations whose analytical expertise is being applied to these materials. This Participants Program has two main objectives. The broad objective is to improve our understanding of fundamental coal liquefaction chemistry to facilitate process improvement and new process development. The specific approach to achieving this objective is to provide a bridge between direct coal liquefaction process development and analytical chemistry by demonstrating the application of various advanced analytical methods to coal liquefaction materials. The methodologies (or techniques) of interest are those which are novel in their application for the support of coal liquefaction and those which have not been fully demonstrated in this application. CONSOL is providing well-documented samples from different

direct coal liquefaction production facilities to the program participants. The participants are required to interpret their analytical data in context to the processing conditions under which the samples were generated. The methodology employed is then evaluated for its usefulness in analyzing direct coal liquefaction derived materials.

Participant's Methodology

The University of Utah used CP/MAS ^{13}C -NMR spectroscopy to derive carbon structural parameters and molecular descriptors for the tetrahydrofuran (THF)-soluble portion of eleven 850 °F+ distillation resids, and one resid which contained ash and insoluble organic material (IOM). The solid-state single pulse Bloch-decay method was determined to provide no additional information with these samples. The samples were produced at the Wilsonville pilot plant. Samples were taken from three locations: between the first- and second-stage reactors, after the second-stage reactor, and at the recycle oil tank. These samples are expected to represent different extents of coal liquefaction. The samples are composites of samples taken over long periods of individual processing runs. Two major processing parameters were varied among the Wilsonville runs: feed coal and reactor configuration (thermal/catalytic vs catalytic/catalytic). The CP/MAS ^{13}C -NMR experimental procedures and the derivation of the carbon structural parameters and molecular descriptors are included on pages 2-6 of the report DOE/PC 89883-65.

Participant's Major Findings

The following principal observations for the application of CP/MAS ^{13}C -NMR spectroscopy to coal liquefaction materials were reported by the University of Utah. An expanded discussion can be found in DOE/PC 89883-65, pages 6 through 12.

Structural parameters derived from the NMR data were used to compare the coal-derived resids with coals similar to the coals from which they were produced. The coals were obtained from the Argonne Premium Coal Program and the Advanced Combustion Engineering Research Center. In most cases, the resids were found to have approximately the same aromatic cluster size (approximately three aromatic rings) as the respective coal. However, the average molecular weight (MW) of the clusters and the average mass per attachment (M_g) is smaller for the resids than

the coals ($MW_{\text{resid}} \approx 258$ vs $MW_{\text{coal}} \approx 329$, and $M_{\delta\text{resid}} \approx 26$ vs $M_{\delta\text{coal}} \approx 34$). In addition, the number of bridges and loops per cluster is smaller for the resids. The number of side chains per cluster was found to be smaller for certain resids for which it was concluded that the bridges or side chains were replaced in the liquefaction process by hydrogen. In the case of the resids produced from subbituminous Wyodak coal, the resids have a higher aromaticity and approximately 50% fewer and shorter side chains than the parent coal.

Some comparison was made of samples obtained from different locations in the Wilsonville plant from the same processing run. It was observed that for most of the samples, the resids had similar structural and lattice parameters. Similarities were more pronounced than differences; the resids are more similar to one another than are the coals. However, these parameters differed from the coal most similar to the feed coal used in the run, as was noted above. In only one case were significant differences noted between samples taken at different points from a single run. Utah reports that their data suggest that the structural changes that occur in the resid are almost complete after the first stage of the two-stage liquefaction process; no significant change was observed in resids obtained from other sampling points in the plant. The one notable exception to these findings was in the samples obtained from a thermal/catalytic run with Illinois No. 6 coal. In this case, there was a significant difference in the interstage and recycle samples. The interstage sample had a higher aromaticity ($f_a = 0.72$ vs 0.63 , ± 0.01), and had a smaller aromatic cluster size ($C = 11$ vs 14 , ± 2.5).

Proton aromaticities obtained indirectly by ^{13}C -NMR correlated well ($R^2 = 0.94$) with the direct ^1H -NMR and elemental analyses measurements of CONSOL on the same samples.

CONSOL Evaluation

The CP/MAS ^{13}C -NMR techniques were shown to be applicable to the analysis of direct coal liquefaction resid samples. Structural parameters were obtained for the THF-soluble resids and one whole resid which contained ash and IOM. Comparison of the structural parameters for the resids with coals comparable to the feed coals used in the processing runs showed structural changes, including removal of the clusters from the infinite lattice by breaking cross links, loss of bridge

mass and hydrogenation. Among the resid samples, the similarities were more pronounced than the differences.

The precision of the CP/MAS ^{13}C -NMR techniques is high; measurements are highly reproducible. Sample preparation time is minimal, requiring only that the solid sample be uniformly ground and packed into the NMR tube. The experimental time required is on the order of 2 to 3 days per sample. The 100 MHz instrument used in this study costs approximately \$300,000. A skilled professional is required for data interpretation.

Further Development

The CP/MAS ^{13}C -NMR technique was shown to be a powerful tool for the elucidation of structural parameters in coal liquefaction derived resids. It was demonstrated that resid samples which contained ash and IOM could be examined without further preparation. It is recommended that an expanded suite of samples be examined by this method, including whole resids (or perhaps full-range liquids) from various points in the liquefaction process and the corresponding feed coals. The structural parameters developed for the resids (or full-range liquids) and coals could form the basis for a comprehensive model of coal liquefaction.

Participant's Statement of Work

Solid-state cross-polarization/magic angle spinning (CP/MAS) ^{13}C -nuclear magnetic resonance (NMR) spectroscopy has been used to examine fossil fuel materials. These analyses have provided a set of parameters from which molecular structure descriptors of materials such as coals and coal pyrolysis tars can be obtained. This technique has not been demonstrated with process-derived direct coal liquefaction materials, or investigated for its ability to answer questions pertaining to the chemistry of direct coal liquefaction. As such, it fits well within the scope of the participants program.

The University of Utah will examine ten direct coal liquefaction derived distillation resid materials by CP/MAS ^{13}C -NMR. From the NMR analysis, the Utah researchers will derive a set of twelve carbon structural parameters for each resid; these twelve parameters will include: fraction of aromatic carbon, fraction of carbonyl carbon, fraction of protonated aromatic carbon, fraction of non-protonated aromatic carbon, etc. Average molecular structural descriptors

then will be derived from these parameters; these descriptors will include: mole fraction of bridgehead carbons, aromatic carbons per cluster, number of attachments per cluster and molecular weight per cluster. Samples have been selected so that the resulting information may be applicable to the understanding of resid reactivity in the direct coal liquefaction process.

The samples will be supplied to the University of Utah with the following information, as available: elemental analyses, ash content, ash elemental analyses, phenolic -OH concentration by FTIR, calorific value, hydrogen classes by ^1H -NMR, and the full history of the sample (plant, process conditions, age, and storage conditions). The ten samples are 850 °F* distillation residual materials. Sample size will be at least 3 g. The ten resid samples will be brittle pitch-like materials that will be supplied as approximately minus 60 mesh powder.

University of Utah Executive Summary

Solid state ^{13}C -NMR spectroscopy experiments have been used to study a set of 11 THF-soluble resid samples obtained from direct liquefaction processing streams at the Wilsonville facility. Structural parameters are derived from the NMR data that characterize the carbon skeletal structure and functional group distribution of the resid samples. These data are compared to similar data obtained on a set of coals of similar type and coal region. Elemental analyses, proton NMR data, and phenolic -OH content of each sample were provided by CONSOL and employed in the analysis of the ^{13}C -NMR data.

The ^{13}C -NMR data indicate that one can elucidate the major structural changes that occur in resid samples derived from different coals. Several structural parameters of the resids are similar to those of comparable "parent" coals. No significant reduction in aromatic cluster size was noted in comparing the resid data with the parent coals. However, it is noted that the number of bridges and loops per cluster is lower in the resids than in the parent coals. The number of side chains per cluster also is lower in the resids derived from subbituminous coals (compared to the "parent" coals) and in the Illinois 6 resids obtained in the catalytic/catalytic mode (i.e., sample Nos. 4, 5 and 6). These results suggest that the resids bear some similarities to the parent coals in terms of cluster size, but exhibit significant changes in other structural parameters such

as number of bridges and loops and, in the case of the subbituminous coal, side chains per cluster. From these data, one could argue that the resids are, on average, similar to the cluster structure of the parent coal except that the resid cluster has been removed from the infinite coal lattice by breaking, on average, one cross link with the subsequent loss of some bridge mass. Furthermore, the data indicate that the similarities in the resids are more pronounced than the differences; there is much more similarity in the resids than is found in the parent coals.

CONSOL EVALUATION AND EXECUTIVE SUMMARY OF FINAL REPORT FROM IOWA STATE UNIVERSITY

Introduction

Under subcontract from CONSOL Inc. (U.S. DOE Contract No. DE-AC22-89PC89883), Iowa State University used ^{31}P -tagged reagents for the speciation and quantification of the labile hydrogen functional groups, specifically the phenolic hydrogen, in tetrahydrofuran (THF)-soluble coal-derived samples. ^{31}P nuclear magnetic resonance (NMR) spectroscopy was used to analyze the derivatized samples. The executive summary authored by the Iowa State researchers is presented here. The following assessment briefly highlights the major findings of the project, and evaluates the potential of the method for application to coal derived materials. These results will be incorporated by CONSOL into a general overview of the application of novel analytical techniques to coal derived materials at the conclusion of this contract.

Summary

In this study, Iowa State University researchers used ^{31}P -tagged reagents to derivatize the labile hydrogen functional groups in the THF-soluble portion of 850 °F⁺ distillation resid materials and the THF-soluble portion of process oils derived from direct coal liquefaction. ^{31}P -NMR was used to analyze the derivatized samples. NMR peak assignments can be made by comparison to model compounds similarly derivatized. Species can be quantified by integration of the NMR signals. Different ^{31}P -tagged reagents can be used to produce different degrees of peak resolution in the NMR spectrum. This, in turn, partially dictates the degree of speciation and/or quantification of species, or classes of compounds, that can be accomplished. Iowa State chose a ^{31}P -tagged reagent ($\text{ClPOCMe}_2\text{CMe}_2\text{O}$) which was shown previously to be particularly useful in the

derivatization of phenols. The derivatized samples all exhibited a small group of peaks attributed to amines and a broad group of peaks in the phenol region. The presence of paramagnetic species in the samples caused the NMR signals to broaden. Electron paramagnetic resonance (EPR) spectra confirmed the presence of paramagnetic organic free radicals in selected samples. Various methods were employed to process the NMR data. The complexity and broadness of the phenol peak, however, made speciation of the phenols impractical. Quantification of the total amount of phenol present in the sample was accomplished by integration. Values obtained agree well with Fourier transform infrared spectroscopic data obtained by CONSOL. Water in the samples also was derivatized by the ^{31}P reagent and quantified. Based on these results, further development of this analytical method as a process development tool may be justified if means are developed to improve resolution and speciate the component phenols.

Program Description

This report describes the work performed at Iowa State University under a subcontract from CONSOL Inc., Research and Development. CONSOL's prime contract to the U.S. Department of Energy (Contract No. DE-AC22-89PC89883, "Coal Liquefaction Process Streams Characterization and Evaluation") established a program for the analysis of direct coal liquefaction derived materials. The program involves a number of participating organizations whose analytical expertise is being applied to these materials. This Participants Program has two main objectives. The broad objective is to improve our understanding of fundamental coal liquefaction chemistry to facilitate process improvement and new process development. The specific approach to achieving this objective is to provide a bridge between direct coal liquefaction process development and analytical chemistry by demonstrating the application of various advanced analytical methods to coal liquefaction materials. The methodologies (or techniques) of interest are those which are novel in their application for the support of coal liquefaction and those which have not been fully demonstrated in this application. CONSOL is providing well-documented samples from different direct coal liquefaction production facilities to the program participants. The participants are required to interpret their analytical data in context to the processing conditions under which the samples were generated. The methodology employed is then evaluated for its usefulness in analyzing direct coal liquefaction derived materials.

Participant's Methodology

Iowa State University used ^{31}P -tagged reagents to speciate and quantify the labile hydrogen functional groups, specifically the phenolic hydrogen, present in the THF-soluble portion of (850 °F) distillation resids and THF-soluble process oils. ^{31}P -NMR was used to analyze the derivatized samples. The samples were produced at the Wilsonville pilot plant. Two major processing parameters were varied among the Wilsonville runs. These were feed coal and reactor configuration (thermal/catalytic vs catalytic/catalytic). Samples from Wilsonville were taken from three locations, between the first- and second-stage reactors, after the second-stage reactor, and at the recycle oil tank. These samples are expected to represent different extents of coal liquefaction. Ten of the samples were composites of samples taken over long periods of single runs. Five samples were obtained from single run periods. The experimental procedures are described on pages 24 through 27 of DOE/PC 89883-62.

Participant's Major Findings

The following principal observations for the application of ^{31}P reagents and ^{31}P -NMR to coal liquefaction materials were reported by Iowa State. An expanded discussion can be found in DOE/PC 89883-62, pages 3 through 15.

A curve-fitting program was applied to deconvolute the broad phenol region (138-144 ppm) of the spectra. Four different sets of parameters were used in the curve-fitting program: 1) line broadening parameter of 0.5 Hz, with no zero-filling factor; this resulted in approximately 100 peaks, making speciation impractical. 2) line-broadening parameter of 0.5 Hz and zero-filling factor; this resulted in narrow line widths, but a very large number of peaks (on the order of 150) in the phenol region. 3) line-broadening parameter of 2.5 Hz and no zero-filling factor; the number of phenol peaks was reduced by an order of magnitude, but the line widths were too broad to allow for speciation. 4) line-broadening parameter of 2.0 Hz and a zero-filling factor; this combination resulted in a small number of peaks that could be fitted; however, line widths were too broad for unambiguous identification of phenols. In all four cases, it was possible to quantify the total phenolic content, which was done by integration. An additional method, a Matched Filter Apodization (MPA) procedure with no zero-filling was used to process the NMR spectrum. This reduced the phenol region to, usually, one peak which was then quantified. Values obtained by the

latter method agreed well with those obtained by CONSOL through the use of an FTIR method.

There appears to be four distinct sets of spectral groupings in the NMR spectra of the fifteen samples. These groups are defined by the presence (or absence) and intensity of peaks (or groups of peaks) at 139.2 ppm, 138.7 ppm, and 137.3 ppm. These four sets appear to correlate with the sampling location in the Wilsonville plant from which the samples were obtained. For example, of the six samples which fall into Group I, five were obtained from the interstage location. Similarly, three of the four samples in Group II were obtained from the second-stage product stream.

The presence of paramagnetic species in the coal-derived samples contributed to line broadening in the NMR spectra. EPR spectroscopy was used to examine the free radicals in the samples. The intensity of the organic free radical signal (at $g = 2.0036$) for different samples was found to correlate to the resolution of the ^{31}P -NMR spectra; the lower the intensity of the free radical signal, the better resolved was the NMR spectra. However, since the sample that was better resolved and had a lower free-radical content also had a lower boiling point, it may be that boiling point, and not free-radical content, primarily affected resolution.

The ^{31}P -tagged reagent used in this study forms an anhydride upon reaction with water. This compound has a distinct peak in the ^{31}P -NMR at 170 ppm. The small amount of water found in the samples most likely arises from adsorption from the atmosphere upon sample handling.

CONSOL Evaluation

The use of ^{31}P -tagged reagents to identify and quantify the labile hydrogen functionalities in coal-derived materials was demonstrated to a limited extent in this project. The total phenol contents determined by this method agree well with values obtained by an established FTIR method. It also is possible with this method to quantify water present in the samples. The method does show potential usefulness for the analysis of direct coal liquefaction resid samples. However, the appropriate choice of reagent and NMR data analysis technique must be further refined so that speciation of the phenolic groups can be made.

The NMR instrument used in this study costs about \$300,000. Materials for reagent synthesis cost approximately \$2.00 per sample. Approximately one week is required to synthesize enough reagent to perform fifty reactions. The ^{31}P -NMR method is amenable to the use of a large variety of solvating agents for the samples, as long as they contain no labile hydrogen. Data manipulation with the MPA approach takes about 1 3/4 hr. Interpretation of the ^{31}P -NMR data requires a skilled professional.

Further Development

This technique appears to be a suitable means to quantify total phenols in coal liquids. However the possibility of phenol speciation was not realized. Future work should be directed toward that goal. Iowa State made the following recommendations for further work: 1) Utilization of different ^{31}P -tagged reagents that will allow for better differentiation of the amine and phenol region of the spectra, 2) Reduction of the free radical content of the samples (perhaps by hydrogenation) to reduce line broadening in the ^{31}P -NMR spectra. However, it would appear that this approach could reduce the phenols. 3) Further evaluation of the ^{31}P -NMR spectral groupings in the phenolic region and their apparent correspondence to sampling location.

Participant's Statement of Work

Derivatization of labile hydrogen groups with phospholane reagents followed by analysis with ^{31}P -NMR spectroscopy is a method which has been used for the investigation of coal and coal pyrolysis products. However, it has not been widely applied to the analysis of direct coal liquefaction derived products, nor has it been demonstrated widely for its ability to answer questions pertaining to the chemistry of coal conversion. As such, it fits well within the scope of the participants program.

The application of phospholane derivatization/ ^{31}P -NMR spectroscopy to a sample set of 15 samples will allow a demonstration of the value of this technique for the speciation and quantitation of the labile hydrogen functional groups present in coal liquefaction-derived materials. These samples have been selected so that the utility of phospholane derivatization/ ^{31}P -NMR for characterizing coal liquefaction resids can be evaluated. Additionally, samples will be supplied so that the behavior of labile hydrogen groups can be evaluated as they pass through

the direct coal liquefaction process. The samples will be supplied to the Iowa State University with the following information, as available: elemental analyses, phenolic -OH concentration by FTIR, calorific value, hydrogen classes by ^1H -NMR, and the full history of the sample (plant, process conditions, age, and storage conditions). Ten of the fifteen samples are tetrahydrofuran (THF)-soluble, non-distillable residual materials. Five of the samples will be the THF-soluble portion of whole process oils. Sample size will be at least 1 g. The resid samples will be brittle pitch-like materials that will be supplied as approximately minus 60 mesh powder. The whole process oils will be viscous liquids.

The phospholane reagents to be used will be selected by the Iowa State University researchers to provide the maximum qualitative and quantitative information on the labile hydrogen compound classes present in the resid samples. These compound classes will include phenols, alcohols, carboxylic acids, thiols and amines. Water content will be determined. Speciation and quantitation of individual compounds will be performed on Reference Nos. 10 and 11, which are distillable oils. Speciation and quantitation of individual compounds will be attempted on the other samples. Individual species or classes of labile hydrogen functional groups will be quantified by integration of the ^{31}P -NMR signals.

The sample set includes five samples (Reference Nos. 7-11) from Wilsonville Run 259G that represent all but one of the major product streams from both the first-stage and two-stage system. This set of samples will be analyzed to examine the behavior of the functional groups as they pass through the reactors in the two-stage liquefaction process.

Iowa State University Executive Summary

Fifteen coal liquefaction products are quantitatively analyzed for phenolics and moisture using the ^{31}P -NMR tagging agent $\text{ClPOCMe}_2\text{CMe}_2\text{O}$. Despite the presence of organic free radicals in these resids, which contributed to the breadth of the derivati phenolic ^{31}P resonances, excellent agreement with the phenolic contents obtained by FTIR spectroscopy was achieved. The best results were obtained by processing the ^{31}P -NMR spectra with an NMRI Matched Filter Apodication program.

Thiols derivatized with 1 give rise to ^{31}P -NMR peaks (209-218 ppm) well outside the range for phenolics (138-144 ppm), and peaks for the former were not detected. Since the alcohol region with 1 (141-149 ppm) overlaps slightly with the phenolic range, the presence of some alcohols such as Ph_3COH and pinacol cannot be ruled out. Aromatic and aliphatic carboxylic acids derivatized with 1 appear to give rise to ^{31}P -NMR peaks in a very narrow range (135-136 ppm). A small ^{31}P -NMR peak at about 132 ppm appeared in all the samples except Nos. 10 and 11. This peak probably is due to amine (130-150 ppm). The origin of the prominent ^{31}P -NMR peak at 137 ppm in samples such as 10, 11 and 15 is not presently clear since it falls just outside the range of carboxylic acids and phenols. While the peak could be due to the presence of amines, it seems unlikely they would be present in such relatively high concentrations. Of course, the 137 ppm peak could be due to a phenol(s) we simply never measured as a model compound.

CONSOL EVALUATION AND EXECUTIVE SUMMARY OF FINAL REPORT FROM THE UNIVERSITY OF KENTUCKY

Introduction

Under subcontract from CONSOL Inc. (U.S. DOE Contract No. DE-AC22-89PC89883), the University of Kentucky studied the use of X-ray absorption fine structure (XAFS) spectroscopy, specifically the least-squares analysis of the X-ray absorption near edge structure (XANES) region of the K-shell XAFS spectra, for the quantitative analysis of the functional forms of organic sulfur in coal derived materials. The University of Kentucky also studied the use of Mössbauer spectroscopy for characterization of the iron-based sulfur-containing components in the coal derived materials. The executive summary authored by the University of Kentucky researchers is presented here. The following assessment briefly highlights the major findings of the project, and evaluates the potential of the method for application to coal derived materials. These results will be incorporated by CONSOL into a general overview of the application of novel analytical techniques to coal derived materials at the conclusion of this contract.

Summary

This study demonstrated the feasibility of using XAFS and Mössbauer spectroscopy for the examination of distillation resid materials derived from direct coal

liquefaction. The least-squares analysis of the XANES region of the K-shell XAFS spectra was shown to be a technique which can be used to determine the sulfur forms in coal liquefaction-derived resid samples. The large amount of pyrrhotite in the resid samples (71 to 99% $\pm$ 10% of the total sulfur) interfered with the precise quantitative analysis of the organic sulfur. However, a spectral subtraction routine was successfully used to provide semi-quantitative results for sulfur species other than the pyrrhotite.

Mössbauer spectroscopy, considered a more accurate method than XAFS for the quantitative analysis of inorganic iron-sulfur species (pyrite, pyrrhotite, iron sulfates), was successfully used to speciate these materials in the coal liquefaction resids. Further application of XAFS and Mössbauer spectroscopy as process development tools appears justified by these results.

Program Description

This report describes the work performed at the University of Kentucky under a subcontract from CONSOL Inc., Research and Development. CONSOL's prime contract to the U.S. Department of Energy (Contract No. DE-AC22-89PC89883, "Coal Liquefaction Process Streams Characterization and Evaluation") established a program for the analysis of direct coal liquefaction derived materials. The program involves a number of participating organizations whose analytical expertise is being applied to these materials. This Participants Program has two main objectives. The broad objective is to improve our understanding of fundamental coal liquefaction chemistry to facilitate process improvement and new process development. The specific approach to achieving this objective is to provide a bridge between direct coal liquefaction process development and analytical chemistry by demonstrating the application of various advanced analytical methods to coal liquefaction materials. The methodologies (or techniques) of interest are those which are novel in their application for the support of coal liquefaction and those which have not been fully demonstrated in this application. CONSOL is providing well-documented samples from different direct coal liquefaction production facilities to the program participants. The participants are required to interpret their analytical data in context to the processing conditions under which the samples were generated. The methodology employed is then evaluated for its usefulness in analyzing direct coal liquefaction derived materials.

Participant's Methodology

The University of Kentucky used XAFS and Mössbauer spectroscopy to analyze five 850 °F* distillation resids. The samples were composite 850 °F* resids of samples taken over long periods of single runs from the Wilsonville pilot plant. These are solids at room temperature, and contain THF-soluble and -insoluble organics and mineral matter. Samples were taken from two locations: between the first- and second-stage reactors and after the second-stage reactor. These samples are expected to represent different extents of coal liquefaction. Two major processing parameters were varied among the Wilsonville runs: feed coal and reactor configuration (thermal/catalytic vs catalytic/catalytic). The experimental details for the sulfur XAFS procedure and the Mössbauer spectroscopy procedure are described on page 2 of DOE/PC 89883-63.

Participant's Major Findings

The following principal observations for the application of XAFS and Mössbauer spectroscopy to coal liquefaction resids were reported by the University of Kentucky. An expanded discussion can be found in DOE/PC 89883-63, pages 2 through 6.

Pyrrhotite was the dominant sulfur species in all five resids, accounting for 71 to 99% ($\pm 10\%$) of the total sulfur in the samples. The large pyrrhotite peak dominated the XANES spectra and partially interfered with regions of the spectra, where the s-p peaks for thiophene and organic sulfide occur. To circumvent the limitations imposed by the pyrrhotite interference, a least-squares fit of the spectra was performed to quantify the sulfur in three broad categories: pyrrhotite, unoxidized organic sulfur, and sulfate (instead of the usual nine or so categories). This approach indicated that the samples contained 0 to 23% ($\pm 5\%$) unoxidized organic sulfur and 1 to 6% ($\pm 3\%$) sulfate sulfur in addition to the pyrrhotite sulfur. In an attempt to better quantify the sulfur species, the pyrrhotite was mathematically subtracted from the spectra and then the pyrrhotite-subtracted spectra were analyzed by the least-squares fitting method. The XANES spectrum of the one resid produced from Wyodak coal was used as the reference pyrrhotite spectrum because the original XANES analysis showed that the sulfur in that sample was virtually all in the form of pyrrhotite. This approach yielded semi-quantitative values for sulfidic, thiophenic, sulfoxide, sulfone and sulfate sulfur in the remaining four resids. Although the results are only semi-

quantitative, some trends can be observed in the data. For example, a comparison of the Illinois No. 6 coal-derived interstage resids from different runs shows that a much higher proportion of the non-pyrrhotite sulfur is thiophenic sulfur in the resid produced by a thermal first stage (Run 250) than the resid produced from a catalytic first stage (Run 257) (78 vs 38%, $\pm 20\%$). The non-pyrrhotite sulfur in the one sample from Pittsburgh seam coal is almost entirely thiophenic (81% $\pm 20\%$) and sulfate (15% $\pm 10\%$).

The Mössbauer spectra of all five samples were similar. A least-squares fit was made of each spectrum and the iron-containing compounds were identified and measured. Pyrrhotite was found to be the dominant iron-bearing phase present, accounting for 84 to 95% $\pm 2\%$ of the total iron. The vacancy content of the pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$) was found to be 6 to 8%, significantly lower than the 9 to 12.5% of most mineral pyrrhotites. Several other iron phases were observed. A ferric phase, which may be either an iron oxide or iron contained in a clay-derived silicate phase, was found in all five resids. Ferrous sulphate (most likely szomolnokite, $\text{FeSO}_4 \cdot \text{H}_2\text{O}$), which may have formed by oxidation of the pyrrhotite after liquefaction, was found in three of the samples. Magnetite was found in the one Wyodak coal derived sample.

The results of the XANES and Mössbauer analyses of the five resid samples were compared to the results of similar analyses of the Argonne Premium coals which correspond most closely to the feed coals used in the liquefaction processing runs. The Argonne coals were examined previously by the researchers at the University of Kentucky. The University of Kentucky observed that the iron species in the Wyodak coal resid must be primarily derived from the iron catalyst used in the processing run because the parent coal has a very low iron content. Additional discussion comparing the resids and coals can be found on pages 4 through 5 of DOE/PC 89883-63.

CONSOL Evaluation

The sulfur XAFS/XANES and Mössbauer techniques were shown to be potentially useful for the quantitative speciation of sulfur forms in direct coal liquefaction resid samples. The dominant pyrrhotite peak in the XAFS spectra partially interfered with the organic sulfur region and reduced confidence in the accuracy of the quantitative data. These experiments demonstrate that for

accurate quantitative speciation of the organic sulfur forms in coal-derived resids, the XAFS/XANES technique should be performed on the inorganic-free portion of the sample. The Mössbauer technique clearly showed that pyrrhotite was the dominant iron-bearing species present in the resids and provided the stoichiometry of the pyrrhotite. Other iron species were also detected, including ferric oxides or silicates, ferrous sulfate and magnetite.

The Mössbauer instrument used in these studies cost approximately \$50,000. It requires approximately one day to prepare and collect data for a single sample by Mössbauer spectroscopy. The sulfur XAFS experiments were conducted at the National Synchrotron Light Source at Brookhaven National Laboratory. Approximate time requirements are 1-2 hr to prepare a sample and about 1 hr to collect data. Cost per sample is approximately \$1000. Data acquisition and interpretation for both methods require a considerable amount of time (on the order of a few hours to one week) and the expertise of a skilled professional.

Further Development

The interference by pyrrhotite in the quantitative determination of the organic sulfur species by XANES indicates that future applications would be better performed with only the organic component of the resid (e.g., the solvent-soluble portion of the resid). The XAFS technique also can be used for the direct speciation of other elements, such as nitrogen and possibly oxygen. Exploration of the applicability of the technique for the quantitative analysis of these heteroatomic species in coal liquids is recommended.

Participant's Statement of Work

X-ray absorption fine structure (XAFS) Spectroscopy has been demonstrated to be a powerful technique for the investigation of sulfur in coal and coal derivatives. The least-squares analysis of the X-ray absorption near edge structure (XANES) region of the K-shell XAFS spectra provides a quantitative analysis of the functional forms of the sulfur. Mössbauer spectroscopy has found numerous applications in coal science, principally for its ability to characterize complex samples containing iron-based components. These techniques have not, however, been demonstrated widely for their ability to answer questions pertaining to the chemistry of coal conversion. As such, they fit well within the scope of the participants program.

The application of XAFS and Mössbauer spectroscopy to a small sample set (5 samples) will allow a demonstration of the value of these techniques for the examination of the sulfur compounds in coal liquefaction-derived resids. XAFS will allow for a quantitative measurement of the sulfur forms in the samples. Since XAFS has reduced sensitivity for the iron-based inorganic sulfur forms, Mössbauer will be used to supplement the XAFS data with quantitative measurements of the iron-based inorganic sulfur forms. This technique for the quantitative determination of sulfur forms may be useful to characterize resids in support of a study of resid reactivity. These samples have been selected so that the utility of the technique for this purpose can be assessed. The samples will be supplied to the University of Kentucky with the following information, as available: elemental analyses, ash content, ash elemental analysis, phenolic OH concentration, calorific value, hydrogen classes by $^1\text{H-NMR}$, and the full history of the sample (plant, process conditions, age, and storage conditions). The five samples are 850 °F distillation residual materials and contain insoluble organic material (IOM) and ash. Sample size will be at least 3 g. The five resid samples will be brittle pitch-like materials that will be supplied as approximately minus 60-mesh powder.

University of Kentucky Executive Summary

The forms of sulfur in five Wilsonville resid samples have been investigated by XANES spectroscopy and Mössbauer spectroscopy. Three of the samples were obtained from liquefaction runs using Illinois 6 coal, and one each from runs using Pittsburgh and Wyodak coals.

Pyrrhotite is the dominant sulfur-containing compound in all five resids. The Mössbauer results show that from 84 to 95% of the iron in the samples is contained in pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$, with $x = 6-8\%$), with minor amounts of ferrous sulfate and other phases present. The raw sulfur K-edge XANES spectra were analyzed into three components: pyrrhotite, unoxidized organic sulfur, and sulfate. On the basis of this analysis, pyrrhotite contained from 71 to 99% of the sulfur in the resids, while unoxidized organic and sulfatic forms accounted for up to 23% and 6% of the sulfur, respectively.

The dominant phase, pyrrhotite, exhibited strong absorption features in the region of the XANES where the s-p peaks for thiophene and organic sulfide occur,

making it difficult to carry out a meaningful analysis of the functional forms of unoxidized organic sulfur. An attempt to physically separate the pyrrhotite from the organic matrix of the resid was not successful. Therefore, a mathematical procedure of subtracting the pyrrhotite XANES from the total resid XANES was developed. The resulting pyrrhotite-subtracted spectra then were analyzed. The results indicated that both sulfidic and thiophenic sulfur functional forms were present in the Illinois 6 resid samples, with thiophenic sulfur being dominant, while only thiophenic sulfur is present in the Pittsburgh seam resid. Too little organic sulfur is present in the Wyodak-Anderson resid to be analyzed by this method, while the accuracy of the Xanes analysis for these pyrrhotite-subtracted spectra is rather poor, the results seem to be reasonable on the basis of previous work on the alteration of sulfur forms resulting from pyrolysis.

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.^{5,7,8}

Section 5

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TABLE 1
SAMPLES ANALYZED - HRI RUN 260-03

LO#	Date	Time	Description	Period
6038	11/20/91		Coal, HRI 5991	1
6039	7/29/92	1330	Coal, HRI 5991 from P-1	13 SD
6040	7/29/92	0745	Start-up Solvent, Wilsonville	start up
6041	7/15/92	0915	Recycle Process Solvent, Tk 4	11
6042	7/29/92	0800	Recycle Process Solvent, Tk 4	13 S/D
6043	11/21-22/91	0600	Naptha Stabilizer Bottoms	2AB
6044	7/17-18/92	0500	Naptha Stabilizer Bottoms	13AB
6045	11/22/91	1410	Filtrate, 0-48	2A
6046	7/17/92	2020	Filtrate, 0-48	13B1
6047	7/5/92	0840	Filter Cake	10A1+A2
6048	7/17/92	0548	Filter Cake	12A
6049	7/18/92	0120	Filter Cake	13B
6095	7/19/92		Coal, HRI 5991, P-1	14A-S/D
6096	10/1/92		Black Thunder Coal, HRI 5887	
6097	7/19/92		PDU Filter Cake, Let Down Line	14A-S/D

TABLE 2
ANALYSIS PLAN - HRI RUN 260-03

LO#	Sample Type (Period)	Analysis									
		Distil- lation	Solu- bility Separa- tion	Dewaxing	¹ H-NMR	IR (c)	MAC (e)	GC/MS	GC/FID	Proximate and Elemental Analysis	Petro- graphy
6036	Coal (1)					✓				✓	
6040	Start-up Solvent (8/u)	✓	✓	✓	✓(a)	✓	✓	✓(f)	✓		
6041	Recycle Solvent (11)	✓	✓	✓	✓(a)	✓	✓	✓(f)	✓		
6042	Recycle Solvent (13)	✓	✓	✓	✓(a)	✓	✓	✓(f)	✓		
6043	NSB (2)				✓(a)	✓		✓			
6044	NSB (13)				✓(a)	✓		✓			
6045	Filtrate (2)	✓	✓	✓	✓(a)	✓	✓	✓(f)	✓		
6046	Filtrate (13)	✓	✓	✓	✓(a)	✓	✓	✓(f)			✓
6047	Filter Cake (10)		✓		✓(b)	✓(d)		✓(g)			
6048	Filter Cake (12)		✓	✓	✓(b)	✓(d)		✓(g)			
6049	Filter Cake (13)		✓		✓(b)	✓(d)		✓(g)			
6095	Coal (14)					✓				✓	✓
6096	Coal					✓				✓	✓
6097	Filter Cake, deposit line (14)		✓		✓(b)	✓(d)		✓(g)		✓	✓

- (a) Chloroform-soluble portion of this sample analyzed by ¹H-NMR
- (b) THF-soluble portion of this samples analyzed in pyridine-d₆ by ¹H-NMR
- (c) Coals analyzed by diffuse reflectance for oxidation index; oil analyzed as whole oils (unless noted) for phenolic -OH conc.
- (d) Tetrahydrofuran-soluble portion of these samples analyzed by IR
- (e) MAC = microautoclave solvent quality test; modified equilibrium conditions (Ref. 2)
- (f) Distillate of this sample analyzed by GC/MS
- (g) Tetrahydrofuran soluble portion of this sample analyzed by GC/MS

TABLE 3
COAL ANALYSES - HRI RUNS 260-03 AND CC-1

	LO-6038 (HRI 5991) Period 1	LO-6095 (HRI 5991) Period 14A	LO-6096 (HRI 5887)	LO-5057 Run CC-1
Moisture, wt % as det.	8.46	7.66	10.30	24.30
Vol. Matter, wt % dry	46.45	43.49	44.04	43.96
Fixed Carbon, wt % dry	46.83	49.06	48.41	48.31
Ash, wt % dry	6.72	7.45	7.55	7.73
Carbon, wt % dry	69.46	68.96	67.54	69.20
Hydrogen, wt % dry	4.68	4.65	4.46	4.96
Nitrogen, wt % dry	1.00	0.94	0.94	0.81
Oxygen, wt % dry (by diff)	17.72	17.50	18.61	16.82
Chlorine, wt % dry	<0.01	<0.01	<0.01	0.08
Sulfur (total), wt % dry	0.42	0.50	0.90	0.40
Sulfur as Sulfate, wt % dry	0.03	0.04	0.14	0.02
Sulfur as Pyrite, wt % dry	0.12	0.15	0.26	0.07
Sulfur as Organic, wt % dry	0.27	0.31	0.50	0.33
Gross Calorific Value, BTU/lb dry	12,669	11,846	11,724	12,859
Oxidation Index*	3.4	3.2	3.1	NA

* Determined by FTIR (Ref. 6)
NA = Not Available

TABLE 3 (Continued)
COAL ANALYSES - HRI RUNS 260-03 AND CC-1

	LO-6038 (HRI 5991) Period 1	LO-6095 (HRI 5991) Period 14A	LO-6096 (HRI 5887)	LO-5057 Run CC-1 (a)
Mineral Matter, vol %, as det	3.8	4.2	4.4	- (a)
Vitrinite Content of Uncontaminated Portion of Coal Samples, vol %, as det.	9.2	78.1	79.5	73.4
Type 2, vol %, as det				2.9
Type 3, vol %, as det	19.0	6.2	1.6	60.2
Type 4, vol %, as det	60.2	64.0	55.6	10.3
Type 5, vol %, as det		7.8	20.6	
Type 6, vol %, as det			1.6	
Exinite, vol %, as det	5.0	4.0	4.5	3.6
Resinite, vol %, as det	0.0	0.0	0.0	-
Semifusinite, vol %, as det	5.4	7.4	6.8	12.5
Micrinite, vol %, as det	5.8	5.5	4.1	8.5
Fusinite, vol %, as det	0.8	0.9	0.9	2.0
Mean Maximum Reflectance (R_o) of uncontaminated coal, %	0.43	0.45	0.48	0.36
Contamination with high vol. coal, vol %	3.0	5.0	3.0	-
Vitrinite Type Analysis of Contamination				-
Type 8, %, normalized		10		-
Type 9, %, normalized	30	50	60	-
Type 10, %, normalized	30	20	30	-
Type 11, %, normalized	20			-
Type 13, %, normalized	20	10	10	-
Type 14, %, normalized		10		-
Mean Max Reflectance (R_o) of contamination, %	1.10	1.05	1.02	-

(a) LO-5057 analysis reported on a mineral-matter-free basis.

TABLE 4
DISTILLATION DATA - HRI RUN 260-03

LO#	Sample Type (Run Period)	850 °F ⁻ Distillate, wt %	850 °F ⁺ Resid, wt %
6040	Start-Up Solvent (S/U)	96.5	2.6
6041	Recycle Solvent (11)	94.3	5.5
6042	Recycle Solvent (13)	94.1	5.4
6045	Filtrate (2)	94.8	5.2
6046	Filtrate (13)	86.2 (84.8) (a)	13.7(15.2) (a)

(a) Duplicate analysis

TABLE 5
MICROAUTOCLAVE SOLVENT QUALITY TESTS (a)

LO#	Sample Type (Run Period)	Coal Conversion, wt % MAF
6040	Start-up Solvent (S/U)	70.3
6041	Recycle Solvent (11)	59.6
6042	Recycle Solvent (13)	56.8
6045	Filtrate (2)	62.2
6046	Filtrate (13)	55.1

(a) Modified Equilibrium Conditions (Reference 2)

TABLE 6
PROTON DISTRIBUTION AND PHENOLIC -OH CONCENTRATION
HRI RUN 260-03

LO#	Sample Type (Run Period)	Proton Distribution, %							Phenolic -OH	
		Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma	Conc., meq/g	Peak cm ⁻¹
6040	Start-up Solvent (S/U)	6.7	5.8	13.5	9.1	20.7	27.1	17.1	0.35	3315
6041	Recycle Solvent (11)	5.4	4.7	9.8	7.3	19.1	33.2	20.6	0.18	3316
6042	Recycle Solvent (13)	4.9	3.9	10.3	7.7	20.0	34.3	19.0	0.10	3322
6043	NSB (2)	0.9	2.7	3.6	4.7	28.6	32.5	27.0	N/D*	-
6044	NSB (13)	1.5	2.6	4.7	5.5	23.0	36.6	26.3	N/D*	-
6045	Filtrate (2)	3.1	4.2	8.7	7.1	20.7	35.0	21.2	<0.10	3330
6046	Filtrate (13)	4.3	2.6	7.9	5.6	18.6	39.4	21.5	<0.10	3325
6047	Filter Cake (10)	6.0	2.9	9.9	6.3	20.8	36.0	18.1	0.10	3309
6048	Filter Cake (12)	5.6	2.8	7.0	5.6	18.1	38.0	22.8	0.11	3311
6049	Filter Cake (13)	5.6	3.0	7.7	6.3	18.8	36.9	21.8	0.12	3306
6097	Filter Cake, deposit line (14)	6.3	2.6	9.6	7.3	19.9	35.9	18.4	0.13	3306

* N/D = not detected

TABLE 7
IDENTIFICATION OF SELECTED PROMINENT PEAKS IN FIGURE 3

Peak No.	Identification	Peak No.	Identification
1	methylcyclohexane	13	methyltetralin
2	ethylcyclohexane	14	unknown (a)
3	solvent contamination	15	dimethyltetralin
4	propylcyclohexane	16	unknown (a)
5	methylpropylcyclohexane	17	tetradecane
6	perhydroindan (a)	18	unknown (a)
7	decalin	19	propyltetralin
8	methylindan	20	pentadecane
9	methyldecalin	20a	butyltetralin
10	tetralin	21	hexadecane
11	dodecane	22	heptadecane
12	methyltetralin	23	unknown (a)

Peak identifications based on searches of the Wiley/NBS Database and CONSOL's library of coal-derived compounds.

(a) Match quality low.

GC/MS Conditions:

Column - 30 m x 0.25 mm fused silica with DB5 coating
 Temperature Program - 35-100 °C @ 35 °/min
 100-320 °C @ 4 °/min
 Mass Spec. - 45-300 amu scan, 70 eV

TABLE 8
IDENTIFICATION OF SELECTED PROMINENT PEAKS IN FIGURE 4

Peak No.	Identification	Peak No.	Identification
1	ethylcyclohexane	15	dimethyltetralin
2	solvent contamination	16	tetradecane
3	propylcyclohexane	17	propyltetralin (a)
4	perhydroindan	18	pentadecane
5	methylmethylethylcyclohexene	19	butyltetralin
6	methylindan	20	tetrahydrobenzindan isomer (a)
7	undecane	21	hexadecane
8	methyldecalin	22	isoprenoid paraffin (a)
9	methylindan	23	heptadecane
10	tetralin	24	pristane
11	dodecane	25	octadecane
12	methyltetralin	26	nonadecane
13	methyltetralin (a)	27	eicosane
14	tridecane	28	heneicosane

Peak identifications based on searches of the Wiley/NBS Database and CONSOL's library of coal-derived compounds.

(a) Match quality low.

GC/MS Conditions:

Column - 30 m x 0.25 mm fused silica with DB5 coating
 Temperature Program - 35-100 °C @ 35 °/min
 100-320 °C @ 4 °/min
 Mass Spec. - 45-300 amu scan, 70 eV

TABLE 9
SOLUBILITY SEPARATION DATA

LO #	Sample Type (Run Period)	THF-Sol, wt % (ash free, wt %)	IOM, wt % (ash free, wt %)	Ash, wt %
6047	Filter Cake (10)	46.6 (56.2)	36.3 (43.8)	17.1
6048	Filter Cake (12)	44.6 (51.5)	39.5 (45.6)	15.9
6049	Filter Cake (13)	51.9 (59.9)	34.7 (40.1)	13.4
6097	Filter Cake, transfer line deposit,(14)	48.0 (57.9)	35.0 (42.2)	17.1
6040	Start-up Solvent, S/U	100.0		
6041	Recycle Solvent (11)	100.0		
6042	Recycle Solvent (13)	99.4		
6045	Filtrate (2)	100.0		
6046	Filtrate (13)	100.0		

TABLES 10A-D

COMPARISON OF KEY DATA BETWEEN THE PRESSURE FILTER LIQUIDS (PFLs) OF HRI RUNS CC-1,¹ CC-2, CC-5, CC-6¹⁰ AND THE RECYCLE OILS, FILTRATES, AND FILTER CAKES FROM HRI RUN 260-03

Table 10A. Microautoclave Tests, THF Coal Conversion, wt % MAF (a)

CC-1 PFLs		260-03 Filtrates	
Run Day	wt % MAF	Period	wt % MAF
6	75.2	2	59.6
10	77.4	11	59.6
13	81.9	13	56.8
16	86.0		
19	83.9		
22	79.7		

(a) modified equilibrium test, Old Ben Mine coal²

Table 10B. Aromatic Proton Distribution, %

CC-1 PFLs					260-03						
Run Day	Whole Sample		850 °F Distillate		Period	Recycle Oil		Filtrate		THF-Sol. Filter Cake	
	Cond	Uncond	Cond	Uncond		Cond	Uncond	Cond	Uncond	Cond	Uncond
6	8.0	3.1	6.1	3.4	2			3.1	4.2		
10	9.4	4.5	7.9	4.6	10					6.0	2.7
13	10.7	3.9	7.3	4.8	11	5.4	4.7				
16	11.6	4.6	7.7	5.2	12					5.6	2.8
19	14.4	5.2	10.6	5.1	13	4.9	3.9	4.3	2.6	5.6	3.0
22	16.4	5.8	12.2	4.9	14					6.3	2.6

TABLE 10C. Resid Content, wt % 850 °F⁺

CC-1 PFLs		260-03		
Run Day	wt % Resid	Period	wt % Resid	
			Recycle Oil	Filtrate
6	24.2			
10	21.9	2		5.2
13	25.6	11	5.5	
16	28.2	13	5.4	13.7
19	29.9			
22	39.8			

TABLES 10A-D (Continued)

COMPARISON OF KEY DATA BETWEEN THE PRESSURE FILTER LIQUIDS (PFLs) OF
HRI RUNS CC-1,¹ CC-2, CC-5, CC-6¹⁰ AND THE RECYCLE OILS,
FILTRATES, AND FILTER CAKES FROM HRI RUN 260-03

TABLE 10D. Phenolic -OH Content, meq/g

CC-1 PFLs			260-03			
Run Day	850°F Distillate	850°F+ Resid	Period	Recycle	Filtrate	THF-Sol Filter Cake
6	0.04	0.14	2		<0.10	
10	0.06	0.24	10			0.10
13	0.07	0.22	11	0.18		
16	0.09	0.26	12			0.11
19	0.13	0.35	13	0.10	<0.10	0.12
22	0.18	0.55	14			0.13

CC-2 PFLs		
6	0.02	0.08
10	0.06	0.17
14	0.07	0.24

CC-5 PFLs		
5	0.09	0.22
9	0.14	0.32
15	0.15	0.38
19	0.14	0.32

CC-6 PFLs		
4	<0.01	0.29
9	0.09	0.53
12	0.16	0.77

TABLE 11

WAX CONTENTS OF SELECTED SAMPLES FROM HRI RUN 260-03,
HRI RUN CC-2, HRI CC-5, HRI CC-6, AND WILSONVILLE RUN 262

Run Number (a)	Sample No.	Sample Type (Run Period)	Dewaxing		Gas Chromatograph		
			% Wax Method A (c)	% Wax Method B (d)	% Straight Chain Paraffin in Whole Oil (f)	% Straight Chain Paraffin in Wax	Wax as a % of Whole Oil (f)
260-03	6040	start-up solvent (S/U)	N/A	59.0	12.8	23.3	54.8
260-03	6041	recycle solvent (11)	23.5	N/A	20.9	39.6 (g)	52.8
260-03	6042	recycle solvent (13)	18.9	49.8	28.1 (j)	60.7 (h,j)	46.3 (j)
260-03	6045	filtrate (2)	31.0	56.9	21.8	44.8 (h)	48.7
260-03	6046	filtrate (13)	42.8	N/A	39.9	70.8 (g)	56.4
260-03	6048	filter cake (12)	N/A	36.6 (i)	18.4	49.2	37.4
CC-2	5336	PFL (10 ABC)	22.0	46.9	27.8	74.7 (h)	37.2
CC-5	5344	PFL (10 ABC)	18.5	21.1	27.0	77.6 (h)	34.8
CC-6 (b)	5349	PFL (4 ABC)	35.3	48.4	20.5	40.5 (h)	50.5
W 262	V131B	recycle solvent (C)	8.7 (e)	28.0 (e)	36.2	76.8 (h)	47.1

- (a) Feed coal for all runs, unless designated otherwise: Wyodak and Anderson seam, Black Thunder Mine coal
- (b) Feed coal Illinois No.6
- (c) -35 °C acetone precipitation procedure
- (d) Column separation procedure only
- (e) Calculated on ash-free basis
- (f) Filtered ash-free oil
- (g) -35 °C acetone precipitation procedure (Method A)-produced wax
- (h) Column only (Method B)-produced wax
- (i) Calculated on a THF-soluble basis
- (j) Average of three analyses.

HRI PDU REACTOR SYSTEM

HRI PDU FILTRATION SECTION

Figure 1. HRI PDU Reactor System with Detail of Filtration Section as Used in Run 260-03.

Figure 2. Temperatures for Reactors 1 and 2, HRI Run 260-03.
(Taken from Reference 3)

Figure 3. Total Ion Chromatograms of Samples Obtained During Start-up and Period 2 of HRI Run 260-03. Identifications refer to n-paraffins.

Figure 4. Total Ion Chromatograms of Samples Obtained During Period 13 of HRI Run 260-03. Identifications refer to n-paraffins.

Figure 5. Total Ion Chromatogram of HRI Run 260-03 Period 2
Naphtha Stabilizer Bottoms (LO-6043).
See Table 7 for peak identifications.

Figure 6. Total Ion Chromatogram of HRI Run 260-03 Period 13
Naphtha Stabilizer Bottoms (LO-6044).
See Table 8 for peak identifications.

Figure 7. Comparison of the Total Ion Chromatograms of Filtrate Samples from HRI Run 260-03 Periods 2 and 13. Identifications refer to n-paraffins.

Figure 8. Total Ion Chromatograms of the THF-Soluble Portion of Three Filter Cakes and a Post-Filter Sample from HRI Run 260-03. Identifications refer to n-paraffins.

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