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Coal Liquefaction Process Streams Characterization and Evaluation,

Quarterly Technical Progress Report
January 1 through March 31, 1993

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

December 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
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COAL LIQUEFACTION PROCESS STREAMS CHARACTERIZATION AND EVALUATION QUARTERLY TECHNICAL PROGRESS REPORT, JANUARY 1 THROUGH MARCH 31, 1993

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

- A set of 18 process samples from HRI CTSL Bench Unit Run CC-16 (227-76) were analyzed to provide information on process performance. Run CC-16 was operated from December 2 through December 14, 1992, with coal from the Burning Star 2 Mine (Illinois 6 seam). The run was made to test and validate Akzo EXP-AO-60 Ni/Mo catalyst. Results are compared with those of previous HRI CTSL bench unit runs made with Burning Star 2 coal and other Ni/Mo catalysts (Runs I-13, I-16, I-17, I-18).

- Microautoclave tests and chemical analyses were performed to measure the reactivity of the standard coal used for determining donor solvent quality of process oils in this contract.

- A brief summary of the status of the Participants Program is given.

- A summary of the final report on a project conducted under Phase II of the the Participants Program by the University of Pittsburgh is presented. Pitt evaluated the use of UV Resonance Raman Spectroscopy for the analysis of coal liquids.

- Two peer-reviewed papers are appended. One paper is authored by researchers at Iowa State University and describes work done under Phase II of the Participants Program to evaluate the use of ^{31}P-NMR spectroscopy for the analysis of coal liquids. The other paper is co-authored by researchers at Western Research Institute and CONSOL and describes work done under Phase I of the Participants Program that consisted of ^{13}C-NMR analyses and hydrogen accounting of Wilsonville samples and operations.

Section 1
EXECUTIVE SUMMARY

HRI CTSL RUN CC-16

Process oil samples from HRI Catalytic Two-Stage Liquefaction (CTSL) Bench Unit Run CC-16 (227-76) were analyzed to provide information on process performance. Run CC-16 was operated in December 1992 with Burning Star 2 Mine (Illinois 6 seam) coal to test and validate Akzo EXP-AO-60 Ni/Mo catalyst (1/16" extrudate). Results were compared with those of four previous HRI CTSL bench unit runs made with Ni/Mo catalysts. Major conclusions from this work are summarized below.

- Akzo EXP-AO-60 gave process oil characteristics in Run CC-16 similar to those of other Ni/Mo catalysts tested in Runs I-13, I-16, I-17, and I-18 (by our analytical and empirical test methods). However, differences in the Run I-13 conditions caused many of the Period 13 comparison samples from Run I-13 to differ from those from the other runs. No distinct performance advantage for any of the catalysts emerges from the process oil characteristics and plant performance. Thus, for commercial coal liquefaction, a number of equivalent catalysts are available from competitive commercial sources. The similarity of run performance and process oil characteristics indicates consistent performance of HRI's bench unit operations over a period of several years.

- Dominant effects on process oil properties in Run CC-16 were catalyst age and higher temperature operation in Periods 10-13 (Condition 2). Properties affected were the aromaticities and phenolic -OH concentrations of most streams and the asphaltene and preasphaltene concentrations of the pressure-filter liquid (PFL) 850°F$^+$ resid. The trends reflect decreasing hydrogenation and defunctionalization of the process streams with increasing catalyst age. Operation at higher temperature conditions seems to have partially offset the effects of catalyst age. The asphaltene and preasphaltene concentrations and phenolic -OH concentration of the PFL 850°F$^+$ resid levelled off after about Period 9, although aromaticity continued to increase.

- The presence of about 40 wt % 850 °F$^+$ resid in the whole PFL improved donor solvent quality by about 5% MAF coal conversion (microautoclave test), relative to the 850°F$^-$ distillate only. Corresponding trends of donor solvent quality and resid concentration suggest that donor solvent quality was related to resid concentration. The donor solvent quality was good for most of the run, about 80% MAF coal conversion in our test from Period 4 on.

- Some selectivity for preasphaltene rejection is exhibited by filtration prior to recycle. The PFC THF solubles (which contain some distillate-range material) are higher in preasphaltenes content than the PFL resid. Though the two processes are distinctly different, this selectivity is similar to that of the ROSE-SR unit at Wilsonville, which selectively rejected preasphaltenes, and to a lesser degree, asphaltenes.

- At HRI's test conditions for Ni/Mo catalysts (Conditions 1 and 2), donor solvent quality of the recycle oil was consistently good in the runs compared.

CALIBRATION AND ANALYSIS OF STANDARD COAL

Chemical analyses and microautoclave tests were performed to monitor oxidation and measure the reactivity of the standard coal (Indiana V, Old Ben Mine No. 1) which is used to determine donor solvent quality of the process oils tested in this contract. Small changes in coal properties were apparent and there were some indications of a decline in coal reactivity, relative to preceding evaluations in 1991 and 1992.

PARTICIPANTS PROGRAM

Phase II is complete. The final report from the University of Pittsburgh project (UV Resonance Raman Spectroscopic analyses) is included in this Technical Report. This technique will require further development before it can be applied to support liquefaction process development. Four of the seven intended Phase III subcontracts are in place. Emphasis in Phase III was shifted toward application of techniques found in Phases I and II to have a high potential for providing process-sensitive chemical information about the coal-liquefaction samples.

Section 2
INTRODUCTION

This is the Technical Progress Report for the fourteenth quarter of activities under DOE Contract No. DE-AC22-89PC89883. It covers the period January 1 through March 31, 1993.

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 to evaluate the techniques or methods include 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. Each activity is summarized, as appropriate in the Executive Summary, Section 1 of this report, and discussed in the Results and Discussion, Section 3 of this report.

- A set of 18 process samples from HRI CTSL Bench Unit Run CC-16 (227-76) were analyzed to provide information on process performance. Run CC-16 was operated from December 2 through December 14, 1992, with Burning Star 2 Mine (Illinois 6 seam) coal. The run was made to test and validate the use of Akzo EXP-AO-60 Ni/Mo catalyst. Results are compared with those of previous HRI CTSL bench unit runs made with Burning Star 2 coal and other Ni/Mo catalysts (Runs I-13, I-16, I-17, I-18).

- Twelve microautoclave tests were made to measure the reactivity of the standard coal (Indiana V, Old Ben Mine No. 1) which is used to determine donor solvent quality of the process oils tested in this contract. The coal was analyzed by chemical analyses to monitor oxidation.

- Substantial progress was made in the Participants Program this quarter. A summary of activities in the Participants Program is presented. The topical report from the University of Pittsburgh was issued, completing Phase II. Pitt evaluated the use of UV Resonance Raman Spectroscopy for the analysis of coal liquids. The CONSOL evaluation and executive summary from Pitt's report are included here. Four of seven intended Phase III subcontracts are in place.

- Two peer-review papers published under the Participants Program are included as Appendix 1 and Appendix 2. "Determination of Total Phenol Concentrations in Coal Liquefaction Resids by ^{31}P-NMR Spectroscopy" was authored by T. Mohan and J. G. Verkade at Iowa State University and published in *Energy & Fuels* **1993**, *7*, 222-226. "N.M.R. Determination of Aromatic Carbon Balances and Hydrogen Utilization in Direct Coal Liquefaction" was co-authored by F. P. Miknis and D. A. Netzel at Western Research Institute and S. D. Brandes, R. A. Winschel, and F. P. Burke at CONSOL and published in *Fuel* **1993**, *72*, 217-224.

- Other work was begun, but not completed this quarter. Analyses were begun on samples from HRI CTSL Run CC-15. Phenolic -OH concentrations were determined on four ASOH (atmospheric still overhead) samples from Run CC-15 to determine whether caustic washing may be desirable when the HRI composite net product from that run is subjected to petroleum inspection tests under the Phase III Participants Program. The samples tested contained about 0.04 to 0.40 meq/g of phenolic -OH. Caustic washing will be conducted as part of the tests.

Section 3
RESULTS AND DISCUSSION

HRI CTSL RUN CC-16

RUN CC-16 BACKGROUND

CONSOL received 18 samples for analysis from HRI Catalytic Two-Stage Liquefaction (CTSL) bench unit Run CC-16. Samples consist of the feed coal, the start-up/make-up oil, pressure-filter liquids (PFLs) from a start-up period and six run periods, and pressure-filter cakes (PFCs), separator overheads (SOH), and atmospheric-still overheads (ASOH) from three run periods.

HRI CTSL Run CC-16,[1-7] also designated Run 227-76, was made in HRI's two-stage ebullated-bed bench unit 227. Run CC-16 was a process variable run designed to test the performance of Amoco EXP-AO-60 Catalyst (Akzo-produced, bimodal 1/16" extrudate, Ni/Mo on alumina) with Burning Star 2 coal (Illinois 6 seam) and, thereby, to validate EXP-AO-60 catalyst as a commercially available catalyst for use in CTSL direct liquefaction.

HRI's specific objectives in Run CC-16 were: 1) to evaluate the performance of EXP-AO-60 catalyst under the CTSL mode of operation, and 2) to compare the performance of this catalyst with that of other Ni/Mo catalysts: Amocat 1C, UOP RCM4, and Shell 317.

A diagram of the CTSL continuous bench unit 227 is given in Figure 1. The nominal throughput of the unit is 20 kg/day. Each reactor has a capacity of 2000 cc. The operating conditions and yields for Run CC-16 are given in Table 1. A mass balance is performed every 8 or 12 hr, and a daily (period) average is reported. Each of the conditions tested is maintained for a minimum of three days (periods) to ensure validity of the data.

The run was 13 days in length, and took place from December 2 through December 14, 1992. Both reactors were charged with the same catalyst. Batch catalyst aging was used; therefore, the catalyst age increased with run time. The unit was operated in a low/high temperature configuration. As in previous tests of Ni/Mo-supported catalyst performance (I-13,[8] I-16,[9] I-17,[9] and I-18[9]), one set of conditions (Condition 1) was used for days 1 through 9 of operation, and a second set of conditions (Condition 2) was used for days 10 through 13 (or longer) of operation. Each day of operation was an operating period. Condition 1 used a solvent/coal ratio of 1.5, reactor temperatures of 750/800 °F, and a continuous atmospheric still (CAS) reboiler temperature of 610 °F. Condition 2 used a lower solvent/coal ratio (1.1), higher reactor temperatures (775/810 °F), and a higher CAS reboiler temperature (625 °F). Condition 2 provided a more severe test of operation at higher catalyst age. Other conditions which were constant throughout the run were hydrogen pressure (approximately 2500 psig), and coal space velocity (46 lb coal/hr/ft^3 (settled) supported catalyst per stage).

The feed coal used in Run CC-16 was Burning Star 2 Mine coal, Illinois 6 seam, HRI No. 6081. The feed coal analysis is given in Table 2. The start-up oil (L-786) was an Illinois 6 coal-derived pressure-filter liquid (PFL) composited from PFL of Runs 227-63 (CC-6), 227-66 (CC-8), and 227-72 (CC-14).[1,3-5] This oil also was used as a make-up oil when the recycle oil inventory was low. The analysis of the start-up/make-up oil is given in Table 3.

HRI indicated[3] that hydrodesulfurization (HDS) during the run was less than anticipated, and was even lower than the hydrodenitrogenation (HDN); this is an unusual occurrence. HRI attributed the low HDS to uptake of sulfur by solid residual material which is concentrated in the pressure filter cake. They checked and confirmed their sulfur analyses, but did not offer any further explanation for the low observed HDS value.

Although some performance differences were noted between runs with the various Ni/Mo catalysts, HRI concluded that the performance of EXP-AO-60 was comparable to that of Shell 317 and Amocat 1C.[1,2] The results validated the use of EXP-AO-60 as a viable commercially-available catalyst for coal liquefaction using the CTSL process.

SAMPLE DESCRIPTION

CONSOL received 18 samples from HRI Catalytic Two-Stage Liquefaction (CTSL) bench unit Run CC-16 for analysis. Samples consisted of: pressure-filter liquids (PFLs) from periods 0C (a start-up period), 4C, 5C, 8C, 9C, 12C, and 13C; pressure-filter cakes (PFCs) from periods 5C, 9C, and 13C; separator overheads (SOH) from periods 5C, 9C, and 13C; atmospheric-still overheads (ASOH) from periods 5C, 9C, and 13C; the feed coal; and the start-up/make-up oil. HRI sample numbers are included in the tables in which each sample first appears.

The pressure-filter liquid (PFL) is a major second-stage product and the major component of the slurry oil. It is obtained by filtering the atmospheric-still bottoms through a pressure filter. The pressure-filter cake (PFC) is the retained material. The separator overhead (SOH) oil and the atmospheric-still overhead (ASOH) oil are distillate net products. All oils are assumed to be solids-free for analytical purposes.

ANALYSES

Elemental analyses were obtained on selected samples (Table 4 and Table 5). Proton distribution analyses were obtained by ^{1}H-NMR for each whole oil sample (Table 8). Each whole oil sample was analyzed by FTIR for phenolic -OH content (Table 11). Each whole PFL and the start-up/make-up oil was tested in the microautoclave at the modified equilibrium conditions (Table 12). Microautoclave coal conversions were calculated assuming that the oils were solids-free. Each whole PFL and the start-up/make-up oil sample was distilled (Table 6) to 320 °C pot/270 °C column/5 torr (850 °F/atm). Each 850 $°F^+$ resid was analyzed by solubility fractionation (Table 7), ^{1}H-NMR (Table 10), and FTIR for phenolic -OH content (Table 11). Each 850 $°F^-$ distillate was analyzed by ^{1}H-NMR (Table 9), and FTIR (Table 11). Each pressure filter cake (PFC) sample was pressed through a 14-mesh screen and mixed thoroughly to ensure sample homogeneity. Aliquots of the PFC samples were sonicated with deuterated pyridine, filtered, and analyzed by ^{1}H-NMR (Table 10). Pressure filter cake samples were extracted with tetrahydrofuran (THF) (Table 6). Each THF-soluble PFC extract was analyzed by solubility fractionation (Table 7), and FTIR for phenolic -OH content (Table 11).

DISCUSSION OF SAMPLE PROPERTIES

Run CC-16 Results

CONSOL's analyses and those reported by HRI[1a] for the Burning Star 2 Mine feed coal are given in Table 2. HRI's values for carbon and oxygen-by-difference may be too low and too high, respectively, for Burning Star 2 Mine coal (rank hvBb or hvCb).

Comparison of the elemental analyses of various process samples (Tables 4 and 5) from Period 4C or 5C to Period 13C shows that hydrogen was consistently lower in samples from the later period. Other elements do not show any consistent trend with run period. The elemental analyses of the solid PFC samples appear to indicate less upgrading later in the run (higher N and S contents).

Analyses of the process stream samples from CC-16 are provided in Tables 6 through 12. To facilitate discussion, most of the analyses are also presented in Figures 3 through 6.

Figure 2 summarizes HRI's performance data for Run CC-16 (Table 1). Notice that the MAF coal conversion stayed constant through Period 8, and then increased slightly through the end of the run. Perhaps this is an effect of higher-temperature operation in Condition 2 near the end of the run. Hydrodesulfurization (HDS) generally decreased through the run, probably a result of catalyst aging. However, distillate product S content did not increase with run time (Table 5). The MAF yield of C4 to 975 °F distillate, the MAF 975 °F$^+$ conversion, and the hydrodenitrogenation (HDN) all showed the same trend: there was an increase from Period 2 to Period 3, followed by a general decline through about Period 7. The values stayed constant through Period 9, and then increased during Periods 11 through 13. The changes in the yield of C4 to 975 °F distillate nearly matched the 975 °F$^+$ conversion changes on a period-by-period basis. The trend displayed by these performance measures (MAF yield of C4 to 975 °F distillate, MAF 975 °F$^+$ conversion, and HDN) seems to represent start-up (Periods 2 to 3), approach to lineout and perhaps catalyst aging (Periods 3 through 7), lineout (Periods 7 through 9), and change to Condition 2 with some catalyst age effect (Periods 11 through 13).

The aromaticities of all streams increased through the run (Figure 3, Tables 8 through 10). This is attributable to two factors: the decreasing hydrogenation activity of the catalyst with increasing catalyst age through the run, and operation at the higher-severity Condition 2 near the end of the run (days 10-13). The initial decline in the aromaticity of the whole PFL and its resid and distillate fractions during start-up period 0 results from the high activity of the system for hydrogenation at very low catalyst age. The higher severity of Condition 2 (Periods 12 and 13) consisted of lower solvent/coal ratio and higher temperature operation of both reactors and of the CAS reboiler. This should result in heavier, less-hydrogenated products and recycle PFL streams, which is what we observe.

The phenolic -OH concentrations of the various streams (Figure 4, Table 11) also decrease on start-up, then increase through the run. In comparison with the aromaticity results, the phenolic -OH concentration of the whole PFL and the 850 °F$^+$ resid portion of the PFL show less of an increase between Condition 1 (Period 9) and Condition 2 (Period 13). Perhaps the increased temperatures or decreased solvent/coal ratio in Condition 2 offsets the effect of increasing catalyst age.

The tetrahydrofuran (THF) soluble portion of each PFC is only slightly more aromatic (Figure 3) and phenolic (Figure 4) than the corresponding whole PFL. HRI confirmed that the PFC contains a significant amount of distillate, in addition to the resid.[10] The 850 °F$^-$ PFL distillates are lower in phenolic -OH than the corresponding ASOH liquids. Similar observations have been made with CC-15 process samples[11] and with distillation fractions of CC-15[11] and Wilsonville Run 260[12] product distillates. This arises from concentration of alkylated phenols in the kerosene boiling range.[13]

Throughout Run CC-16, there were general trends of decreasing concentrations of oils (hexane soluble), and increasing concentrations of asphaltenes (hexane insoluble-benzene soluble) and preasphaltenes (benzene insoluble-pyridine soluble) in the PFL 850 °F$^+$ resid (Figure 5, Table 7). The concentrations of oils, asphaltenes, and preasphaltenes in the PFL resid all seem to level off somewhat after Period 8 or 9. This levelling off in Condition 2, rather than increasing further with increased catalyst age, may be an effect of increased defunctionalization with increased reactor temperature. With only a few samples, it is not possible to determine if the PFC samples exhibit any similar general trend. It is apparent from the data (Figure 5) that the PFC THF-solubles (which contain some distillate-range material) contain more preasphaltenes than the PFL resid. Thus, some selectivity for preasphaltene rejection is exhibited by filtration prior to recycle. Even though they are different processes, this selectivity is similar to that of the ROSE-SR unit at Wilsonville, which selectively rejected preasphaltenes, and to a lesser degree, asphaltenes.

Although the preasphaltene concentration in the Period 9 THF-soluble PFC sample is high, it was confirmed by repeat analysis. The THF extraction of the PFC was not repeated, however. The PFC preasphaltene data, including this value, appear to show catalyst aging effects from Period 5 to Period 9, and the effect of higher severity conditions in Condition 2 that, to a large degree, corrected for catalyst age.

The donor solvent quality (Mod-EQ microautoclave test) of the whole PFL decreased on start-up, but increased to a consistently good value of about 80% by Period 4 (Figure 6, Table 12). The solvent quality of the PFL distillate was consistent at about 70 to 75% in the samples tested. Therefore, the addition of the PFL resid improved solvent quality by about 5% absolute MAF coal conversion. The parallel trends of whole PFL solvent quality and 850 °F^+ resid concentration in the PFL (Figure 6, Tables 6 and 12) is commonly observed in CONSOL's analyses of HRI samples. This suggests that the changes in solvent quality in Run CC-16 were largely governed by resid concentration.

Comparison of CC-16 with Other CTSL Runs

Because CC-16 was a catalyst performance run made at conditions similar to prior catalyst performance runs at HRI, it is useful to compare these results with those of comparable runs made with other catalysts. HRI made such a comparison of plant performance in presentations at two Proof-of-Concept Technical Review Meetings.[1,2] The previously-described conditions, which were held constant throughout Run CC-16 and described as Conditions 1 and 2, were equivalent to those used in prior HRI CTSL Runs I-13,[8] I-16,[9] I-17,[9] and I-18[9] made with supported Ni/Mo catalysts. The most notable difference is Run I-13, which used a greater number of run conditions. The conditions for catalyst testing were fixed by HRI for Run I-16 and all subsequent runs. However, the I-13 comparison period differs in some conditions from those of Runs I-16, I-17, I-18 and CC-16. The table below gives those differences.

RUN I-13 EXCEPTIONS TO Ni/Mo CATALYST RUN COMPARISON

Text Description	Period 13, Condition 2	
Run	**I-13**	**I-16, I-17, I-18, CC-16**
Actual Run Period*	18	13
Actual Condition No.	4	2
2nd Stage Temp., °F	800	810

*Catalyst age is approximately proportional to run period.

Note: All other conditions for the comparison periods were equivalent between I-13 and the other runs.

HRI indicated[2] that some differences in bench unit configuration or operation existed among some of the runs. These were not considered to be particularly significant, especially since run results were equivalent for five runs. Supported Ni/Mo catalysts tested in these runs were: Akzo-produced EXP-AO-60 (designed to be equivalent to Amocat 1C) in Run CC-16; 1/16" extrudate Amocat 1C in Run I-13; 1/32" extrudate Amocat 1C in Run I-16; 1/20" spherical UOP RCM4 in Run I-17; and 1/32" extrudate Shell 317 in Run I-18. All of the catalysts have a bimodal pore distribution, except the spherical UOP catalyst.

In light of HRI's findings that the supported Ni/Mo catalysts tested in Runs I-13, I-16, I-17, I-18, and CC-16 gave very similar process performance,[1,2] it is of interest to determine if the analytical characteristics of corresponding process samples from each run are also similar. This case provides an excellent opportunity to look for similarities in sample characteristics based on similarities in performance for runs made several years apart (nearly seven years from Run I-13 to Run CC-16).

Our general conclusion is that the corresponding process samples from the comparable Ni/Mo catalyst runs are very similar in characteristics. A detailed comparison is made in Tables 13 and 14 and Figures 7 through 10. Period (Day) 9 in each of the runs was the last day of operation of Condition 1. Likewise, Period (Day) 13 in each of the runs was the last day at Condition 2. Thus, the properties of the Period 9 samples from each of the runs will be compared with each other. Similarly, the properties of the Period 13 samples from each of the runs will be compared with each other. This will give the best inter-run comparison available at both Condition 1 and Condition 2. The I-13 samples were also obtained from the last day of operation at those conditions. However, the run days do not correspond. Consequently, at the end of the condition, catalyst age and reaction temperature were not the same. The Run I-13 Period 13 results often were different from the other samples, attributable to this difference in second-stage temperature and catalyst age. Prior run results were previously reported for the individual Runs I-13,[8] I-16,[9] I-17,[9] and I-18.[9]

As shown in Figure 7 and Tables 13 and 14, the Period 9 and Period 13 whole PFLs and their 850 °F$^+$ resid and 850 °F$^-$ distillate fractions were quite consistent in hydrogen aromaticity measured by ^{1}H-NMR. Run-to-run variation was typically about 2 to 3% of total protons, but was as high as about 5% of total protons in some cases, such as the Period 9 whole PFLs. The Run I-13 Period 9 and Period 13 PFLs and their fractions are consistently slightly higher than corresponding samples from the other runs. The reason for this is not obvious in the case of the I-13 Period 9 samples. In the I-13 Period 13 (actually period 18) samples, it is attributable to high catalyst age. As is expected with higher catalyst age and higher temperature, the Period 13 samples are consistently more aromatic than their Period 9 counterparts.

The phenolic -OH concentrations (Figure 8, Tables 13 and 14) were quite consistent. Except for the Period 13 samples from I-13, run-to-run variation was 0.1 meq OH/g or less. The I-13 (Period 13) PFL fractions are significantly higher in -OH concentration than corresponding samples from the other runs, as a result of the relatively lower second-stage temperature and higher catalyst age used to produce the I-13 sample. In contrast to the aromaticity results, the Period 13 samples are only slightly more phenolic than their Period 9 counterparts. Thus, the higher-severity conditions in Condition 2 (Period 13) appear to be effective in countering the detrimental effect of catalyst aging on phenolic -OH concentration.

The concentrations of oils, asphaltenes, and preasphaltenes in the PFL 850°F$^+$ resid fraction are consistent within about 5 wt % (Figure 9, Tables 13 and 14). Similar to the phenolic -OH results, the higher severity in Period 13 largely offsets the expected increase in asphaltenes and preasphaltenes from catalyst aging.

The donor solvent qualities (MAF coal conversion in a standard microautoclave test) and 850 °F^{+} resid contents of the whole PFLs were very consistent among all the runs (Figure 10, Tables 13 and 14). No significant difference is observed between the Period 9 and Period 13 samples. This level of donor solvent quality would be rated as "good".

Other properties, such as hydroaromatic donor hydrogen content and paraffinic hydrogen content from the proton distribution, are compared in Tables 13 and 14. These show that the corresponding process oils from each of the Ni/Mo catalyst runs are similar in overall hydrogen (proton) distribution, not just in aromaticity.

In summary, EXP-AO-60 produced process oils in Run CC-16 with sample characteristics similar to those produced in Runs I-13, I-16, I-17, and I-18 using other Ni/Mo catalysts tested. Considering this and the equivalence in plant performance, no catalyst emerges with a distinct performance advantage. This is encouraging news for commercialization of coal liquefaction. It implies that a number of effective commercial catalysts could be available from competitive sources.

The conclusion from an analytical perspective is that similar run performance gave similar process oil characteristics. This supports our experience that the characterization methods we use routinely are relevant to process performance. These results also verify the consistent performance of HRI's bench unit operations, in spite of some operational changes, over an interval of several years.

At the conditions HRI chose for catalyst testing (Conditions 1 and 2), donor solvent quality of the recycle oil has been consistently good in all of the runs compared.

CALIBRATION AND ANALYSIS OF STANDARD COAL

Routine microautoclave solvent quality assays are made with a single standard coal: Old Ben No. 1 Mine, Indiana V seam. The current batch of coal was received in November 1988. In April 1990, this coal batch was found to be rapidly deteriorating and it was repacked for long-term storage in air-tight, N_2-purged plastic bags in batches of 500g.[14] At the time of sealing, the coal was retested. Reported here are the chemical analyses and microautoclave test results from a recently opened plastic bag (January 1993). Comparison is made to the analyses of the as-received coal (November 1988), the analyses made upon resealing the coal in April 1990, and the analyses made one and two years later in March 1991 and March 1992.

The degree of deterioration of the coal sample via weathering is indicated by alteration in the oxygen functional-group distribution and an increase in total and organic oxygen content.[15] Pyritic sulfur is known to slowly convert to sulfate; this and a loss of calorific value often are the only perceptible changes in the chemical analysis of the coal sample. The analyses given in Table 15 show that the coal has a similar analysis to the batch tested in March 1991. There is a slight increase in sulfate sulfur content. The calorific value is intermediate between the as-received (1/88) value and the samples tested in subsequent years. It is worthy of note that since the coal was stored in sealed bags, although there has been no significant oxidation of the coal, the moisture content is slowly declining.

Generally, it has been found that oxidation results in a decrease in liquefaction yields.[16,17] In order to determine the relative decline in performance of this coal, batch microautoclave tests have been periodically made using this coal and solvents containing varying ratios of tetralin and 1-methylnaphthalene. Three commonly used sets of test conditions were employed.[18] The results of the most recent tests, and tests made ten, twenty-two and thirty-three months earlier, are given in Table 16. The coal conversions obtained with these tests can be used as reference points for liquefaction solvents tested with this coal. Similar data for earlier (1979 and 1981) batches of the same coal were previously reported.[18-21]

The repeatability of the microautoclave assay was shown to have a standard deviation of 1.2% absolute.[18] Eight of the twelve data points are within this 1.2% deviation of the average. The other four are lower than the average. The overall average (bottom row in Table 16) also is slightly lower for the recent set of tests. Thus, though there are some indications that the coal's reactivity toward conversion may be declining, comparison with the sample tested in February 1990, March 1991, and March 1992 show no significant change in coal conversion in the tests performed in January 1993.

PARTICIPANTS PROGRAM STATUS

PARTICIPANTS PROGRAM

The following items were accomplished in the fourteenth quarter of this contract.

Phase II

The final report for the University of Pittsburgh project was issued. The CONSOL evaluation and the Pitt Executive Summary are included herein. Pitt evaluated UV Resonance Raman Spectroscopy for analysis of coal liquids. This completes Phase II.

Phase III

A statement of work was prepared for a project with the National Institute for Petroleum and Energy Research (NIPER) to conduct inspection tests on HRI net product oils. The proposed statement of work and budget were approved by DOE. The subcontract was accepted by NIPER. The sample designated for testing (net product from HRI Run CC-15) was shipped directly from HRI to NIPER. Preliminary distillation of the sample has shown that it contains <0.4 wt% of the 650 °F$^+$ fraction.

Statements of work were approved by DOE for additional research with SRI International for analysis by field ionization mass spectrometry (FIMS) and the University of Utah for CP/MAS ^{13}C-NMR analyses. These methods were explored in Phases I and II, respectively, and found to provide considerable information about the process-derived samples. Subcontracts were subsequently placed with SRI International and the University of Utah. Samples for SRI and Utah were chosen to contain considerable overlap. Both sample sets include samples from HRI Run CC-15. It is intended that the application of these methods to this set of samples will maximize the information available about the process. Analytical and processing information for the samples sets are being assembled for transmittal to the two research groups.

A statement of work for a project with the University of Pittsburgh for measurement of hydrogen donor ability of resids was approved by DOE and a subcontract was initiated. Samples were chosen and shipped. Analytical and processing information for the samples set are being assembled for transmittal to the University of Pittsburgh.

A visit was made to the Pennsylvania State University to clarify the proposed work plan. A subsequently revised statement of work for 2-D high performance liquid chromatography (HPLC) and HPLC/mass spectrometry (MS) analysis of whole process oils was submitted for DOE approval. Samples for the Penn State program have been set aside for shipment pending approval.

A statement of work was drafted for a subcontract with the University of Delaware to explore resid reactivity measurements using the University's short time batch reactor (STBR).

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

INTRODUCTION

Under subcontract from CONSOL Inc. (U.S. DOE Contract No. DE-AC22-89PC89883), the University of Pittsburgh studied the use of ultraviolet resonance Raman (UVRR) spectroscopy for the characterization of coal liquefaction resids. The full report authored by the University of Pittsburgh researchers was issued.[22] 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 suggests that with further development the UVRR spectroscopy method may prove useful for the examination of the aromatic and unsaturated species in distillation resid materials derived from direct coal liquefaction. The technique, which was previously used for the examination of polycyclic aromatic hydrocarbons (PAH) in bio-medical materials, petroleum, and polymer systems, was applied to the tetrahydrofuran (THF)-soluble portion of six 850 °F$^+$ distillation resids. The results of this study indicate that the UVRR method may, with additional development, become a useful tool for the analysis of the PAHs in coal-derived materials.

PROGRAM DESCRIPTION

This report describes the work performed at the University of Pittsburgh 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 Pittsburgh used UV resonance Raman spectroscopy with a continuous wave (CW) laser source for the examination of the tetrahydrofuran (THF)-soluble portion of six $850°F^+$ distillation resids. The samples were produced at the Wilsonville pilot plant. Samples were taken from two locations: between the reactors, and after the second-stage reactor. 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 UVRR experiments utilizing the CW UV laser are described on pages 8 through 9 of the full report.[22]

PARTICIPANT'S MAJOR FINDINGS

The following principal observations for the application of UVRR spectroscopy to coal liquefaction materials were reported by the University of Pittsburgh. An expanded discussion can be found in the full report,[22] pages 10 through 13.

The THF-soluble samples were resolubilized in THF and examined. These same samples were extracted with acetonitrile and examined as solutions. The acetonitrile-extraction residues were solubilized in THF and also examined. It was found that the Raman spectrum of the material extracted into the acetonitrile fraction was different than that of the whole samples and contains species that absorb less strongly than the original samples. It was possible to distinguish differences in the spectra of the THF-soluble and acetonitrile-soluble portion of each sample. In addition, the acetonitrile-extraction residues (resolubilized in THF) have a larger bandwidth for the 1630 cm^{-1} peak and the shoulder at 1560 cm^{-1} is absent. This is especially true for the Run 257 second-stage product, the Run 260 second-stage product, and the Run 261 interstage sample. There was, however, little sample-to-sample difference evident among the THF-soluble or acetonitrile-soluble portions of the samples. The broad peaks evident in all the spectra indicate that numerous species are adsorbing in the same region.

In this study it was found that the solid resid samples could be examined without solubilization. It was found, however, that the solid samples must be spun under the laser light to prevent localized heating. Further study with the solid samples was not pursued under this contract.

CONSOL EVALUATION

In this study, a brief exploration of the UVRR spectroscopy technique was made with direct coal liquefaction-derived materials. It was found that the materials can be examined in the solid state; however, the parameters of measurement were not fully explored in this study. Neither identification and quantification of the species present in the samples, nor speciation by aromatic ring conjugation was accomplished. Higher resolution spectra would be required to accomplish either. In addition, a complete library of reference spectra constructed with model compounds would be required to thoroughly complete this task. It is believed that the ease of examining samples as solids will be advantageous for future work.

The Raman spectrometer used in these studies costs on the order of $200,000. It is not, presently, commercially available equipment. The time required to produce a single spectrum is about five minutes.

FURTHER DEVELOPMENT

The UVRR spectroscopy technique was explored in this project. A number of avenues for further research are suggested based on the major findings presented here. 1) It was found that solid coal-derived resid materials can be examined by the UVRR technique without solubilization. This would be the preferred method to use in any future work with resids. 2) The use of the next generation of instrumentation, which is becoming commercially available and has higher resolution, would be advantageous in determining the species present in the coal-derived materials. The author recommends the following techniques to obtain higher resolution with the present instrumentation 1) "Raman hole burning", 2) "saturation" techniques and 3) collection of spectra at low temperature. Additionally, the author specifies the need to assemble a reference library of Raman spectra from suitable model compounds before molecular speciation can be routinely accomplished with complex mixtures such as coal-derived resids.

PARTICIPANT'S STATEMENT OF WORK

UV Resonance Raman Spectroscopy (UVRRS) is a technique which has been used for the investigation of bio-medical materials, petroleum, and polymers. It also has been used to examine several coal-derived liquids. It has not, however, been demonstrated for its ability to answer questions pertaining to the chemistry of coal conversion. The UVRRS technique has the potential to speciate and quantify the various conjugated aromatic ring structures in coal liquids. This information, not readily obtainable by other routes, should be of value for understanding factors affecting resid properties and reactivity. As such, it fits well within the scope of the participants program.

The application of UVRRS to a set of six samples will allow a demonstration of the value of this technique for the examination, speciation, and quantitation of the polyaromatic hydrocarbon structures in coal liquefaction-derived resids. These samples have been selected (see attached list) so that the utility of UVRRS for characterizing liquefaction resids can be evaluated. The samples will be supplied to the University of Pittsburgh with the following information, as available: elemental analyses, ash content, ash elemental analysis, phenolic OH concentration, calorific value, hydrogen classes by ^{1}H-NMR, and the full history of the sample (plant, process conditions, age, and storage conditions). The six samples are tetrahydrofuran (THF)-soluble, non-distillable residual materials. Sample size will be at least 10g. The samples will be brittle pitch-like materials that will be supplied as approximately minus 60 mesh powder.

The samples will be solubilized in a good solvent for coal liquids (THF or pyridine), cast as a film on a support which can be moved past the focal point of the laser to prevent localized heating, then analyzed by the UVRRS technique.

The six samples will be characterized by groups of differing ring conjugation (separately 2, 3, and 4 conjugated-ring groups, and possibly 5 and 6 conjugated-ring groups). Speciation of compounds within these groups also will be attempted.

UNIVERSITY OF PITTSBURGH EXECUTIVE SUMMARY

We demonstrated the utility of UV resonance Raman spectroscopy to study aromatic and unsaturated species in coal liquid residuals. The samples examined were obtained from different coal liquefaction runs utilizing different coals. Some of the differences involved either two stages of catalytic hydrogenation or only one stage.

UV resonance Raman spectroscopy is a new technique which is being developed for uses in analytical chemistry and biochemistry as well as for fundamental physical chemical studies. It involves exciting samples with UV light and examining the frequencies and intensities of the Raman scattered light. Polycyclic aromatic hydrocarbons (PAH) are intense UV Raman scatters. We have demonstrated that it is easy to study them at low concentrations and in complex environments. Previous studies demonstrated we could monitor PAH in coal-derived liquids. In this study we examined coal residuals.

We utilized a new continuous wave (CW) laser source which we demonstrated had important advantages for these types of studies. We demonstrated that we could examine the solid residuals using this laser, and that the only requirement is that we must spin the sample to distribute the sample heating. We also examined the residuals dissolved in tetrahydrofuran (THF), a solvent in which they are completely soluble. We also extracted the residuals with acetonitrile and compared the Raman spectra of the acetonitrile solubles, to the complete residuals in THF solution and the acetonitrile extracted solid residual dissolved in THF. We see differences between the spectra of the different samples.

Although we detect differences, we do not have sufficient information to correlate the spectral differences to particular components. UV resonance Raman spectroscopy is a new technique which does not as yet have a large library of reference compounds. The incisive use of this technique for these kinds of studies will require measuring extracts of the residuals and the creation of a library of reference compounds.

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.[18,20]

Section 5

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TABLE 1

HRI CTSL RUN CC-16 OPERATING SUMMARY

Coal: Illinois 6 HRI No. 6061
Catalyst: AKZO AO-60 HRI No. 6043

Period No.	1	2	3	4	5	6
Date, 1992 (Start of Period)	12/2	12/03	12/04	12/05	12/06	12/07
Hr of Run (End of Period)	24	48	72	96	120	144
Stg 2 Cat Age, lb Dry Coal/lb Cat	13	33	54	74	94	114
1st Stg Temp, °F	707	749	751	750	751	749
2nd Stg Temp, °F	741	799	800	799	800	801
Unit Back Pressure, psig	2476	2497	2493	2493	2495	2492
Space Vel, lb Coal/hr/ft^3 (Stg 2) Cat	30.0	45.8	45.8	45.1	45.6	45.3
<u>wt % Dry Coal</u>						
PFL Recycle	368.7	150.1	122.9	137.5	150.1	150.1
PFL to Buffer to Stg 1	41.0	16.0	18.9	19.0	15.4	13.8
PFL to Buffer to Stg 2	41.2	14.0	16.8	20.6	18.5	18.4
Make-up Oil	0.0	0.0	27.2	12.6	0.0	0.0
Material Balance, % (Gross)	88.83	95.11	101.22	99.06	100.59	99.43
<u>Estimated Normalized Yields, wt % Dry Fresh Feed</u>						
C_1-C_3 in Gases		5.79	5.41	5.54	5.91	5.76
C_4-C_7 in Gases		4.75	3.99	3.81	4.10	4.17
IBP-390 °F in Liquids		17.76	17.56	14.17	12.54	12.58
390-500 °F in Liquids		13.78	16.06	10.83	8.94	8.76
500-650 °F in Liquids		30.39	37.87	25.34	21.75	21.21
650-850 °F in Liquids		1.38	-0.93	7.81	11.88	14.12
850-975 °F in Liquids		-0.06	-1.05	2.52	3.52	4.32
Toluene Sol 975 °F$^+$ Oil		-0.07	-3.07	2.19	5.73	7.10
Toluene Insol 975 °F$^+$ Oil		-0.01	0.00	0.00	0.04	0.06
Unconverted Coal		7.87	6.96	8.03	7.11	7.04
Ash		10.61	10.61	10.61	10.61	10.61
Water		10.93	9.56	11.48	10.03	6.34
CO		0.09	0.14	0.13	0.10	0.10
CO_2		0.04	0.03	0.11	0.07	0.04
NH_3		1.35	1.46	1.36	1.30	1.28
H_2S		3.11	3.03	2.93	2.95	2.90
Total (100 + H_2 Reacted)		107.70	107.65	106.85	106.57	106.40
<u>Process Performance</u>						
C_4-975 °F Dist, wt % MAF Coal		76.1	82.2	72.1	70.2	72.9
975 °F$^+$ Conversion, wt % MAF		91.3	95.6	88.6	85.6	84.1
Coal Conversion, wt % MAF		91.2	92.2	91.0	92.0	92.1
HDS, wt %		81.1	78.9	76.5	76.9	75.5
HDN, wt %		90.5	97.8	91.3	87.0	86.0

Source: Reference 3

TABLE 1 (Cont'd)

HRI CTSL RUN CC-16 OPERATING SUMMARY

Coal: Illinois 6 HRI No. 6081
Catalyst: AKZO AO-60 HRI No. 6043

Period No.	7	8	9	10	11	12	13
Date, 1992 (Start of Period)	12/08	12/09	12/10	12/11	12/12	12/13	12/14
Hr of Run (End of Period)	168	192	216	240	264	288	312
Stg 2 Cat Age, lb Dry Coal/lb Cat	134	154	174	194	214	234	253
1st Stg Temp, °F	750	752	752	768	775	777	777
2nd Stg Temp, °F	799	799	800	807	809	811	810
Unit Back Pressure, psig	2496	2504	2504	2502	2504	2502	2496
Space Vel, lb Coal/hr/ft^3 (Stg 2) Cat	45.6	46.2	46.2	44.4	44.9	45.8	43.8
wt % Dry Coal							
PFL Recycle	150.1	150.1	148.4	109.9	109.9	107.3	99.0
PFL to Buffer to Stg 1	12.4	12.1	14.5	16.4	14.8	16.5	14.6
PFL to Buffer to Stg 2	19.5	35.4	16.5	16.1	14.6	15.6	14.7
Make-up Oil	0.0	0.0	0.0	0.0	0.0	2.6	10.9
Material Balance, % (Gross)	99.35	97.72	98.47	95.54	99.27	96.53	98.22
Estimated Normalized Yields, wt % Dry Fresh Feed							
C_1-C_3 in Gases	5.34	5.65	5.81		8.27	8.12	7.89
C_4-C_7 in Gases	3.42	3.91	3.78		4.06	4.18	4.14
IBP-390 °F in Liquids	13.03	12.87	13.54		17.74	18.11	18.06
390-500 °F in Liquids	8.95	8.80	9.15		11.01	11.09	11.16
500-650 °F in Liquids	18.21	18.40	19.13		22.79	22.72	22.85
650-850 °F in Liquids	13.68	12.78	12.56		7.93	7.73	9.70
850-975 °F in Liquids	3.97	3.73	3.77		1.75	1.69	2.23
Toluene Sol 975 °F$^+$ Oil	7.51	7.37	7.23		3.35	2.98	3.94
Toluene Insol 975 °F$^+$ Oil	0.08	0.08	0.13		0.05	0.09	0.23
Unconverted Coal	7.81	6.89	6.67		5.80	5.88	5.24
Ash	10.61	10.61	10.61		10.61	10.61	10.61
Water	9.23	10.88	9.67		9.22	9.47	6.43
CO	0.14	0.12	0.08		0.17	0.10	0.17
CO_2	0.04	0.04	0.04		0.04	0.04	0.04
NH_3	1.23	1.24	1.24		1.32	1.33	1.33
H_2S	2.92	2.92	2.89		2.78	2.81	2.84
Total (100 + H_2 Reacted)	106.20	106.30	106.29		106.89	106.95	106.85
Process Performance							
C_4-975 °F Dist, wt % MAF Coal	68.5	67.7	69.3		73.0	73.3	76.2
975 °F$^+$ Conversion, wt % MAF	82.8	84.0	84.3		89.7	90.0	89.5
Coal Conversion, wt % MAF	91.3	92.3	92.5		93.5	93.4	94.1
HDS, wt %	76.1	76.1	75.3		72.4	73.3	74.0
HDN, wt %	82.6	83.0	82.9		88.3	88.8	88.8

Source: Reference 3

TABLE 2

ANALYSES OF BURNING STAR 2 COAL
HRI CTSL Run CC-16

HRI Sample No. 6081 (LO 6153)	Results	
	HRI(a)	CONSOL (b)
Moisture Content, wt %	2.97	1.89
Volatile Matter, wt % (MF)	39.05	39.38
Fixed Carbon, wt % (MF)	50.34	49.26
Ash Content, wt % (MF)	10.61	11.36
Ultimate Analysis, wt % (MF)		
Carbon	69.48	71.10
Hydrogen	4.39	4.82
Sulfur	3.68	3.61
Nitrogen	1.25	1.30
Chlorine		0.079
Oxygen (by difference)	10.59	7.73
Sulfur, Total		
Sulfur, Pyritic		1.77
Sulfur, Sulfate		0.06
Sulfur, Organic (by Difference)		1.78
Elemental, wt % of Ash		
Na_2O		0.48
K_2O		1.82
CaO		8.03
MgO		0.85
Fe_2O_3		21.79
TiO_2		0.86
P_2O_5		0.04
SiO_2		43.96
Al_2O_3		17.78
SO_3		3.90
Unaccounted		0.49
Calorific Value, Btu/lb dry basis		12468

(a) Analyses reported by HRI in Reference 1a.
(b) Analyses performed by CONSOL R&D

TABLE 3

ANALYSES OF START-UP/MAKE-UP SOLVENT
HRI CTSL Run CC-16

HRI No.	L-786
API Gravity	2.0
Elemental Analysis, wt %	
Carbon	89.95
Hydrogen	8.69
Sulfur	0.143
Nitrogen	0.55
ASTM D-1160 Distillation, wt %	
IBP, °F	537°C
IBP-650 °F	9.15
650-850 °F	46.42
850-975 °F	14.34
975 °F+	29.95

Note: Analyses reported by HRI in Reference 1.

TABLE 4

ANALYSIS OF SELECTED PFC SAMPLES FROM HRI RUN CC-16

Analysis	Results (a)	
	Period 5C, LO-6168	Period 13C, LO-6170
Ultimate Analysis, wt % Ash-Free Basis, except as noted		
Carbon	87.94	89.12
Hydrogen	8.31	7.72
Nitrogen	0.57	0.90
Chlorine	0.161	0.214
Oxygen (by diff.) (SO_3-free ash basis)	-0.84 (1.63)	-3.35 (-0.72)
Sulfur	3.86	5.40
Ash, wt % As-Determined (SO_3-free)	32.17 (29.70)	40.17 (37.54)
Elemental, wt % of Ash		
Na_2O	0.48	0.50
K_2O	1.77	1.79
CaO	5.96	5.38
MgO	0.90	0.88
Fe_2O_3	19.49	20.30
TiO_2	0.76	0.70
P_2O_5	0.06	0.04
SiO_2	44.15	45.37
Al_2O_3	18.17	18.28
SO_3	7.67	6.54
Unaccounted	0.59	0.22

(a) Analyses performed by CONSOL R&D.

TABLE 5

ELEMENTAL ANALYSES OF SELECTED LIQUID SAMPLES FROM HRI RUN CC-16

Sample Type	PFL	PFL	PFL	ASOH/SOH(a)	ASOH/SOH(a)	ASOH	ASOH	SOH	SOH
Period	4C	5C	13C	5C	13C	5C	13C	5C	13C
Sample No.	LO-6156	LO-6157	LO-6161	-	-	LO-6165	LO-6167	LO-6162	LO-6164
Ultimate Analysis, wt % As-Determined									
Carbon	89.59	90.01	89.14	86.59	86.88	86.83	87.21	83.72	83.95
Hydrogen	9.91	9.87	8.85	12.58	12.25	12.05	11.53	13.23	13.10
Nitrogen	0.31	0.30	0.35	0.12	0.09	0.17	0.17	0.09	0.21
Chlorine	ND	<0.010	<0.010	<0.010	<0.010	0.017	<0.010	0.012	<0.010
Sulfur	<0.03	<0.03	0.06	<0.03	<0.03	<0.03	<0.03	0.05	0.04
Oxygen (by difference)	0.19	-0.18	1.60	0.71	0.78	0.93	1.09	2.90	2.70

Note: Analyses performed by CONSOL R&D, samples were assumed to be free of moisture and ash
ND = Not Determined

(a) Blend of the two components in the ratio produced in the designated operating period: 33.9% SOH, 66.1% ASOH in Period 5; 38.1% SOH, 61.9% ASOH in Period 13.

TABLE 6

DISTILLATION AND THF PRESSURE FILTRATION RESULTS
HRI CTSL RUN CC-16

	wt % of Sample	
Period	**850 °F$^-$ Dist.**	**850 °F$^+$ Resid**
<u>Pressure-Filter Liquids</u>		
0C	87.4	11.5
4C	63.6	35.4
5C	61.1	38.5
8C	56.8	43.1
9C	59.0	40.7
12C	58.7	41.0
13C	58.2	41.3
Make-Up Oil	69.8	29.6

	wt % of Sample		
Period	**THF-Solubles**	**IOM**	**Ash**
<u>Pressure-Filter Cake</u>			
5C	49.8	19.1	31.1
9C	50.5	18.5	31.0
13C	43.6	17.9	38.5

TABLE 7

SOLUBLE FRACTIONATION ANALYSIS OF 850 °F$^+$ PFL RESIDS AND PFC EXTRACTS
HRI CTSL RUN CC-16

Period	wt % of 850 °F$^+$ Resid		
	Oils	Asphaltenes	Preasphaltenes
<u>Pressure-Filter Liquids</u>			
0C	92.7	5.5	1.7
4C	86.9	10.2	3.0
5C	86.7	9.9	3.4
8C	79.7	12.7	7.5
9C	76.5	14.7	8.8
12C	76.5	15.6	7.9
13C	75.5	15.9	8.6
Make-Up Oil	69.2	19.7	11.1
<u>THF Extract from Pressure-Filter Cake</u>			
5C	83.3	10.4	6.3
9C	56.2*	11.6*	32.2*
13C	71.7	12.8	15.5

*Average values from two runs.

TABLE 8

PROTON DISTRIBUTION OF WHOLE SAMPLES HRI CTSL RUN CC-16

Period	Sample No. Lo-	Proton Distribution, %						
		Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
Pressure-Filter Liquid								
OC	6155	2.9	2.9	8.7	7.2	18.7	37.9	21.8
4C	6156	8.9	4.0	12.8	7.5	20.0	28.7	18.1
5C	6157	9.5	3.8	13.8	7.9	20.7	27.5	16.8
8C	6158	9.9	4.5	14.1	8.3	20.7	26.2	16.3
9C	6159	10.4	4.4	14.9	7.9	20.4	25.7	16.4
12C	6160	13.1	5.4	14.9	8.4	18.8	23.5	15.9
13C	6161	12.9	5.6	14.5	8.4	18.6	24.0	16.1
Separator Overheads								
5C	6162	2.0	2.7	4.0	4.7	24.6	34.1	27.8
9C	6163	2.4	2.7	4.8	5.4	28.3	28.3	28.0
13C	6164	2.7	3.0	5.2	5.7	27.5	30.1	25.9
Atmospheric Still Bottoms								
5C	6165	2.0	4.5	7.7	7.0	24.8	30.5	23.4
9C	6166	2.7	5.2	8.7	7.9	24.5	28.9	22.2
13C	6167	3.9	5.8	10.4	8.6	23.9	27.5	20.0
Start-up/Make-up Oil								
L-786	6154	9.2	4.5	12.3	7.7	18.6	29.4	18.2
Pressure-Filter Cake (a)								
5C	6168	11.6	2.8	14.4	7.7	22.1	27.0	14.5
9C	6169	13.3	4.0	15.4	7.9	20.9	24.5	14.1
13C	6170	16.6	3.4	16.1	8.1	20.2	23.2	12.4

(a) Filtered pyridine extract, run in 99.96% d_5-pyridine.

TABLE 9

PROTON DISTRIBUTION OF 850 °F$^-$ DISTILLATES HRI CTSL RUN CC-16

Period	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
Pressure-Filter Liquid							
OC	2.1	3.4	8.8	7.2	18.6	39.0	20.9
4C	6.5	3.7	12.3	7.6	22.1	31.2	16.7
5C	7.1	3.9	12.9	7.8	22.0	29.5	16.8
8C	7.2	4.4	13.3	8.0	22.6	28.3	16.1
9C	7.1	4.5	12.9	7.7	21.9	28.8	17.1
12C	9.9	4.5	13.5	7.6	21.6	26.4	16.5
13C	9.6	5.0	13.3	8.0	20.7	27.5	15.9
Start-up/Make-up Oil							
L-786	6.8	4.3	11.5	7.7	20.6	31.7	17.3

TABLE 10

PROTON DISTRIBUTION OF 850 °F$^+$ RESIDS HRI CTSL RUN CC-16

Period	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
Pressure-Filter Liquid							
OC	8.4	3.1	17.7	9.2	21.8	26.3	13.4
4C	14.6	3.6	17.8	8.5	20.5	23.0	12.1
5C	15.2	4.1	17.8	8.6	20.0	22.4	11.8
8C	15.4	4.9	18.1	9.0	19.4	21.3	12.0
9C	15.5	6.2	17.6	9.2	19.0	20.7	11.8
12C	19.7	6.3	18.7	9.3	17.7	18.1	10.2
13C	20.7	6.3	18.6	9.4	17.6	17.9	9.5
Start-up/Make-up Oil							
L-786	17.9	6.7	18.5	8.9	17.0	20.3	10.6

TABLE 11

PHENOLIC -OH CONCENTRATIONS OF WHOLE SAMPLES, DISTILLATES, THF-SOLUBLE RESIDS
HRI CTSL RUN CC-16

Sample Type	Period	Phenolic -OH Concentration, meq/g		
		Whole Samples	850 °F$^-$ Dist	850 °F$^+$ Resid
Pressure Filter Liquids (PFL)	0C	0.04	0.03	0.17
	4C	0.12	0.06	0.24
	5C	0.14	0.06	0.24
	8C	0.23	0.08	0.43
	9C	0.28	0.09	0.51
	12C	0.28	0.11	0.55
	13C	0.30	0.12	0.56
Separation Overheads (SOH)	5C	0.05		
	9C	0.06		
	13C	0.08		
Atmospheric Still Overheads (ASOH)	5C	0.08		
	9C	0.12		
	13C	0.14		
Start-up/Make-up Oil	L-786	0.29	0.14	0.70
		THF-Sols		
Pressure Filter Cake (PFC)	5C	0.17		
	9C	0.33		
	13C	0.41		

TABLE 12

MICROAUTOCLAVE TESTS WITH WHOLE SAMPLES

	THF Coal Conversion, wt % MAF
Pressure-Filter Liquids	
0C	57.6
4C	77.1
5C	79.8
8C	84.2
9C	83.7
12C	82.3
13C	85.3
Make-up Oil	80.5

TABLE 13

COMPARISON OF CONDITION 1 SAMPLES FROM HRI RUN CC-16 WITH RUNS WITH Ni/Mo CATALYSTS

Run	I-13	I-16	I-17	I-18	CC-16
Catalyst	Am 1C 1/16" Extr.	Am 1C 1/32" Extr.	RCM-4 1/20" Sph.	Sh 317 1/32" Extr.	EXP-AO-60 1/16" Extr.
Whole PFL					
Aromaticity (a), % of Protons	16.9	13.3	14.3	13.8	14.8
Hydroaromaticity (b), % of Protons	20.5	22.6	22.0	21.8	20.4
Paraffinicity (c), % of Protons	39.5	42.7	41.3	43.1	42.1
Phenolic -OH Concentration, meq/g Sample (c = calculated from components, a = actual)	0.32c	0.24c	0.29c	0.27c	0.26c, 0.28a
Concentration of 850 °F$^+$ Resid, wt %	46.5	39.5	44.8	43.4	40.7
Donor Solvent Quality, % MAF Coal Conversion in Mod-EQ Test	83.4	81.7	81.0	81.8	83.7
PFL 850 °F$^-$ Distillate					
Aromaticity (a), % of Protons	12.9	10.2	11.1	10.4	11.6
Hydroaromaticity (b), % of Protons	22.3	23.4	23.6	24.1	21.9
Paraffinicity (c), % of Protons	44.4	46.8	45.4	45.2	45.9
Phenolic -OH Concentration, meq/g Sample	0.11	0.07	0.07	0.07	0.09
Calculated Donor Solvent Quality (d), %	80.9	81.0	81.9	82.8	80.8
PFL 850 °F$^+$ Resid					
Aromaticity (a), % of Protons	22.7	19.3	20.0	19.8	21.7
Hydroaromaticity (b), % of Protons	19.8	20.7	20.0	20.8	19.0
Paraffinicity (c), % of Protons	28.5	32.9	33.0	31.4	32.5
Phenolic -OH Concentration, meq/g Sample	0.57	0.49	0.56	0.54	0.51
Oils, wt % of THF-Soluble 850 °F$^+$ Resid	77.8	77.1	71.4	75.7	76.5
Asphaltenes, wt % of THF-Soluble 850 °F$^+$ Resid	16.2	16.3	19.2	19.5	14.7
Preasphaltenes, wt % of THF-Soluble 850 °F$^+$ Resid	6.0	6.6	9.4	4.8	8.8

(a) Defined as % condensed + uncondensed aromatic protons.
(b) Defined as % cyclic beta protons.
(c) Defined as % alkyl beta + gamma protons.
(d) Calculated from the proton distribution obtained from the NMR spectrum.

TABLE 14

COMPARISON OF CONDITION 2 SAMPLES FROM HRI RUN CC-16 WITH RUNS WITH Ni/Mo CATALYSTS

Run	I-13	I-16	I-17	I-18	CC-16
Catalyst	Am 1C 1/16" Extr.	Am 1C 1/32" Extr.	RCM-4 1/20" Sph.	Sh 317 1/32" Extr.	EXP-AO-60 1/16" Extr.
Whole PFL					
Aromaticity (a), % of Protons	20.4	17.6	17.7	17.4	18.5
Hydroaromaticity (b), % of Protons	19.9	20.3	21.1	21.0	18.6
Paraffinicity (c), % of Protons	33.9	38.8	39.2	37.2	40.1
Phenolic -OH Concentration, meq/g Sample (c = calculated from components, a = actual)	0.46c	0.27c	0.27c	0.32c	0.30c, 0.30a
Concentration of 850 °F$^+$ Resid, wt %	46.7	43.3	43.5	43.6	41.3
Donor Solvent Quality, % MAF Coal Conversion in Mod-EQ Test	79.9	82.3	82.2	80.8	85.3
PFL 850 °F$^-$ Distillate					
Aromaticity (a), % of Protons	15.6	14.0	13.5	13.0	14.6
Hydroaromaticity (b), % of Protons	21.7	21.9	22.3	22.9	20.7
Paraffinicity (c), % of Protons	39.9	41.6	42.5	42.5	43.4
Phenolic -OH Concentration, meq/g Sample	0.23	0.09	0.09	0.11	0.12
Calculated Donor Solvent Quality (d), %	84.1	83.0	82.6	83.2	80.5
PFL 850 °F$^+$ Resid					
Aromaticity (a), % of Protons	28.8	25.4	24.3	25.1	27.0
Hydroaromaticity (b), % of Protons	16.9	19.2	19.2	18.8	17.6
Paraffinicity (c), % of Protons	24.8	26.8	28.8	27.3	27.4
Phenolic -OH Concentration, meq/g Sample	0.73	0.51	0.51	0.59	0.56
Oils, wt % of THF-Soluble 850 °F$^+$ Resid	75.4	75.3	74.4	75.0	75.5
Asphaltenes, wt % of THF-Soluble 850 °F$^+$ Resid	18.7	18.6	18.9	18.4	15.9
Preasphaltenes, wt % of THF-Soluble 850 °F$^+$ Resid	5.9	6.2	6.7	6.6	8.6

(a) Defined as % condensed + uncondensed aromatic protons.
(b) Defined as % cyclic beta protons.
(c) Defined as % alkyl beta + gamma protons.
(d) Calculated from the proton distribution obtained from the NMR spectrum.

TABLE 15

ANALYSIS OF 1988 BATCH OF OLD BEN NO. 1 MINE, INDIANA V COAL

	Sample Date				
	11/88 (a)	4/90 (b)	3/91 (c)	3/92 (c)	1/93 (c)
Moisture, wt % as determined	8.67	8.24	7.69	7.09	6.96
Proximate, wt % dry basis					
Volatile Matter	41.24	41.17	41.29	41.62	40.97
Fixed Carbon	49.53	49.69	49.65	49.43	50.02
Oxidized Ash	9.23	9.14	9.06	8.95	9.01
Ultimate, wt % dry basis					
Carbon	71.35	71.91	71.11	71.22	72.03
Hydrogen	5.04	4.98	4.99	5.00	4.98
Nitrogen	1.43	1.49	1.38	1.44	1.54
Oxygen (diff.)	9.03	8.70	9.57	9.61	8.70
Sulfur, Total	3.87	3.78	3.85	3.73	3.74
Pyritic	1.59	1.04	1.15	1.08	1.13
Sulfate	0.10	0.57	0.66	0.63	0.70
Organic (diff.)	2.18	2.17	2.04	2.02	1.91
Chlorine	0.05	N/A	0.04	0.05	N/A
Oxidized Ash	9.23	9.14	9.06	8.95	9.01
Elemental, wt % oxidized ash					
Na_2O	0.44		0.55		0.52
K_2O	2.12		2.21		2.20
CaO	4.78		4.86		4.90
MgO	0.81		0.83		0.86
Fe_2O_3	26.94		27.32		27.56
TiO_2	0.89		0.92		0.92
P_2O_5	0.18		0.18		0.14
SiO_2	39.57		39.44		40.06
Al_2O_3	18.82		19.17		18.75
SO_3	3.12		3.30		2.89
Unaccounted	2.33		1.22		1.20
Calorific Value, dry (HHV), Btu/lb	13,154	12,799	12,788	12,745	12,908

(a) As-received sample
(b) Sample stored in plastic bucket
(c) Sample stored (from 4/90) in heat-sealed, nitrogen-purged, plastic bag.

TABLE 16

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

	Solvent		% MAF Conversion				
Test	Tetralin, wt %	1-Methyl-Naphthalene wt %	2/1/90	3/5/91	3/24/92	1/19/93	Avg
KIN	0	100	55.0	57.2	-	-	56.1
KIN	5	95	63.9	65.3	64.3	62.8 (b)	64.1
KIN	10	90	68.1	69.6	-	-	68.9
KIN	25	75	75.8	74.9	73.6	73.6	74.5
KIN	50	50	76.1	77.1	78.3	76.1	76.9
KIN	100	0	71.7	72.4	71.8	71.3	71.8
EQ	0	100	48.9	49.6	-	-	49.3
EQ	5	95	60.7	60.3	60.0	58.2 (b)	59.5
EQ	10	90	68.4	68.3	-	-	68.4
EQ	25	75	63.9 (a)	74.2	74.1	76.0	74.8
EQ	50	50	81.1	82.3	81.6	81.2	81.6
EQ	100	0	85.9	85.7	87.1	84.2	85.7
MOD-EQ	0	100	48.7	48.7	-	-	48.7
MOD-EQ	5	95	57.4	55.3	57.9	56.4	56.7
MOD-EQ	10	90	63.5	63.2	-	-	63.4
MOD-EQ	25	75	71.7	71.2	71.9	72.9	71.9
MOD-EQ	50	50	82.8	80.6	80.5	81.5	81.4
MOD-EQ	100	0	87.3	88.3	87.2	85.4	87.1
Avg of Common Tests	-	-	74.1 (c)	74.0	74.0	73.3	73.8

KIN = Kinetic Test: 12g solvent, 1.5g coal, 10 min, 750°F
EQ = Equilibrium Test: 10g solvent, 5g coal, 30 min, 750°F
MOD-EQ = Modified Equilibrium Test, 9g solvent, 6g coal, 30 min, 750°F

(a) This value suspect, excluded from average
(b) This value is an average of two test results
(c) This average obtained by substituting the value 74.8 for the data point foot-noted "a"

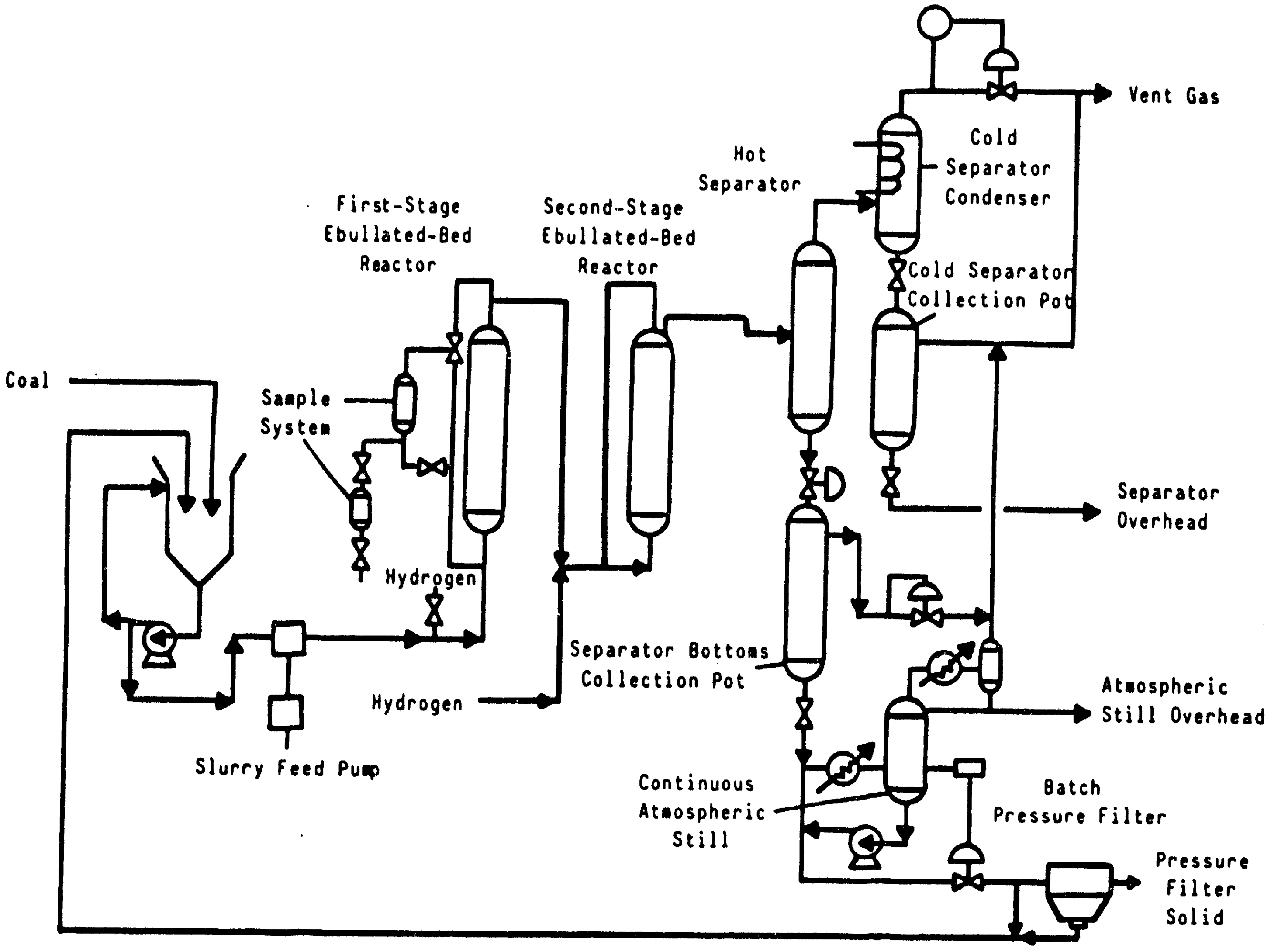


Figure 1. Ebullated-Bed Bench Unit 227.
Source: Reference 7

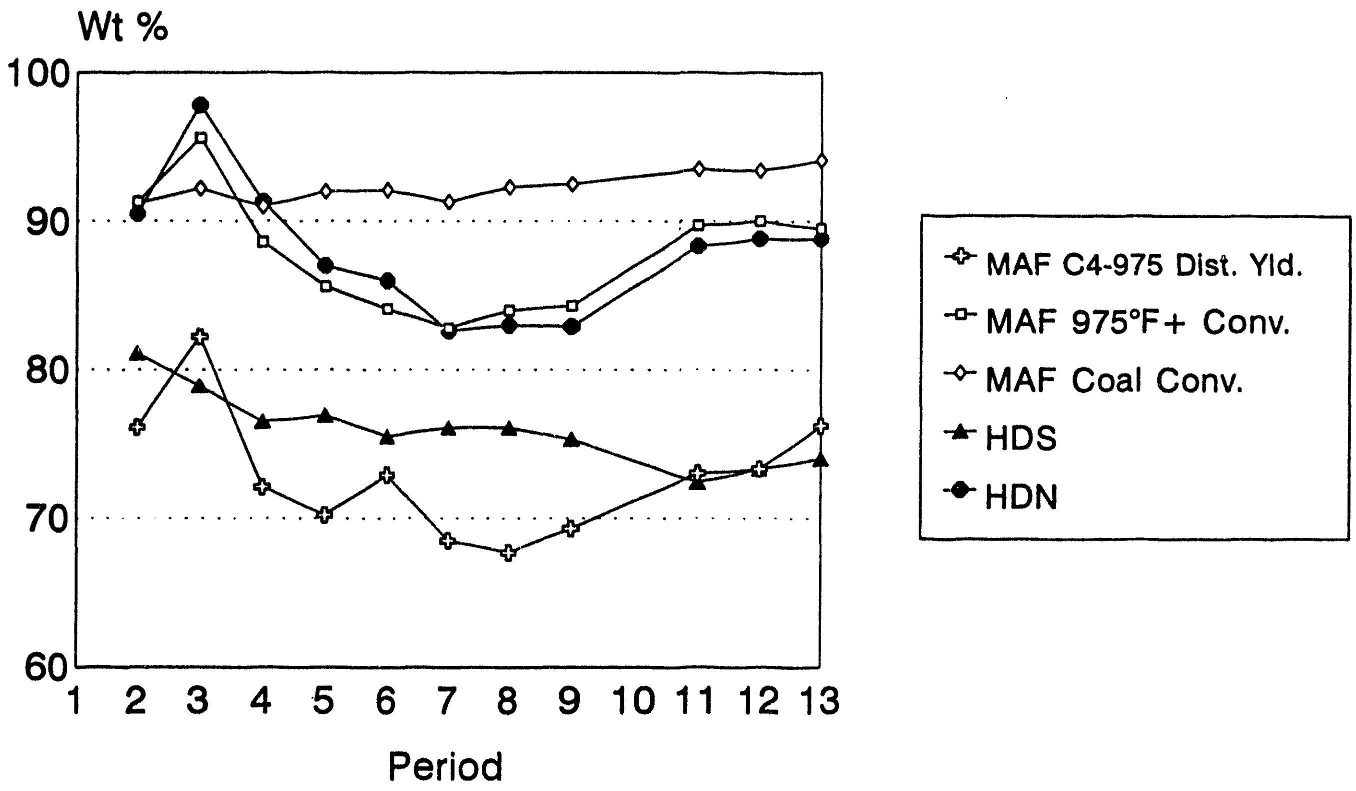


Figure 2. Run CC-16 Unit Performance - HRI Results.

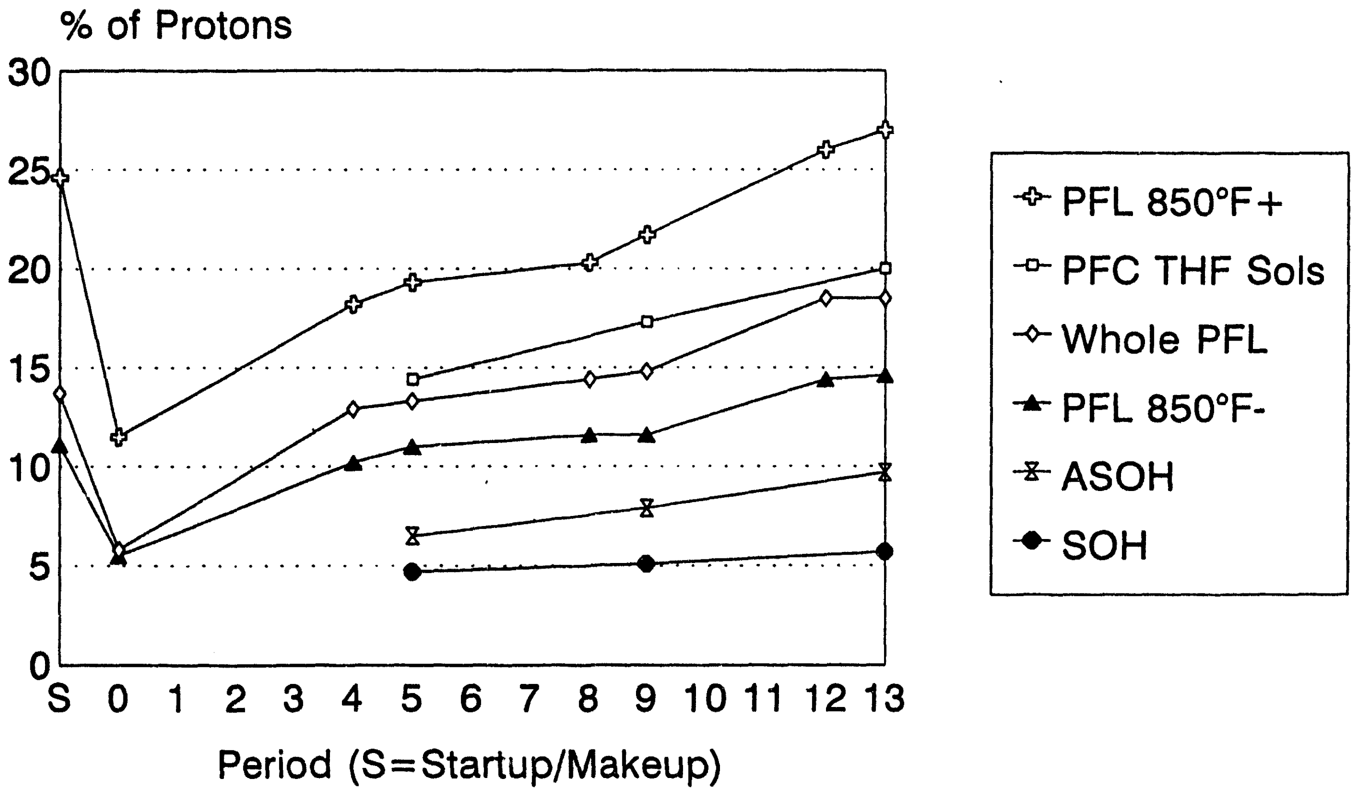


Figure 3. HRI Run CC-16 Process Stream Properties - Hydrogen Aromaticity.

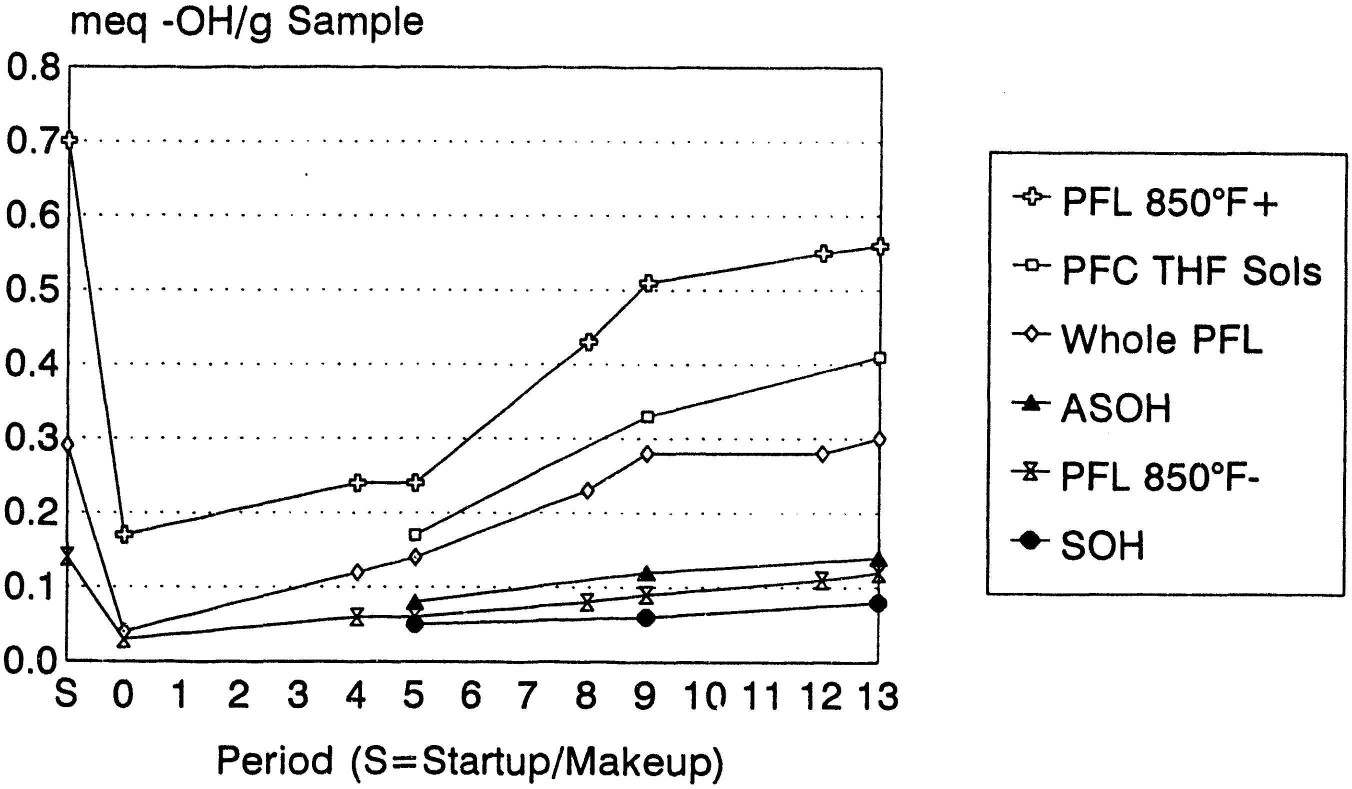


Figure 4. HRI Run CC-16 Process Stream Properties - Phenolic -OH Concentration.

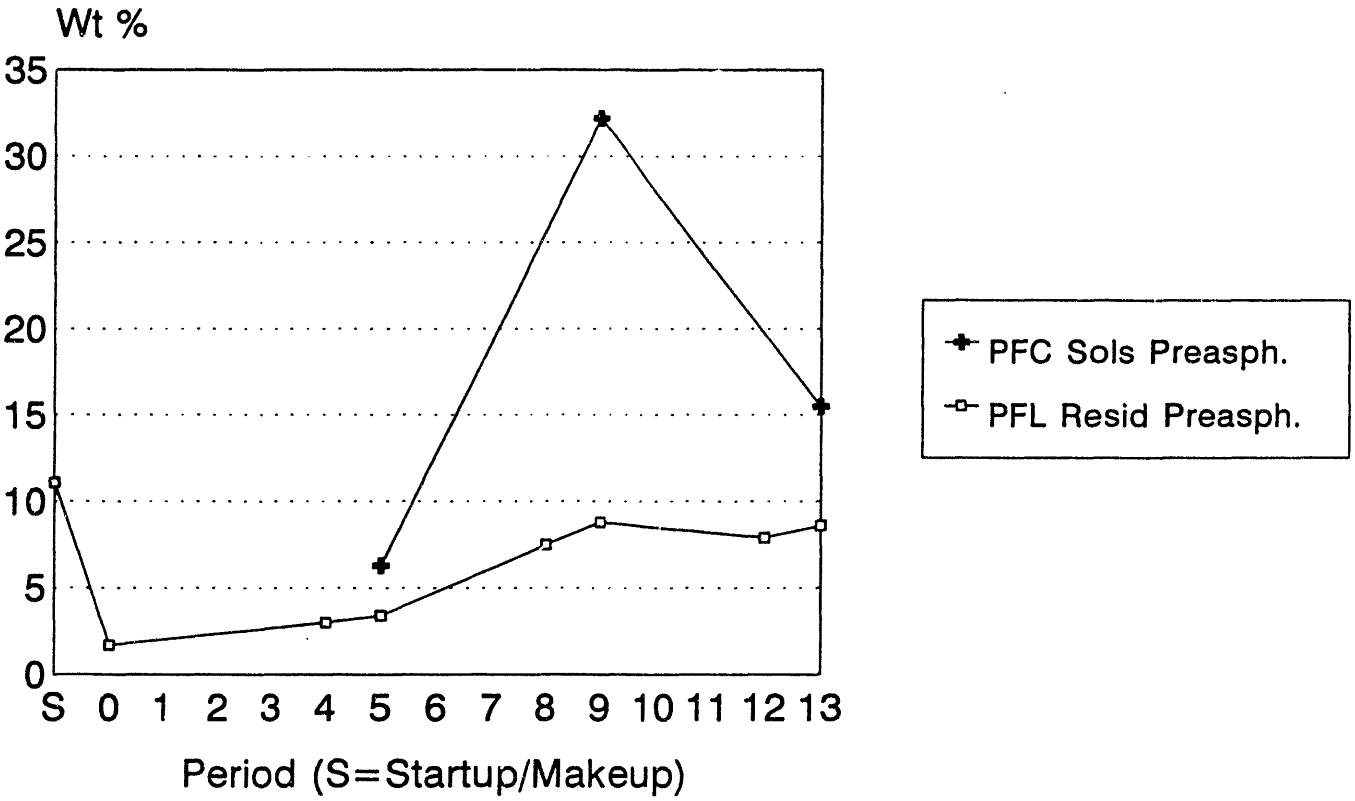
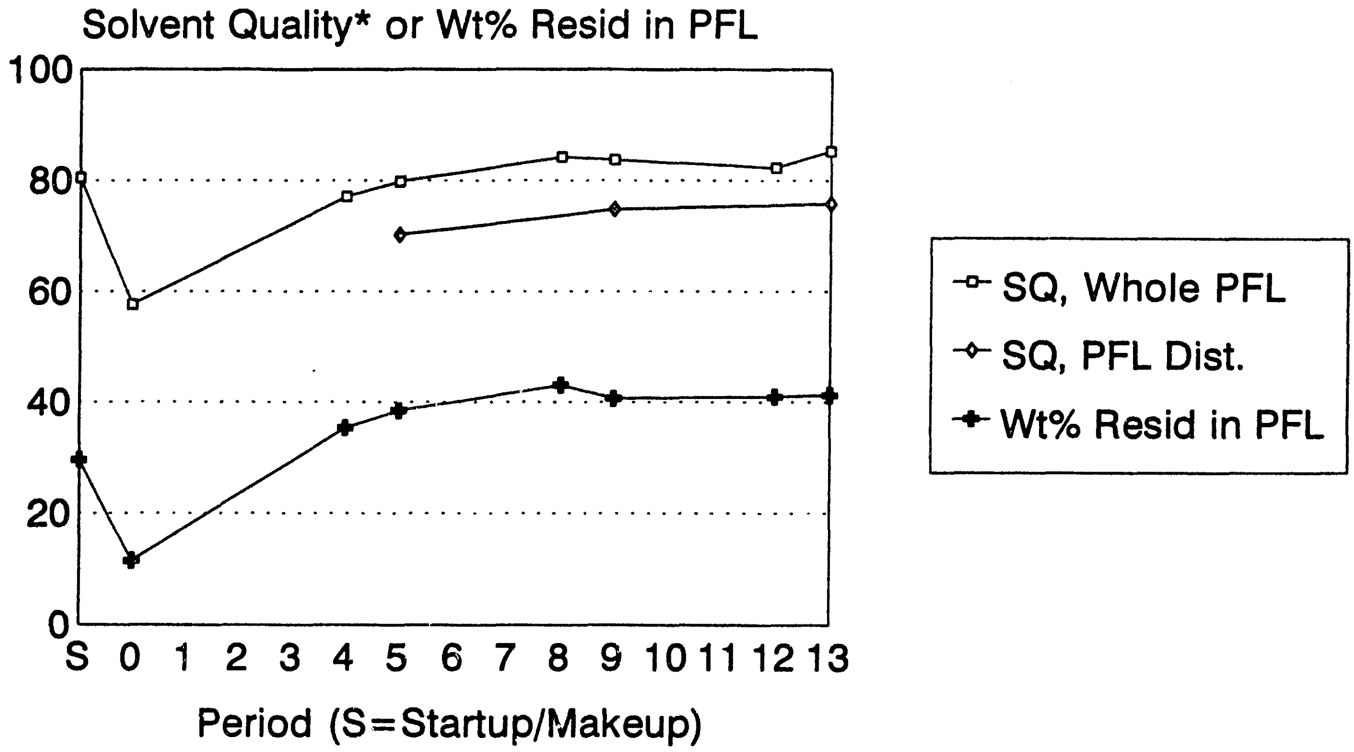


Figure 5. HRI Run CC-16 Process Stream Properties - Solubility Fractions of PFL 850 °F$^+$ Resid and PFC THF Solubles.



* Wt% Conversion of Standard Indiana V Coal at Mod-EQ Microautoclave Conditions

Figure 6. HRI Run CC-16 PFL Properties - Solvent Quality Effects of 850 °F^+ in Whole PFL.

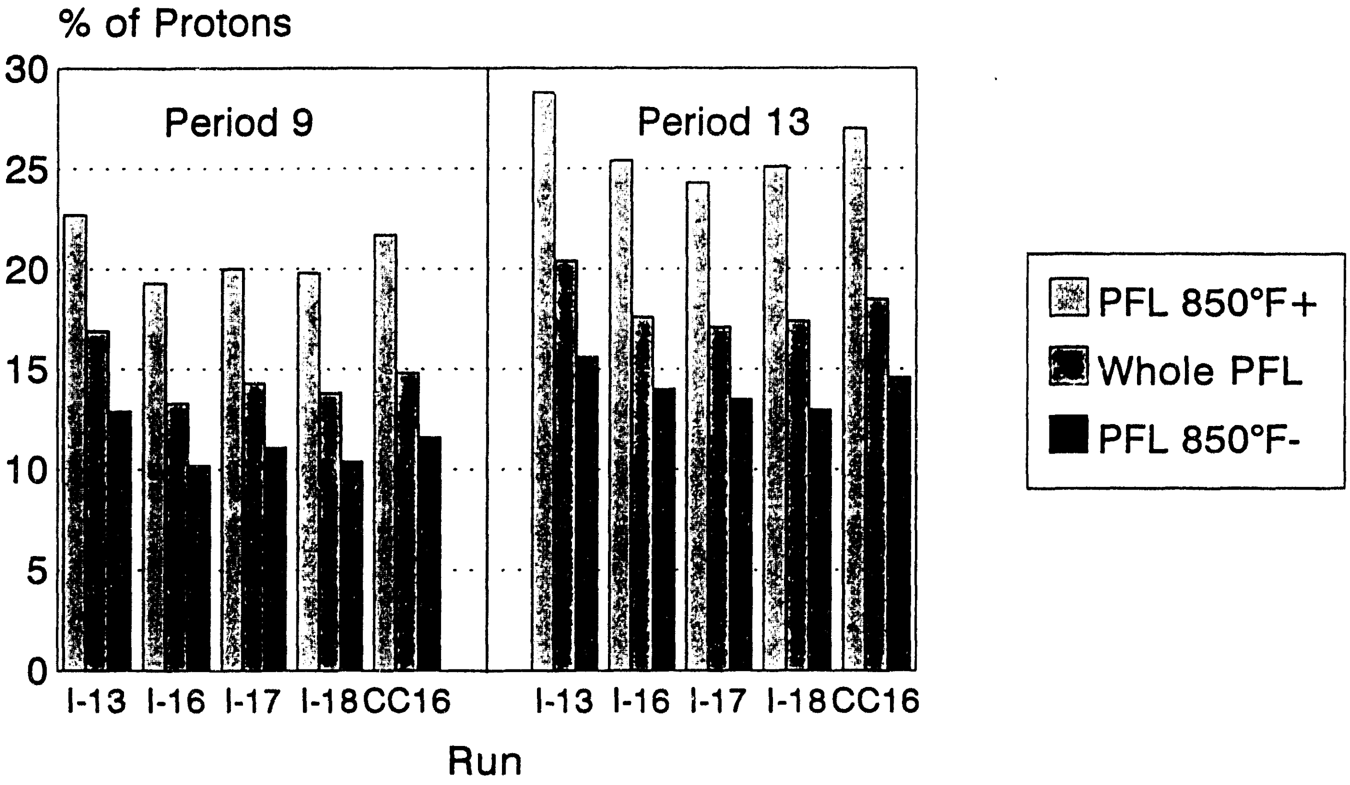


Figure 7. HRI Run CC-16 vs Other Runs - PFL Hydrogen Aromaticity.

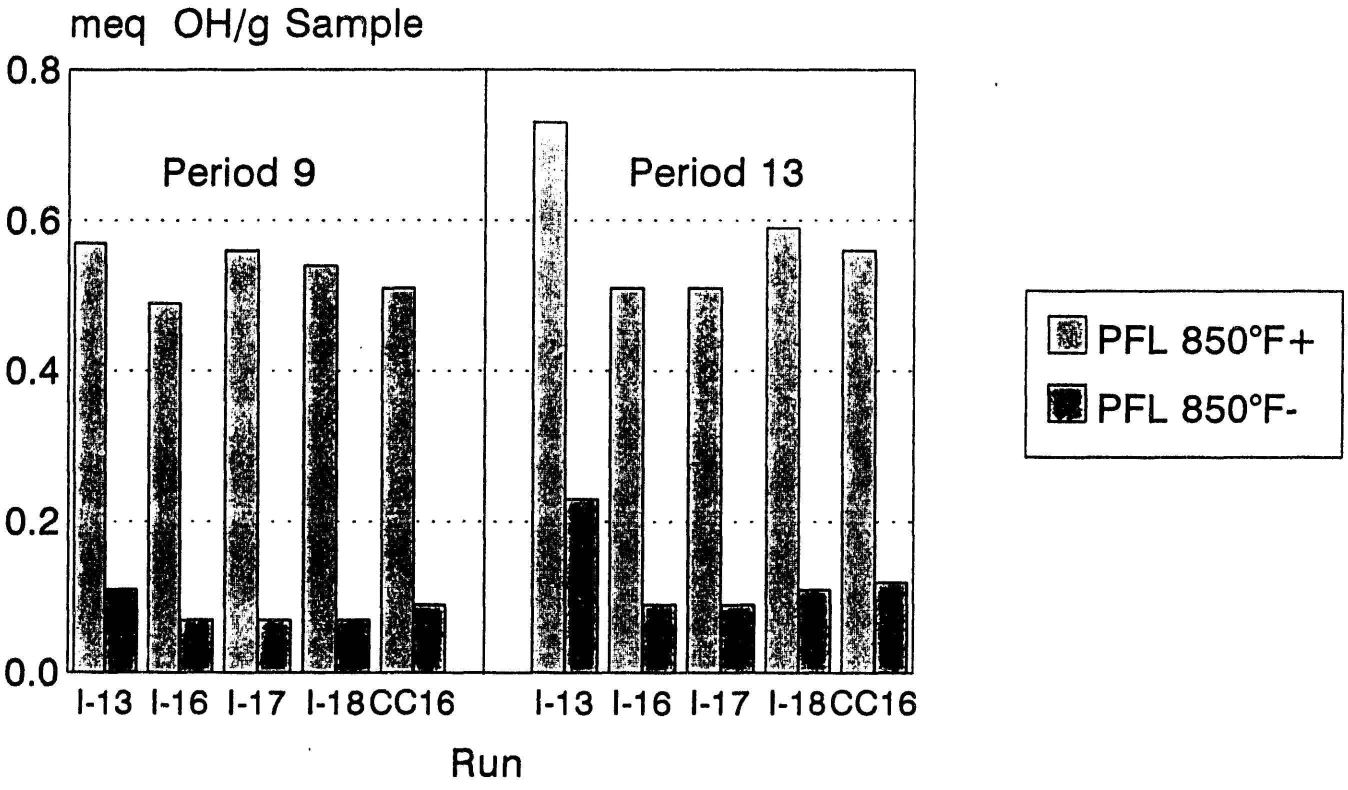


Figure 8. HRI Run CC-16 vs Other Runs - PFL Phenolic -OH Concentration.

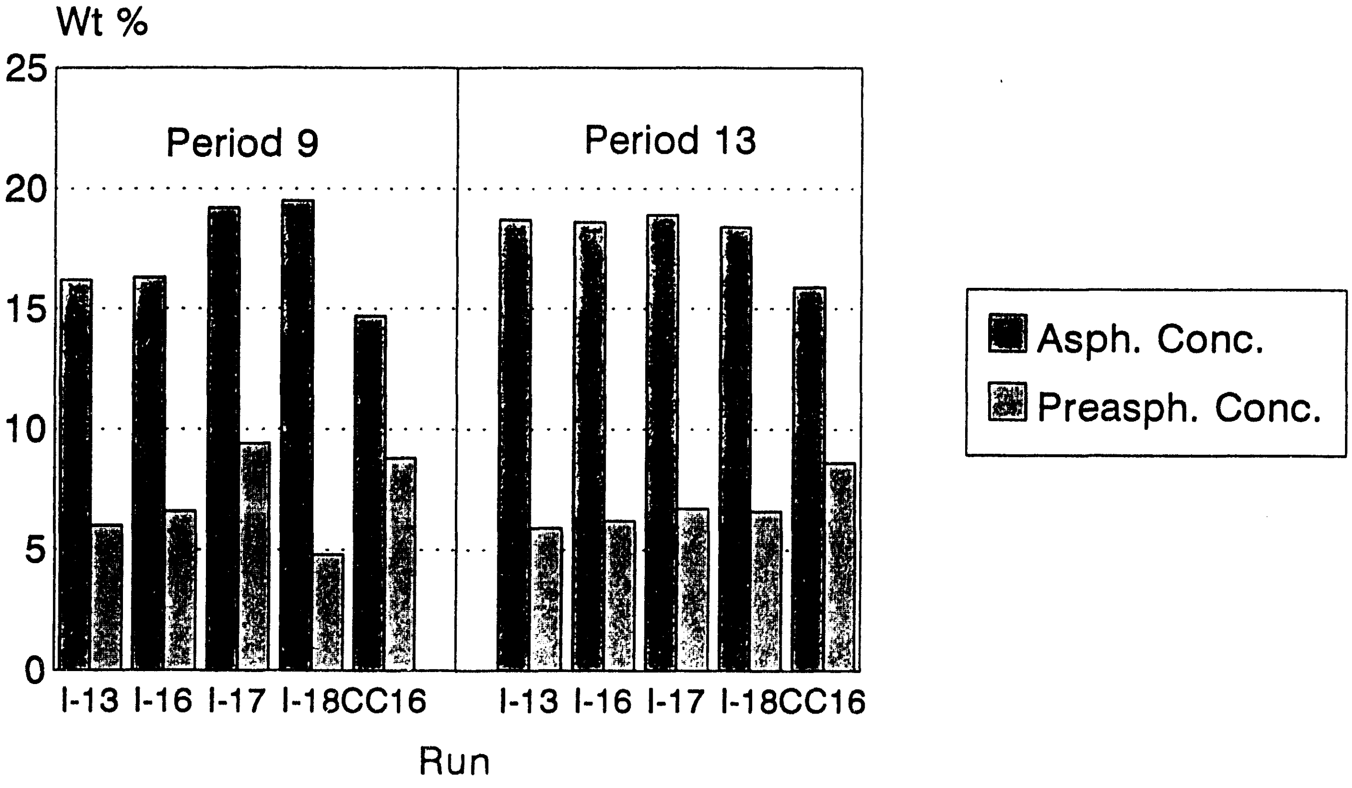


Figure 9. HRI Run CC-16 vs Other Runs - Solubility Fractions of PFL 850 °F $^+$ Resid.

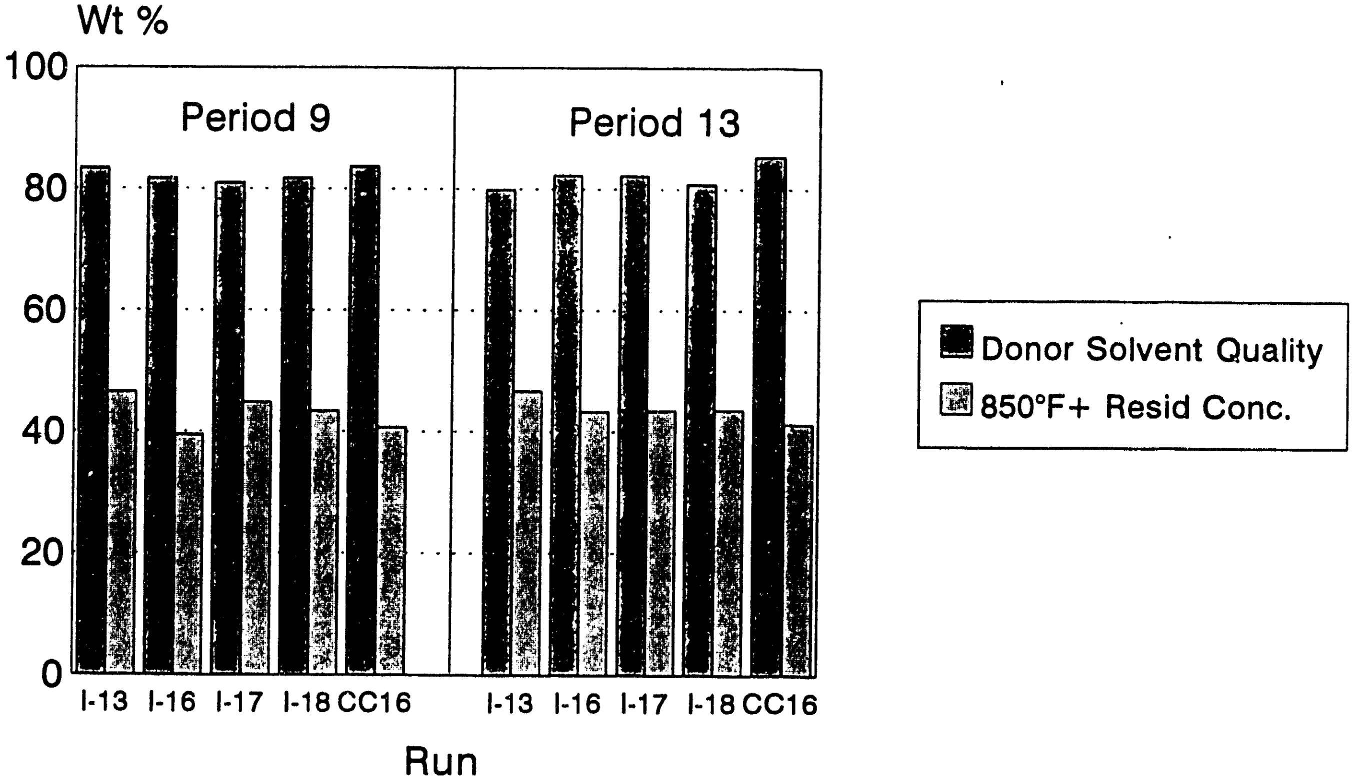


Figure 10. HRI Run CC-16 vs Other Runs - Solvent Quality and 850 °F^+ Resid Concentration of PFL.

APPENDIX 1

Determination of Total Phenol Concentrations in Coal Liquefaction Resids by ^{31}P-NMR Spectroscopy

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Determination of Total Phenol Concentrations in Coal Liquefaction Resids by ^{31}P NMR Spectroscopy

T. Mohan and J. G. Verkade*

Department of Chemistry and Ames Laboratory, Iowa State University, Ames, Iowa 50011

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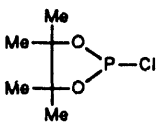
Fifteen coal liquefaction resids are quantitatively analyzed for phenolics and moisture using the ^{31}P NMR tagging agent $Cl\overline{POCMe_2CMe_2O}$. Despite the presence of organic free radicals in these resids, which contributed to the breadth of the derivatized phenolic ^{31}P resonances, excellent 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 NMR1 matched filter apodization program.

Introduction

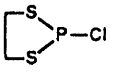
Coal liquefaction processes require monitoring of process performance. One approach to accomplishing this goal is to selectively quantitate a chemical component such as phenolic OH. With the use of FTIR spectroscopy, the phenolic OH contents in a wide range of coal liquefaction samples were quantitatively assessed by employing THF as a solvent.[1a,b] Comparison of the FTIR results with those from similar studies using a ^{19}F NMR tagging reagent[2] revealed that there was good agreement for many samples but substantial disagreement in samples containing high phenolic contents (ca. 2.0 mequiv/g).[1d] On the other hand, quantitations of phenolic OH contents in a series of H-coal distillates and vacuum bottoms by three NMR tagging techniques (^{19}F, ^{29}Si, and ^{31}P) compared favorably.[3] In that study, $Cl(O)PPh_2$ was concluded to be the reagent of choice because of the stability of its phenolic derivatives (compared with the instability over time of the corresponding derivatives of $F_3CC(O)Cl$) and the 100% natural abundance of ^{31}P compared with ^{29}Si (4.70%).

In previous publications[4-9] we have described a variety of NMR spectroscopic tagging reagents for the speciation and quantitation of compounds containing labile hydrogen functional groups, and in particular the potential usefulness of reagents 1[5,6,9] and 2[7-9] in the determination of phenols. Herein, we apply reagent 1 to the determination of the total phenol content in a series of 15 coal liquefaction resids and we compare our results with those obtained for the same samples by FTIR spectroscopy.[1a,b] The FTIR method was chosen as the standard of reference because of its high precision (±0.09 mequiv/g) and low average error (±0.1 mequiv/g[1b]), coupled with the observation that the ^{19}F NMR method is not suitable for coal resids.[1c,2a] We also demonstrate the usefulness of reagent 1 in determining the moisture contents of these liquefaction resids. In the reaction associated with this analysis, the reagent 1 derivatizes water to form the anhydride of 1, namely 3.[9]

Although 2 provides more than twice the ^{31}P NMR dispersion for phenols,[7-9] reagent 1 was chosen for this study because the peaks were too severely broadened by paramagnetic impurities for reagent 2 to be very useful.



1



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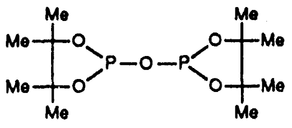

3

Experimental Section

Reagents. Chloroform-*d* (Aldrich) was stored over activated molecular sieves before use. *l*-Menthol (Aldrich) was used as received. All the phenols used in this study were recrystallized from ethanol before use. Triethylamine (Kodak) was distilled over anhydrous KOH pellets and stored under nitrogen. 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, 1, was prepared according to a literature procedure[10] and was purified by distillation; bp 39–41 °C at 1 mmHg (lit.[9] 81–82.5 °C at 15 mmHg; lit.[10] 77–78 °C at 12 mmHg).

Model Mixtures. Model mixtures of phenols were prepared by weighing the phenols directly into a 10 mm diameter NMR tube together with a weighed amount of the internal standard, *l*-menthol and the relaxagent, $Cr(acac)_3$ (1 mol % based on reagent 1). The mixture was dissolved in chloroform-*d* (4.0 mL) and after the addition of triethylamine (0.5 mL, 3.6 mmol), the phenols and *l*-menthol were reacted with reagent 1 (0.50 mL, 3.2 mmol) at 10 °C for about 1 h. The ^{31}P NMR spectrum was then obtained. Further data for a typical model phenol mixture are given in Table I.

Coal Liquefaction Resids. The origins of the coal liquefaction samples employed in this study are listed in Table II. Samples 10 and 11 are liquids, while all the rest are solids. All

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(1) (a) Robbins, G. A.; Winschel, R. A.; Burke, F. P. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* 1985, *30*, 155. (b) Winschel, R. A.; Robbins, G. A.; Burke, F. P. Technical Progress Report, July–Sept. 1985, DOE/PC 70018-13, December, 1985. (c) Burke, F. P.; Winschel, R. A. Technical Report, Oct. 1, 1983–Mar. 31, 1984, DOE Contract No. DE-AC22-80PC30027, March, 1985. (d) Robbins, G. A., private communication.

(2) (a) Winschel, R. A.; Burke, F. P. "Recycle Slurry Oil Characterization Report: 10/1/82-3/31/83"; DOe Contract No. DE-AC22-80PC30027, February, 1984. (b) Winschel, R. A. and Burke, F. P. "Recycle Slurry Oil Characterization-Second Annual Report"; DOE Contract No. DE-AC22-80-PC30027, August, 1983.

(3) Dadey, E. J.; Smith, S. L.; Davis, B. H. *Energy Fuels* 1988, *2*, 326.

(4) Schiff, D. E.; Verkade, J. G.; Metzler, R. M.;Squires, T. G.; Venier, C. G. *Appl. Spectrosc.* 1986, *40*, 348.

(5) Wroblewski, A. E.; Markuszweski, R.; Verkade, J. G. *Prepr. Pap—Am. Chem. Soc., Div. Fuel Chem.* 1987, *32*, 302.

(6) Wroblewski, A. E.; Lensink, C.; Markuszweski, R.; Verkade, J. G. *Energy Fuels*, 1988, 2, 765.

(7) Lensink, C.; Verkade, J. G. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* 1988, *33*, 906.

(8) Lensink, C.; Verkade, J. G. *Energy Fuels*, 1990, *4*, 197.

(9) Wroblewski, A. E.; Lensink, C.; Verkade, J. G. *Energy Fuels* 1991, *5*, 491.

(10) Zwierzak, A. *Can. J. Chem.* 1961, *45*, 2501.

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Table I. Quantitative ^{31}P NMR Analysis of Phenol Mixture Using Reagent 1[a]

				mmol found		
compound	mg	mmol (calcd)	$\delta^{31}P$ (ppm)	0.5 Hz[b]	2.0 Hz[c]	MFA[d]
2,3,6-trimethylphenol	19.6	0.144	143.64	0.143	0.149	0.152
2,6-dimethylphenol	17.0	0.139	143.09	0.138	0.140	0.145
3,4-dimethylphenol	28.4	0.232	138.77	0.234	0.223	0.230

[a] *l*-Menthol (18.7 mg, 0.120 mmol) was used as internal standard, 1 mol % (based on 1) of $Cr(acac)_3$ (9.6 mg) was used as relaxagent. [b] Calculated after processing with a line-broadening factor of 0.5 Hz. [c] Calculated after processing with a line-broadening factor of 2.0 Hz. [d] Calculated after processing with matched filter apodization.

Table II. Coal Liquefaction Resid Samples[a] Studied Using NMR Tagging Reagent 1

sample no.	run no.	sample designator	sampling point
1[b]	250[e]	R1236	interstage
2[b]	250[e]	V131B	recycle stream
3[b]	257[e]	R1235	interstage
4[b]	257[e]	V1067	second stage product
5[b]	257[e]	V131B	recycle stream
6[b]	255[f]	R1236	interstage
7[c]	259 G[g]	R1235	interstage
8[c]	259 G[g]	V1067	second stage product
9[c]	259 G[g]	V131B	recycle stream
10[d]	259 G[g]	V161 + V182	light net product
11[d]	259 G[g]	V164	interstage separator overhead
12[b]	260 ABC[h]	R1235	interstage
13[b]	260 ABC[h]	V1067	second stage product
14[b]	260 ABC[h]	V131B	recycle stream
15[b]	260 DEF[h]	R1235	interstage

[a] Wilsonville pilot plant samples provided by CONSOL Inc., 4000 Brownsville Road, Library, PA 15129. [b] THF-soluble portions of solid 850 °F+ materials ("residue"). [c] THF-soluble portions of whole process oils. [d] Whole process oils. [e] Using Illinois No. 6 Burning Star No. 2 Mine. [f] Using Texas Lignite. [g] Using Pittsburgh Seam Ireland Mine. [h] Using Wyodak and Anderson Seam Black Thunder Mine.

the manipulations involving the liquefaction materials were carried out in a drybox or a glovebag filled with dry nitrogen to avoid contamination with external moisture. The samples (280.5–650.9 mg) were weighed directly into previously weighed NMR tubes containing 13.5–33.4 mg of *l*-menthol and 1 mol % (based on reagent 1) of $Cr(acac)_3$. The contents were then dissolved in chloroform-*d* (4.0 mL), and triethylamine was added (0.50 mL, 3.6 mmol) followed by reagent 1 (0.50 mL, 3.2 mmol) after the sample was cooled below 10 °C. After about 2 h at 10 °C, the NMR spectrum was obtained.

NMR Instrumentation and Processing. ^{31}P NMR spectra of the derivatized model mixtures and coal liquefaction resids were obtained on a Bruker WM-200 spectrometer operating at 81.0 MHz. The spectrometer was interfaced with an ASPECT 2000 computer. The following acquisition parameters were employed: broad band decoupling; pulse width, $\pi/2$, 26 μs; sweep width, 4864 Hz; memory size, 16K; relaxation delay, 3.0 s; acquisition time, 1.69 s; number of scans 64 for the model mixtures and 1000 in the case of the coal liquefaction samples.

Integrations were performed on a DEC Mini Computer using the NMR1 program. After base line correction and zero filling (if required, see later), the FID was processed in three ways: using a line broadening factor of 0.5 Hz, 2.0 Hz, and a factor automatically selected by the NMR1 matched filter apodization (MFA) program. In the MFA program the line broadening factor is set equal to a calculated line width based on the equation of a theoretical Lorentzian line. The line width, and hence the line broadening factor, is determined from the sum of all the frequencies in the FID.[11] The MFA line broadening factors ranged from 2.5 to 8.3 Hz for the coal liquefaction samples and it was 6.6 Hz for the model phenol mixtures.

The broad derivatized phenolics region of the ^{31}P spectra of the coal liquefaction samples was curve-fitted in its entirety. With a line broadening factor of 0.5 Hz, zero filling[12] was required for about half of the samples in order to achieve convergence. The number of peaks at convergence ranged from 40 to 150. To reach convergence in samples not zero filled, it was necessary to delete peaks with large line widths (>500 Hz) and no integral or intensity value. By employing a 2.0-Hz line broadening factor, the number of data points to process is diminished, thus reducing the time required for iterations. Again, however, zero filling was always required to achieve convergence. Using MFA, convergence was reached more quickly and zero filling was never required.

The quantities of phenolics, amines, and H_2O in mequiv/g of coal liquefaction sample relative to that of *l*-menthol present (in mequiv/g of coal liquefaction sample) were then calculated from the integrals (see eq 1 in Results and Discussion).

EPR Instrumentation. EPR spectra were recorded at 292 K on a Bruker ER-200D spectrometer operating at a frequency of 9.450 78 GHz and interfaced with an ASPECT 2000 computer. The sweep widths were maintained in the range 2700 to 3700 G. The EPR spectrum of sample no. 11 was obtained as its solution in chloroform while that of sample no. 12 was obtained on the solution used for ^{31}P NMR spectroscopy. Both samples gave a single resonance at a *g* value of 2.0036, calculated by the relation $g = h\nu/\beta H$.

Results and Discussion

To obtain reliable quantitative data from ^{31}P NMR spectroscopy, the following five conditions must be satisfied:

1. Complete derivatization with the NMR tagging reagent, as was shown earlier for reagents such as 1,[9] must be achieved.

2. Thermal equilibrium must be reached by the nuclei to be quantitated. This was accomplished by using relaxation delays at least 5 times greater than the longest T_1.[11] In the present study this delay was fixed at 3.0 s.

3. To reduce the relaxation time of the derivatized phenols to less than 0.5 s, 1 mol % of $Cr(acac)_3$ (based on reagent 1) should be employed.

4. The recommended[11] signal-to-noise ratio of greater than 250 was achieved by optimizing the number of scans to 64 for the model phenol mixtures and to 1000 scans for the derivatized coal resid samples. In the case of some samples, signal-to-noise ratios of up to 5000 were achieved.

5. Broad-band decoupling should be employed to eliminate errors that are likely to arise from the nuclear Overhauser effect.

In this study, the concentration of each phenol in the model mixture was calculated as

$$\frac{\text{mequiv of phenolic O}}{\text{g of coal material}} = \frac{I_{\text{derivatized phenol}}}{I_{\text{derivatized }l\text{-menthol}}} \frac{\text{mequiv of }l\text{-menthol O}}{\text{g of coal material}} \quad (1)$$

where *I* refers to the relative intensity of the integral for the derivatized phenolic region and the mequiv of *l*-menthol oxygen is calculated from the weight of *l*-menthol used and its molecular weight. The mequiv values of amine nitrogen and moisture oxygen were calculated analogously, except in the latter case, where half of the corresponding integral was taken, since there are two replaceable

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[11] Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Pergamon: London, 1986.

[12] In this procedure as many pseudo data points as the computer memory allows are introduced in order to achieve smooth curve fitting.[11] This procedure did not adversely affect quantitation, however.

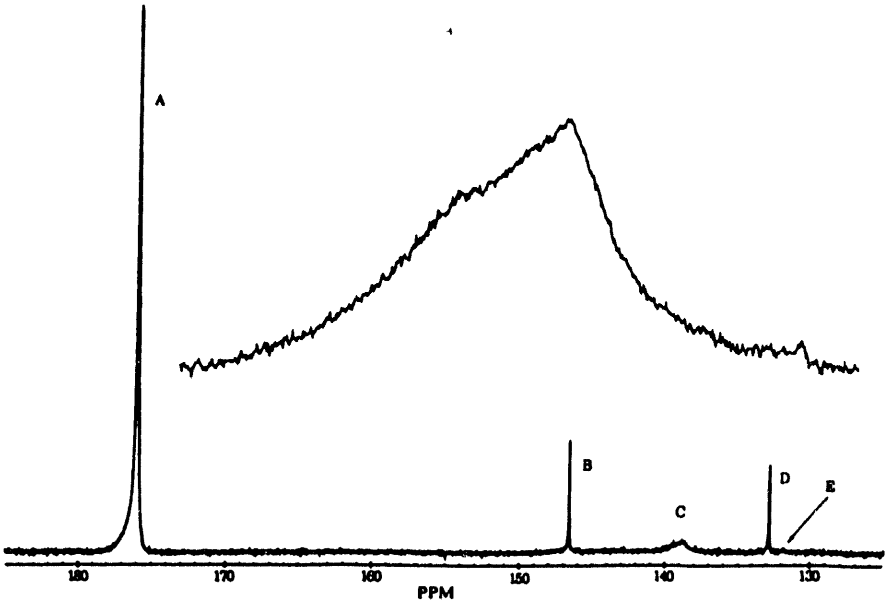

Figure 1. An 81.0-MHz ^{31}P NMR spectrum of a typical coal resid sample (no. 12) studied herein which was derivatized with 1. The letters A–D designate the resonances for 1, derivatized *l*-menthol, derivatized phenolics, and derivatized water (3), respectively. The small resonances labeled E at 132 ppm (see text) are assigned to derivatized amines. An expansion of the ^{31}P region of the phenolics (137–141 ppm) in a typical coal resid sample (no. 12) derivatized with 1 is shown in the inset.

Figure 2. Contributing peaks calculated by the NMR1 curve-fitting procedure for the phenolic region of a typical coal resid sample (no. 12) derivatized with 1, using a line-broadening factor of 0.5 Hz and zero-filling to achieve convergence.

hydrogens in H_2O and 3 is formed. The choice of *l*-menthol as the internal standard was addressed earlier.[9]

A number of model mixtures containing different phenols was prepared in order to optimize the NMR parameters. The results obtained with an example of such a model mixture are tabulated in Table I. The use of more than 1 mol % of $Cr(acac)_3$ relative to 1 increased the line widths of the individual signals, thereby introducing further error into the quantitative data.

The ^{31}P NMR spectra of the derivatized coal resid samples in Table II featured three predominating sharp peaks labeled A, B, and D in Figure 1, corresponding to excess reagent 1 at 179.5 ppm,[9] derivatized *l*-menthol at 146.6 ppm[9] and anhydride 3 at 132.9 ppm[9] arising from the moisture present in the coal sample, respectively. A broad signal C appeared in the derivatized phenolic region (138–144 ppm[9]). In the inset of Figure 1 is shown an expansion of the latter set of signals. The ^{31}P NMR spectrum of this region after processing the FID with an apodization (line broadening) parameter of 0.5 Hz prior to Fourier transformation revealed the presence in this region of more than 100 peaks in the typical case. Application of the NMR1 curve-fitting program then gave rise to spectra resembling Figure 2 in the typical case. However, the line widths of these signals varied from as low as 0.4 Hz to as high as 197 Hz, which rendered the unequivocal identification of the phenols impractical. In about half of the samples, convergence could be achieved only by processing the FID with a zero-filling factor. In these cases, even though the line widths were small (0.81 Hz), the number of peaks was again unrealistically large (e.g., 148 for sample 12), making speciation impractical. Moreover, the FID of the two liquid samples examined (no. 10 and 11 in Table II) could be processed to a smooth curve only with a line broadening factor of 2.5 Hz, although without zero filling. Here the number of peaks was found to be smaller (e.g., 13 for sample 11), but in view of their large line width, unequivocal assignments to specific derivatized phenols were not possible. However, total phenolic contents could be calculated from the integrals of the signals and they have been listed in Table III. A ^{31}P NMR spectrum obtained on the Unity 500 instrument at 202 MHz also failed to resolve the broad signal C adequately for speciation of phenolics.

In view of the aforementioned difficulties and the long iteration time (as much as 5 h) for processing the FID using a line broadening factor of 0.5 Hz, an attempt was made to reduce the number of peaks (and hence the iteration time) by processing the FID's of the resid samples with a line-broadening factor of 2.0 Hz and zero filling in hopes of achieving at least partial speciation. The curve-fitting was successfully achieved in all cases except the liquid samples 10 and 11. As expected, the number of peaks was reduced, but the line widths resulting from the curve-fitting procedure were again found to be too large for unambiguous identification of phenol derivatives. However, as before, the total phenol contents could still be calculated by this approach and they are also collected in Table III.

The persistent broadness of the ^{31}P NMR spectra in the derivatized phenolic region prompted us to test for the presence of free radicals which are expected to broaden the signals. An EPR spectrum obtained on one such sample (no. 12) clearly indicated the presence of organic free radicals on the basis of the *g* factor (2.0036). The EPR spectrum of sample no. 11, a liquid, also revealed a signal at the same *g* value. The decreased intensity of the signal by a factor of ca. 5 compared with sample 12 is in accord with the appearance of a better-resolved ^{31}P NMR spectrum for sample 11. This result strongly suggested

Table III. Phenolic, Amino, and Moisture Contents^{a} of Coal Liquefaction Samples

		by ^{31}P NMR			phenolic error^{g}	
sample no.	phenolic by FTIR^{b}	phenolic	amino	moisture	excluding amino	including amino
1	1.07	1.02^{c}	0.01^{c}	0.13^{c}	−0.05	−0.04
		1.13^{d}	0.10^{d}	0.13^{d}	+0.06	+0.16
		1.07^{e}	0^{e}	0.12^{e}	0	0
2	0.74	0.63^{c}	0.03^{c}	0.07^{c}	−0.11	−0.08
		0.77^{d}	0.01^{d}	0.07^{d}	+0.03	+0.04
		0.72^{e}	0.02^{e}	0.07^{e}	−0.02	0
3	0.68	0.60^{c}	0^{c}	0.13^{c}	−0.08	−0.08
		0.68^{d}	0.02^{d}	0.12^{d}	−0.00	+0.02
		0.64^{e}	0.02^{e}	0.11^{e}	−0.04	−0.02
4	0.57	0.43^{c}	0.10^{c}	0.06^{c}	−0.14	−0.04
		0.40^{d}	0.02^{d}	0.09^{d}	−0.17	−0.15
		0.42^{e}	0.02^{e}	0.08^{e}	−0.15	−0.13
5	0.50	0.34^{c}	0.03^{c}	0.10^{c}	−0.16	−0.13
		0.37^{d}	0.04^{d}	0.10^{d}	−0.13	−0.09
		0.39^{e}	0.04^{e}	0.09^{e}	−0.11	−0.07
6	1.04	0.85^{c}	0.10^{c}	0.10^{c}	−0.19	−0.09
		1.00^{d}	0.01^{d}	0.10^{d}	−0.04	−0.03
		0.98^{e}	0^{e}	0.10^{e}	−0.06	−0.06
7	0.60	0.58^{c}	0^{c}	0.10^{c}	−0.02	−0.02
		0.60^{d}	0.01^{d}	0.10^{d}	0	+0.01
		0.57^{e}	0^{e}	0.09^{e}	−0.03	−0.03
8	0.42	0.30^{c}	0.03^{c}	0.09^{c}	−0.12	−0.09
		0.37^{d}	0.01^{d}	0.09^{d}	−0.05	−0.04
		0.41^{e}	0.02^{e}	0.09^{e}	−0.01	+0.01
9	0.60	0.48^{c}	0.02^{c}	0.11^{c}	−0.12	−0.10
		0.30^{d}	0.01^{d}	0.11^{d}	−0.30	−0.29
		0.28^{e}	0^{e}	0.10^{e}	−0.32	−0.32
10	0.18	0.29^{e}	0^{e}	0.06^{e}	+0.11	+0.11
		0.27^{f}	0^{f}	0.06^{f}	+0.09	+0.09
11	0.27	0.33^{e}	0^{e}	0.09^{e}	+0.05	+0.05
		0.51^{f}	0^{f}	0.05^{f}	+0.24	+0.24
12	0.97	0.97^{c}	0.08^{c}	0.13^{c}	0	+0.08
		0.90^{d}	0.02^{d}	0.13^{d}	−0.07	−0.05
		0.84^{e}	0^{e}	0.12^{e}	−0.13	−0.13
13	0.70	0.41^{c}	0.21^{c}	0.11^{c}	−0.29	−0.08
		0.48^{d}	0^{d}	0.10^{d}	−0.22	−0.22
		0.64^{e}	0.01^{e}	0.10^{e}	−0.06	−0.05
14	0.71	0.69^{c}	0.04^{c}	0.17^{c}	−0.02	+0.02
		0.44^{d}	0.03^{d}	0.10^{d}	−0.27	−0.24
		0.60^{e}	0.04^{e}	0.09^{e}	−0.11	−0.06
15	0.95	0.78^{c}	0^{c}	0.18^{c}	−0.17	−0.17
		0.92^{d}	0.03^{d}	0.18^{d}	−0.03	0
		1.00^{e}	0.03^{e}	0.17^{e}	+0.05	+0.08

[a] mequiv/g. [b] See ref 1a,b. [c] FID processed with 0.5-Hz line-broadening factor. [d] FID processed with 2.0-Hz line-broadening factor. [e] FID processed with matched filter apodization. [f] FID processed with 2.5-Hz line-broadening factor. [g] In mequiv/g of coal resid sample.

that attempts to resolve the broad derivatized phenolic signal would be of little use for the speciation of derivatized phenols.

We then attempted to determine the total phenolic content using a simple function which processes the FID's by a matched filter apodization procedure in order to at least determine the total phenol content as expeditiously as possible. Using this program (which required no zero filling), the broad signal C was generally identified by the program as a single peak (although in some cases by as many as three or four peaks) and the phenolic contents were calculated after the curve-fitting procedure which could now be accomplished almost instantaneously. The results are collected in Table III.

Table III summarizes the total phenolic contents calculated by the three different ^{31}P NMR analysis methods employed here, thus allowing a comparison with values reported for these samples by FTIR spectroscopy.[1a,b] The average error in the latter method was determined to be ±0.1 mequiv/g coal liquefaction sample with a reproducibility of ±0.09 mequiv/g.[1b] In Table IV are summarized the average errors (relative to the FTIR data) associated with the three line-broadening factor methods used in our ^{31}P NMR analyses. From this table it is seen that the average error decreases for all three line-broadening treatments when the amine contents are included. Since secondary amines (including pyrroles) also absorb in the phenolic OH region in the IR,[1a,b,d] we believe the amine contributions found in the present work should be included in the phenolic contents for comparison with the FTIR results. In that case, the average error for the MFA line-broadening analysis appears to match the FTIR results most closely.[13] The reproducibility of our technique was tested by using three separately weighed aliquots of sample no. 2. The average precisions using the 0.5 Hz, 2.0 Hz and MFA line broadening approaches are ±0.02, ±0.06, and ±0.05 mequiv/g. These figures compare very well with the ±0.09 mequiv/g precision observed for the FTIR method.[1d]

Table IV. Average Errors^{a} in Phenolic Contents by ^{31}P NMR Spectroscopy

line-broadening treatment	excluding amino	including amino
0.5 Hz	−0.11	−0.06
2.0 Hz	−0.09	−0.07
MFA	−0.04	−0.03

[a] In mequiv/g coal resid samples.

We note here that the agreement between our ^{31}P NMR method with the FTIR technique on resid samples is much better than that found in a comparison of a ^{19}F NMR tagging approach[1c] with the FTIR method, for the analysis of phenolics in a series of distillates which have the advantage that free radicals are largely absent. Thus, the ^{19}F NMR tagging method resulted in underestimates of the FTIR-determined phenolic contents, ranging from 0.07 to 1.12 mequiv/g,[1c] compared with ca. −0.04, −0.03 mequiv/g using the MFA approach (Table IV). It is interesting that the sample giving the largest deviation from the FTIR determination (no. 9) gave essentially the same ^{31}P NMR-determined phenol values upon repetition of the NMR measurements on a fresh sample.

Moisture is reported not to interfere in the FTIR method for phenolics[1a,b] since the water peaks (when observed) are generally found to be 170 cm^{-1} or more to higher wavenumbers.[1d] Because the preparation of the FTIR samples took place in air, some contamination of the samples by moisture is inevitable. Since our preparations rigorously excluded air, we believe the small rather constant H_2O contents observed in the samples studied here (Table III) strongly suggest that the moisture arises from the liquefaction process and/or is absorbed by the sample during the preparation procedure. Interestingly, inclusion of both the amine and moisture contents with the phenolic analyses produce average errors of +0.05, +0.04, and +0.06 mequiv/g for our line-broadening treatments using 0.5 Hz, 2.0 Hz, and MFA, respectively. It should be noted here that in contrast to the coal resid samples, for which the average error in the phenolic

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(13) It should be noted that we have not been able to identify the compounds responsible for the peaks in this portion of the amine region. Moreover, it cannot be concluded that the derivatized phenolic region in our spectra is uncontaminated by derivatized amines, since the derivatized amine region is large (130–150 ppm).

Table V. Relationship of Spectral Grouping and Appearance to Sampling Point

spectral group	samples	sampling point	spectral appearance		
			139.2 ppm	138.7 ppm	137.3 ppm
I	1, 3, 6, 7, 12	interstage	mod intense shoulder	mod narrow peak	low-intensity peak
	2	recycle stream			
II	4, 8, 13	second stage product	intense shoulder	mod narrow peak	mod-intensity peak
	9	recycle stream			
III	5, 14	recycle stream	intense broad shoulder	mod narrow peak	high-intensity peak
	15	interstage			
IV	10	light net product	group of peaks	group of peaks	high-intensity peak
	11	interstage separator overhead			

contents determined by ^{31}P NMR analysis decreased using a 0.5 Hz, then a 2.0 Hz, and finally an MFA line-broadening factor, the same series of analyses for the model phenol mixture in Table I gave an increase in average error from 0.00 to ±0.03 to ±0.13 mequiv/g of phenol mixture. We believe this result indicates that spectra consisting of non (paramagnetically) broadened, nonoverlapping peaks, wherein all the peaks are approximately equally sharp, are best analyzed with a small line-broadening factor (i.e., 0.5 Hz in the present instance).

Finally, we note that a comparison of the ^{31}P NMR's of the phenolic regions for each of the 15 samples derivatized with 1 reveals four rather distinct spectral appearances or "fingerprints" as shown in Table V. Our EPR results suggest that only the liquid samples have sufficiently low concentrations of radicals to give rise to distinct sets of peaks at ~139.2 and ~138.7 ppm. Thus, our technique gives a qualitative indication of relative radical concentrations. Moreover, there appears to be a partial correlation of spectral appearance (i.e., spectral groups I–IV in Table V) with sampling point as shown in this table. Thus, five out of six of the samples in spectral group I are from the interstage, three out of four in group II are second stage products, two out of three of the samples from group III are from recycle streams, and both light oils fall in group IV.

Conclusions

From this study the following can be concluded: (1) Our ^{31}P NMR tagging method is applicable to the analysis of phenolic contents of coal liquefaction samples despite the relatively low concentrations of these compounds and despite the presence of organic free radicals which broaden the spectra. (2) The average errors for all three apodization methods employed here to analyze the derivatized phenolic region of the ^{31}P NMR spectra are at least as favorable as those for the FTIR method (±0.1 mequiv/g), and by inclusion of the amine content found outside of this region, the NMR method using the MFA line-broadening approach appears to be somewhat better (−0.03 mequiv/g, Table IV). By comparison, the data given in the earlier report using Cl(O)PPh$_2$ as a ^{31}P NMR tagging reagent indicates that the agreement among the ^{31}P, ^{29}Si, and ^{19}F NMR tagging results for five coal liquids averaged 0.15 mequiv/g.[3] (3) By also including the small intrinsic water contents found in the samples studied, the average error moves from slightly negative to slightly positive. (4) The ^{31}P NMR analysis reported here, which takes about $1^{3}/_{4}$ h per sample when the MFA analysis approach is used, is not as rapid as the FTIR method which takes approximately 15 min per sample.[1a,b] However, our ^{31}P NMR approach is about as rapid as that reported with Cl(O)-PPh$_2$.[3] (5) The ^{31}P NMR method described permits the simultaneous analysis of moisture, since interference of moisture is categorically absent, as is also the case for the reagent Cl(O)PPh$_2$.[3] (6) The ^{31}P NMR method is amenable to a large variety of solvents, including pyridine,[9] as long as they contain no labile hydrogen functional groups. (7) The ^{31}P NMR method works well for resid samples, in contrast to the ^{19}F NMR method.[1c,2a]

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APPENDIX 2

NMR Determination of Aromatic Carbon Balances and Hydrogen Utilization in Direct Coal Liquefaction

N.m.r. determination of aromatic carbon balances and hydrogen utilization in direct coal liquefaction

Francis P. Miknis, Daniel A. Netzel, Susan D. Brandes*
Richard A. Winschel* and Francis P. Burke*
Western Research Institute, Box 3395, University Station, Laramie, WY 82071, USA
**CONSOL Inc., 4000 Brownsville Road, Library, PA 15129, USA*
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Solid- and liquid-state ^{13}C n.m.r. measurements were made on a suite of samples obtained from different stages of a coal liquefaction run at the Wilsonville Two-Stage Advanced Coal Liquefaction Research and Development Facility. The n.m.r. measurements were combined with elemental analysis and mass balance data to measure aromatic carbon balances and hydrogen utilization for Wilsonville coal liquefaction run 259G. This was a catalytic/catalytic integrated two-stage liquefaction run on a deeply cleaned, Pittsburgh seam, high volatile bituminous (hvAb) coal from the Ireland mine in West Virginia, USA. The n.m.r. measurements showed that on the basis of the feed coal, about 58% of the aromatic carbons in Pittsburgh coal were hydrogenated during two-stage liquefaction, and 55% of the hydrogenation occurred during the second stage. A net of 68.1 mol of hydrogen per 100 mol of coal carbon was consumed during the first stage of Wilsonville run 259G. This amounted to 69% of the total overall two-stage hydrogen consumption. Matrix cleavage and hydrogenation reactions accounted for 31% and 27%, respectively, of the total first-stage hydrogen consumption. Hydrogenation reactions accounted for most (69%) of the hydrogen consumed during the second stage, and accounted for 40% of the overall two-stage total hydrogen consumption. Most of the total hydrogen consumed for hydrocarbon gas generation (70%), and for heteroatom removal and heterogas production (71%) occurred in the first stage. Overall hydrogen consumption was 14% for hydrocarbon gas production and 27% for heteroatom removal and heterogas production.

(Keywords: n.m.r. determination; aromatic; coal liquefaction)

Coals are hydrogen-deficient fossil fuels that have a highly aromatic carbon structure[1,2]. They do not readily convert to liquid products during heating as do, for example, Colorado oil shales, which are hydrogen-rich because of their highly aliphatic carbon content[3]. In addition, coals have a macromolecular structure attendant with various cross-links that can contain heteroatoms and that can affect their conversion properties[4]. Thus, in order to convert coal to useful liquid products, hydrogen must be added or carbon must be removed, usually at elevated temperatures, in order to disrupt the macromolecular network and to stabilize and reduce the molecular weights of the fragments.

Reactions of hydrogen are important in all stages of liquefaction. Hydrogen chemistry and utilization are very important for design of coal liquefaction processes because of the impact of hydrogen consumption on process economics. In fact, investigation of more efficient ways to produce, use, or recover hydrogen has been given a high priority for research by the US Department of Energy Coal Liquefaction Research Needs assessment panel[5]. Therefore, a key to developing a successful coal liquefaction process is an understanding of how hydrogen is used among the different reaction modes that yield the final products.

The hydrogen consumed in coal liquefaction is employed in a variety of free-radical and non-free-radical processes[6]. Hydrogenation, hydrogenolysis and heteroatom removal are particularly important hydrogen-consuming reactions. In addition, reactions of carbon moieties that form aromatic carbon in the residue or redistribute the aromatic carbon in the residue (condensation reactions) are detrimental to yields. These reactions may occur in the solid or semisolid residue, and thus have been difficult to examine because techniques for direct measurement of carbon structural changes in solid coals or residues have not been available. With the introduction of solid-state n.m.r. techniques, this situation has changed considerably[7-9].

Reviews on the application of solid-state n.m.r. techniques to the study of coals have been published[7-10]. To a large extent, these techniques have been applied to the study of the carbon structure of coal and how it changes with rank, the origin and evolution of coal, and the behaviour of coal under various heating and processing conditions. Most of the latter studies have used n.m.r. to determine changes in carbon aromaticity during coal liquefaction[6,11-13] or pyrolysis[14-16].

In this paper n.m.r. measurements made on whole coals, product oils and distillates, residues and insoluble

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fractions obtained from a liquefaction experiment at the Wilsonville Two-Stage Advanced Liquefaction Research and Development Facility are reported. The objectives of this study are to provide process developers with data that are important for closing aromaticity balances, and for understanding the chemistry of hydrogen utilization during coal liquefaction. Such data are important for process development but are difficult, if not impossible, to acquire by any other means. This paper is an example of what can be done when analytical data are combined with process data. Although the results reported here are for a specific liquefaction run at Wilsonville, the methodology can be applied to any liquefaction process to acquire data that can provide an understanding of some of the process chemistry of coal liquefaction.

EXPERIMENTAL

N.m.r. measurements

Solid-state n.m.r. measurements were made with a Chemagnetics CMX 100/200 solids n.m.r. spectrometer. Carbon aromaticity measurements were made at a ^{13}C frequency of 25 MHz using the technique of cross polarization (CP) with magic-angle spinning (MAS) and high-power decoupling. A zirconia bullet spinner 9.5 mm in diameter was used. Spinning rates were between 3.5 and 4.2 kHz. A total of 10 800 transients were collected for each CP/MAS spectrum. Other n.m.r. parameters were a 90° pulse width of 5 μs, a contact time of 1 ms and a pulse delay of 1 s. These parameters are typical for CP/MAS measurements of coals[2,17].

Liquid-state ^{13}C n.m.r. measurements were made on a Jeol GSX-270 n.m.r. spectrometer. The conditions for recording a ^{13}C n.m.r. spectrum were 320 scans, 9.3 μs pulse width (90°), 0.8 s acquisition time, a pulse delay of 10 s, 32 k time-domain data points and gated decoupling with the decoupler on during data acquisition. ^{13}C spectra were obtained on samples containing $\sim$0.05 M chromium(III) acetylacetonate as a relaxation agent.

All n.m.r. spectra were phased manually and integrated using the instrument's computer software. For the CP/MAS ^{13}C aromaticity measurements, the integrations covered the range from 340 to -80 ppm. This large range was required to include contributions to the aromatic carbon integrals from spinning sidebands centred at $\sim$300 and ~ -40 ppm. For all the samples, the region between 340 and 90 ppm was considered as the aromatic carbon region. Any contributions from carbonyl carbons in the region 165–210 ppm were also included. The region between 90 and -20 ppm was considered the aliphatic carbon region. The integrated sideband intensity between -20 and -80 ppm was added to the aromatic carbon integral.

Samples

Six well-documented samples were examined. These samples were chosen as part of a programme designed to create stronger bridges between direct coal liquefaction process development and analytical chemistry[18]. Under this programme, samples obtained from process development units were provided to analytical researchers for testing. The results of their examinations were interpreted in the context of the liquefaction process. The results reported in this paper are taken from such a study[19].

The set of samples were obtained from Wilsonville coal liquefaction run 259G[20]. Run 259G was operated for 5 days from 30 April 1990 to 4 May 1990 in the catalytic/catalytic integrated two-stage liquefaction (CC-ITSL) configuration with ash recycle, with deeply cleaned, Pittsburgh seam, high volatile bituminous coal (hvAb) from the Ireland mine in West Virginia. A summary of the operating conditions and overall two-stage liquefaction yields for period G are given in *Table 1*. The samples consisted of the starting coal and process oils from various stages of the liquefaction process. Solid- and liquid-state ^{13}C n.m.r. aromaticity measurements were made on these samples. Carbon aromaticities for two 'oil' samples (*Table 2*) were determined by CP/MAS, because these materials were solid at room temperature. These measurements and the elemental analyses and mass balance data were used to determine a carbon aromaticity mass balance and to determine the modes of hydrogen utilization by modification of the method of Finseth *et al.*[6]. The elemental compositions and the n.m.r. aromaticity measurements are summarized in *Table 2*. The steady-state material balance data from period G of run 259 are provided in *Table 3*.

RESULTS AND DISCUSSION

Aromatic carbon balances

In principle, the calculation of aromatic carbon balances is straightforward. All that is necessary is knowledge of the carbon values of all the materials entering and leaving a reactor, knowledge of the aromatic carbon fractions of the same materials, and a mass balance across the reactor so that the conversion of coal to gas, liquid and solid products can be obtained. The amount of aromatic carbon, on a mass basis, for a given product is obtained by multiplying the per cent carbon by the aromaticity, and this value is multiplied by the yield of that product. The net production (aromatization) or destruction (hydrogenation) of aromatic

Table 1 Conditions and yields for Wilsonville run 259G[a] for representative operating period (30 April 1990–4 May 1990)

Coal	
Feed rate (kg h^{-1}, mf)	104.5
Ash (wt%, mf)	4.4
Conc. in slurry (wt%, mf)	30.0
Process solvent (wt%)	
566°C$^+$ resid.	40.3
Cresol insolubles (CI)	12.0
First stage	
Average reaction temp. (°C)	440
Inlet H_2 partial pressure (MPa)	19
Space velocity	
(kg feed h^{-1}-kg cat.)	1.8
(kg mf coal h^{-1}-m^3 cat.)	452
Catalyst type	Shell 324
Catalyst age (kg (resid + CI)/kg cat.)	1141 ± 16
(kg mf coal/kg cat.)	487 ± 6
Catalyst replacement rate (kg/mg mf coal)	2
Second stage	
Average reaction temp. (°C)	421
Inlet H_2 partial pressure (MPa)	17
Space velocity	
(kg feed h^{-1}-kg cat.)	1.7
(kg mf coal h^{-1}-m^3 cat.)	452
Catalyst type	Shell 324
Catalyst age (kg (resid + CI)/kg cat.)	924 ± 13
(kg mf coal/kg cat.)	490 ± 6
Catalyst replacement rate (kg/mg mf coal)	2

[a] Data from Reference 20

Table 2 Sample description, elemental analysis and carbon aromaticities, Wilsonville run 259G

Sample no.	Descriptor	Coal	Element (wt%, maf) C	H	N	O	S	Carbon aromaticity
1	Raw coal	Pittsburgh	81.2	6.0	1.4	8.1	3.3	0.69
2	Process distillate, V161 + V182	Pittsburgh	86.4	13.0	0.1	0.4	0.0	0.26[a]
3	Interstage product oil, R1235	Pittsburgh	89.3	7.4	0.3	1.9	1.1	0.72
4	Recycle product oil, V131B	Pittsburgh	90.6	7.7	0.2	0.6	0.8	0.71
5	Separator overhead product oil	Pittsburgh	86.7	11.9	0.2	1.1	0.1	0.27[a]
6	Ash concentrate	Pittsburgh	85.5	4.6	1.2	3.6	5.2	0.91

[a] Liquid-state n.m.r. measurement

Table 3 Overall steady-state material balance two-stage liquefaction system and first-stage reactor system[a] (basis: 100 kg h^{-1} maf coal)

Two-stage system + deasher Stream	($kg\,h^{-1}$)	Sample no.	First stage Stream	($kg\,h^{-1}$)	Sample no.
Input			*Input*		
Coal (maf)	100	1	Coal (maf)	100	1
Coal ash	4.58		Coal ash	4.58	
H_2	6.73		H_2	4.65	
Seal oil[b]	2.61		Seal oil[b]	1.46	
Total	113.92		V1074	124.91	4
			Ashy recycle	114.76	
			Deasher resid.	19.35	
			Total	369.71	
Output			*Output*		
CO, CO_2	0.43		CO, CO_2	0.43	
H_2O	6.66		H_2O	6.64	
NH_3	1.35		NH_3	0.55	
H_2S	2.93		H_2S	1.78	
C_1–C_3	8.87		C_1–C_3	6.12	
C_4–C_6	4.09		C_4–C_6	3.01	
V140[c]	0.98		V140[c]	0.98	
Deasher resid.[c]	2.73		V164	35.34	5
Ash conc.	13.10	6	R1235	314.85	3
V164	35.34	2	Total	369.70	
V182[d]	−18.22				
V1078	39.85				
V1074	16.69				
Ash recycle[c,e]	−0.87				
Total	113.93				

[a] Data are for run 259, period G, day 2 May 1990

[b] The small amount of this additive is ignored in the material balance calculations

c The small flow of this product is ignored in the material balance calculations

[d] The negative value is the result of an accounting convention at Wilsonville. It is from this stream that all non-coal-derived materials that are introduced into the system are negated from the overall material balance

[e] The negative value indicates an inventory draw-down

carbon across a reactor is obtained by difference between the output and input aromatic carbons.

Carbon aromaticity balances were made for Wilsonville coal liquefaction run 259G and are summarized in *Table 4*. The data are reported on the basis of 100 kg maf coal. The carbon aromaticity balance across the first-stage reactor shows a deficit of 14.1 kg of aromatic carbon (output − input). This represents the amount of aromatic carbon that was hydrogenated in the first stage of liquefaction during run 259G. The overall carbon aromaticity balance across the first- and second-stage reactors shows a deficit of 32.7 kg of aromatic carbon. On the basis of the feed coal, this means that 58% of the original aromatic carbon in the Pittsburgh coal was hydrogenated during the Wilsonville two-stage liquefaction run 259G. The amount of aromatic carbon hydrogenated during the second stage of liquefaction can be obtained by subtracting the first-stage aromatic carbon deficit from the overall deficit. This gives a value of 18.6 kg of aromatic carbon that was hydrogenated during the second stage of liquefaction.

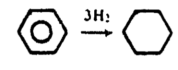
The aromatic carbon balance data (*Table 4*) show that 57% of the hydrogenation of aromatic carbon occurs in the second stage of liquefaction. Presumably, this causes a reduction in molecular weight of the products. It also contributes to the increase in the H/C ratio of the final liquid product (1.81 net product oil product versus 1.07 total first-stage liquid product). This is consistent with the idea that the first stage of liquefaction involves coal dissolution and the second stage involves primarily liquids upgrading. Data on the modes of hydrogen utilization, which are discussed in the next section, support these ideas.

Hydrogen utilization during liquefaction

The chemical reactions that are present in all stages of coal liquefaction are reactions of hydrogen. There are a number of ways in which hydrogen participates in the direct liquefaction of coal[6,11–13]. These include hydrogenolysis, alkyl bond scission and hydrogenation:

$$\text{hydrogenolysis} \quad \text{R-O-R}' \xrightarrow{2H_2} \text{RH} + \text{HR}' + H_2O \quad (1)$$

$$\text{alkyl bond scission} \quad \text{R-R}' \xrightarrow{H_2} \text{RH} + \text{HR}' \quad (2)$$

hydrogenation  (3)

These reactions consume hydrogen during the liquefaction process. In hydrogenolysis, hydrogen is used to remove heteroatoms. In alkyl bond scission, the molecular weights of the liquefaction fragments are reduced. During hydrogenation, aromatic rings are saturated.

The product carbon aromaticities from hydrogenolysis and alkyl bond scission are generally the same as that of the reactants (coal + solvent), whereas hydrogenation produces a product of different aromaticity than the starting materials[11]. Also, aromatization, which is the reverse of hydrogenation, and condensation, which is the reverse of bond scission, are potential sources of hydrogen during liquefaction.

Table 4 Summary of aromatic carbon mass balance data (basis: 100 kg maf coal)

Sample no.	Descriptor	Process stage	Sample (kg, maf)	Carbon (wt%, maf)	Carbon aromaticity	Aromatic carbon (kg)	Total aromatic carbon (kg)
Wilsonville run 259G[a]							
Input							
1	Pittsburgh coal	First	100	81.2	0.69	56.0	
4	Recycle product oil	First	242.5	90.6	0.71	156.0	212.0
Output							
3	Process oil	First	294.0	89.3	0.72	189.0	
5	Separator overhead	First	35.3	86.7	0.27	8.3	
	Product oil						197.3
							$\Delta = -14.7$
Wilsonville run 259G[a]							
Input							
1	Pittsburgh coal	Overall two-stage	100	81.2	0.69	56.0	
							56.0
Output							
2	Process distillate	Overall two-stage	73.7	86.4	0.26	16.6	
6	Ash concentrate	Overall two-stage	8.6	85.5	0.91	6.7	
							23.3
							$\Delta = -32.7$

[a] Several additional minor inputs and outputs not accounted, see material balance (*Table 3*)

Finseth *et al.*[6] proposed a method to monitor the changes in hydrogen utilization during coal liquefaction. This method incorporates a variety of analytical methods that are already available or currently under development. In the method of Finseth *et al.*[6], the total hydrogen incorporated in the carbonaceous products during liquefaction is given by:

$$\Delta H_T = \Delta H_C + \Delta H_{hyd} \qquad (4)$$

where ΔH_T = total hydrogen incorporated, ΔH_C = hydrogen incorporated in bond cleavage reactions (Equations (1) and (2)) and ΔH_{hyd} = hydrogen incorporated by hydrogenation (Equation (3)).

The term ΔH_T is determined by classical elemental analysis; ΔH_{hyd} can be determined by combining solid- and liquid-state ^{13}C n.m.r. measurements with elemental analysis measurements of the solid and liquid products and reactants. There is no satisfactory method to measure ΔH_C, the number of bonds broken during the reaction. However, ΔH_C can be further divided into: bond cleavage associated with heteroatom removal, ΔH_{NOS} (Equation (1)); alkyl bond scission (Equation (2)) which results in C_1–C_4 hydrocarbon gases, ΔH_{C1-C4}; and alkyl bond scission in the slurry mixture that yields non-volatile solid and liquid products, ΔH_{matrix}:

$$\Delta H_C = \Delta H_{NOS} + \Delta H_{C1-C4} + \Delta H_{matrix} \qquad (5)$$

Substituting Equation (5) into Equation (4) yields:

$$\Delta H_T = \Delta H_{hyd} + \Delta H_{NOS} + \Delta H_{C1-C4} + \Delta H_{matrix} \qquad (6)$$

Thus, measurement of hydrogen incorporation during coal liquefaction is reduced to measuring ΔH_T by elemental analysis, measuring ΔH_{hyd} by high resolution ^{13}C n.m.r. aromaticity measurements in the solid and liquid reactants and products, and measuring ΔH_{C1-C4} by quantitative gas analyses. The term ΔH_{matrix} is then determined by difference. If this term is negative, hydrogen is liberated because of condensation reactions; if ΔH_{matrix} is positive, then thermolysis reactions consume hydrogen during liquefaction.

Finseth's method is designed to determine hydrogen incorporated in the carbonaceous product, but does not account for hydrogen incorporated in the heteroatomic gaseous products (H_2O, H_2S, NH_3). We modified the method to include that hydrogen, ΔH_{NOS}(gas). ΔH_{NOS}(gas) was determined from the measured yields and calculated hydrogen contents of H_2O, H_2S and NH_3. ΔH_T was taken as the measured overall hydrogen consumption during the liquefaction test. For the calculations of the light hydrocarbons, we made some additional assumptions. Data were available for C_1–C_3 and C_4–C_6 hydrocarbon gas yields, so hydrogen utilization was determined for both hydrocarbon groups. Thus,

$$\Delta H_T = \Delta H_{hyd} + \Delta H_{NOS} + \Delta H_{NOS}(\text{gas}) + \Delta H_{C1-C3} + \Delta H_{C4-C6} + \Delta H_{matrix} \qquad (7)$$

These data are calculated using the assumptions of Finseth *et al.*[6] that, on average, one hydrogen atom is incorporated into the organic product for every heteroatom removed from the feed material; hydrogenation consumes one hydrogen atom for every carbon atom reduced (each 0.01 change in aromaticity); and two hydrogen atoms are consumed per mole of light hydrocarbons formed. The rationale for these assumptions is discussed in greater detail by Finseth *et al.*[6], Lett *et al.*[21] and by Beret and Reynolds[22], who also used the method for determining hydrogen incorporation in petroleum residuum hydroconversion. Finseth's method does not account for production of carbon oxides; however, in period G of run 259, the carbon oxide yields were very low (*Table 6*). Apparently, any carbon oxides initially

Table 5 Hydrogen utilization accounting calculation, Wilsonville run 259G, first stage (basis: 100 kg maf coal)

	Inputs				Outputs					
	Dry coal	Recycle oil	Gas	Total	Interstage oil	Separator overhead	Gas	Total	Δ, out – in	
Sample no.	1	4	–	–	3	5	–	–		
Mass (kg)	104.6	260.5[a]	4.6	369.7	314.8	36.3[b]	18.5	369.7	–	NA
Elementals (kg)										
C	81.2	221.0	–	302.3	262.6	31.5	8.2[c]	302.3	–	–
H	6.0	18.9	4.6	29.5	21.8	4.3	3.3[c]	29.5	–	–
N	1.4	0.4	–	1.8	0.9	0.1	0.8[c]	1.8	–	–
O (diff.)	8.1	1.6	–	9.7	5.5	0.4	4.1[c]	10.0	0.3 kg	–
S	3.3	2.0	–	5.3	3.2	0.0	2.1[c]	5.3	–	–
Ash	4.6	16.6	–	21.2	20.8	–	–	20.8	–0.4 kg	NA
Gases (kg)										
H_2	–	–	4.6	4.6	–	–	–	–	–4.6 kg	
C_1–C_3	–	–	–	–	–	–	6.1	6.1	6.1 kg	0.28 kmol[d]
C_4–C_6	–	–	–	–	–	–	3.0	3.0	3.0 kg	0.04 kmol[e]
CO_x	–	–	–	–	–	–	0.4	0.4	0.4 kg	0.01 kmol[f]
H_2O	–	–	–	–	–	–	6.6	6.6	6.6 kg	0.37 kmol
NH_3	–	–	–	–	–	–	0.6	0.6	0.6 kg	0.03 kmol
H_2S	–	–	–	–	–	–	1.8	1.8	1.8 kg	0.05 kmol
Carbon aromaticity, f_a	0.69	0.71	–	0.70	0.72	0.27	–	0.65[g]	–0.05	–1.26 kmol[h]

[a] Seal oil (1.46 kg) accounted here
[b] V-140 oil (0.98 kg) accounted here
[c] By difference
[d] Assumes molecular weight of 21.9
[e] Assumes molecular weight of 66.2
[f] Assumes CO_2
[g] Total f_a includes carbonaceous gases, for which $f_a = 0$
[h] Change in f_a represents mol H consumed by saturation per mol of carbon. Carbon = 302.3 kg = 25.2 kmol; therefore, $-0.05 \times 25.2 = 1.26$ kmol H

produced were hydrogenated to water and methane in the presence of the active hydrogenation catalyst that was present in each reactor.

This calculation method was applied to the data from Wilsonville run 259G (*Tables 5–8*). *Tables 5* and *6* provide the weighted elemental analyses needed for normalization to the basis of 100 mol of coal carbon in the products and feed. *Table 7* compares the products and feed materials on the normalized basis. The data in *Table 7* and Equation (7) were used to determine the hydrogen utilization among the various modes of consumption listed in *Table 8*. On a weight basis, the distribution of C_1–C_3 gases was assumed to be 50% C_1, 30% C_2 and 20% C_3. This gave an average molecular weight of 21.9 g mol^{-1}, which was used in the conversion from a weight per cent basis (*Tables 5* and *6*) to moles (*Table 7*). The distribution of C_4–C_6 hydrocarbons was also assumed to be 50, 30 and 20 wt%, respectively. This gave an average molecular weight of 67.8 g mol^{-1} for this fraction.

The hydrogen utilization during Wilsonville run 259G is summarized in *Table 8*. A number of observations can be made from these data. Overall, 99.0 mol of hydrogen atoms were consumed per 100 mol of coal carbon over the two stages of liquefaction. Of this amount, 68.1 mol or 69% was consumed during the first stage, and 30.9 mol, or 31% was consumed in the second stage. Matrix cleavage reactions accounted for 31% of the total first-stage hydrogen utilization, and hydrogenation accounted for 27% during this stage. However, hydrogenation reactions accounted for 40% of the overall hydrogen consumption. Hydrogenation dominated the hydrogen consumption during the second stage of liquefaction, accounting for 69% of the total second-stage hydrogen consumption. These data are consistent with the notion that hydrogen consumption during the first stage involves molecular weight reduction of the products, whereas during the second stage, most of the hydrogen is used for product upgrading.

Hydrogen consumption for hydrocarbon gas production (C_1–C_3 plus C_4–C_6) remained relatively constant over both stages of liquefaction. Overall, 14% of the total two-stage hydrogen consumption was used for hydrocarbon gas production; this same percentage (14%) of total first-stage hydrogen consumption and total second-stage hydrogen consumption was used for hydrocarbon gas production. However, most (70%) of the total hydrogen consumed for hydrocarbon gas production is used during the first stage.

Heteroatom removal and heterogas production consumed large amounts of hydrogen, accounting for 27% of the overall hydrogen consumption. Proportionately, about the same amount of the total hydrogen consumption in the second stage (25%) and the first stage (28%) was utilized for heteroatom removal and heterogas production. As illustrated in *Tables 5* and *6*, water is the principal heterogas produced in the first stage, whereas H_2S and NH_3 production are of greater relative import-

Table 6 Hydrogen utilization accounting calculations, Wilsonville run 259G, overall two-stage (basis: 100 kg maf coal)

	Inputs			Outputs				Δ, out − in	
	Dry coal	Gas	Total	net product oil	Ash concentrate	Gas	Total		
Sample no.	1	–	–	2	6	–	–		
Mass (kg)	104.6	6.7	111.3	72.0[a]	15.0[b]	24.3	111.3	–	NA
Elementals (kg)									
C	81.2	–	81.2	62.2	8.4	10.6[c]	81.2	–	–
H	6.0	6.7	12.7	9.4	0.5	2.8[c]	12.7	–	–
N	1.4	–	1.4	0.1	0.1	1.2[c]	1.4	–	–
O (diff.)	8.1	–	8.1	0.3	0.4	6.9[c]	7.6	0.5 kg	–
S	3.3	–	3.3	0.0	0.5	2.8[c]	3.3	–	–
Ash	4.6	–	4.6	–	5.1	–	5.1	0.5 kg	NA
Gases (kg)									
H_2	–	6.7	6.7	–	–	–	–	−6.7 kg	−6.7 kmol
C_1–C_3	–	–	–	–	–	8.9	8.9	8.9 kg	0.41 kmol[d]
C_4–C_6	–	–	–	–	–	4.1	4.1	4.1 kg	0.06 kmol[e]
CO_x	–	–	–	–	–	0.4	0.4	0.4 kg	0.01 kmol[f]
H_2O	–	–	–	–	–	6.7	6.7	6.7 kg	0.40 kmol
NH_3	–	–	–	–	–	1.4	1.4	1.4 kg	0.08 kmol
H_2S	–	–	–	–	–	2.9	2.9	2.9 kg	0.09 kmol
Carbon aromaticity, f_a	0.691	–	0.69	0.26	0.91	–	0.29[g]	−0.40	−2.71 kmol[h]

[a] V-140 oil (0.98 kg) and seal oil (−2.61 kg) accounted here

[b] Deasher resid (2.73 kg) and ash recycle (−0.87 kg) accounted here

[c] By difference

[d] Assumes molecular weight of 21.9

[e] Assumes molecular weight of 66.2

[f] Assumes CO_2

[g] Total f_a includes carbonaceous gases, for which $f_a = 0$

[h] Change in f_a represents mol H consumed by saturation per mol of carbon. Carbon = 81.2 kg = 6.8 kmol; therefore, −0.40 × 6.8 = −2.71 kmol H

ance in the second stage. (The values for the second stage are obtained by taking the difference of the values in *Tables 5* and *6*.)

The data in *Table 8* suggest that a small amount of hydrogen (2.3 mol/100 mol of coal carbon) is liberated from condensation reactions during the second stage of liquefaction. However, as noted earlier, the hydrogen consumed for matrix cleavage reactions is obtained by difference (Equation (7)). The small amount of condensation calculated for the second stage may reflect the fact that this number was obtained by difference and that cumulative errors in elemental, gas and n.m.r. analyses, mass balances, and the assumptions all contribute to the accuracy of the hydrogen consumption value assigned to matrix cleavage.

Finally, it must be emphasized that this method only treats the net chemistry of hydrogen utilization and cannot determine whether internally produced hydrogen or the hydrogen atmosphere actually provides the hydrogen that is consumed. Nevertheless, the method is useful for relating processing conditions to the overall process chemistry, and for exploiting this information to optimize process conditions for a desired product slate.

SUMMARY AND CONCLUSIONS

This study showed by that combining solid- and liquid-state ^{13}C n.m.r. measurements with elemental analyses and mass balance data, greater insight into the chemistry of coal liquefaction processes can be obtained. By measuring the increase or decrease of aromatic carbon in the various liquefaction products, the degree of hydrogenation at different stages of liquefaction and under various conditions can be ascertained. Application of these procedures to Wilsonville run 259G showed an overall deficit of 32.7 kg of aromatic carbon. Relative to the starting coal, this means that 58% of the original aromatic carbon in Pittsburgh coal was hydrogenated during the overall two-stage liquefaction.

The net hydrogen consumption among different hydrogen-consuming reactions was also determined. The data from Wilsonville run 259G showed that, during two-stage liquefaction, most of the hydrogen was consumed for hydrogenation of aromatic rings (40%), followed by heteroatom removal and heterogas production (27%), matrix cleavage (cracking) reactions (18%), hydrocarbon gas production (14%). Matrix cleavage is the major consumer of hydrogen in the first stage, accounting for 31% of the total first-stage hydrogen consumption. Hydrogenation is the major consumer of hydrogen during the second stage, accounting for 69% of the total second-stage hydrogen consumption. Oxygen is the major heteroatom removed in the first stage, whereas sulphur and nitrogen removal is more predominant in the second stage. The data indicate that during period G of run 259, the high-temperature first stage functioned to hydrocrack and deoxygenate the coal slurry, whereas the lower-temperature second stage functioned to hydrogenate and further reduce the nitrogen and sulphur contents of the slurry oil.

The combination of n.m.r. measurements with elemental analyses and process conversion data provides a powerful method to study coal liquefaction processes. The measurements can be used in a straightforward manner to obtain information about the degree of hydrogenation, modes of hydrogen utilization, and to some extent the degree of condensation/retrograde reactions that occur during coal liquefaction. In addition, with a suitable suite of samples that vary as a function of time, temperature and other process conditions, it should be possible to develop kinetic models and other predictive relationships for coal liquefaction based on structural parameters.

Table 7 Hydrogen utilization accounting calculations, Wilsonville run 259G

	Input	Output[a]	Δ	H utilization
	(mol/100 mol of feedstock carbon)			
First stage				
Analysis (mol/100 mol feed C)				
C	100.00	100.00	–	
H	98.8	113.4	14.6	14.6
N	0.5	0.3	−0.2	1.4
O	2.4	1.5	−0.9	
S	0.7	0.4	−0.3	
Gas yield (mol/100 mol feed C)				
C_1–C_3	–	1.1	1.1	
C_4–C_6	–	0.2	0.2	2.6
Carbon aromaticity, f_a	0.70	0.65	−0.05	5.0
Overall two stage				
Analysis (mol/100 mol coal C)				
C	100.00	100.00	–	
H	88.7	170.5	81.8	81.8
N	1.5	0.2	−1.3	9.5
O	7.5	0.6	−6.9	
S	1.5	0.2	−1.3	
Gas yield (mol/100 mol coal C)				
C_1–C_3	–	6.0	6.0	
C_4–C_6	–	0.9	0.9	13.8
Carbon aromaticity, f_a	0.69	0.29	−0.40	40

[a] Includes liquid streams plus non-heteroatom gases

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Table 8 Hydrogen utilization accounting results Wilsonville run 259G

	Hydrogen utilization by organic products			
	First stage		Overall two stage	Second stage (by diff.)
	(mol H/100 mol slurry carbon)	(mol H/100 mol coal carbon[a])	(mol H/100 mol coal carbon[a])	(mol H/100 mol coal carbon[a])
C_1–C_3 production	2.2	8.2	12.0	3.8
C_4–C_6 production	0.4	1.5	1.8	0.3
Heteroatom removal	1.4[b]	5.2[b]	9.5[b]	4.3[b]
Hydrogenation	5.0	18.6	40.0	21.4
Matrix cleavage	5.6	20.8	18.5	−2.3
Heterogas production	3.7	13.8	17.2	3.4
Total	18.3	68.1	99.0	30.9

[a] Coal carbon/slurry carbon ratio = 81.2/302.3

[b] Refers to H added to carbonaceous products to replace carbon–heteroatom bonds

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