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Coal Liquefaction Process Streams Characterization and Evaluation,

Quarterly Technical Progress Report
July 1 through September 30, 1993

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

March 1994

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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, JULY 1 THROUGH SEPTEMBER 30, 1993**

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

- Fifty-eight process samples from HRI CTSL Bench Unit Run CC-15 (227-75) were analyzed to provide information on process performance. Run CC-15 was operated for 14 periods (days) from October 21 through November 3, 1992 in the thermal/catalytic configuration with Black Thunder Mine (Wyodak and Anderson seams) coal and Shell S-317 Ni/Mo supported extrudate catalyst. The run was made to test performance with and without a dispersed hydrous iron hydroxide catalyst precursor impregnated in the coal. Results are compared with those of previous HRI CTSL bench unit Run CC-1, which was operated in the catalytic/catalytic configuration, also with Shell S-317 catalyst.
- Several HRI Run CC-15 product distillate fractions prepared by the National Institute for Petroleum and Energy Research (NIPER) for petroleum inspection tests were further characterized by CONSOL. These characterization data are presented.
- Microautoclave tests and chemical analyses were performed to evaluate the solvent quality of two potential solvents for Alberta Research Council (ARC).
- Eight product samples from catalytic dehydrogenation experiments were characterized for the University of Pittsburgh.
- A description is presented of the thermogravimetric analysis (TGA) method for determination of resid concentration/resid conversion, which was adapted for use in-house from HRI's standard method.
- A brief summary of the status of the Participants Program is given.
- Two papers, based on work performed under this contract, are appended. Both were authored by CONSOL researchers. One paper was from the DOE Coal Liquefaction and Gas Conversion Contractor's Conference, September 27-29, 1993, Pittsburgh, PA, and the other paper was from the DOE workshop "Direct Liquefaction: Focused Research for Improved Economics", September 27, 1993, Pittsburgh, PA.

Section 1

EXECUTIVE SUMMARY

A set of 58 process samples from HRI CTSL Bench Unit Run CC-15 (also known as Run 227-75) were analyzed to provide information on process performance. Run CC-15 was operated in the thermal/catalytic configuration with Black Thunder Mine (Wyodak and Anderson seams) coal and Shell S-317 Ni/Mo supported extrudate catalyst in the second-stage reactor. The run was made to test performance with and without a dispersed hydrous iron hydroxide catalyst precursor impregnated in the coal. Results are compared with those of previous HRI CTSL bench unit Run CC-1, which was operated in the catalytic/catalytic configuration, also with Shell S-317 catalyst.

HRI Run CC-15 had three major operating variables: catalyst age, the use (or not) of iron-impregnated coal, and pretreater temperature (which had no significant effect on oil properties). Deactivation of the second-stage supported catalyst was the dominant influence on most of the changes in oil properties over the course of the run. Consequences of the increased catalyst age were increases in aromaticity and phenolic -OH concentration and decreases in hydrogen donor content and paraffinic hydrogen content in most process streams, including product distillates. Donor solvent quality of the whole pressure filter liquid (PFL) increased through the first six or eight days of the run, at which point it apparently stabilized.

The effect of suspending the use of iron-impregnated coal in Condition 3 is most apparent in the interstage (first stage) samples. Interstage oils from Condition 3 have higher aromaticity, lower phenolic -OH content in the solubles, and poorer solvent quality, evidently resulting from decreased hydrogenation of the interstage sample (especially the resid portion). The presence of supported catalyst in the second stage largely mitigated any effect on the properties of the PFL, pressure filter cake (PFC) and product distillate samples. The proton distribution data suggest that it was primarily the condensed-ring components of the resid which were hydrogenated less effectively when the untreated coal was used in Condition 3, relative to the use of Fe-treated coal in Conditions 2 and 4.

The lower SO₃-free ash concentration in the PFC from Condition 3, when untreated coal was used, reflects the higher IOM/ash ratio resulting from the lower coal conversion in Condition 3, and addition of the catalyst in Conditions 2 and 4 (which increased the ash content). Evidently most of the observed differences in PFC ash elemental and sulfur and nitrogen concentrations are direct consequences of coal treatment. The PFLs and net product distillates showed no consistent or significant effect on elemental composition resulting from the coal treatment.

Results from Run CC-15 period 8 were compared with those of period 16 of the previous HRI CTSL bench unit run, which was operated in the catalytic/catalytic configuration with Shell S-317 catalyst (Run CC-1). The PFL and interstage (INT) samples from Run CC-15 period 8 PFL were lower in donor solvent quality, slightly lower in aromaticity and hydroaromaticity, and were higher in paraffinicity and phenolic -OH concentration than their Run CC-1 period 16 counterparts. Although the dispersed Fe catalyst in Run CC-15 evidently provided good hydrogenation, it produced a lower-quality recycle solvent. Deoxygenation was much lower in operation with the dispersed Fe in Run CC-15 than in supported catalyst operation in Run CC-1. The higher first-stage temperature in Run CC-1 probably contributed to the apparently higher deoxygenation and hydrocracking in that run.

CHARACTERIZATION OF HRI CTSL RUN CC-15 NET PRODUCT AND FRACTIONS

CONSOL characterized the net product oil from HRI CTSL Run CC-15 and its fractions produced by the National Institute for Petroleum and Energy Research (NIPER) after the petroleum inspection tests were completed. ¹H-NMR, phenolic -OH and GC/MS data were collected. The crude oil and the four distillation fractions have low concentrations of phenolics; as expected, the kerosene cut has the highest concentration of phenolics. The HRI CTSL Run CC-15 net product oil (crude) has a lower boiling-point distribution, contains more hydrogen, is less aromatic, and less phenolic than the net products of Wilsonville Runs 259G and 260D examined previously in this contract.^{10,19-21} In addition, the boiling-point fractions (naphtha, kerosene, etc.) of the Run CC-15 net product are more enriched in hydrogen, are less aromatic and contain less phenolic and total oxygen (by difference) than the respective fractions from Wilsonville Runs 259G and 260D. NIPER used caustic washing to extract the phenolic compounds from the naphtha and kerosene fractions of the net product of Run CC-15. CONSOL's

analyses show that the caustic washing method employed was reasonably efficient and selective for removal of phenolics. The specific phenolic compound types present in the cresylic fractions (alkali extract) were identified: C₀- to C₃-phenols in the naphtha fraction and C₁- to C₄-phenols and indanol in the kerosene fraction.

ALBERTA RESEARCH COUNCIL CANDIDATE LIQUEFACTION OILS

Alberta Research Council sent two candidate liquefaction oils, both from Wilsonville Run 263, and requested information about their donor solvent quality. The oil identified as V-178 +320°C was much lighter than authentic plant recycle solvents. The V-1074 oil was much lighter than expected for this stream, but was equivalent by our characterization methods to the recycle heavy distillate materials we previously analyzed from the slurry-catalyst-only portion of Run 263 (Periods A through H). The oils have roughly equivalent donor quality, which we rate as "fair", based on standard microautoclave tests. We recommend the V-1074 oil as the preferred liquefaction solvent.

THERMOGRAVIMETRIC ANALYSIS (TGA) METHOD FOR THE DETERMINATION OF 975 °F* ASTM D-1160 DISTILLATION EQUIVALENT VALUES

A thermogravimetric analysis (TGA) method for the determination of 975 °F* ASTM D-1160 distillation equivalence values developed by HRI, Inc. was modified for use in-house. The modified test gave self-consistent results, with acceptably small standard deviations. These values compared well to those obtained by HRI with the same samples with their TGA method, and with an ASTM D-1160 distillation. The method is now available for use on a routine basis.

PARTICIPANTS PROGRAM

The first Phase III project of the Participants Program was completed this quarter. This project was for petroleum inspection tests of net product oils produced in HRI Run CC-15. The seventh and final subcontract was placed (with NIPER) for another set of petroleum inspection tests on the net product oil from HRI Run CMSL-2. The Pennsylvania State University and the University of Utah requested and received no-cost time extensions for their projects. A trip was made to Penn State to discuss the progress of their work. A draft final report was received from the University of Pittsburgh. Work is progressing at the University of Delaware and SRI International.

Section 2

INTRODUCTION

This is the Technical Progress Report for the sixteenth quarter of activities under DOE Contract No. DE-AC22-89PC89883. It covers the period July 1 through September 30, 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 (Section 3) of this report.

- A set of 58 process samples from HRI CTSL Bench Unit Run CC-15 (227-75) were analyzed to provide information on process performance. Run CC-15 was operated for 14 periods (days) in the thermal/catalytic configuration in October and November of 1992 with Black Thunder Mine (Wyodak and Anderson seams) coal and Shell S-317 Ni/Mo supported extrudate catalyst. The run was made to test performance with and without coal impregnated with a dispersed hydrous iron hydroxide catalyst precursor. Results are compared with those of previous HRI CTSL bench unit Run CC-1, which was operated in the catalytic/catalytic configuration with Shell S-317 catalyst.
- The net product oil from HRI Run CC-15 and four distillate fractions prepared from it by the National Institute for Petroleum and Energy Research (NIPER) for petroleum inspection tests were further characterized by CONSOL. These results are presented.
- A description is presented of our thermogravimetric analysis (TGA) method adapted from one routinely used by HRI for determination of 975 °F⁺ resid concentration/resid conversion in small samples.
- At DOE's request, microautoclave tests and chemical analyses were performed to evaluate the solvent quality of two potential coal liquefaction solvents for Alberta Research Council.
- Eight product samples from catalytic dehydrogenation experiments were characterized for the University of Pittsburgh.
- Substantial progress was made in the Participants Program this quarter. A summary of activities in the Participants Program is presented. Three more Phase III subcontracts are in place, bringing the total to six out of the seven planned subcontracts.

- One DOE workshop presentation and one 1993 DOE Contractors' Review Conference paper are appended. The presentation entitled "Economic Benefits of Process Stream Characterization", presented by R. A. Winschel at the DOE workshop "Direct Liquefaction: Focused Research for Improved Economics", September 27, 1993, Pittsburgh, PA, is included as Appendix 1. F. P. Burke also participated in the Workshop by chairing one of the sessions. The paper entitled "Coal Liquefaction Process Streams Characterization and Evaluation: an Analytical Characterization Case Study", authored by S. D. Brandes, G. A. Robbins, R. A. Winschel, and F. P. Burke, is included as Appendix 2. It includes work performed under both the Base and Participants Programs.
- Work in progress, but not complete, consists of process stream characterization on samples from Wilsonville Run 263.

Section 3
RESULTS AND DISCUSSION

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HRI CTSL RUN CC-15

HRI RUN CC-15 BACKGROUND

CONSOL received 58 samples from HRI Catalytic Two-Stage Liquefaction (CTSL) bench unit Run CC-15 for analysis. Samples consisted of the feed coals, the start-up/make-up oil, interstage (INT) samples (actually first-stage reactor inventory samples) from three run periods, pressure-filter liquids (PFLs), pressure-filter cakes (PFCs), separator overheads (SOHs), and atmospheric-still overheads (ASOHs) from thirteen run periods.

HRI Catalytic Two-Stage Liquefaction (CTSL) Run CC-15,^{1,2,3} also called Run 227-75, was made in HRI's two-stage ebullated bed bench scale unit 227. The run was divided into four operating conditions, each lasting several days (Table 1). Each day is considered a run period. The objective of the run was to test a predispersed (impregnated) hydrated iron oxide catalyst prepared by the method of incipient wetness, as developed by the U.S. Department of Energy, Pittsburgh Energy Technology Center.⁴ The feed coal was Wyodak and Anderson seam, Black Thunder Mine subbituminous coal. The pretreated coal, which had an iron content of 0.57 to 0.65 wt % according to HRI (Table 2), was used in run periods 1-5, 6-8, and 12-14 (Conditions 1, 2, and 4, respectively). An untreated sample of the same coal was used in run periods 9-11 (Condition 3); the untreated coal had an iron content of 0.20 wt % according to HRI. The analyses of the coal and the pretreated coal can be found in Table 2. The pretreated coal has an elevated N content (about 2.7% vs. about 1% MAF) as a result of the catalyst incorporation procedure.¹

Start-up and make-up oil for Run CC-15 was a filtered process-derived liquid produced in the HRI process development unit during Run 260-03, which also used Black Thunder Mine coal. Analyses of the start-up oil are given in Table 3. The liquefaction tests were conducted in HRI's 20 kg/day continuous flow unit 227 (Figure 1). To activate the iron catalyst precursor (FeOOH), the impregnated Black Thunder Mine coal was pretreated with H₂S in a pretreatment reactor at 275 °C (522 °F) in Condition 1 and 290 °C (570 °F) in Conditions 2 through 4. During the liquefaction, the first stage reactor temperature was maintained at

about 427 °C (800 °F) and the second stage reactor temperature was held at about 413 °C (775 °F). Throughout the test, the first stage reactor was operated thermally (i.e., without supported catalyst). Shell S-317 NiMo catalyst was present in the second-stage reactor. The test was conducted using constant space velocity of about 43 lb coal/h/ft³ of settled supported catalyst. Catalyst age increased as the run progressed (batch catalyst operation). Operating conditions are given in Table 1.

Yields and process performance results from HRI are given in Table 1 for all of the run conditions. Although the values in Table 1 indicate that desulfurization was low (even negative), HRI found the actual organic desulfurization to be over 90%.^{1a} The low removal of total sulfur is due to high sulfur uptake by the solid residual material, which is concentrated in the pressure filter cake. It is presumed that the sulfur is trapped as iron and calcium sulfides in the filter cake. Coal conversion and distillate yields in this run were higher in Conditions 1, 2, and 4 when iron-impregnated coal was used than in Condition 3 when it was not used. Although there was no apparent effect of catalyst deactivation as the run progressed on coal conversion, the catalyst deactivation is evident in the performance data for distillate yield and conversion of 975 °F* resid, which both decreased.

BENCH UNIT DESCRIPTION HRI RUN CC-15^{1,5}

In the two-stage catalytic process as configured for Run CC-15 (Figure 1), coal was slurried with process-derived heavy recycle oils and brought to the slurry preparation section on a bi-hourly basis. The slurry was pressurized, mixed with hydrogen, and fed to the pretreater. Sulfur was added in the form of liquefied hydrogen sulfide to ensure proper sulfidation of the catalyst precursor, as well as to maintain the supported catalyst in the sulfided state. The pretreater was operated at 275 °C (522 °F) in Condition 1 and 290 °C (570 °F) in Conditions 2 to 4. The slurry then passed directly into the first-stage thermal reactor. The first stage was operated at a temperature of about 427 °C (800 °F).

The first-stage products pass directly to the second stage, without any separation, for hydrotreatment, liquefaction, and heteroatom removal. The severity of this stage can be regulated to control distillate yield and product selectivity.

In Run CC-15, the second-stage temperature was maintained at about 413 °C (775 °F).

The first-stage reactor is a back-mixed reactor (with slurry catalyst) and the second-stage reactor is a conventional ebullated-bed reactor. Utilization of the 1/32" extrudate catalyst allowed fluidized catalyst operation over a wide range of slurry oil viscosity and density. The solids content and residual oil composition in the recycle stream can be varied for optimum process performance. In Run CC-15, the slurry oil was composed of filtered atmospheric still bottoms, with no solids recycle. Mass balance was performed every 8 or 12 hours and a daily (period) average was reported. Each of the conditions tested was maintained for a minimum of three days (periods) to ensure validity of the data.

SAMPLE DESCRIPTION

CONSOL received a suite of 58 samples from all four run conditions (thirteen periods) of HRI Catalytic Two-Stage Liquefaction (CTSL) bench unit Run CC-15. These included start-up solvent, coal, and process and product stream samples. Pressure-filter liquids (PFLs) which we received were all daily composites of three plant shifts, and consequently were designated ABC after the period number (for example, the 8ABC PFL is composited from 8A, 8B, and 8C PFL samples). PFLs were received from periods 2ABC through 14ABC. Pressure-filter cakes (PFCs), separator overheads (SOH), and atmospheric-still overheads (ASOH) were received from periods 2A through 14A. Interstage oils (INT) were obtained from periods 9A, 12A, and 15A. In addition, samples of the untreated feed coal, the treated feed coal, and the start-up/make-up oil were received. HRI sample numbers are included in the tables in which each sample first appears.

First-stage oils (also called interstage oils, INT) are samples of the first-stage reactor inventory obtained from the recirculation stream on the ebullating bed. 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 sampling procedure used by HRI is to complete the material balance of the last period in a condition, then to take the first-stage sample while maintaining constant operating conditions. As a result, each first-stage sample corresponds most closely to the PFL sample taken one sub-period

earlier. For this reason, the 9A, 12A, and 15A INT samples represent periods 8 (Condition 2), 11 (Condition 3), and 14 (Condition 4), respectively. The inter-stage oils and corresponding PFL, PFC, and ASOH/SOH blend samples constitute twelve samples chosen for elemental and advanced analyses, representative of the corresponding conditions. CONSOL produced the ASOH/SOH blends by blending the two light net distillate product oil samples, the separator overhead (SOH) and atmospheric still overhead (ASOH) sample, in the proportions in which they were produced (according to HRI's reported yields). Thus, each blend represented a net oil product for that period.

ANALYSES

All oils were assumed to be solids-free for analytical purposes. Elemental analyses were obtained on selected samples (Tables 4 and 5). Proton distribution analyses were obtained by ^1H -NMR for each whole oil sample (Tables 8-10). Each whole oil sample was analyzed by FTIR for phenolic -OH content (Table 11). Each whole PFL and INT 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 INT, one whole PFL, and the start-up/make-up oil sample were distilled (Table 6) to 320 °C pot/270 °C column/ 5 torr (850 °F/atm). Each INT 850 °F⁺ resid was analyzed by ^1H -NMR (Table 9). Each INT 850 °F⁻ distillate was analyzed by ^1H -NMR (Table 9), and FTIR (Table 11). The 850 °F⁺ distillation bottoms samples were extracted with tetrahydrofuran (THF) (Table 6). Each THF-soluble extract was analyzed by FTIR for phenolic -OH content (Table 11). From each THF-insoluble filter cake a sample was ashed, and the insoluble organic matter (IOM, also called Unconverted Coal, or UC) content was calculated by difference. 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 ^1H -NMR (Table 8). Pressure filter cake samples also 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).

In addition to these routine analyses, several promising advanced analytical techniques were applied to selected Run CC-15 process stream samples under the Participants Program of this contract. These special analyses include field

ionization mass spectrometry (FIMS) and solid state cross polarization/magic angle spinning (CP/MAS) ^{13}C -nuclear magnetic resonance (NMR) spectroscopy. Additionally, standard petroleum inspection tests were used to evaluate the quality of the net product oils from Run CC-15. These studies were designed to demonstrate, in a systematic manner, application of these methods to support coal liquefaction process development. Analytical data from these studies are discussed and interpreted in relation to Run CC-15 process conditions and performance, briefly in the paper in Appendix 2, and in more detail in Topical Reports.^{6,7,8} No further discussion of those analyses will be given here.

RUN CC-15 SAMPLE PROPERTIES

Overall Run

CONSOL characterized all of the Run CC-15 process oil samples by several routine methods, such as ^1H -NMR spectroscopy, phenolic -OH determination by Fourier transform infrared (FTIR) spectroscopy, and solvent quality determinations, as appropriate. The results of characterization by several of these methods are presented in Figures 2 through 5 for several process streams. These results provide a general overview of the run. This is followed by a more detailed discussion of the characterization of the samples selected for additional analyses (data in Figures 6 through 11).

It is apparent from the ^1H -NMR data (Figure 2, Tables 8-10) that there is a general trend of increasing aromaticity of all samples except the whole interstage oils for the duration of the run. This reflects the dominant effect of supported catalyst deactivation with respect to hydrogenation. The trends showing increased aromaticity of the SOH and ASOH samples as the run progressed are less pronounced and the rates of increase are lower than the trends for the PFL and PFC samples (Figure 2). During Condition 3 (Periods 9, 10, and 11), there appears to be a significantly sharp increase in aromaticity of the PFL and PFC samples. This may reflect the absence of the dispersed catalyst. However, during Period 9 an unusually large amount of makeup oil was required in the recycle feed (~20 wt % of the recycle feed was makeup). This significant quantity of the less aromatic make-up oil could decrease the aromaticity of the PFL sample obtained from period 9. The apparent sharp increase is accounted for by a return in periods 10 and 11 to a lower make-up oil to process-derived oil ratio in the system.

Along with the general upward trends in aromatic proton concentration, there are corresponding downward trends in hydroaromatic and paraffinic proton concentrations in the PFL and INT samples. The cyclic beta protons (which include much of the donatable hydrogen), and paraffinic protons (represented by the sum of the alkyl beta and gamma protons) are shown in Figure 3. These trends can be expected to accompany the decreasing hydrogenation activity of the catalyst. The decrease in paraffinics concentration is observed in the distillate products, as well as in the PFL, PFC, and whole interstage samples (evident from Tables 8-10, not all data shown in Figure 3). The start-up/make-up oil was quite high in paraffinic hydrogen. Two factors may contribute to the decrease in hydrogen donors with decreasing hydrogenation activity of the catalyst. One factor is inadequate re-hydrogenation of depleted donors. The second factor is a greater demand on the solvent for donatable hydrogen, if hydrogen is less readily available from other sources.

It is evident that there is also a general trend of increasing phenolic -OH concentration of all samples except the whole interstage oil throughout the run (Figure 4 and Table 11). This reflects the effect of catalyst deactivation with respect to deoxygenation. In contrast to the aromaticity results, the phenolic -OH concentration increases smoothly through the run, with no apparent irregularities. The whole interstage samples are more aromatic and phenolic than their PFL and PFC counterparts (Figures 2 and 4, Tables 8, 9, and 11).

The phenolic -OH contents of the ASOH and SOH samples generally follow that of the corresponding PFL through the run (Figure 4 and Table 11). In spite of having a lower boiling point distribution and lower aromaticity, the ASOH samples are consistently higher in phenolic -OH than the corresponding whole PFLs. This arises from concentration of alkylated phenols in the kerosene cut boiling range.⁹ This was seen previously in distillation fractions from Wilsonville Run 260¹⁰ and in the HRI Run CC-15 product fractions.⁸

Donor solvent quality of the whole PFL, as measured by a standard microautoclave assay, increased from the poor value of the start-up oil (56% MAF coal) to a moderately good value of about 80% MAF coal conversion by Period 8 (Figure 5, Table 12). After Period 8, the donor quality of the whole PFL stayed relatively constant. A small decrease in Periods 11 and 12 may be related to the

discontinuation of the Fe catalyst in Periods 9 through 11. There is a significant loss in donor solvent quality of the whole interstage oil (from 74 to 62%) during the operation with untreated coal (Condition 3).

Period 8, 11, and 14 Samples

The set of twelve PFL, PFC, and interstage samples representing Conditions 2, 3 and 4 (Periods 8, 11, and 14) are discussed here in more detail. Treated coal was used in both Conditions 2 and 4, but the supported catalyst age was greater in Condition 4 than in Condition 2. In Condition 3, the untreated coal was used, and the supported catalyst age was intermediate between the Condition 2 and Condition 4 values. Any property of a Condition 3 sample that falls significantly above or below the midpoint of the Condition 2 and Condition 4 values indicates a probable effect of the use of untreated coal.

The total proton aromaticity and condensed-ring aromatic hydrogen content by $^1\text{H-NMR}$ are shown in Figures 6 and 7, respectively, for the Condition 2, 3, and 4 samples (based on data in Tables 8-9). Included in the graphs are data for the CONSOL-generated 850 °F⁻ distillate and 850 °F⁺ resid fractions of the whole interstage sample. The PFC and PFL aromaticities for the Condition 3 sample are consistent with a linear increase in aromaticity as the run progressed. The whole interstage sample from Condition 3 is substantially more aromatic than the interstage samples from Conditions 2 or 4. The corresponding interstage distillate fraction shows no aromaticity increase from Condition 2 to Condition 3; however, the interstage resid shows a large aromaticity increase. The data shown in Figure 7 indicate that the higher aromaticities were from higher concentrations of condensed aromatic protons. This indicates that condensed-ring components of the resid were hydrogenated less effectively when the untreated coal was used in Condition 3, relative to the use of Fe-treated coal in Conditions 2 and 4. The effect was more pronounced in the interstage samples than in the PFL or PFC samples because the supported catalyst in the second stage provides a levelling effect.

The hydroaromatic hydrogen donor (cyclic beta hydrogen) content of the samples (including the CONSOL-generated interstage 850 °F⁻ distillate and 850 °F⁺ resid fractions) are shown in Figure 8. The PFC sample shows a steady decline in donor content from Condition 2 to 3 to 4. The remaining samples in Figure 8 show a

consistent loss in donor hydrogen content in Condition 3, relative to Conditions 2 and 4. The greatest losses in donor content from Conditions 2 and 4 to Condition 3 took place in the whole interstage sample and in the interstage resid. This is consistent with the total and condensed aromaticity results, in indicating relatively more hydrogenation when the treated coal was fed.

Paraffinic hydrogen content (as measured by the sum of alkyl beta and gamma protons) of the samples is shown in Figure 9. Relative to the midpoint of the Condition 2 and 4 data, the Condition 3 paraffinic hydrogen is low for the PFC, PFL, and interstage resid samples, high for the interstage distillate sample and as expected for the whole interstage samples. This provides further indication of lower hydrogenation in the PFC, PFL, and interstage resid samples during Condition 3, when untreated coal was fed. The reason for the higher interstage distillate paraffinic content during Condition 3 is not clear. The data indicate that it occurred at the expense of cyclic beta hydrogen, and not of aromatic hydrogen, however.

Taken together, the hydrogen distribution data indicate that the lower hydrogenation activity in the first stage, as a result of using untreated coal, primarily affected the interstage resid properties, with less (or no) effect on other samples or process streams.

The donor solvent quality as measured by microautoclave assay is shown in Figure 10 for the whole PFL and interstage samples representing Conditions 2, 3, and 4. There is a significant loss in donor solvent quality (from about 75% to about 62%) of the whole interstage oil during the operation with untreated coal (Condition 3). The hydrogen distribution data presented above make it clear that the high aromaticity and low donor content of the interstage oil produced during Condition 3 were largely responsible for its low donor solvent quality. Since the largest effects on aromaticity and cyclic beta were seen in the interstage resid fraction, the resid quality evidently significantly affects solvent quality.

The phenolic -OH concentrations of the samples representing Conditions 2, 3, and 4 are shown in Figure 11. The whole interstage samples and their 850 °F⁺ resid fractions are more aromatic and phenolic than their interstage distillate,

PFL, and PFC counterparts (Figures 6 and 11). The interstage distillates are higher in phenolic -OH concentration than the corresponding whole PFL and PFC samples (Figure 11), in spite of having the same or lower aromaticity (Figure 6). The PFC and PFL samples show no significant effect of the use of untreated coal in Condition 3 on phenolic -OH concentration (Figure 11). However, the whole interstage oil and its distillate and resid fractions show a lower phenolic -OH concentration in Condition 3 when untreated coal was used. This is unexpected, since hydrogenation (as indicated by aromaticity) and deoxygenation (as indicated by phenolic -OH concentration) frequently show the same response to liquefaction variables (except temperature). Some possible explanations are offered below for the observed response of lower phenolic -OH concentration of the interstage stream and each of its fractions when the untreated coal was used. Our data provide little or no direct evidence to support a particular explanation.

M. Farcasiu proposed¹¹ (based on model compound studies¹²) that the iron catalyst in use in Conditions 2 and 4 may promote fast cracking of the low-rank coal, but does not catalyze dehydroxylation to hydroaromatic structures. This would explain the higher phenolic -OH content at Conditions 2 and 4. In the case of Condition 3, the absence of the iron catalysts inhibits the cracking reaction.

Another possibility is that the increased hydrogenation activity (due to dispersed catalyst) in the first stage is effective in converting ethers to phenols. Without the dispersed catalyst from the impregnation treatment, fewer ethers are converted. Malhotra and McMillen¹³ have pointed out that the solvent plays an important role in breaking strong bonds (such as ether bonds) thermal reactions. They also indicated that stabilizing rearrangements of phenolic structures may play a role in solvent-promoted retrograde reactions. In practice, high coal conversion with extensive retrogressive reaction is not readily distinguished from mere low coal conversion. Since coal conversion was lower in Condition 3, it is possible that the converted coal is relatively lower in phenolic -OH because less-reactive components were not converted, or because less asphaltenic and preasphaltenic material was generated. We previously noted in Wilsonville runs that coal conversion preferentially increased the concentration of phenolic, preasphaltenic resid components.¹⁴ The oxygen-by-difference values (Tables 4 and 5) are not reliable enough to shed any light on this possibility.

Ultimate and Ash Elemental Analyses of Period 8, 11, and 14 Samples

Ultimate and ash elemental analyses were obtained on the period 8, 11, and 14 samples (Tables 4 and 5). Period 9A PFL and PFC samples were also analyzed. Since period 9A was transitional from Condition 2 to 3, properties of the 9A PFL and PFC samples may be expected to lie between those of the corresponding period 8A and 11A samples. In fact, the analyses of the period 9A PFL and PFC samples are generally similar to their period 8A counterparts.

Relative to periods 8 and 14, the period 11A PFC was lower in ash content. This seems to result directly from addition of the catalyst in periods 8 and 14, and indirectly from a higher IOM/ash ratio as a consequence of the lower coal conversion HRI experienced when the untreated coal was used (Table 1). Also in period 11, the PFC was lower in S and N contents. Ammonium nitrate is used in the catalyst preparation and it is believed that N is incorporated into the treated coal used in periods 8 and 14.¹ Evidently, much of the additional sulfiding agent used in combination with the dispersed catalyst was retained in the filter cake. The period 11A PFC ash was lower in Fe_2O_3 and SO_3 contents. This is directly related to the addition of Fe-based catalyst and subsequent S retention in the filter cake in periods 8A and 14A.

Some of the effects of coal treatment observed in the PFC analyses are evident in the interstage sample analyses. Relative to the period 9A and 15A interstage samples, the period 12A interstage sample was lower in ash and higher in organics (especially carbon content), and lower in N (S was low in the period 12A and 15A samples, relative to the period 9A sample). The ash and sulfur changes are much larger in the PFC than in the interstage samples, because the ash and sulfur are much more concentrated in the PFC. The interstage ash elemental concentrations showed the same qualitative changes with coal treatment as did those of the PFC.

The PFL and product distillate samples showed little effect of pretreated coal use (Table 5). The PFLs were all low in S content, and their C, H, and N contents showed no consistent trend with coal pretreatment. The ASOH/SOH blend was slightly low in N in period 11A. The SOH in period 11 was low in C by $\approx 0.5\%$, and slightly high in S, relative to the comparison samples from periods 8 and 14.

The higher organics concentration and lower ash concentration in the PFC sample from period 11, when untreated coal was used, reflect the higher IOM/ash ratio resulting from the lower coal conversion HRI experienced, and addition of the catalyst in periods 8 and 14 (increasing the ash content). Evidently most of the observed differences in PFC ash elemental and S and N concentrations are direct consequences of coal treatment vs. non-treatment. Ash elemental compositions of the interstage samples generally showed many of the same differences, but less consistently than PFC compositions. In the PFLs and net product distillates, virtually no consistent or significant effect on elemental composition is evident from coal treatment vs. non-treatment. In the net products, the possible exceptions are slightly lower N content in the period 11 ASOH/SOH blend, and slightly higher S and lower C concentrations in the period 11 SOH. Product oil quality is addressed more comprehensively in the petroleum inspection tests mentioned earlier in this report (see Appendix 2), and reported in detail elsewhere.⁸

Comparison of Process Stream Properties from Runs CC-15 and CC-1

HRI reported¹ a comparison of Run CC-15 and Run CC-7 to evaluate thermal/catalytic and catalytic/thermal configurations and two different Fe dispersed catalysts. They also reported¹⁵ a comparison of catalytic/catalytic vs. thermal/catalytic operations with no catalyst, and Fe, Mo, and Mo/Fe dispersed catalysts in Runs CC-1, CC-15, and CMSL-1. We previously reported analyses for Run CC-1,¹⁶ but have not analyzed samples from Run CC-7 or CMSL-1. Here we compare period 8 of Run CC-15 (Fe-treated coal, thermal/catalytic operation) with period 16 of Run CC-1 (catalytic/catalytic), as HRI did. HRI also included in their comparison¹⁵ period 11 of Run CC-15 (untreated coal, thermal/catalytic); we have already made that comparison with the period 8 samples in the previous section. The conditions used to produce the samples for comparison are shown in Table 13 (reproduced from the HRI paper¹⁵). HRI found that Run CC-15 period 8 was similar in many respects to Run CC-1 period 16: coal conversion, resid conversion and distillate yield were about the same, within about 2%. In Run CC-15 period 8, there was about 4% more light distillate and 3% less heavy distillate than in Run CC-1 period 16. HRI also found that the resid content of the PFL increased with catalyst age and was higher in Run CC-15 than in Run CC-1.

Table 14 shows the comparison data for the whole PFL, the whole INT and its distillate and resid fractions, and the SOH. The Run CC-15 period 8 PFL and INT samples were lower in donor solvent quality, slightly lower in aromaticity and hydroaromaticity, and were higher in paraffinicity and phenolic -OH concentration than their Run CC-1 period 16 counterparts. Although the dispersed Fe in Run CC-15 evidently provided good hydrogenation (as indicated by lower aromaticity), the hydrogen distribution (as indicated by the hydroaromaticity and paraffinicity) provided a lower-quality recycle solvent, relative to that produced with the supported catalyst in Run CC-1. Perhaps too much overall hydrogenation, or too little cracking led to the higher concentrations of paraffins and lower concentrations of hydroaromatic donors in Run CC-15. Deoxygenation was much lower in operation with the dispersed Fe in Run CC-15 than in supported catalyst operation in Run CC-1. The higher first-stage temperature in Run CC-1 probably also had a role in the apparently higher deoxygenation and hydrocracking in Run CC-1.

CHARACTERIZATION OF HRI CTSL RUN CC-15 NET PRODUCT AND FRACTIONS

INTRODUCTION

The net product oil (crude oil) from HRI Run CC-15 and three of its four distillation fractions were returned to CONSOL by National Institute for Petroleum and Energy Research (NIPER) in August, 1993, after NIPER completed the petroleum inspection tests on them.⁸ There was an insufficient amount of the 638 °F⁺ fraction for return to CONSOL. Also returned were the two caustic-washed distillation fractions and the recovered cresylics (caustic extract) fractions from them. CONSOL supplementally characterized the returned samples. CONSOL's characterization included ¹H-NMR analysis and determination of the phenolic -OH concentrations by FTIR spectroscopy on each fraction and gas chromatography/mass spectroscopy (GC/MS) analysis of the cresylic fractions. The results of these analyses are reported here.

PROCEDURE

Standard procedures were used for the determination of phenolic -OH concentrations¹⁷ and ¹H-NMR proton distributions.¹⁸ The NMR proton distributions are area percentages, normalized by omitting the area of the hydroxyl peak. Omitting the hydroxyl peak is inconsequential for most samples; however, since the cresylic fractions had intense hydroxyl peaks, this omission did affect their reported proton distributions. GC/MS analyses were performed with an HP 5970 system equipped with a 30 m x 0.25 mm DB-5 column (0.25 μm film thickness). The GC conditions were: injection port at 300 °C; column 5 min at 35 °C then to 100 °C at 35 °C/min, then to 320 °C at 4 °C/min; 20 psig of He carrier gas; scan from 45 to 300 amu. Splitless injection was used. The samples were injected as 1% solutions in tetrahydrofuran. The mass spectra were searched against the Wiley/NBS mass spectral library. Identifications are based on the search results supplemented in some cases by retention times.

CHARACTERIZATION OF STRAIGHT-RUN FRACTIONS

The ¹H-NMR proton distributions and phenolic -OH concentrations are shown in Table 15. Also shown in Table 15 are the yield of each fraction and its hydrogen and oxygen-by-difference contents, as determined by NIPER.⁸ Phenolic oxygen contents, calculated from the phenolic -OH concentrations, are also shown. In general, the fractions contain less hydrogen and become more aromatic with increasing boiling point. The phenolic oxygen is concentrated in the kerosene

fraction, as has been observed in the earlier coal-derived crudes analyzed under this contract¹⁹⁻²¹ and by other workers⁹ with different coal-derived syncrudes. However, the phenolic -OH concentration is quite low in all fractions.

The HRI CTSL Run CC-15 net product (crude) has a lower boiling-point distribution, it contains more hydrogen and it is less aromatic and less phenolic than the net products of Wilsonville Runs 259G^{19,20} and 260D.²¹ Also, in general, each of the individual boiling-point fractions (naphtha, kerosene, etc.) of the Run CC-15 product are more enriched in hydrogen, are less aromatic and contain less phenolic and total (by difference) oxygen than the respective fractions from Wilsonville Runs 259G and 260D.

CHARACTERIZATION OF THE CAUSTIC WASHED FRACTIONS

Coal-derived synthetic crude oils frequently contain high concentrations of oxygen-containing compounds, particularly phenols, relative to conventional petroleum crude oils. Though these phenols are found at elevated concentrations in all of the distillation fractions (e.g., naphtha, kerosene, etc.), they are most frequently concentrated in the kerosene fraction (b.p. approx. 380 x 510 °F).⁹ Phenolic compounds must be reduced to low concentrations to produce finished transportation fuels. In a typical modern petroleum refining scheme, this would be accomplished by hydrotreating. However, because coal liquids have high concentrations of phenols, it may be advantageous to reduce their concentration by some route other than hydrotreating, for example, by caustic extraction. This route for removal of phenols could have several advantages over the hydrotreating route: it would reduce overall hydrogen consumption, it could produce a valuable by-product (cresylic acid) and it would simultaneously strip from the oil mercaptans and hydrogen sulfide in addition to phenols. Indeed, caustic washing was once a popular unit operation in petroleum refineries because of its ability to sweeten light distillates.²² As part of the petroleum inspection tests, NIPER caustic washed the naphtha and kerosene fractions to remove phenolics (cresylics). The cresylic fractions were recovered. CONSOL analyzed the recovered cresylics to examine the effectiveness of caustic washing for removal of phenols from the HRI CTSL Run CC-15 net product fractions.

Caustic washing effectively reduced the phenolic concentrations (by essentially 100 %) in both fractions, as shown in Table 15. In both cases, the yield of the

cresylic fraction was 2 to 4% of the straight-run fraction and this cresylic fraction contained all of the phenolic functionality of the original fraction. The proton distributions of the caustic-washed fractions are nearly the same as those of the respective straight-run fractions. However, the proton distributions of the cresylics are distinctly different; they show high concentrations of aromatics (particularly uncondensed aromatics) and alkyl alpha protons and low concentrations of paraffinic (alkyl beta and gamma) protons, as expected for phenolics-rich materials. The phenolic oxygen concentrations of the cresylics are extremely high at 8.9 and 7.7 wt %, respectively, for the naphtha and kerosene cresylics. This compares to 14.8% for pure cresol, 13.1% for pure xylenol and 11.8% for pure C₃-phenol. Thus, it appears that roughly half by weight of the recovered cresylics are phenolic compounds.

The results of the GC/MS analyses are summarized in Table 16. The naphtha cresylic fraction is composed of C₀- to C₃-phenols and it appears to be nearly pure; i.e., there are no major non-phenolic components. The kerosene cresylic fraction is composed of C₁- to C₄-phenols and indanol; it too appears to be fairly pure, although there are some hydrocarbon components present.

The crude and each of its fractions shows an amine peak more prominently than the phenol peak in the infrared spectrum (THF solution). We have seen identifiable amine features primarily in spectra of light (net distillate) products from HRI. In these samples, the amine probably contributes to the reported phenolic -OH concentration, causing it to be high. The caustic washed naphtha and kerosene fractions show no discernable phenol peak, but distinct amine peaks. In these samples, the phenolic compounds evidently are so low in concentration that the amine compounds are detected. Apparently, the amines are overshadowed in the IR spectrum by the phenolics in many coal liquids, especially the heavier distillates and resids. These results are consistent with the apparent difficulty experienced by many researchers in removal of nitrogen by hydrotreatment.

ALBERTA RESEARCH COUNCIL CANDIDATE LIQUEFACTION OILS

Alberta Research Council (ARC) sent two candidate liquefaction oils and requested information about their solvent quality.²³ CONSOL characterized the oils at DOE's request. The oils were identified as V-178 +320 °C and V-1074 samples from Wilsonville Run 263 with Black Thunder Coal. Based on the information provided by ARC (Table 17), the V-178 +320 °C is much lighter than authentic plant recycle solvents. The V-1074 is the Wilsonville heavy distillate component of the recycle, but this particular sample also is much lighter than expected. Typically, one would expect to see V-1074 essentially devoid of 650 °F- material and containing a modest amount of material in the 650 x 750 °F range (about 5% in Run 263).

The results of CONSOL's characterization of the two Wilsonville solvents are given in Table 18. The solvents are moderately paraffinic (alkyl beta + gamma protons), and seem fairly typical of Black Thunder heavy distillates in this regard. The V-178 +320 °C is at the low end in total aromaticity for a liquefaction solvent, but the V-1074 is fairly typical in aromaticity for this plant stream. A good donor solvent will typically have about 19% cyclic beta protons or more, so these solvents appear deficient in hydroaromatic donor species. The V-1074 is quite low in these donors. The standard microautoclave tests of donor solvent quality show the two oils to be more-or-less equivalent, although the V-1074 is slightly better than the V-178 +320 °C (though at borderline statistical significance). It appears that the higher aromaticity and consequent higher physical solvency of the V-1074 is enough to make up for its low hydroaromatic content, relative to the V-178 +320 °C. In the context of the range of donor solvent qualities we have observed over the years, these would be considered "fair" quality. Both solvents are quite high in phenolic -OH concentrations. The higher value of the V-178 +320 °C phenolic -OH peak location reflects its highly aliphatic and lower-boiling character.

In summary, the V-1074 sample is equivalent by our characterization methods to the recycle heavy distillate materials we have analyzed from periods A through H of Run 263 (when no supported catalyst was used in the second stage), in spite of the presence of lower-boiling material in the ARC sample. We have not analyzed lighter materials from Run 263. However, the characteristics of the V-

178 +320 °C sample seem reasonable for that boiling range. The solvents have roughly equivalent donor quality, which we would rate as "fair". Based on our experience, the V-1074 sample is the preferred liquefaction solvent.

SAMPLES FROM THE UNIVERSITY OF PITTSBURGH

Elemental analyses were requested by Dr. I. Wender of the University of Pittsburgh on eight samples produced by catalytic dehydrogenation reaction. Four samples (Nos. 1 through 4) were produced in Run 26 under DOE Grant No. RA2-91PC91035. The remaining four samples (5 through 8) were produced in Run 32 under DOE contract No. DE-AC22-91PC91054. Table 19 summarizes the results of the analyses.

THERMOGRAVIMETRIC ANALYSIS (TGA) METHOD FOR THE DETERMINATION OF 975 °F* ASTM D-1160 DISTILLATION EQUIVALENT VALUES

A thermogravimetric analysis (TGA) method for the determination of the equivalent 975 °F* (ASTM 1160) distillation bottoms value, based on a method developed and routinely used at HRI, Inc., was developed for use in-house. The equipment used at HRI is different than that which is available at CONSOL R&D. Therefore, it was necessary to modify the HRI method to achieve comparable results.

The CONSOL TGA method uses a DuPont 951 TGA. The TA-PC control and data acquisition system are PC-based and use software developed by MC-Squared Thermal Systems. The software and data-interface module were supplied by Instrument Specialists, Inc., Antioch, IL.

Conditions established for the TGA experiment are as follows:

Temperature Ramp, °C	Final Actual Temperature, °C	Heating Rate, °C/min	Hold Time, min.	Atmosphere
30 - 105	110	40	3	N ₂
105 - 363	375	40	2	N ₂
363 - 732	732	100	3	O ₂

It should be noted that for each interchangeable furnace, the heating profiles are slightly different. The temperature limits given in the above table may be altered by one or two degrees to compensate. The programmed values differ from the actual values achieved because of temperature overshoot obtained as a result of the furnace design and the relatively high heating rate. The data point for the 975 °F* equivalence is obtained at the beginning of the 2-minute hold time, once 375 °C is achieved, as compared to HRI's practice of taking the data point after holding the sample at 375 °C for a number of minutes. The much slower heating rate used here, versus that which is used by HRI, brings the sample to the 975 °F* equivalent point coincidentally with the achievement of 375 °C. The 2-minute hold time is used to line-out the furnace at 375 °C before changing to an O₂ atmosphere. Sample size used for preliminary work was 6 to 10 mg. The method is being standardized on 10.0 mg (±0.5 mg).

Multiple TGA experiments were run using a coal liquid material supplied by HRI. The values obtained by HRI for the 975 °F+ fraction of this material are: 28.80, 28.90, 28.55, 30.43, 27.55, 29.42, 27.73, 29.11, and 29.18 wt % (mean = 28.85 wt %, standard deviation = 0.87 wt %). Values obtained using the method detailed above are: 30.9, 27.9, 24.2, 30.4, 30.9, 31.5 wt % (mean = 29.3 wt %, standard deviation = 2.7 wt %). Thus, the two laboratories gave results that are statistically indistinguishable.

In addition to the HRI standard sample, four samples produced at the Wilsonville facility from Runs 258 and 262 also were chosen to be standard samples. These four samples of coal-derived materials are two whole oil samples (Wilsonville Run 262 Period E, V-1074, and Wilsonville Run 258 Period K, V-131B) and two resid samples (Wilsonville Run 262 Period E V-130 deashed resid, and Wilsonville Run 262 Period E V-1082 ashy resid). These materials contain a wide range of ash and resid contents. All four of these materials were analyzed by HRI Inc. by their (well-established) TGA method. HRI also analyzed two samples by ASTM D-1160 distillation. The HRI data are presented in the table below. In addition, we conducted TGA analyses on these materials using the method which we developed in-house. As can be seen in the table, we reproduce the HRI values fairly well.

Sample (Wilsonville Run Period and Stream)	HRI TGA Value (average of 2 determinations)		HRI ASTM D-1160 Value	CONSOL TGA Value (average of ≥10 determinations)	
	975 °F+, wt %	Ash, wt %	975°F+, wt %	975 °F+, wt %	Ash, wt %
262 E, V130	84.34	0.00	84.56	83.76 ±3.49	1.70 ±0.35
262 E, V1082	87.51	19.64		90.74 ±2.29	18.63 ±0.66
262 E, V1074	1.47	0.01		3.07 ±1.35	1.19 ±0.61
258 K, V131B	56.80	10.24	54.47	57.92 ±2.23	10.01 ±1.13

These tests confirm the goodness of the empirical method as adapted for CONSOL's use. The method is now available to the Program on a routine basis.

Aliquots of these four samples were sent to SRI International to assist in the development of a method employing large-scale (1.5 g sample size) TGA.

PARTICIPANTS PROGRAM STATUS

The first Phase III subcontract of the Participants Program was completed this quarter. This subcontract was with the National Institute of Petroleum and Energy Research (NIPER) for petroleum inspection tests on the net product oils of HRI CTSL Run CC-15. The results of these tests are described in the paper presented at the DOE Coal Liquefaction and Gas Conversion Contractor's Conference, September 27-29, 1993 (Appendix 2). The conclusions NIPER reached from this work are that the net product oil obtained from HRI Run CC-15 is a very light, low-sulfur crude. It is potentially acceptable as a refinery feed. The CTSL Run CC-15 oil is of a much higher quality than the net product oil from Wilsonville Run 260D, which also used Black Thunder Mine subbituminous coal, based on comparison to a set of petroleum inspection tests performed under Phase II of the Participants Program. The full report from NIPER, with CONSOL evaluation, will be issued as a Topical Report.

A second subcontract was placed with NIPER for another set of petroleum inspection tests. In consultation with Burns and Roe Services Corp. and DOE, it was decided to perform these tests on the net product oils from HRI Run CMSL-2 instead of Run CC-16. Both runs were made with Burning Star 2 coal, but Run CMSL-2 was made at what is considered by HRI to be state-of-the-art liquefaction conditions. Approximately 6 gal of a blend of atmospheric still overhead (ASOH) and separator overhead (SOH) from Run CMSL-2, periods 8, 9, 11, and 12 were sent directly from HRI to NIPER for the tests. In contrast to the first set of tests, the distillation cuts were designated to include a heavy naphtha "swing cut" (350-400 °F). After determination of the yield and specific gravity, the light (IBP-180 °F) and medium (180-350 °F) naphtha cuts will be blended before further analyses are performed. NIPER reported that after the initial distillation, it was apparent that there would be an insufficient amount of the swing cut to perform all tests which were specified in the statement of work. It was decided, on consultation with Burns and Roe, to eliminate the JFTOT thermal stability test on the caustic washed portion of this fraction. If there still is not enough material, then the JFTOT test on the straight-run fraction also will be eliminated from the work plan. The results of these analyses will be issued with the data from the first set of petroleum inspection tests in the same Topical Report.

The Pennsylvania State University subcontract was delayed due to equipment failure. Penn State is using normal-phase high performance liquid chromatography (HPLC) with ultraviolet (UV) diode array detection to examine five ash-free direct liquefaction process-derived samples. The UV detector was found to be not functioning properly. CONSOL agreed to a no-cost extension from August 31 to October 31, 1993. Additional work is dependent on producing the HPLC fractions and will include elucidation of HPLC-derived fractional components by gas chromatography/mass spectrometry and high resolution mass spectrometry. We visited Penn State to discuss the progress of the work. A trip report describing the visit is appended (Appendix 3).

The University of Utah requested and was granted a second no-cost subcontract extension for their project, which entails ^{13}C -NMR analysis of samples from HRI CTSL Run CC-15. Some data were received from Utah in the form of a progress report. A draft final report is now expected from Utah by November 30, 1993.

A first draft report from the University of Pittsburgh was received and reviewed. Comments were offered to the authors. The project with the University of Pittsburgh concerns evaluation of the hydrogen donor ability of coal liquid resids by catalytic dehydrogenation. Pitt provided a second draft final report which was reviewed thoroughly and returned to the authors for revision.

A draft final report was received from SRI International. SRI used field ionization mass spectrometry (FIMS) to analyze the process-derived samples from HRI CTSL Run CC-15 and Run CC-16. The report is being reviewed. Revisions will be requested of the authors and the final version of the report will be issued as a Topical Report in the next quarter.

The University of Delaware project for the evaluation of their short-time batch reactor (STBR) system to produce data for kinetic (and mechanistic) modeling of resid reactivity is progressing well. We made a second visit to Delaware to discuss project plans. Delaware issued an interim report. In it they described some preliminary experiments for the establishment of operating conditions. The planned work-up procedure was revised to accommodate the nature of the coal-liquefaction resids. Delaware has decided to use an oil-free, but presulfided catalyst (which was prepared originally for Wilsonville Run 260) in their

experimental work instead of producing a sulfided catalyst in-house. Approximately 2 lb of oil-free Shell 324 Ni/Mo catalyst was prepared for Delaware by Soxhlet extracting it with THF, grinding it to pass a 60 Tyler mesh screen, and sealing it in plastic-lined aluminum bags under vacuum. The extraction and grinding procedures were carried out under N_2 . The analysis of the washed catalyst is given in Table 20. The full history of the catalyst sample was sent to Delaware.

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.^{17,18,24-27}

Section 5

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TABLE 1
HRI CTSL RUN CC-15 OPERATING SUMMARY

Condition No.	1					2		
Period No.	1	2	3	4	5	6	7	8
Date, 1992 (Start of Period)	10/21	10/22	10/23	10/24	10/25	10/26	10/27	10/28
Hr of Run (End of Period)	24	48	72	97	121	145	169	193
Stg 3 Cat Age, lb Dry Coal/lb Cat	26	57	85	115	144	172	200	228
1st Stg Temp, °F	523	520	523	523	522	558	567	568
2nd Stg Temp, °F	788	800	799	799	799	801	801	801
3rd Stg Temp, °F	767	774	775	775	775	776	784	774
Unit Back Pressure, psig	2491	2503	2506	2505	2505	2501	2494	2502
Space Vel, lb Coal/hr/ft ³ (Stg 2) Cat	38.0	45.4	41.7	42.5	42.3	42.0	39.9	41.7
<u>wt % Dry Coal</u>								
PFL Recycle	142.2	164.0	144.1	162.4	167.0	167.0	155.4	162.6
PFL to Buffer to Stg 1	3.3	3.7	4.0	4.0	4.3	4.0	4.4	4.1
PFL to Buffer to Stg 2 & 3	9.9	9.3	12.2	9.9	9.5	9.7	9.3	8.5
Make-up Oil	39.3	3.1	22.9	4.6	0.0	3.9	11.6	4.5
H ₂ S	6.5	6.5	6.2	2.9	3.5	2.9	3.3	3.6
Material Balance, % (Gross)	85.81	95.23	97.08	99.30	97.36	98.53	99.42	97.25
<u>Estimated Normalized Yields,</u> <u>wt % Dry Fresh Feed</u>								
C ₁ -C ₃ in Gases					9.94			10.13
C ₄ -C ₇ in Gases					2.80			2.91
IBP-390 °F in Liquids					16.26			16.36
390-500 °F in Liquids					13.67			13.30
500-650 °F in Liquids					17.55			17.59
650-850 °F in Liquids					10.04			7.99
850-975 °F in Liquids					1.81			2.07
Toluene-Sol 975 °F ⁺ Oil					3.75			4.61
Toluene-Insol 975 °F ⁺ Oil					0.04			0.06
Unconverted Coal					6.50			6.87
Ash					6.03			6.03
Water					15.52			16.41
CO					0.74			0.67
CO ₂					1.37			0.91
NH ₃					2.71			2.62
H ₂ S					-0.02			-0.07
Total (100 + H ₂ Reacted)					108.72			108.46
<u>Process Performance</u>								
C ₄ -975 °F Dist, wt % MAF Coal					66.1			64.1
975 °F ⁺ Conversion, wt % MAF					89.1			87.7
Coal Conversion, wt % MAF		91.6	92.2	92.1	93.1		93.2	92.7
HDS, wt %					-3.1			-15.2
HDN, wt %					90.0			87.1

Coal: Black Thunder coal - L-780 (Fe-treated) (Periods 1-8, 12-14)
HRI-5828 (untreated) (Periods 9-11)

Catalyst: 3rd Stage - Shell S-317 NiMo Catalyst (HRI-5394)

Source: Reference 3

TABLE 1 (Cont'd)
HRI CTSL RUN CC-15 OPERATING SUMMARY

Condition No.	3			4		
Period No.	9	10	11	12	13	14
Date, 1992 (Start of Period)	10/29	10/30	10/31	11/01	11/02	11/03
Hr of Run (End of Period)	217	241	265	289	313	337
Stg 32 Cat Age, lb Dry Coal/lb Cat	257	286	316	345	374	403
1st Stg Temp, °F	567	567	566	566	566	566
2nd Stg Temp, °F	801	800	801	801	801	800
3rd Stg Temp, °F	773	774	775	775	773	773
Unit Back Pressure, psig	2499	2497	2499	2496	2495	2492
Space Vel, lb Coal/hr/ft ³ (Stg 2) Cat	42.6	43.2	43.7	42.8	42.8	42.7
<u>wt % Dry Coal</u>						
PFL Recycle	143.8	162.1	162.8	165.4	167.0	167.0
PFL to Buffer to Stg 1	4.4	4.3	4.7	4.5	4.4	4.3
PFL to Buffer to Stg 2 & 3	7.7	9.1	10.7	10.1	9.7	10.1
Make-up Oil	37.7	4.2	3.5	5.5	0.0	0.0
H ₂ S	3.1	3.1	3.2	3.1	3.1	3.0
Material Balance, % (Gross)	93.31	100.41	98.98	101.26	99.97	100.08
<u>Estimated Normalized Yields,</u> <u>wt % Dry Fresh Feed</u>						
C ₁ -C ₃ in Gases			9.94		9.68	9.86
C ₄ -C ₇ in Gases			3.00		3.00	2.57
IBP-390 °F in Liquids			15.61		14.98	14.69
390-500 °F in Liquids			12.22		11.58	11.12
500-650 °F in Liquids			14.98		16.25	15.70
650-850 °F in Liquids			6.66		9.20	10.08
850-975 °F in Liquids			1.66		2.25	2.43
Toluene Sol 975 °F ⁺ Oil			5.33		6.13	6.81
Toluene Insol 975 °F ⁺ Oil			0.33		0.14	0.17
Unconverted Coal			9.40		7.46	6.85
Ash			5.71		6.03	6.03
Water			19.33		17.08	17.43
CO			0.80		0.75	0.74
CO ₂			1.88		0.95	0.97
NH ₃			0.73		2.49	2.49
H ₂ S			0.25		-0.09	-0.10
Total (100 + H ₂ Reacted)			107.82		107.88	107.84
<u>Process Performance</u>						
C ₄ -975 °F Dist, wt % MAF Coal			57.4		60.9	60.2
975 °F ⁺ Conversion, wt % MAF			84.0		85.4	85.3
Coal Conversion, wt % MAF		91.3	90.0		92.1	92.7
HDS, wt %			48.8		-19.3	-19.8
HDN, wt %			66.6		82.7	82.6

Coal: Black Thunder coal - L-780 (Fe-treated) (Periods 1-8, 12-14)
HRI-5828 (untreated) (Periods 9-11)

Catalyst: 3rd Stage - Shell S-317 NiMo Catalyst (HRI-5394)

Source: Reference 3

TABLE 2
ANALYSES OF BLACK THUNDER MINE COAL
AND IRON-IMPREGNATED BLACK THUNDER MINE COAL
HRI CTSL RUN CC-15

HRI Sample No.	5828		L-780	
	HRI (a)	CONSOL (b)	HRI (a)	CONSOL (b)
Moisture Content, wt %	8.41	5.59	8.81	11.20
Volatile Matter, wt % (MF)		43.21		43.51
Ash Content, wt % (MF)	6.95	7.15	7.15	6.58
Ash Content, SO ₃ -free, wt %	5.71	6.14	6.03	5.56
Ultimate Analysis, wt % (MAF, SO ₃ -free ash basis)				
Carbon	72.51	72.14	72.38	72.05
Hydrogen	4.08	4.88	4.31	4.92
Sulfur	0.51	0.51	0.49	0.47
Nitrogen	0.95	1.04	2.64	2.70
Oxygen (by difference)	21.95	21.43	20.18	19.86
Iron Content, wt % (MF)	0.20	0.33	0.57 to 0.65	0.75
Elemental, wt % of Ash				
Na ₂ O		0.83		0.56
K ₂ O		0.44		0.24
CaO		19.86		20.77
MgO		3.96		4.23
Fe ₂ O ₃		6.56		16.36
TiO ₂		1.08		1.02
P ₂ O ₅		0.89		0.79
SiO ₂		36.17		27.22
Al ₂ O ₃		15.26		11.46
SO ₃		14.16		15.43
Unaccounted		0.79		1.92
Calorific Value, Btu/lb dry basis		11528		11595

- (a) Analyses reported in Reference 1
(b) Analyses performed by CONSOL R&D
(c) Range as reported by HRI

TABLE 3
ANALYSES OF START-UP SOLVENT¹
HRI CTSL RUN CC-15

HRI No.	L-769
API Gravity	10.1
Elemental Analysis, wt %	
Carbon	88.95
Hydrogen	10.08
Sulfur	0.06
Nitrogen	0.34
ASTM D-1160 Distillation	
IBP	318°C
5, Vol %	339°C
10, Vol %	345°C
20, Vol %	358°C
30, Vol %	366°C
40, Vol %	376°C
50, Vol %	385°C
60, Vol %	398°C
70, Vol %	416°C
80, Vol %	449°C
90, Vol %	479°C
95, Vol %	517°C
96, Vol %	524°C

TABLE 4
ANALYSES OF SOLIDS-CONTAINING SAMPLES FROM HRI RUN CC-15

Sample	PFC	PFC	PFC	PFC	INT	INT	INT
Period	8A	9A	11A	14A	9A	12A	15A
HRI Sample No.	LO-6108	LO-6148	LO-6109	LO-6152	LO-6181	LO-6182	LO-6183
Ultimate Analysis, wt % As-Determined							
Carbon	60.36	60.10	69.06	63.36	84.19	88.28	85.20
Hydrogen	5.39	5.41	5.80	5.36	8.28	8.16	7.83
Nitrogen	0.76	0.75	0.62	0.81	0.96	0.66	1.05
Chlorine	<0.010	0.023	<0.010	0.019	0.010	0.023	0.018
Sulfur	2.41	2.20	0.82	2.20	0.42	0.28	0.28
Ash, Including SO ₃	31.64	30.79	20.33	29.28	4.84	3.72	4.71
Ash, SO ₃ -Free	25.38	26.69	18.35	24.07	4.07	3.31	3.97
Oxygen (by Diff.), SO ₃ -Free	5.70	4.83	5.35	4.18	2.07	-0.71	1.65
Elemental, wt % of Ash							
Na ₂ O	0.51	0.56	1.08	0.65	0.57	0.90	0.56
K ₂ O	0.22	0.22	0.36	0.19	0.23	0.34	0.23
CaO	22.20	21.30	24.59	21.68	17.44	21.42	17.12
MgO	4.57	4.41	5.14	4.26	3.61	4.05	3.54
Fe ₂ O ₃	17.79	17.14	7.09	17.97	15.14	7.43	14.93
TiO ₂	1.06	1.10	1.35	1.10	0.94	1.12	0.90
P ₂ O ₅	0.86	0.82	1.21	0.82	0.66	0.89	0.67
SiO ₂	21.73	28.20	30.44	23.09	33.82	37.63	33.51
Al ₂ O ₃	11.77	11.96	17.27	11.50	10.69	14.44	11.24
SO ₃	19.79	13.32	9.73	17.81	16.01	11.11	15.62
Unaccounted	-0.50	0.97	1.74	0.93	0.89	0.67	1.68

(a) Analyses performed by CONSOL R&D; samples were assumed to be free of moisture.

TABLE 5

ANALYSES OF SOLIDS-FREE LIQUID SAMPLES FROM HRI RUN CC-15

Sample Type	PFL	PFL(a)	PFL	PFL	ASOH/ SOH(b)	ASOH/ SOH(b)	ASOH/ SOH(b)	ASOH	ASOH	ASOH	SOH	SOH	SOH
Period	8ABC	9ABC	11ABC	14ABC	8A	11A	14A	8A	11A	14A	8A	11A	14A
Sample No.	LO- 6113	LO- 6119	LO- 6115	LO- 6122	-	-	-	LO- 6105	LO- 6106	LO- 6142	LO- 6102	LO- 6103	LO- 6132
Ultimate Analysis, wt % As-Determined													
Carbon	88.88	89.71	89.35	86.14	86.39	86.09	86.27	87.11	87.44	86.18	84.34	83.81	84.42
Hydrogen	9.98	9.92	9.07	9.04	13.04	12.83	12.47	12.42	12.30	11.93	12.91	13.04	12.88
Nitrogen	0.56	0.57	0.54	0.81	0.40	0.28	0.53	0.34	0.31	0.60	0.30	0.25	0.32
Chlorine	0.022	0.015	<0.010	0.022	<0.010	<0.010	<0.010	<0.01 0	0.016	0.019	0.012	<0.010	0.022
Sulfur	0.03	<0.03	<0.03	<0.03	<0.03	0.06	<0.03	0.03	<0.03	0.04	0.04	0.10	<0.03
Oxygen (by difference)	0.53	-0.24	1.00	3.96	0.13	0.73	0.69	0.09	-0.10	1.23	2.40	2.79	2.33

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

- (a) A sample of the 850 °F⁺ fraction had the following analysis (wt % as-determined): C, 91.01%; H, 7.46%; N, 1.12%; S, 0.03%; and O (Diff), 0.38%.
- (b) Blend of the two components in the ratio produced in the designated operating period. Blends were: 69.95 wt % SOH, 30.05 wt % ASOH (Period 8); 71.04 wt % SOH, 28.96 wt % ASOH (Period 11); and 69.38 wt % SOH, 30.62 wt % ASOH (Period 14).

TABLE 6
DISTILLATION AND FRACTIONATION OF SAMPLES
HRI RUN CC-15

Run Day	wt % of Sample			
	850 °F ⁻ Distillate	THF-Soluble 850 °F ⁺ Resid	IOM	Ash
<u>Pressure Filter Cakes</u>				
2A			36.6	30.4
3A			28.9	33.1
4A			27.3	32.4
5A			25.6	31.6
6A			24.6	32.9
7A			22.6	31.9
8A			24.1(a)	31.0(a)
9A			25.1	31.2
10A			26.8	20.1
11A			30.3(a)	19.5(a)
12A			29.6	19.6
13A			22.2	26.5
14A			23.6(a)	28.8(a)
<u>Pressure Filter Liquids</u>				
8ABC			0.12	0.03
9ABC	71.6	28.4	0.09 (0.26)*	0.01 (0.01)*
11ABC			1.15	0.01
14ABC			0.74	0.03
<u>Interstage</u>				
9A	52.2	36.8	5.5	4.6
12A	50.5	37.1	6.0	4.2
15A	45.8	41.2	8.9	3.8

* Measured in whole sample.

a) Average of duplicate determinations.

TABLE 7
SOLUBILITY FRACTIONATION OF PFC SAMPLES
HRI RUN CC-15

Run Day	wt % of THF-Soluble Portion of PFC		
	Oils	Asphaltenes	Preasphaltenes
2A	87.3	7.1	5.7
3A	80.3	12.8	6.9
4A	75.1	16.7	8.2
5A	71.5	19.2	9.3
6A	69.0	20.2	10.8
7A	69.6	20.5	9.9
8A	67.5	23.0	9.5
9A	69.3	21.3	9.4
10A	67.6	21.3	11.1
11A	64.5	23.1	12.4
12A	63.5	22.8	13.7
13A	66.6	23.2	10.2
14A	63.3	24.6	12.1

TABLE 8

**PROTON DISTRIBUTION OF MAKE-UP OIL, PFL, AND PFC EXTRACT SAMPLES
HRI RUN CC-15**

Run Day	Sample No.	Proton Distribution, %						
		Cond Arom	Uncond Arom	Cyclo Alpha	Alkyl Alpha	Cyclo Beta	Alkyl Beta	Gamma
Pressure Filter Liquids								
2ABC	6116	4.8	3.1	9.4	6.6	19.0	38.1	19.0
3ABC	6117	6.3	3.5	12.2	7.3	19.2	35.2	16.4
4ABC	6110	7.4	3.7	11.3	7.1	18.9	34.7	17.0
5ABC	6111	8.0	4.2	11.9	7.6	18.2	33.0	17.1
6ABC	6118	9.6	4.2	14.6	8.1	18.8	30.3	14.3
7ABC	6112	8.6	5.0	12.3	8.2	18.2	32.1	15.6
8ABC	6113	9.7	5.1	12.0	7.5	17.2	31.9	16.6
9ABC	6119	10.3	4.0	14.4	8.2	17.7	29.8	15.5
10ABC	6114	12.1	4.9	14.8	8.5	17.2	29.1	13.4
11ABC	6115	13.8	4.7	15.8	8.6	16.2	27.2	12.9
12ABC	6120	13.4	5.7	16.1	9.1	17.0	27.0	11.6
13ABC	6121	13.3	5.6	16.2	9.1	17.4	26.3	12.0
14ABC	6122	13.3	6.2	13.9	8.4	16.7	27.6	13.9
Pressure Filter Cake								
2A	6143	7.5	2.4	11.7	7.0	20.5	33.2	17.7
3A	6144	8.4	2.4	12.6	7.7	15.8	37.2	15.9
4A	6145	9.5	2.2	14.3	8.2	21.1	30.8	13.9
5A	6107	11.1	2.6	15.4	8.4	20.1	29.5	12.8
6A	6146	11.2	3.7	16.3	9.3	20.3	25.6	13.6
7A	6147	12.0	3.3	14.9	7.9	19.3	28.6	14.0
8A	6108	12.3	3.7	13.8	7.8	17.8	29.0	15.6
9A	6148	11.7	3.2	14.8	8.4	19.4	28.2	14.3
10A	6149	13.3	3.5	14.3	8.0	22.5	25.6	12.9
11A	6109	15.3	4.6	14.8	8.6	16.6	26.8	13.4
12A	6150	16.9	3.9	16.1	8.8	16.9	25.0	12.3
13A	6151	12.7	7.1	15.6	9.5	16.2	22.5	16.4
14A	6152	15.4	5.0	14.5	8.6	16.4	25.4	14.8
Make-Up Oil								
L-769	6100	4.0	3.7	8.7	6.7	19.3	36.1	21.6

TABLE 9
PROTON DISTRIBUTION OF INTERSTAGE SAMPLES
HRI RUN CC-15

Run Day	Sample No.	Proton Distribution, %						
		Cond Arom	Uncond Arom	Cyclo Alpha	Alkyl Alpha	Cyclo Beta	Alkyl Beta	Gamma
Interstage - Whole Samples								
9A	6181	13.2	6.4	12.8	8.6	15.3	28.5	15.0
12A	6182	20.5	5.8	11.2	7.7	13.2	26.8	14.8
15A	6183	15.0	8.0	13.9	8.9	14.5	25.6	14.1
Interstage - Distillates								
9A		10.6	4.7	13.0	8.6	16.8	31.9	14.4
12A		11.1	4.9	11.1	8.2	16.1	32.5	16.2
15A		11.7	5.3	15.3	9.4	17.4	28.6	12.3
Interstage - Resid								
9A		28.4	3.1	20.6	9.3	15.1	16.5	7.0
12A		34.5	5.6	20.2	8.9	11.6	12.6	6.6
15A		29.4	3.5	21.2	9.4	14.5	15.3	6.8

TABLE 10
PROTON DISTRIBUTION OF NET PRODUCT DISTILLATE SAMPLES
HRI RUN CC-15

Run Day	Sample No.	Proton Distribution, %						
		Cond Arom	Uncond Arom	Cyclo Alpha	Alkyl Alpha	Cyclo Beta	Alkyl Beta	Gamma
Separator Overheads								
2A	6123	1.2	2.4	3.5	4.9	22.1	37.6	28.3
3A	6124	1.4	2.9	4.9	5.7	24.3	34.7	26.1
4A	6125	1.4	3.3	5.5	5.5	24.9	34.6	24.7
5A	6101	1.3	3.4	4.7	5.4	23.9	33.9	27.5
6A	6126	2.2	3.4	6.4	6.0	25.6	33.1	23.4
7A	6127	1.8	3.5	6.5	6.1	25.9	32.6	23.6
8A	6102	1.8	3.8	4.7	5.2	22.2	35.7	26.6
9A	6128	1.9	3.2	6.2	6.2	23.3	34.1	25.0
10A	6129	2.1	4.0	6.0	6.4	23.6	33.3	24.6
11A	6103	2.8	3.5	6.6	6.3	22.0	33.3	25.5
12A	6130	2.6	3.9	6.2	6.2	23.6	33.1	24.3
13A	6131	2.1	4.1	6.0	6.3	24.9	32.4	24.2
14A	6132	2.1	3.2	5.0	6.1	24.2	32.6	26.8
Atmospheric Still Overheads								
2A	6133	1.5	3.3	6.3	6.4	20.7	36.7	25.0
3A	6134	2.0	4.2	8.0	7.4	21.8	34.2	22.4
4A	6135	2.5	4.5	9.2	8.0	22.7	31.7	21.2
5A	6104	1.5	5.1	6.0	7.1	21.9	33.9	24.6
6A	6136	2.8	5.6	10.0	8.5	23.7	30.3	19.2
7A	6137	2.8	5.6	10.5	8.8	24.1	30.5	17.6
8A	6105	1.8	5.4	7.6	7.8	23.1	32.5	21.7
9A	6138	2.0	5.3	8.3	8.6	22.4	30.7	22.7
10A	6139	3.0	5.7	11.5	9.2	23.9	29.8	16.8
11A	6106	2.4	5.5	10.7	8.4	20.3	30.0	22.8
12A	6140	3.5	6.0	11.6	9.6	23.4	28.8	17.0
13A	6141	3.2	6.4	12.0	9.7	24.0	28.0	16.7
14A	6142	2.5	6.4	9.9	9.2	21.4	28.8	21.8
ASOH/SOH Blends								
8A	(70% SOH + 30% ASOH)	2.5	4.2	7.4	6.6	25.1	31.9	22.9
11A	(71% SOH + 29% ASOH)	3.3	4.6	8.4	7.4	25.8	31.4	19.0
14A	(69.4% SOH + 30.6% ASOH)	2.8	4.4	7.5	7.0	24.8	30.8	22.8

TABLE 11
PHENOLIC -OH CONCENTRATIONS
HRI RUN CC-15

Make-Up Oil			
Sample		Conc., meq/g	
L-769		0.08	

Whole PFL		THF Extract of Whole PFC	
Run Day	Conc., meq/g	Run Day	Conc., meq/g
2ABC	0.07	2A	0.08
3ABC	0.10	3A	0.12
4ABC	0.13	4A	0.18
5ABC	0.16	5A	0.21
6ABC	0.18	6A	0.24
7ABC	0.19	7A	0.24
8ABC	0.21(a)	8A	0.27(a)
9ABC	0.20	9A	0.23
10ABC	0.22	10A	0.28
11ABC	0.23(a)	11A	0.30(a)
12ABC	0.23	12A	0.31
13ABC	0.28	13A	0.32
14ABC	0.29(a)	14A	0.38(a)

Run Day	Interstage Sample Conc., meq/g		
	Whole	850 °F Dist.	850 °F Resid
9A	0.61	0.43	0.95
12A	0.49	0.36	0.85
15A	0.62	0.55	0.91

Run Day	Sample Conc., meq/g		
	SOH	ASOH	ASOH/SOH Blend
2A	0.03	0.05	
3A	0.08	0.12	
4A	0.10	0.17	
5A	0.10	0.19	
6A	0.12	0.22	
7A	0.12	0.22	
8A	0.13	0.24	0.17
9A	0.13	0.25	
10A	0.13	0.27	
11A	0.15	0.30	0.20
12A	0.15	0.31	
13A	0.18	0.35	
14A	0.20	0.39	0.25

(a) Average of duplicate values

TABLE 12
MICROAUTOCLAVE TESTS WITH WHOLE SAMPLES
HRI RUN CC-15

Run Day	THF Coal Conversion wt % MAF
<u>Pressure Filter Liquids</u>	
2ABC	54.1
3ABC	59.6
4ABC	65.6
5ABC	71.5
6ABC	74.6
7ABC	77.0
8ABC	80.3
9ABC	78.3
10ABC	80.7
11ABC	75.4
12ABC	76.1
13ABC	81.2
14ABC	77.8
<u>Interstage</u>	
9A	73.9
12A	61.7
15A	75.2
<u>Make-Up Oil</u>	
L-769	55.0

Standard Modified-Equilibrium (Mod-EQ) test conditions are:

9 g sample, 6 g Old Ben No. 1 Mine Coal (Indiana V seam), 750 °F,
30 min.

TABLE 13
CONDITIONS OF RUN PERIODS CHOSEN FOR COMPARISON
OF SAMPLES FROM HRI RUNS CC-15 AND CC-1

Run	CC-15	CC-1
Period (Day)	8	16
Catalyst Age, lb coal/lb cat	228	384
First-Stage Catalyst	Dispersed Fe	Shell S-317
Second-Stage Catalyst	Shell S-317	Shell S-317
First-Stage Temperature, °F	801	817
Second-Stage Temperature, °F	774	767
Relative Space Velocity (Ref. 1)	0.91	1.00

TABLE 14
COMPARISON OF SAMPLE PROPERTIES
FROM HRI RUNS CC-15 PERIOD 8 AND CC-1 PERIOD 16

Run Period	CC-15 8	CC-1 16
<u>Whole PFL</u>		
Aromaticity (a), % of Protons	14.8	16.2
Hydroaromaticity (b), % of Protons	17.2	18.6
Paraffinicity (c), % of Protons	48.5	42.1
Phenolic -OH Concentration, meq/g Sample (c = calc'd from components, a = actual)	0.21a	0.14c
Concentration of 850°F ⁺ Resid, wt %	28.4(d)	28.2
Donor Solvent Quality, % MAF Coal	80.3	86.0
Conversion in Mod-EQ Test		
<u>Whole INT</u>		
Aromaticity (a), % of Protons	19.6	20.4
Hydroaromaticity (b), % of Protons	15.3	16.7
Paraffinicity (c), % of Protons	43.5	39.1
Phenolic -OH Concentration, meq/g Sample (c = calc'd from components, a = actual)	0.61a	0.28c
Concentration of 850°F ⁺ Resid, wt %	36.8	38.9
Donor Solvent Quality, % MAF Coal	73.9	80.6
Conversion in Mod-EQ Test		
<u>INT 850°F⁻ Distillate</u>		
Aromaticity (a), % of Protons	15.3	15.8
Hydroaromaticity (b), % of Protons	16.8	18.5
Paraffinicity (c), % of Protons	46.3	44.2
Phenolic -OH Concentration, meq/g Sample	0.43	0.15
<u>INT 850°F⁺ Resid</u>		
Aromaticity (a), % of Protons	31.5	33.3
Hydroaromaticity (b), % of Protons	15.1	14.5
Paraffinicity (c), % of Protons	23.5	23.5
Phenolic -OH Concentration, meq/g Sample	0.95	0.49
<u>SOH</u>		
Aromaticity (a), % of Protons	5.6	6.6
Hydroaromaticity (b), % of Protons	22.2	24.2
Paraffinicity (c), % of Protons	62.3	55.2
Phenolic -OH Concentration, meq/g Sample	0.13	0.05

- (a) Defined as % condensed + uncondensed aromatic protons.
(b) Defined as % cyclic beta protons.
(c) Defined as % alkyl beta + gamma protons.
(d) From distillation of the period 9 sample.

TABLE 15

ANALYSIS OF HRI CTSL RUN CC-15
NET PRODUCT AND FRACTIONS

Fraction	Yield, wt % of Crude (a)	H Content, wt % (a)	Proton Distribution, % (b)							Phenolic -OH		Oxygen Content, wt %	
			Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma	Conc., meq/g	Peak Max, ν , cm^{-1}	Phenoic	Total, by diff. (a)
Crude Oil	100.0	12.52	3.1	4.4	8.6	7.6	24.2	28.2	23.9	0.18(c)	-	0.29	0.41
Naphtha, IBP-380 °F	40.2	13.96	1.4	2.1	3.4	4.8	29.3	30.5	28.4	0.13(c)	-	0.21	0.00
Kerosene, 380-510 °F	33.4	11.77	3.1	6.8	10.7	9.7	20.6	28.1	20.9	0.24(c)	-	0.38	0.75
Diesel Fuel, 510-638 °F	22.5	11.37	4.4	5.3	13.3	9.3	20.2	29.3	18.1	0.10(c)	-	0.16	0.77
Residuum, 638 °F+	2.7	10.28	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.86
Unaccounted	1.2												
Naphtha, Caustic Washed	37.3(d)	13.77	1.6	2.0	4.1	5.7	30.0	29.6	27.0	-(f)	-	-	0.01
Kerosene, Caustic Washed	30.7(e)	11.68	3.2	6.4	11.3	10.0	21.2	27.6	20.4	-(f)	-	-	0.23
Naphtha Cresylics	1.0(d)	ND	6.6	37.3	6.4	25.0	8.3	10.2	6.2	5.56	3309	8.90	ND
Kerosene Cresylics	1.3(e)	ND	4.1	19.3	15.9	20.6	12.5	17.7	9.8	4.68	3316	7.49	ND

(a) Data from NIPER, Reference 8.

(b) Hydroxyl peaks omitted from proton distributions in all cases.

(c) Amines observed; probable contribution to reported phenolic -OH concentration.

(d) 1.9 wt % of crude in naphtha fraction was unrecovered from caustic wash.

(e) 1.4 wt % of crude in kerosene fraction was unrecovered from caustic wash.

(f) Amine observed; no phenols detected.

ND = Not determined.

TABLE 16
COMPOSITIONS OF CRESYLIC FRACTIONS BY GC/MS
HRI CTSL RUN CC-15 CRUDE OIL FRACTIONS

Compound	Naphtha Cresylic Fraction		Kerosene Cresylic Fraction	
	No. of Resolved Peaks	Relative Peak Area, (Largest Peak = 100)	No. of Resolved Peaks	Relative Peak Area, (Largest Peak = 100)
Phenol	1	56	-	-
o-cresol	1	90	-	-
m/p-cresol	1	100	1	3
Dimethyl phenol	5	90	6	97
Ethyl phenol	2	72	2	63
C ₃ -phenols	6	16	12	387
C ₄ -phenols	-	-	12	182
Indanol	-	-	1	33

NOTE: Few hydrocarbon contaminants were found in the naphtha cresylic fraction.
The kerosene cresylic fraction contained numerous hydrocarbon components.

TABLE 17

ALBERTA RESEARCH COUNCIL CHARACTERIZATION DATA
PROPERTIES OF WILSONVILLE SOLVENTS

	V-178 +320 °C Cut	V-1074 Blend
Run No.	263?	263
Carbon	88.3	87.8
Hydrogen	9.5	8.5
Nitrogen	0.96	0.85
Sulfur	360 ppm	0.05
Molybdenum	1 ppm	
Boiling Range	IBP 262 50% 340 Final 459	256 404 535 °C
NMR		
Hydroaromatics	24	
Aromatics	8	
C ₁₃ Aromatics	33	

All data wt % unless otherwise stated.

TABLE 18

CONSOL's CHARACTERIZATION DATA ON
ALBERTA RESEARCH COUNCIL SAMPLES

Sample ID	Proton Distribution, %							Phenolic -OH		Donor Solvent Assay*
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma	Conc., meq OH/g Sample	Peak Location, ν , cm ⁻¹	% MAF Conversion
V178 +320 °C	9.7	6.8	15.6	9.9	17.1	28.4	12.5	0.81	3313	72.2
V-1074 2-5 Blend	15.6	7.9	16.5	8.7	13.2	24.5	13.5	1.05	3304	74.8

* Microautoclave test at Modified-Equilibrium Conditions: 6 g Old Ben No. 1 (Ind. V) coal, 9 g solvent, 30 min, 750 °F

TABLE 19
ELEMENTAL ANALYSES OF UNIVERSITY OF PITTSBURGH SAMPLES

Sample Number	Product Fraction	wt %, as determined			
		C	H	N	S, total
1	THF-Soluble	85.19	10.70	0.49	2.78
2	THF-Insoluble	71.94	4.06	1.82	7.15
3	n-Pentane Soluble	84.92	10.97	0.45	2.72
4	n-Pentane-Insoluble	88.25	5.41	1.97	5.27
5	THF-Soluble	85.10	10.64	0.87	2.19
6	THF-Insoluble	62.92	6.29	1.52	8.76
7	n-Pentane Soluble	85.46	11.66	0.53	1.97
8	n-Pentane Insoluble	87.59	6.26	1.91	3.20

TABLE 20
ANALYSIS OF SHELL 324 CATALYST
PRESULFIDED AND WASHED IN TETRAHYDROFURAN
GROUND TO PASS 60 MESH

Ultimate Analysis, wt %, as det.	
Carbon	3.00
Hydrogen	1.06
Nitrogen	0.24
Sulfur	8.05
Nickel	2.08
Molybdenum	10.5

Figure 1. HRI Two-Stage Ebullated Bed Bench-Scale Unit 227
Configured for Run CC-15.

Figure 2. Proton Aromaticity of Process Stream Samples During HRI CTSL Run CC-15.

Figure 3. Proton Hydroaromaticity and Paraffinicity of Process Stream Samples During HRI CTSL Run CC-15.

Figure 4. Phenolic -OH Concentration of Process Stream Samples During HRI CTSL Run CC-15.

Figure 5. Donor Solvent Quality of Whole PFL and INT Process Stream Samples During HRI CTSL Run CC-15.

Figure 6. Proton Aromaticity of Process Stream Samples
During Conditions 2-4 of HRI CTSL Run CC-15.

Figure 7. Condensed Aromatic Proton Content of Process Stream Samples During Conditions 2-4 of HRI CTSL Run CC-15.

Figure 8. Proton Hydroaromaticity of Process Stream Samples During Conditions 2-4 of HRI CTSL Run CC-15.

Figure 9. Proton Paraffinicity of Process Stream Samples During Conditions 2-4 of HRI CTSL Run CC-15.

Figure 10. Donor Solvent Quality of Process Stream Samples
During Conditions 2-4 of HRI CTSL Run CC-15.

Figure 11. Phenolic -OH Concentration of Process Stream Samples During Conditions 2-4 of HRI CTSL Run CC-15.

APPENDIX 1

**ECONOMIC BENEFITS OF
PROCESS STREAM
CHARACTERIZATION**

**R. A. WINSCHEL
CONSOL Inc.**

**DIRECT LIQUEFACTION: FOCUSED RESEARCH FOR IMPROVED ECONOMICS
PITTSBURGH, PA
SEPTEMBER 27, 1993**

OBJECTIVES OF CHARACTERIZATION IN LIQUFACTION PROCESS DEVELOPMENT

- ✓ MASS/ELEMENTAL/COMPONENT BALANCES
- ✓ YIELDS AND CONVERSIONS
- ✓ PROCESS MONITORING
- ✓ PROCESS INTERPRETATION
- ✓ PROCESS OPTIONS

**COLIRN PANEL
HIGH PRIORITY RESEARCH RECOMMENDATIONS
FOR DIRECT LIQUEFACTION**

- DEVELOP KINETIC MODELS OF LIQUEFACTION
- DEVELOP COAL STRUCTURE/REACTIVITY RELATIONSHIP
- IDENTIFY RETROGRADE REACTION STRUCTURES, MECHANISMS, KINETICS
- STUDY MECHANISMS OF CATALYTIC HYDRO AND CRACKING REACTIONS AND INVESTIGATE HOMOGENEOUS/DISPERSED CATALYSTS
- IMPROVE HYDROGEN UTILIZATION
- ROLE OF MINERAL MATTER

EXAMPLES OF LIQUEFACTION TECHNOLOGY IMPACTS ON LIQUEFACTION COSTS

- ✓ REACTOR THROUGHPUT
- ✓ PRODUCT YIELD/SELECTIVITY/QUALITY
- ✓ H₂ UTILIZATION
- ✓ PROCESS SEVERITY
- ✓ CATALYST USAGE
- ✓ COAL PROPERTIES

COST FACTORS AND INFORMATION NEEDS

COST FACTORS	INFORMATION NEEDS					
	KINETIC MODEL	COAL STRUCTURE/ REACTIVITY	RETRO- GRADE REACTIONS	CATALYSTS	H ₂ UTILIZA- TION	MINERALS
COAL COSTS		++				
COAL PREP	+	++				+
REACTOR THROUGHPUT	++	++	++	++		+
H ₂ USAGE	+				++	
CATALYST USE	+		+	++		
PROD. SEPARATION			+			++
PROD. YIELD/SELECTIVITY	++	+	+		+	
PRODUCT QUALITY				++	++	
PROCESS CONTROL	+				+	

+POTENTIAL IMPACT

++LARGE POTENTIAL IMPACT

ANALYTICAL TOOLS AND TARGET INFORMATION NEEDS

ANALYTICAL TOOL	INFORMATION NEEDS					
	KINETIC MODEL	COAL STRUCTURE/ REACTIVITY	RETRO- GRADE REACTIONS	CATALYSTS	H ₂ UTILI- ZATION	MINERALS
PRODUCT INSPECTION TESTS				✓	✓	
¹³ C-NMR	✓	✓	✓		✓	
MASS SPECTROMETRY	✓	✓	✓			
HETEROATOM SPECIATION	✓	✓	✓		✓	
SEPARATIONS	✓	✓				
FLUORESCENCE MICROSCOPY	✓					✓
TEM/STEM				✓		✓
ESR	✓	✓	✓			

ANALYTICAL TOOLS AND COST FACTORS

TOOL (PARTICIPANT)	COST FACTORS								
	COAL COSTS	COAL PREP	REACTOR THROUGH-PUT	H USE	CATALYST USE	PRODUCT SEPARATION	PRODUCT YIELD/ SELECTIVITY	PRODUCT QUALITY	PROCESS CONTROL
PRODUCT INSPECTION TESTS				+	+		+	+	
¹³ C-NMR			+	+			+	+	
MASS SPEC			+	+	+	+	+		
HETEROATOM SPECIATION			+	+			+	+	
SEPARATIONS	+		+	+	+	+	+		
FLUOR. MICROSCOPY			+				+		+
TEM/STEM					+				
ESR			+	+	+				

+ = SUCCESSFULLY DEMONSTRATED FOR APPLICATION

D = DEVELOPMENT NEEDED FOR SUCCESSFUL DEMONSTRATION

PROPOSED PLANS

- ✓ SUPPORT PROOF-OF-CONCEPT PROGRAM
- ✓ RESID CONVERSION KINETICS

RESID CONVERSION KINETICS APPROACH

- 1. DEVELOP STD METHOD FOR RELATIVE RESID REACTIVITY
AND APPLY TO BROAD RANGE OF RESIDS**
- 2. CORRELATE RELATIVE REACTIVITY WITH MOLECULAR
COMPOSITION DATA AND OTHER CHARACTERISTICS**
- 3. GENERATE FUNDAMENTAL RESID CONVERSION
KINETICS FROM EXPERIMENTAL DATA**
- 4. CONSTRUCT MATHAMATICAL MODEL TO PREDICT
RESID REACTIVITY FROM CHARACTERISTICS**

APPENDIX 3

CONSOL Inc.

INTEROFFICE COMMUNICATION

TO : R. A. Winschel

DATE : August 18, 1993

FROM : S. D. Brandes

AT(OFFICE) : R&D - Library

SUBJECT : Trip to Penn State, July 22, 1993

I visited Penn State to discuss the progress of work on our subcontract with them under Phase III of the Participants Program. Present at the meeting were Dr. Hatcher and three of his graduate students who are working on different aspects of the project; David Clifford is responsible for the HPLC separations and data, Lei Hou is working with the GC/MS, and Dan McKinney will be operating the high resolution mass spectrometer (HRMS) (he is now learning how to use the instrument).

Progress to date includes: 1) The parameters of the HPLC solvent gradient have been established to provide a good separation of a set of 21 model compounds with the Hypersil Green PAH-2 column. This compound set includes the 17 compound-set from EPA protocol #610, which contains aromatic species with up to six condensed rings. 2) The established conditions were used to separate the five coal liquids. Results were very good. Clear baseline, separation was achieved in a number of regions of the chromatogram. The results were presented both as three dimensional plots (I vs. t vs. λ) and two dimensional slices of I vs. t at a number of wavelengths. There are some obvious differences in the chromatograms of the different samples. Dr. Hatcher believes that these are the best LC separations he has ever seen of coal liquids and he is planning to publish the results in the near future.

Some questions still remain as to how much of the sample is going into and getting through the column, and the quantity of each eluted fraction. Originally, 3 mg of material was dissolved in 25 mL of solvent and determinations were made that suggest >99% was dissolved; however, this concentration proved to be too dilute for HPLC separation and UV detection purposes. The currently used concentration is 10 mg in 1 mL. This produces a "muddy" solution. Filtering and determination of the amount of soluble material has not been done, but will be. Fractions will be collected from the column, the eluting solvent driven off under N_2 , and weighed. Dr. Hatcher believes this can be done accurately enough to close a mass balance on the column. He also believes this will be superior to just adding standards to the samples for quantification, because some compounds in the samples will not be detected by the UV spectrometer.

GC/MS data were presented. There was nothing unusual in these chromatograms. There were the usual problems associated with using a library data search for compound assignments. Dr. Hatcher and Hou will spend some time looking at the mass spectra of the individual peaks to confirm assignments. Although the HPLC separation elutes material in the region that the work with the standards identifies as being >5 ring compounds, these compounds are not identified in the GC/MS. This is being attributed to a combination of low concentration of these

August 18, 1993

compounds in the samples and a low sensitivity in the high mass region. Dr. Hatcher is quite sure that when work starts with the HRMS, these materials will be distinguishable.

The question of which fractions should be examined by the HRMS was discussed. I recommended that, based on examination of the HPLC data, they should concentrate their efforts, at least to start, on the biggest differences among the samples. For example, the ratio of peaks in one chromatogram was very different than in another. Thus these two eluted fractions would be good candidates for the MS. I reminded them that their goal was to show the utility of the method for process development and recommended that they think about why these samples were different (i.e., different feed coals, different catalyst age, different processing units, etc.) and try to interpret their results on that basis.

I was shown the data station for the HPLC. They are using a very impressive piece of software from Millipore/Waters called Millennium 2010. This software allows for real-time data acquisition and compilation, data display in 2- and 3-D modes, peak identification based on the UV spectrum and a resident library, and much more.

S. D. Brandes

SDB:1s

cc: F. Kennedy
F. P. Burke
G. A. Robbins
Technical Records (1621-16)

DATE

FILMED

6/27/94

END