**Coal Liquefaction Process
Streams Characterization
and Evaluation**

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**Quarterly Technical Progress
Report, January 1 through
March 31, 1992**

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

August 1992

CONSOL Inc.
Research & Development
4000 Brownsville Road
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Prepared for the:

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

U.S. DOE Patent Clearance was provided by
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ABSTRACT

COAL LIQUEFACTION PROCESS STREAMS CHARACTERIZATION AND EVALUATION, QUARTERLY TECHNICAL PROGRESS REPORT, JANUARY 1 THROUGH MARCH 31, 1992

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

- Process oils from Wilsonville Run 262 were analyzed to provide information on process performance. Run 262 was operated from July 10 through September 30, 1991, in the thermal/catalytic Close-Coupled Integrated Two-Stage Liquefaction (CC-ITSL) configuration with ash recycle. The feed coal was Black Thunder Mine subbituminous coal. The high/low temperature sequence was used. Each reactor was operated at 50% of the available reactor volume. The interstage separator was in use throughout the run. The second-stage reactor was charged with aged Criterion 324 catalyst (Ni/Mo on 1/16" alumina extrudate support). Slurry catalysts and sulfiding agent were fed to the first-stage reactor. Molyvan L is an organometallic compound which contains 8.1% Mo, and is commercially available as an oil-soluble lubricant additive. It was used in Run 262 as a dispersed hydrogenation catalyst precursor, primarily to alleviate deposition problems which plagued past runs with Black Thunder coal. One test was made with little supported catalyst in the second stage.
- The role of phenolic groups in donor solvent properties was examined. In this study, four samples from direct liquefaction process oils were subjected to O-methylation of the phenolic groups, followed by chemical analysis and solvent quality testing.
- The status of the Participants Program is described.
- Summaries of the final reports under the Participants Program from Advanced Fuel Research and the National Institute for Petroleum and Energy Research are presented. Two technical presentations are appended.

Section 1

INTRODUCTION

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

OVERVIEW

Direct coal liquefaction is a complicated chemical process. Recent advances in the technology, which significantly reduced the product costs, have come about through an improved fundamental understanding of liquefaction chemistry. Further improvements are possible, and will depend on continued advances in our knowledge of process chemistry. Supplying this knowledge requires the use of a variety of the tools of analytical chemistry applied to the appropriate samples, and interpretation of the analytical data in context to process development.

The Research and Development Department of CONSOL Inc. (CONSOL) is conducting a three-year project to characterize process and product streams from direct coal liquefaction process development programs sponsored by the Department of Energy. In this project, 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 a subcontracted project team.

In addition to samples from current process development programs, CONSOL maintains a bank of coal liquids samples from the SRC-I, H-Coal, ITSL (Lummus and Wilsonville) and HRI-CTSL coal liquefaction programs, and the Lummus, HRI and UOP coprocessing development programs. These samples, which represent important stages in the recent development of coal liquefaction technology, are also used in the analytical program.

CONTRACT OBJECTIVES

CONSOL is conducting a three-year program to characterize process and product streams from direct coal liquefaction process development projects. The program objectives are two-fold: 1) to obtain and provide appropriate samples of coal liquids for the evaluation of analytical methodology, and 2) to support ongoing DOE-sponsored coal liquefaction process development efforts. The two broad objectives have considerable overlap and together serve to provide a bridge between process development and analytical chemistry.

More specifically, the first objective is to identify, collect, and disburse appropriate samples of coal liquids for analysis by techniques that hold promise, but are not fully demonstrated, for use in liquefaction process development efforts. Samples are chosen from ongoing DOE-funded liquefaction and coprocessing projects and from CONSOL's collection of coal liquids produced during the past ten years. Samples are chosen based on their relevance to process development programs, and are well-documented in terms of feedstocks, sampling location, time and operating conditions. The samples chosen are sufficient to judge the applicability of the analytical methods being evaluated. These process oils are analyzed by CONSOL in a base characterization program using techniques established in previous CONSOL research. Selected samples also are provided to project team participants (as subcontractors), other researchers active in the analysis of coal liquids, who characterize them using a range of methods beyond those used in the base program. Subcontracts to approximately 16 organizations that have specialized analytical capabilities are a major aspect of this work. Individual analytical specialists from the subcontractors take a major role in interpreting their own results in context to the liquefaction process, and not merely provide data. This portion of the program includes an evaluation of the utility of promising analytical techniques for providing useful information for coal liquefaction process development; those results will be applied to ongoing development efforts. This evaluation will be based on the usefulness of an analytical method in process monitoring, to obtain specific chemical information, and as judged by precision and accuracy.

The second objective is to support the process developers. This includes support in the form of providing results and interpretation of data obtained with the analytical techniques being assessed. However, more directly, appropriate process oils are being characterized in the base program by a variety of standard techniques that have proven relevance to development efforts. The results from these more routine analyses aid plant operations and planning. Also, these results provide the data needed to select appropriate samples for the non-routine techniques and provide a set of data for correlations with the results of the more exploratory techniques.

CONTRACT ACTIVITIES - THIS PERIOD

Contract activities for this quarter are listed below. Each topic is summarized and discussed in detail under a separate heading in Section 2, Discussion. Because each topic is summarized, where appropriate, in the corresponding section of the Discussion, no overall Summary section is provided in this report.

- Twenty-one process oils from Wilsonville Run 262 were analyzed to provide information on process performance. Run 262 operated from July 10 through September 30, 1991, in the thermal/catalytic Close-Coupled Integrated Two-Stage Liquefaction (CC-ITSL) configuration with ash recycle. The feed coal was Black Thunder Mine sub-bituminous coal. The high/low temperature sequence was used. Each reactor used 50% of the available reactor volume. The interstage separator was in use throughout the run. The second-stage reactor was charged with aged Criterion 324 catalyst (Ni/Mo on 1/16" alumina extrudate support). Slurry catalysts (Molyvan L and a disposable iron oxide) and a sulfiding agent were fed to the first-stage reactor. Molyvan L, an organometallic compound which contains 8.1% Mo, is an oil-soluble lubricant additive which was used in Run 262 as a dispersed hydrogenation catalyst precursor. Its use was expected to alleviate deposition problems which plagued past runs with Black Thunder coal. One test was made with little supported catalyst in the second stage. The objectives for Run 262 were to evaluate the performance of a dispersed molybdenum catalyst

processing a low-rank coal, and to investigate and eliminate the solids buildup that usually occurs during low-rank coal liquefaction at Wilsonville. Run 262 was the first Wilsonville run to use the dispersed Mo catalyst.

- The role of phenolic groups in donor solvent properties was examined. In this study, four samples of direct liquefaction process oils were subjected to O-methylation of the phenolic groups, followed by chemical analysis and solvent quality testing.
- A status report is given here of progress made in the Participants Program during the tenth quarter. The final reports were received from Advanced Fuel Research and the National Institute for Petroleum and Energy Research, completing their subcontracts under Phase I of the Participants Program. Those reports are summarized here. They are being issued as topical reports. All Phase I contracts are now complete. The Virginia Polytechnic Institute and State University and SRI International final reports were issued.
- SRI International prepared a paper for presentation at the 203rd National Meeting of the American Chemical Society on work performed under the Participants Program. A copy of the preprint is included in this report as Appendix 1.
- Under Phase II of the Participants Program, purchase order contracts were issued to four potential participants. Contracts were signed and initiated with the University of Chicago, the University of Utah, Iowa State University, and Vander Sande Associates. This completes the contingent of participant team members for Phase II. Complete sample sets were sent to each subcontractor. Analytical data and processing information has been issued to all but one subcontractor. Work is progressing on all Phase II subcontracts.
- Ongoing work, in addition to the Participants Program, includes the analysis of samples from Wilsonville Run 263 (begun this quarter), and "calibration" of the standard coal.

- A paper entitled "Agglomeration of Low-Rank Coal As A Pretreatment For Direct Coal Liquefaction" was accepted for publication in a special issue of *Fuel*. It is included as Appendix 2 of this report.

Section 2

RESULTS AND DISCUSSION

WILSONVILLE RUN 262

SUMMARY

CONSOL analyzed twenty-one process oils from Wilsonville Run 262 which was operated in the thermal/catalytic Close-Coupled Integrated Two-Stage Liquefaction (CC-ITSL) configuration with ash recycle. The feed coal was Black Thunder Mine subbituminous coal and 1/16" Criterion 324 (Ni/Mo) catalyst was used in the second-stage reactor. Other conditions included 50% reactor volumes in use, interstage separator in use, and a high/low temperature sequence. Molyvan L, an organometallic compound which contains 8.1% Mo, and iron oxide slurry catalysts and a sulfiding agent were fed to the first-stage reactor. One test was made with little supported catalyst in the second stage. The major results from CONSOL's analyses are summarized below.

- During Run 262, there was a general increase in 850°F⁺ resid concentration and a corresponding decrease in distillate concentration in the process streams from period A through period F. The THF-soluble 850°F⁺ resid showed a general decrease in the oil (hexane-soluble) concentration and increases in the asphaltene and preasphaltene concentrations through the run. Hydrogen aromaticity of the distillate and resid components of all streams increased from period B on. Distillate hydrogen donor (hydroaromatic) content decreased throughout the run. Distillate paraffinic hydrogen content was generally lowest at the beginning and end of the run, and highest in periods B through D. The concentration of phenolic -OH in the distillate and resid portion of most streams stayed fairly constant through period D or E, and then increased. However, the interstage distillate increased in phenolic -OH concentration through the run, except for a decrease from period C2 to D. Donor solvent quality (by microautoclave solvent donor assay) generally decreased through the run; however, it increased again after period D or E.

- Most of the trends in process oil properties indicate decreasing distillate and resid quality as Run 262 progressed. In spite of confounding variables, changes in certain variables seemed to dominate the oil properties. There were concurrent increases in second-stage temperature and coal feed rate as the run progressed. The slurry Mo concentration generally decreased through the run. In the last run period, most of the supported catalyst was removed from the second stage. Most of these changes are expected to worsen oil properties. Recycle resid concentration also generally increased through the run, but because the changes were rather small and their expected impact on oil properties is uncertain, changes in recycle resid concentration did not appear to play a major role in determining overall oil properties during the run.
- In contrast to Runs 258 to 261, there was relatively little THF-soluble 850°F⁺ conversion provided by the second stage in Run 262. In general, the soluble resid and components showed first-stage and total net yields (negative conversions), but higher second-stage conversions. Only the preasphaltenes and phenolic -OH showed consistently positive second-stage conversions which increased the corresponding average total conversions. These results indicate a significant role of the second stage in removal of preasphaltenes and in resid deoxygenation. The total system conversion of resid + UC in Run 262 averaged about 20 %. The average total conversions of the THF-soluble resid and most of its components were negative in Runs 262 and 258 (which also processed subbituminous coal), but were positive in Run 260, the prior run to use only Black Thunder coal. Resid component conversions seem to show some sensitivity to changes in process conditions within Run 262. However, the identification and utility of such responses may be obscured by high variability in the calculated conversions.
- CONSOL results show a general decline in first-stage coal + IOM conversion through Run 262. Wilsonville results for first-stage coal conversion show a similar trend, except for one or two periods. This and the higher organic rejection in periods D through F may be

evident in the elevated IOM content in the interstage samples from periods D through F. Upward trends in coal feed rate, second-stage temperature, resid concentration and a downward trend in slurry Mo concentration through the run may have influenced the trend in first-stage coal conversion. No particular process variable stands out, however, as being a primary influence.

- The average ratios of CONSOL conversions to Wilsonville conversions in Run 262 were compared with those from earlier runs. A CONSOL/Wilsonville conversion ratio lower than one indicates a relatively smaller percentage conversion of 850 x 1050°F material than of 1050°F⁺ material (resulting from low 850 x 1050°F conversion or, alternatively, high conversion of 1050°F⁺, including unconverted coal). The ratios for virtually every period of Run 262 for the first and second stage were quite low relative to past Wilsonville CC-ITSL runs (since Run 250). The total conversion ratios in Run 262 (averaging 0.58) were consistently much lower than those observed in the past. Since resid extinction was achieved in most run periods, conversion of 1050°F⁺ can be regarded as high. Perhaps at the relatively high coal feed rates used in Run 262, there was a net production of 850 x 1050°F boiling material (measured as distillate at Wilsonville), made from 1050°F⁺, but not effectively converted further to 850°F⁻. Perhaps the 850 x 1050°F material was highly paraffinic and was not easily cracked to lighter products.
- Periods B and D had first-stage conversions and conversion ratios higher than the remaining Run 262 periods (and conversion ratios more typical of past CC-ITSL Wilsonville runs), but had second-stage conversions and conversion ratios which were considerably low relative to the rest of Run 262. It is not clear why periods B and D stand out in this regard. Both periods followed a decreases in the slurry Mo concentration and preceded increases in coal feed rate and second-stage temperature. The total 850°F⁺ conversions for periods B and D were very similar to those of the rest of the run, however. This suggests that there may have been problems with the interstage samples or analyses from those periods.

- Rate constants and activities in each reactor stage from Run 262 were compared with those from other CC-ITSL runs. Overall, it appears that the conversion activities for Run 262 are relatively low. Periods B and D both gave 850°F⁺ resid + UC conversion activities which were relatively high in the first stage and relatively low in the second stage (perhaps from non-representative samples). The second-stage conversion activity was relatively high in period C1. Omitting the results from periods B and D, the average conversion activity ($\times 10^7$) was 1.48 ± 0.19 in the first stage and 1.41 ± 0.63 in the second stage. If period C1 is also left out, we obtain an average of 1.50 ± 0.21 for the first stage and 1.13 ± 0.18 for the second stage.
- After period E, almost all of the supported catalyst was withdrawn from the second reactor, and the slurry Mo concentration was increased from 100 ppm to 200 ppm. A comparison of results from period E was made with those from period F (which was considered unstable). Differences in the distillate, resid, and IOM content of the process streams were minor. Changes in proton distribution, ranging from slight to large, indicate less hydrogenation in period F, as one would expect. Significant increases in the phenolic -OH concentrations of all the distillates and resids occurred, indicating that deoxygenation is an important role of the supported catalyst, in addition to hydrogenation. The phenolic -OH removed from the distillate in the second stage decreased by about 0.20 meq/g from period E to period F. The interstage and product distillate donor solvent quality increased from period E to period F, probably from a decrease in paraffinic material in the solvent.
- Conversion of 850°F⁺ resid and its components and kinetic rate constants were also compared before (period E) and after (period F) withdrawal of most of the second-stage catalyst. Although Wilsonville found the second-stage and total resid + UC conversion to be lower in period F than in period E, CONSOL found them to be the same (Wilsonville measures 1050°F⁺, CONSOL measures 850°F⁺). Perhaps a decrease in the conversion of oils and an increase in the conversion

of preasphaltenes and phenolic -OH from period E to period F resulted from the improvement in solvent quality, and/or the increase in slurry Mo concentration. There were virtually no changes in the rate constants and activities for 850°F⁺ resid conversion from period E to period F. A synthesis of CONSOL and Wilsonville results indicates that second-stage and total conversions of 850 x 1050°F material relative to conversion of 1050°F⁺ material must have been relatively higher in period F than in period E. This is evident especially in the ratio of CONSOL-to-Wilsonville second-stage conversion, which increased from 0.362 in period E to 0.796 in period F.

- Oil characteristics and resid conversion results obtained by CONSOL for Run 262 samples were compared with results from previous runs made with Black Thunder coal (periods 258H, 258M, 260C, 260D, 262B, and 262E, all thermal/catalytic, except catalytic/thermal period 260D). Periods B and E span most of the range of operating conditions and oil properties observed during the run. Many conditions differed among the comparison periods. Run 262 was unique in its use of the Molyvan L slurry catalyst precursor. Iron oxide and a sulfiding agent was used in each of the comparison periods. The Run 262 distillate solvent quality indexes were relatively low. Except for some of the resid -OH concentrations, many of the properties indicated that process oils from periods 262B and 262E were upgraded more than oils from the other periods. The Run 262 oils were similar in many ways to those from 260D, or in some cases to those from 260C. Although 850°F⁺ resid conversions were low in the Run 262 periods, the first-stage kinetic rate constant and activity for conversion of 850°F⁺ resid in 262E were similar to those from 260C.
- As part of a study of the activity and chemical nature of the catalytic Mo species derived from Molyvan L, the concentration of major and selected trace elements were determined in several samples derived from the R-1235 sample from period 262A. Virtually all (97%) of the Mo present in the whole oil was found in the

distillation resid and 93% was found in the THF-insoluble portion of the distillation resid. Perhaps the molybdenum not accounted for was present in the whole oil in a THF-soluble form, or it was insoluble, but passed through the filter which had a particle retention size of $2.5\mu\text{m}$.

- From periods C1 to C2, a decrease in the recycle resid concentration had no definitive impact on process oil properties, although Wilsonville observed changes in yields.
- From period C2 to period D, the slurry Mo concentration was decreased from 500 to 200 ppm. There was a decrease in resid concentration (and increase in distillate concentration) in the interstage and product streams. The interstage and product distillate decreased in phenolic -OH concentration, but the interstage resid increased in phenolic -OH concentration. The decrease in slurry Mo concentration appeared to consistently reduce distillate donor solvent quality.
- From period D to period E, the coal feed rate and second-stage temperature were increased, and the slurry Mo concentration was decreased. The general increase in resid concentration and distillate and resid aromaticity and phenolic -OH concentration seems to result from the changes in coal feed rate and Mo concentration.
- From period A (transitional) to period B, there was an increase in resid recycle concentration and a decrease in slurry Mo concentration. CONSOL data showed increases in the 850°F^+ resid content of all streams. The recycle and interstage resids increased in oil (hexane-solubles) concentration from period A to B, whereas the product resid decreased in oil content. This increase in the oil component may be attributable to a higher recycle rate of deashed resid (which is relatively reduced in preasphaltenes, and perhaps asphaltenes). Proton distributions indicate increased hydrogenation in period B, but no clear cause is evident. The resid fraction of

all streams decreased slightly in phenolic -OH, indicating slightly better deoxygenation in period B. The donor solvent quality decreased from period A to period B, probably from increased paraffinicity and decreased hydroaromaticity.

- From period B to period C1, the coal feed rate and the second-stage temperature were increased and resid injection was discontinued. There was a step-increase in the resid preasphaltene concentrations in all streams. The observed changes from period B to period C1 generally point to a slight worsening of process oil properties at the higher coal feed rate and second-stage temperature.
- From period A to B, the ash content of the recycle stream decreased by nearly 2 wt %. From period B to period C1, the ash content of all the streams increased by 1 to 3 wt %. From period C2 to D, the ash content of all the streams decreased by 1-2 wt %. The cause of these changes is not completely clear, but may be related to changes in the ash content of the feed coal, though small (Table 1). Of course, unidentified changes in the process which affect inventories and flows of recycle solvent components, etc. will also affect the concentration of ash in the process streams.
- The 850°F⁺ resid concentrations determined by CONSOL for the V-131B samples were 10-16 wt % higher than Wilsonville's reported resid concentrations. Wilsonville uses a distillation endpoint of about 1050°F, whereas CONSOL uses an endpoint of 850°F. Thus, CONSOL reports 850 x 1050°F material as resid, and Wilsonville reports it as distillate.
- The sum of IOM and ash values obtained by CONSOL for the V-131B samples from periods C1 and C2 (Table 2, Figure 3) were about 4 wt % higher than Wilsonville's measured CI concentrations. All of CONSOL's values were higher than those of Wilsonville, but most were higher by less than 1 wt %. Our analyses were obtained from a true composite over each material balance period, whereas Wilsonville's values were combined from daily operation analyses.

WILSONVILLE RUN 262 OVERVIEW

CONSOL analyzed 21 process oils from Wilsonville Run 262, which was operated with subbituminous coal from the Black Thunder mine and with slurry and supported catalysts in the first and second reactor stages, respectively.¹ One test was made nominally without the supported catalyst in the second stage (see below). Run 262 was operated from July 10 through September 30, 1991, in the Close-Coupled Integrated Two-Stage Liquefaction (CC-ITSL) configuration with ash recycle. The high/low temperature sequence was used throughout the run, except for a one-day test during operation with most of the supported catalyst removed from the second reactor. Molyvan L slurry catalyst precursor was fed to the first stage along with disposable iron oxide catalyst (and dimethyl disulfide, DMDS, as a sulfiding agent). In theory, the iron oxide promotes coal conversion, whereas the Mo catalyst provides mild hydrogenation activity. The latter is intended to help prevent the coking which contributed to interstage deposition in past runs with this coal.² Molyvan L is an oil-soluble lubricant additive (friction reducer, antioxidant, antiwear and extreme pressure agent) produced by R. T. Vanderbilt Company. It consists of the organometallic compound molybdenum di(2-ethylhexyl) phosphorodithioate in a petroleum oil. It contains 8.1% Mo, 12.3% S, and 6.4% P by weight. Presumably, under liquefaction conditions, the soluble Molyvan L turns into finely divided, well-dispersed particles of MoS₂. The supported catalyst used in the second stage was Criterion 324 (Ni/Mo on 1/16" extrudate unimodal alumina support). Criterion 324 is an equivalent version of Shell 324 produced in Europe.

Run 262 was made using 50% of the available volume of each reactor. The interstage separator was in use throughout the run. The major operating variables were catalyst variables (concentration of slurry catalyst, presence or absence of supported catalyst), second-stage reactor temperature, coal feed rate (and consequently, space velocity), and resid concentration in the recycle solvent. The ashy recycle stream was V-1082 bottoms.

The resid injection system was used through period B, but its use was discontinued after that. This system, which provides a way to inject most of the resid directly without mixing it as a pasting solvent component, was designed to lower the recycle resid inventory requirements for the plant, and thereby to decrease the plant's equilibration time. Its use was discontinued because plugging occurred and because it introduced variability into the composition of the reactor feed. The resid injection system was found not to improve resid conversion reactivity.

In the last run period (period F), the supported catalyst was withdrawn from the second reactor so that operability with only slurry catalyst could be tested. However, a small quantity of about 30 lb of supported catalyst (originally 170 lb) remained in the reactor during the test. Although yields were poor and the period was unstable, operability without supported catalyst (except for the 30 lb) was demonstrated. A brief low/high temperature test allowed planning for Run 263 operation without supported catalyst. A decline in pasting solvent quality was noted after supported catalyst was removed from the second stage.

The objectives for Run 262 were: 1) to evaluate the performance of a dispersed molybdenum catalyst while processing a low-rank coal, and 2) to investigate and eliminate solids buildup while processing a low-rank coal.

All-distillate product slates were obtained in periods A, B, C1, D and E. Resid yields were -4 to 3 wt % MAF coal. This was the first Wilsonville run in which most operating periods were considered all-distillate (resid yield 0 ± 5 wt % MAF). The highest distillate yield was obtained in period C1, which gave 65 wt % distillate and -4 wt % resid yield. Organic rejection was 17 wt % in period C1. Wilsonville noted that Molyvan L dispersed catalyst improved resid and coal conversions, allowing operation at lower temperature and higher space velocity. Decreasing the Mo concentration from 1000 to 100 ppm appeared to have no effect on resid conversion, but did decrease coal conversion. Supported catalyst (Criterion 324) in the second stage allowed lower-temperature operation

of the interstage heater, due to exothermic heat release in the second stage.

Higher distillate production rates were projected at zero resid yield for period 262C1 and 262E relative to periods 251-IIB and 258HI in which no slurry Mo catalyst was used. Wilsonville staff believe¹ that some of the benefits observed when using the dispersed catalyst with Black Thunder coal would also improve the liquefaction of lignite.

Run 262 demonstrated some success in preventing deposition in the interstage piping. The plant was shut down once to inspect and clean the interstage separator (V-1258), which at that time was not working well. The deposition was much less severe than in previous runs. A soft mass of relatively low-ash content (22-32% vs 56-67% in Runs 258 and 260) and a hard, floating mass were removed from the interstage separator. These were distinctly different from the problem deposits previously found. Removed from the interstage separator at the end of the run were a thin deposit from the wall and a solid mass from the bottom. Some deposition did occur in the first-stage reactor, as well. However, Wilsonville found no deposition in transfer lines or in the second-stage reactor during Run 262.

Wilsonville reported the production of waxy product oils in this run.¹ Operators experienced problems with gelling of V-164 (first-stage distillate) and V-1078 (second-stage distillate) samples, particularly on cool nights. This had never been a problem in the past. The paraffins were separated by mixing samples with cold acetone, placing them in the freezer for three hours, and then filtering the product. Gas chromatography was used to identify n-paraffins from C₁₆ to C₃₂ in the white product. The V-164 and V-1078 (undistilled product) samples contained 2-7 wt % paraffins in periods A through D, and 8-9 wt % paraffins in periods E and F. There seemed to be a general increase in paraffin content in these streams throughout the run. Wilsonville measured 7-28 wt % paraffins in the V-1074 recycle distillate from periods A-D and 12-16 wt % in the V-1074 oil from periods E and F.¹ The

paraffin concentration in the V-1074 increased to a peak around period D and then decreased.

On September 30 (the last day of the run), the low/high temperature sequence was tested to determine operability. The reactor temperatures were changed to 810/825°F and the coal feed rate was decreased from 350 to 300 MF lb/hr. Coal conversion increased, but the reaction exotherm decreased. The interstage preheater outlet was at its operational maximum when the coal rate was 300 MF lb/hr. The test indicated that operation in low/high mode is achievable. In contrast, in Run 260, the highest second-stage reactor temperature that could be obtained was only 804°F when low/high operation was tried.

Total post-run recovery of supported catalyst was only 76.2%. It was speculated that the catalyst was crushed by impingement of the feed flow against the top face of the plenum chamber, which was found to have grooves eroded in it.

Operating conditions and yields¹ for material balance periods appear in Table 1. A simplified flow scheme³ of the Wilsonville plant, as configured for Run 262, appears in Figure 1. More detail on the part of the plant involving the major distillate streams is shown in Figure 2.

PLANT DESCRIPTION

During Run 262, the Wilsonville plant was operated in the thermal/catalytic (with regard to supported catalyst) CC-ITSL mode with ash recycle. The standard plant configuration, as used during most of the run, is described below. Exceptions to the standard configuration are described after that for operation with the resid injection system. For standard operation, coal was slurried with a mixture of second-stage vacuum-flashed bottoms (ashy resid, V-1082 bottoms), second-stage heavy distillate (V-1074), and deashed second-stage product resid (V-130). The pasting solvent stream is called V-131B. CONSOL received a sample of this stream. The slurry was fed with hydrogen through the preheater and first-stage backmixed reactor (R-1235). Run 262 was made with the interstage separator (V-1258) in place. The interstage separator removed

the gas and light products from the first-stage products prior to processing in the second stage. The liquid portion of the separator overheads was sent to the product distillation system. The separator bottoms were sent to the second stage, along with make-up hydrogen. Each interstage sample received by CONSOL consisted of the feed to the second stage. The second-stage ebullated-bed reactor was R-1236. Gases and light oils were separated from the second-stage product in an atmospheric flash (V-1250). The atmospheric flash bottoms (V-1067) were separated in a vacuum flash into distillate (V-1082 overheads) and resid (V-1082 bottoms). Samples of the V-1067 material, received by CONSOL, contain ash, IOM, resid and distillate-range material, and represent the recycled material prior to fractionation into distillate, ashy resid, deashed resid components, and subsequent recycle. A portion of the V-1082 bottoms stream was recycled to the first stage as a component of the pasting solvent. The remainder of the V-1082 bottoms stream was deashed in the Kerr-McGee ROSE-SR (formerly called Critical Solvent Deashing) unit, which rejected an ash concentrate and produced a deashed resid product (V-130). The deashed resid was recycled back to V-131B as the second component of the pasting solvent. The atmospheric flash overhead liquids and the V-1082 overheads were sent to the distillation system (consisting of the T-105 atmospheric tower, followed by the T-102 vacuum tower), which produced naphtha (V-161, the T-105 overheads), middle-distillate (V-182, the T-102 overheads), and heavy distillate (V-1074, the T-102 bottoms). The heavy distillate was recycled as the third component of the pasting solvent. The withdrawal tube flush during Run 262 consisted of T-102 vacuum column bottoms (V-1074), the heavy gas oil used for recycle. Previously, the lighter V-182 material had been used.

In operations without resid injection (August 16 through the end of the run on September 30), all the components of the recycle oil (process or pasting solvent) were combined in V-131B to make the slurry oil. The slurry was prepared batchwise in V-101A by adding the coal. During resid injection (July 12 through August 16), the oil used for slurry preparation consisted of distillate only, or distillate plus some deashed resid. The remaining deashed and ashy resid required to achieve the target composition for the recycle material was injected separately through pump

P-1090 (for deashed resid) and through pump P-1091 (for V-1082 bottoms). Slurry was still prepared batchwise in V-101A, but the oil used to prepare coal slurry contained no ashy resid (some batches may have contained no resid at all).

ABBREVIATED HISTORY OF RUN 262

This section is paraphrased from Wilsonville technical review meeting handouts.¹ Run 262 began on July 10, 1991, in the thermal/catalytic CC-ITSL mode feeding Black Thunder mine subbituminous coal. Because of operating difficulties, July 12 was the first full day of operation. The first-stage reactor was R-1235 and the second-stage reactor was R-1236. Both reactors were configured to use 50% of the available reactor volume. The interstage separator (V-1258) was in use throughout the run. The second-stage reactor was charged with 145 lb (dry) of Criterion 324 1/16-inch (Ni/Mo) catalyst that had been aged during Run 260 to an age of 628 lb MF coal/lb cat, or 1470 lb resid+CI/lb cat. A subsequent addition of catalyst on July 14 brought the reactor catalyst charge to 170 lb. The start-up solvent was produced in Run 261 from Burning Star 2 mine (Illinois 6 seam) bituminous coal. Start-up (target) conditions were: 250 MF lb/hr coal feed rate, 30 wt % MF coal in the slurry (2.33 solvent/MF coal ratio), 40 wt % resid and 12 wt % cresol insolubles (CI) in the recycle solvent, and 825/760°F reactor temperatures. Slurry catalysts and sulfiding agent were fed to the first-stage reactor as follows: iron oxide (2 wt % of the MF coal) was mixed with the coal slurry and Molyvan L (Mo was 1000 ppm on MF coal) was mixed with dimethyl disulfide (DMDS) sulfiding agent and injected into the feed line before the first-stage preheater.

A chronological account of the run follows:

- 7/10/91: Run 262 started.
- 7/11: An outage was caused by a leak in the line between the vacuum flash feed tank (V-1067) and the vacuum flash tank (V-1082).
- 7/12: Resid injection was begun.
- 7/12-15: The vent system on the slurry mix tank had a poor vacuum, which caused problems with preparing coal slurry.

- 7/12-17: The best operation of resid injection occurred with 45 wt % coal in the slurry, which was lower than the target. This caused the coal concentration in the total feed to be lower than the target of 30 wt %.
- 7/12-22: Multiple operational problems occurred. The centrifugal pumps on vacuum flash unit V-1082 would not circulate due to a restriction, and leaks were present in the V-1082 overheads condenser (E-1012). These resulted in a high solvent content in the ROSE-SR feed. The ROSE-SR unit was not deashing well and eventually plugged because of continued ash carryover. Poor deashing was attributed to the high solvent content of the feed, and perhaps unusual feed characteristics from dispersed Mo catalyst. The ashy resid recycle pumps (P-1091) used in resid injection were leaking or not pumping.
- 7/13: Two brief power outages occurred.
- 7/16-20: Improvement or fair condition was reported for operation of units.
- 7/17-19: Increasing the coal concentration in the slurry to 46-48 wt % was attempted. After this, the coal slurry concentration was set to 45% due to circulation pump problems and other slurry preparation problems.
- 7/17-20: Balance period A was transitional for several reasons. The actual resid concentration in the recycle solvent was much lower than the target value, there was ash carryover in the ROSE-SR unit, and there was inconsistency in hydrogen consumption during this period.
- 7/20-8/16: The flow rates for the ashy resid pumps were inconsistent.
- 7/22-8/6: The plant was down because of plugging in the ROSE-SR unit. The vacuum flash unit overhead condenser (E-1012) was sent for repairs of the leaks.
- 8/6: The run was restarted.
- 8/6-15: The ashy resid pumps (P-1091) leaked and had reduced flow rates.
- 8/7: The Mo concentration was decreased from 1000 to 500 ppm.
- 8/8-9,14-15: Balance period B
- 8/10-12: The plant was down because of a leak in the recycle hydrogen compressor (C-1206). The overhead condenser on the vacuum distillation column (T-102) failed. Some water entered the reactors.

- 8/12: The run was restarted with the T-102 vacuum distillation column bypassed. Atmospheric distillation column (T-105) bottoms were sent to V-178, the T-102 product vessel. The vacuum flash overheads (V-1072) were sent to the T-102 bottoms product vessel (V-1074) for recycle.
- 8/13: The recycle hydrogen compressor (C-1206) was temporarily out of service.
- 8/15: Problems were encountered with the resid injection system. The T-102 vacuum distillation column was put back in service.
- 8/16: Because of plugging of the resid injection system, resid injection was discontinued for the remainder of Run 262. The coal feed rate was increased from 250 to 300 MF lb/hr. The feed rate of DMDS and Molyvan L was inadvertently set for the lower value, however.
- 8/16-18: Ash in the recycle was low because of the transition from resid injection to the standard practice of blending slurry batchwise in V-101A. (Deashed and ashy resid inventories were low.) Because of this and the low DMDS/Molyvan L feed rate, coal conversion was low.
- 8/19: The second-stage temperature was increased from 760 to 790°F. The DMDS and Molyvan L addition rate was increased to the proper value for this coal feed rate (see entry for August 16).
- 8/22-23: Balance period C1 (Period C was split into periods C1 and C2 to account for differences in recycle resid concentration.)
- 8/22-28: Solids buildup in the interstage separator (V-1258) was apparent. See detail in daily entries.
- 8/22: The level control valve on V-1258 could not control the flow. Some gas blew through to the second stage. The V-1258 density/level gauge showed a high level, suggesting the presence of solids. These caused a run upset.
- 8/23: The bypass on the V-1258 level valve plugged and was not repairable.
- 8/23-28: Continued indications of solid deposition.
- 8/24-25: Balance period C2
- 8/26-27: The temperature reading in the middle of V-1258 was low. This is usually an indication of solids in the separator.
- 8/27: Numerous power outages occurred.

8/28: The Mo concentration was decreased from 500 to 200 ppm.

8/29-9/6: The V-1258 level was very difficult to control. The plant was shut down for inspection and cleaning of the interstage separator (V-1258) and associated piping. A catalyst withdrawal was made before plant was taken down. The corresponding catalyst addition was made on Sep 6. A large clump of deposited material was found in the bottom of the V-1258 separator vessel. The V-1258 level valve had a worn trim.

9/3: The viscosities of the contents of V-101A and B became high. T-102 overhead distillate was used to dilute the tank contents.

9/6: The run was restarted.

9/7: The ebullating pump (P-1222) for the first-stage reactor (R-1235) failed.

9/8-12: Balance period D

9/8: 27 lb of catalyst was added to the second-stage reactor (R-1236) to replace catalyst removed during the shutdown.

9/9: The V-1258 level valve plugged, causing a loss of flow and an upset.

9/13: The second-stage reactor temperature was increased from 790 to 810°F, since the interstage preheater outlet temperature was low enough to permit it. The coal feed rate was also increased from 300 to 350 MF lb/hr, so that resid inventory would not be depleted. The Mo concentration was decreased from 200 to 100 ppm.

9/16: The target recycle solvent composition was increased from 40 to 42 wt % resid. Since Wilsonville consistently measured resid in the pasting solvent to be about 2 wt % lower than the target concentration, this would enable them to blend to 40% actual resid concentration.

9/18-22: Balance period E

9/18: A brief shutdown of the first-stage preheater (B-1200) caused a temperature upset in the reactors.

9/19: A brief power outage occurred. The waxy nature of the V-1258 and V-1250 overhead streams caused plugging. Steam tracing of the lines was needed and performed.

9/23: The Mo concentration was increased from 100 to 300 ppm for 1/2 day, then reduced back to 200 ppm. Most of the Criterion 324 supported catalyst was removed from the second-stage reactor (R-1236), according to the run plan.

92.2 lb dry catalyst was withdrawn and it was assumed that ca. 60 lb remained. At the end of the run, however, only 29 lb dry catalyst was found. After withdrawal of the supported catalyst, reactor exotherms decreased and resid inventory increased rapidly.

9/24, 26-27, 29:

Balance period F was considered unstable because one of the major streams (the feed to the V-1079 vacuum flash unit) was not measurable because the dump pot malfunctioned on September 24. The flow rate of this stream was estimated until end of run by a material balance around the V-1082 vacuum flash vessel.

9/24-29: The first-stage distillate overheads (V-164) and the second-stage atmospheric flash overheads (V-1078) were reported to have a waxy gel-like consistency after September 24. This coincided with removal of catalyst from the second stage and with the onset of colder weather. Toward the end of the run, the lines from V-105 (V-1258 overheads) to V-164 to V-160 had plugging problems from the waxy material. The waxy material also caused level control problems in V-1251 (atmospheric flash overheads separation vessel) on September 25-29.

9/28: Circulation was lost in V-101B, causing a brief feed outage. This resulted in low reactor temperatures.

9/30: To test operability in the low/high temperature mode, the first-stage reactor (R-1235) temperature was decreased from 825 to 810°F and the second-stage reactor (R-1236) temperature was increased from 810 to 825°F. The coal feed rate was decreased from 350 to 300 MF lb/hr for 5 1/2 hours, then later increased to 360 MF lb/hr.

10/1: Run 262 ended.

SAMPLE DESCRIPTIONS

CONSOL received 21 process oil samples from Run 262. The process oils consisted of a recycle oil (V-131B) sample, an interstage oil (R-1235) sample, and the second-stage flashed bottoms product oil (V-1067) sample composited from each of the seven material balance periods A through F. Prior to Run 261, CONSOL received daily composite or individual daily samples from Wilsonville runs. At CONSOL's request, Wilsonville personnel composited samples over the complete material balance period for each sample beginning with the Run 261. This was done to reduce

uncertainty in interpretation of analytical results from one period to another. The samples from periods A and B (resid injection) designated V-131B actually were composited to represent the entire recycle feed (including injected resid, but without the fresh coal), and not just the slurry oil.

ANALYSES

Proton distributions were obtained by $^1\text{H-NMR}$ for each of the V-131B, interstage and V-1067 whole samples (Tables 8-10). All the whole samples were tested in the microautoclave at the modified equilibrium conditions (Table 18). Prior experience has shown that the whole-sample microautoclave results may show high variability when the samples have high solids concentrations, as was the case in Run 262. The whole samples were distilled (Tables 2-4) to 320°C pot/ 270°C column/5 torr (850°F/atm). Each 850°F^+ resid was analyzed by solubility fractionation (Tables 5-7), $^1\text{H-NMR}$ (Tables 14-16) and FTIR for phenolic -OH content (Table 17). Each 850°F^- distillate was analyzed by $^1\text{H-NMR}$ (Tables 11-13) and FTIR (Table 17). Microautoclave tests were made at the modified equilibrium conditions with each 850°F^- distillate (Table 18).

Details of the sample work-up and analytical procedures have been presented elsewhere.^{4,5} All samples for proton distribution by NMR were dissolved in 99.96% deuterated pyridine (whole or resid samples) or in CDCl_3 (distillate samples). Integrations were performed electronically. Response factors used for flame ionization detection of solubility fractions were those previously used for Run 258 samples which were also produced from Black Thunder coal. A different set of response factors is used for each feed coal used to produce an oil sample.

PROCESS OIL PROPERTIES

Process oil properties are presented in Tables 2 through 18 and in Figures 3 through 14. The discussion is most easily followed by referring to the figures. The following are general observations made about process oil properties during Run 262. Key differences in conditions of material balance periods are summarized here as a reference for comparison of oil properties.

- From period A (transitional) to period B, there was an increase in the resid concentration in the process solvent from 32.1 to 37.7 wt % and a decrease in the Mo concentration from 1000 to 500 ppm (MF coal basis). During part of period B, the vacuum tower T-102 was bypassed.
- From period B to period C1, the coal feed rate was increased from 247.7 to 301.4 MF lb/hr and the second-stage temperature was increased from 761 to 790°F. In addition, resid injection was discontinued after period B.
- From period C1 to period C2, the resid concentration was decreased from 39.1 to 35.8 wt %.
- From period C2 to period D, the Mo concentration was decreased from 500 to 200 ppm.
- From period D to period E, the coal feed rate was increased from 299.7 to 346.2 MF lb/hr, the second-stage temperature was increased from 790 to 810°F, and the Mo concentration was decreased from 200 to 100 ppm.
- From period E to period F (unstable), the supported catalyst was removed from the second stage (except for the residual 30 lb) and the added precursor Mo concentration was increased from 100 to 200 ppm.

Between periods B and C1, between periods D and E, and between periods E and F, the resid concentration in the process (recycle) solvent varied by 2-3 wt %, but was considered to be constant. The coal feed rate changes were accompanied by simultaneous changes in the second-stage reactor temperature. The second-stage reactor temperature was set to 760, 790, or 810°F, respectively, when the coal feed rate was set to 250, 300, or 350 MF lb/hr. It is intended that the higher reaction temperature compensate for the shorter residence time at a higher coal feed rate. The only unconfounded variable changes were from period C1 to

period C2 (decrease in recycle resid concentration) and from period C2 to period D (decrease in the Mo concentration). Between periods, operational changes usually involved more than a single variable. However, oil properties generally did not change substantially during the run. Consequently, they will be discussed in a general way. A few specific cases will be singled out for more discussion. A separate discussion will be given comparing period E with period F. Period F was unique in Run 262 because most of the supported catalyst was removed from the second stage.

Component distributions of the whole process oils are shown in Figures 3-5 and given in Tables 2-4. From period A to B, the ash content of the recycle stream decreased by nearly 2 wt %. From period B to period C1, the ash content of all the streams increased by 1 to 3 wt %. From period C2 to D, the ash content of all the streams decreased by 1-2 wt %. The reason for these changes in observed ash content is not completely clear, but may be related to changes in the ash content of the feed coal, although the changes in feed coal ash content as seen in Table 1 are small. Of course, unidentified changes in the process which affect inventories and flows of recycle solvent components, etc. will also affect the concentration of ash in the process streams. The 850°F⁺ resid concentrations determined by CONSOL for the V-131B samples were 10-16 wt % higher than Wilsonville's reported resid concentrations. Wilsonville uses a distillation endpoint of about 1050°F, whereas CONSOL uses an endpoint of 850°F. Thus, CONSOL reports 850 x 1050°F material as resid, and Wilsonville reports it as distillate.⁶ Changes in resid and distillate concentration of the process streams will be discussed along with other changes in oil properties.

The sum of IOM and ash values obtained by CONSOL for the V-131B samples from periods C1 and C2 (Table 2, Figure 3) were about 4 wt % higher than Wilsonville's measured CI concentrations. All of CONSOL's values were higher than those of Wilsonville, but most were higher by less than 1 wt %. Our analyses were obtained from a true composite over each material balance period, whereas Wilsonville's values were combined from

daily operation analyses or flow rates. Wilsonville uses cresol to define solubility, whereas CONSOL uses THF.

During Run 262, there was an increase in 850°F⁺ resid concentration and a corresponding decrease in distillate concentration in all streams (i.e., recycle, interstage, and product) from period A through period F (Figures 3-5, Tables 2-4). All three streams showed a general decrease in the concentration of oils (hexane-solubles) in the THF-soluble 850°F⁺ resid through the run, with corresponding increases in the asphaltene (benzene-solubles) and preasphaltene (benzene-insoluble, pyridine-solubles) concentrations (Figures 6-8, Tables 5-7). Hydrogen aromaticity (Figures 9-11) of the distillate (Tables 11-13) and resid (Tables 14-16) components of all streams generally decreased from period A to period B, but then increased from period B through the end of the run. Distillate hydrogen donor (hydroaromatic) content decreased throughout the run (Figures 9-11, Tables 11-13). Distillate paraffinic hydrogen content was generally lowest at the beginning and end of the run, and highest in periods B through D (Figures 9-11, Tables 11-13). The concentration of phenolic -OH in the distillate and resid portion of most streams stayed fairly constant through period D or E, and then increased (Figure 12, Table 17). An exception was the interstage distillate, which increased in phenolic -OH concentration from period A through C2, dropped from period C2 to D, and increased from period D through F. Distillate donor solvent quality (coal conversion in a microautoclave solvent donor assay) generally decreased through period D or E, then increased (Figure 13, Table 18). There were relative maxima in distillate donor solvent quality during periods A, C2, and F. To some degree, these appear to be related to lower paraffinic hydrogen, especially in periods A and F. Past work at CONSOL has shown paraffinic hydrogen to be detrimental to donor quality.^{7,8}

Most of the trends in process oil properties indicate decreasing distillate and resid quality as Run 262 progressed. In spite of confounding variables, changes in certain variables seemed to dominate the oil properties. There were concurrent increases in second-stage temperature and coal feed rate as the run progressed. There was a general decrease

in slurry Mo concentration as the run progressed. In the last run period, most of the supported catalyst was removed from the second stage. These are changes that one might expect to worsen oil properties. There also was an increase in recycle resid concentration from period A through C1, a decrease from period C1 to C2, and then another increase from period C2 through F. Some of these recycle resid concentration changes were rather small, and their impact on oil properties is uncertain. Therefore, changes in recycle resid concentration did not play an obvious role in determining overall oil properties during the run.

Some specific changes in oil properties from one period to another are worth noting. A number of oil properties changed substantially from period A to period B. The transitional nature of period A may have contributed to observed differences in oil properties, in addition to changes in operating variables. There was an increase in resid recycle concentration and a decrease in slurry Mo concentration between periods A and B. CONSOL data show increases in the 850°F⁺ resid content of all streams (Figures 3-5, Tables 2-4). The recycle and interstage resids increased in oil (hexane-solubles) concentration from period A to B, whereas the product resid decreased in oil content (Figures 6-8, Tables 5-7). This increase in the oil component of the recycle resid is understandable, when we consider that the cresol-insoluble (CI) concentration (from V-1082 bottoms, the deasher feed) was fixed in the recycle solvent composition at about 19 wt %. The 5 wt % additional resid in the recycle solvent in period B must consist of deashed resid from the ROSE-SR unit. The deasher selectively rejects the asphaltene and preasphaltene components of the resid, along with the ash. (Compare the preasphaltenes in the recycle resids to those of the product resids in Tables 5-7.) Therefore, the additional deashed resid in period B is enriched in the oil component. Proton distributions (Figures 9-11, Tables 11-16) show a decrease in distillate and resid aromaticity, a decrease in distillate hydroaromaticity, and an increase in distillate paraffinicity of all streams from period A to B. These effects indicate increased hydrogenation in period B, but no clear cause is evident. The phenolic -OH concentration of the resid fraction of all streams decreased slightly (Figure 12, Table 17), indicating slightly better deoxygenation

in period B. The distillate donor solvent quality decreased from period A to period B (Figure 13, Table 18), probably from increased paraffinicity and decreased hydroaromaticity.

From period B to period C1, the coal feed rate and the second-stage temperature were increased and resid injection was discontinued. There was an increase in THF-soluble resid concentration and a decrease in the distillate concentration in the interstage sample (Figure 5). There was a step increase in the resid preasphaltene concentrations and a decrease in the oil content of the resids in all streams (Figures 6-8). Distillate and resid aromaticity increased by a small amount (Figures 9-11). There was an increase in interstage distillate hydroaromaticity (Figures 9-11). From period B to C1, there were small increases in the phenolic -OH concentration of the resid streams (Figure 12). The distillate donor solvent quality (Figure 13) decreased slightly from period B to period C1. The observed changes from period B to period C1 generally point to a slight worsening of process oil properties at the higher coal feed rate and second-stage temperature.

From periods C1 to C2, the target recycle resid concentration decreased by about 3 wt %, although there was only a slight decrease in the resid concentration in the recycle solvent, as measured by CONSOL (Table 2, Figure 3). However, the product solvent showed an increase in the resid content, and a decrease in the distillate content (Table 3, Figure 4). Perhaps the change in recycle resid concentration was too small to have a definitive impact on oil characteristics. Wilsonville did observe changes in yields, however, as a result of the resid concentration decrease.

From period C2 to period D, the slurry Mo concentration was decreased from 500 to 200 ppm. There was a decrease in resid concentration (and increase in distillate concentration) in the interstage and product streams (Figures 4-5). There was a substantial decrease and increase, respectively, in the interstage distillate and resid phenolic -OH concentrations (Figure 12). The product distillate also decreased in phenolic -OH concentration. Distillates from all three process streams

decreased in donor solvent quality from period C2 to period D (Figure 13). Although the responses of many oil properties were inconsistent, the decrease in slurry Mo concentration appeared to consistently reduce distillate donor solvent quality.

From period D to period E, the coal feed rate and second-stage temperature were increased, and the slurry Mo concentration was decreased. All three streams increased in resid concentration (Figures 3-5). There was a significant increase in distillate and resid aromaticity from period D to period E (Figures 9-11), except in the product distillate, which did not change. The phenolic -OH concentration increased by a significant amount in the product resid and the interstage and product distillates (Figure 12). The general increase in resid concentration and distillate and resid aromaticity and phenolic -OH concentration seems to result from the coal feed rate increase and Mo concentration decrease.

A major change in operating conditions occurred from period E to F. This is when most of the supported catalyst was removed from the second reactor, and the slurry Mo concentration was increased. Results of operation, before and after this change, will be described in more detail in a later section.

850°F⁺ RESID CONVERSION AND KINETICS

CONSOL analyses of the process oils were used to calculate conversions (forced ash balance method) of the 850°F⁺ material and its various components in each reactor stage (Table 19, Figures 14-19). The 850°F⁺ conversions then were used to calculate conversion rate constants and conversion activities (Table 20, Figure 20). The conversion and kinetic calculations were made as described elsewhere.⁹ Briefly, the following equations are used in the calculations:

$$C = \text{Conversion} = \left(\frac{850^{\circ}\text{F}^{+} \text{ In/Ash In} - 850^{\circ}\text{F}^{+} \text{ Out/Ash Out}}{850^{\circ}\text{F}^{+} \text{ In/Ash In}} \right) \times 100\%$$

$$K = \text{Rate Constant} = \text{WHSV} \left(\frac{C}{100 - C} \right)$$

$$A = \text{Conversion Activity} = K e^{E_{\text{act}}/RT},$$

where E_{act} is assumed to be 23,500 cal/mol, as has been used in the past at CONSOL.⁸ In the first equation and in the figures and discussion to follow, 850°F⁺ refers to the organic portion of the distillation bottoms consisting of IOM and THF-soluble resid. For convenience and consistency, the catalytic stage WHSV was used to calculate the rate constant for the thermal stage. Also note that no catalytic stage WHSV was given for period F, in which virtually all of the supported catalyst was removed from the second stage. For simplicity, the WHSV for period E (6.6 lb feed/hr lb cat.) was used in the period F rate calculations. The coal feed rates and the thermal space rates were the same in these two periods (space rates were 91.5C in period E, 90.6C in period F in units of lb MF coal/hr/ft³, where C is a constant).

Conversions of 850°F⁺ resid and its components calculated for each reactor stage and the total system are given in Table 19. Figure 14 shows the first-stage and total THF-soluble 850°F⁺ and coal + IOM conversions for Run 262. As is typically observed, the second stage provided very little additional conversion of coal + IOM. In past runs the second stage typically provided a substantial part of the THF-soluble 850°F⁺ conversion. However, in Run 262, there was relatively little THF-soluble 850°F⁺ conversion provided by the second stage (Figure 14, Table 19). Variations in 850°F⁺ conversion with run period can be seen in Figures 15-19. Also presented are average conversions and standard deviations for the run. The results for the balance periods may show high variability, because the conversion calculated for the resid solubility components (Table 19, Figures 16-19) are subject to error accumulated from determination of total THF-solubles, IOM, ash, and the solubility fractions. The average and standard deviation may provide a more reliable indication of the conversions. The soluble resid and its oil, asphaltene, preasphaltene, and phenolic -OH components (Figures 15-19) show first-stage and total net yields (negative conversions), but higher second-stage conversions. The second-stage conversions of THF-solubles (Figure 15), and the oil (Figure 16) and asphaltene (Figure 17)

components each average to approximately zero over the run, the result being that the average first-stage conversion and average total conversion are virtually equal for each of these resid fractions. On the other hand, the second-stage conversions of preasphaltenes and phenolic -OH were consistently positive (Figures 18 and 19), and the corresponding average total conversions were greater than the average first-stage conversions. In Run 260¹⁰, the average total conversion of the THF-soluble resid and its components were positive (except for preasphaltene conversion, which was negative). In Runs 262 and 258¹¹, the average total conversion of the THF-soluble resid and all its components were negative. Thus, there was a net overall yield (negative conversion) of 850°F+ THF-soluble resid in Run 262 (note that the 850 x 1050°F material is reported as distillate at Wilsonville). This results from the conversion of coal + IOM to solubles. When they are combined as one component (resid + UC), the total conversion is positive, averaging about 20%. The second-stage conversion of THF-soluble resid and its components is nearly always greater than the first-stage conversion, because most of the coal solubilization is done in the first stage. In the second stage, little additional coal solubilization occurs, and the net conversion of THF-soluble resid is higher (and typically positive). The Run 262 results indicate that the second stage played a significant role in removal of preasphaltenes and in resid deoxygenation.

Conversion of various components through the run will be discussed briefly in more detail. CONSOL results show a general decline in first-stage coal + IOM conversion through the run (Figure 14). Wilsonville results for first-stage coal conversion show a similar trend, except for one or two periods (Table 1). The interstage sample IOM content (Figure 5) seems to reflect this in periods D through F. Perhaps this is also related to the higher organic rejection (yield of ash-free solid product in Table 1) in periods D through F. As discussed in an earlier section, there were upward trends in coal feed rate, second-stage temperature, resid concentration and a downward trend in slurry Mo concentration through the run which may have influenced the trend in first-stage coal conversion. No particular process variable stands out from the crowd, however, as being a primary influence.

Periods B and D, which appeared somewhat unusual, were similar in regard to resid component conversion. Period B had high first-stage conversions of THF-soluble resid and each of its components relative to the rest of the run periods (Figures 15-19). Period D had high first-stage conversion of THF-soluble resid and each of its components except asphaltenes relative to the other run periods. In periods B and D, the high first-stage conversions of the oil and asphaltene components were typically accompanied by corresponding low second-stage conversions. Other than the possibility that the interstage samples were not representative, there is no obvious explanation for these results. Periods C1 and E, which represent increases in second-stage temperatures and coal feed rates, relative to corresponding prior periods, also show some features in common. Both periods had high second-stage and total conversions of oils, relative to those in other run periods (Figure 16). In period C1, the second-stage and total conversions of THF-soluble resid and of asphaltenes also were high (Figures 15 and 17). In contrast, period E had a high first-stage conversion of oils and a high second-stage conversion of preasphaltenes (Figures 16 and 18). Periods A and C2, in which recycle resid concentrations were relatively low, had low total conversions of THF-soluble resid and of the oils fraction (Figures 15 and 16). Period A additionally had high conversions of preasphaltenes in both stages and the total system, perhaps because of the high dispersed Mo concentration in period A (Figure 18). (Periods B, D and F also had high first-stage and total preasphaltene conversions (Figure 18) and high first-stage phenolic -OH conversions (Figure 19).) These results seem to indicate some sensitivity of the resid component conversions to changes in process conditions. However, the identification and utility of such responses may be obscured by high variability in the calculated conversions.

In Table 20, the 850°F⁺ resid + UC conversions obtained by CONSOL are compared with those obtained by Wilsonville. The associated kinetic rate constants and conversion activities obtained by CONSOL also are given. The conversions obtained by CONSOL are different from those obtained by Wilsonville because of a difference in laboratory distillation conditions. CONSOL uses an 850°F atmospheric equivalent distillation

endpoint, whereas Wilsonville uses a 1050°F atmospheric equivalent endpoint. Therefore, CONSOL calculates conversion of 850°F⁺ material, but Wilsonville calculates conversion of 1050°F⁺ material. The effect of this difference on measured conversions has been discussed elsewhere.⁹

The average ratios of CONSOL conversions to Wilsonville conversions are compared below.

RATIO CONSOL/WILSONVILLE CONVERSIONS OF RESID + UC

Period	First Stage	Second Stage	Total
262 (all)	0.68 $\pm$ 0.18	0.23 $\pm$ 0.70	0.58 $\pm$ 0.07
262B-E	0.72 $\pm$ 0.21	0.04 $\pm$ 0.76	0.55 $\pm$ 0.07
262A,C1,C2,E,F (second-stage conversions were all positive)	0.58 $\pm$ 0.04	0.58 $\pm$ 0.20	0.60 $\pm$ 0.08
262F	0.56	0.80	0.64
260C ¹⁰	1.01 (thermal)	0.67 (catalytic)	0.92
260D-F ¹⁰	0.96 $\pm$ 0.18 (catalytic)	1.79 $\pm$ 0.72 (thermal)	1.13 $\pm$ 0.10
Average Runs 250-259 ²⁰	0.98 $\pm$ 0.10	0.85 $\pm$ 0.16	0.94 $\pm$ 0.06

The ratios for virtually every period of Run 262 (Table 20) for the first and second stage and total system were low relative to past Wilsonville runs. Only in periods B and, perhaps, D were the first-stage ratios typical of past runs. Likewise, only in periods C1 and F were the second-stage ratios typical of past runs. The total conversion ratios in Run 262 were consistently much lower than ever observed in the past.

A CONSOL/Wilsonville conversion ratio lower than one indicates that the percentage conversion of 850 x 1050°F material is relatively smaller than the percentage conversion of 1050°F⁺ material. This indicates low 850 x 1050°F conversion or, alternatively, high conversion of 1050°F⁺ (including unconverted coal). Since resid extinction was achieved in most run periods, it appears that conversion of 1050°F⁺ can be regarded as high. Perhaps at the relatively high coal feed rates used in Run 262, there was a net production of 850 x 1050°F boiling material (measured as distillate at Wilsonville), because it was being made from 1050°F⁺, but was not effectively converted further to 850°F⁻. One possible explanation for these unexpected results is that the 850 x 1050°F material may have been highly paraffinic and was not easily cracked to lighter

distillate. Although Wilsonville found evidence of paraffins in all the distillates, they did not report a high concentration of the 850 x 1050°F material in the distillates.

Periods B and D, in which the first-stage conversion ratios were more typical of past Wilsonville runs, had first-stage conversions and conversion ratios higher than the remaining Run 262 periods, but had second-stage conversions and conversion ratios which were considerably low relative to the rest of Run 262. It is not clear why periods B and D might stand out in this regard. Both periods followed a decreases in the slurry Mo concentration and preceded increases in coal feed rate and second-stage temperature. The total 850°F conversions for periods B and D were very similar to those of the rest of the run, however. This suggests that there may have been problems with the interstage samples or analyses from those periods.

The kinetic rate constants and conversion activities for each reactor stage are given in Table 20 and the activities are plotted in Figure 20. These results are not surprising, in light of the discussion of resid component conversions above. Periods B and D gave relatively high 850°F resid + UC conversion activities in the first stage, while those for the second stage during those periods were low. The second-stage conversion activity was relatively high in period C1. Omitting the results from periods B and D, the average conversion activity ($\times 10^7$) was 1.48 ± 0.19 in the first stage and 1.41 ± 0.63 in the second stage. If period C1 is also left out, we obtain an average of 1.50 ± 0.21 for the first stage and 1.13 ± 0.18 for the second stage. As the latter set of averages indicates, it is typically observed that the 850°F resid + UC activity of the thermal first stage is higher than that of the second stage. This seems to result from the primary role the first stage plays in converting coal to solubles. The conversion of coal + IOM dominates the conversion of resid. Rate constants and activities in each catalyst stage from Run 262 are compared below with those from other runs.

RATE CONSTANTS AND ACTIVITIES FOR CONVERSION OF RESID + UC

Period	First Stage Rate Constant	Second Stage Rate Constant	First Stage Activity $\times 10^7$	Second Stage Activity $\times 10^7$
262 A,C1,C2,E,F (B and D omitted)	0.94 ± 0.12	0.57 ± 0.25	1.48 ± 0.19	1.41 ± 0.63
262 A,C2,E,F (B, C1, and D omitted)	0.95 ± 0.14	0.47 ± 0.08	1.50 ± 0.21	1.13 ± 0.18
262F	0.96	0.56	1.53	1.08
260C ¹⁰	1.17 (thermal)	0.99 (catalytic)	1.84 (thermal)	0.99 (catalytic)
260D-F ¹⁰	1.25 ± 0.32 (catalytic)	0.54 ± 0.34 (thermal)	3.47 ± 1.38 (catalytic)	1.30 ± 0.74 (thermal)
Average Runs 251-II, 251-III (Wyodak) ²⁹	1.96	0.22	3.52	2.32
Average Runs 250-257 (Bituminous) ²⁹	1.33 ± 0.36	0.61 ± 0.11	2.73 ± 0.75	2.30 ± 0.81

The average first-stage rate constant during Run 262 was somewhat low, relative to the other runs listed. The average second-stage rate constant during Run 262 was similar to the bituminous average, higher than the Wyodak average, and lower than the period 260C result. The average first-stage activity during Run 262 was somewhat low, relative to 260C, and quite low relative to the other runs listed. The average second-stage activity during Run 262 was much lower than the bituminous and Wyodak averages, but slightly higher than the period 260C average. Overall, it appears that the conversion activities for Run 262 are low relative to previous Wilsonville runs.

EFFECT OF SUPPORTED CATALYST WITHDRAWAL FROM THE SECOND STAGE

After period E, almost all of the supported catalyst was withdrawn from the second reactor, and the slurry Mo concentration was increased from 100 ppm to 200 ppm for period F. (Period F was considered unstable.) The resid preasphaltene content increased by a small amount in the recycle sample. Changes from period E to period F in proton distribution in all three streams were quite consistent: there was an increase in resid and distillate aromaticity, a decrease in distillate hydro-aromaticity, and a decrease in distillate paraffinicity (Figures 9-11, Tables 11-16). These changes ranged from slight to large, depending on the sample and property involved. The changes in proton distribution indicate less hydrogenation in period F, as one would expect. There were

significant increases in the phenolic -OH concentrations of distillate and resids from all the streams (Figure 12, Table 17). This indicates that deoxygenation is an important role of the supported catalyst, in addition to hydrogenation. The phenolic -OH removed from the distillate by the second stage decreased from 0.54 meq/g in period E to 0.32 meq/g in period F (obtained by subtracting the V-1067 value from the corresponding R-1235 value in Table 17). The interstage and product distillate donor solvent quality increased from period E to period F, probably from a decrease in paraffinic material in the solvent.

Although Wilsonville found the second-stage and total resid + UC conversion to be lower in period F than in period E, CONSOL found them to be the same (Table 20, Wilsonville measures 1050°F⁺, CONSOL measures 850°F⁺). Conversion of oils (hexane-solubles) decreased a significant amount in the first stage and total system, and by a small amount in the second stage (Figure 16, Table 19). Conversion of preasphaltenes increased substantially in the first stage and total system, and by a small amount in the second stage (Figure 18, Table 19). Phenolic -OH conversion in the first stage and total system likewise showed an increase from period E to period F (Figure 19). Perhaps this resulted from the improvement in solvent quality, and/or the increase in slurry Mo concentration. There were virtually no changes in the first- and second-stage rate constants and activities for 850°F⁺ resid conversion from period E to period F (Figure 20, Table 20). Since Wilsonville observed a decrease in (1050°F⁺) resid + UC conversion in the second stage and total system, but CONSOL did not observe a decrease in 850°F⁺ conversion, conversion of 850 x 1050°F material relative to conversion of 1050°F⁺ material must have been relatively higher in period F than in period E (Table 20). This is evident in Table 20, where the ratio of CONSOL to Wilsonville second-stage conversion increased from 0.36 in period E to 0.80 in period F. Both Wilsonville and CONSOL results show no change in the resid + UC conversion in the first stage from period E to period F (Table 20).

COMPARISON OF OILS FROM RUN 262 WITH OILS FROM RUNS 260 AND 258

To provide some perspective on oil properties and performance during Run 262, oil characteristics and resid conversion results obtained by CONSOL for Run 262 samples will be compared with results from previous runs made with Black Thunder coal. Two periods from each of Runs 258, 260 and 262 will be compared. Table 21 gives the operating conditions for periods 258H, 258M, 260C, 262B, and 262E (thermal/catalytic), and 260D (catalytic/thermal). Reactor volumes in use were 50% in each reactor during periods of Runs 258 and 262, but were 100% in the thermal stage and 75% in the catalytic stage in the Run 260 periods. Periods B and E represent extremes in several run conditions during Run 262: second-stage temperature, coal feed rate, space velocity, and slurry Mo concentration, and they span most of the range of oil properties observed during the run. Relative to Run 262, the Run 258 periods had higher first-stage temperatures, intermediate second-stage temperatures, lower-to-equal coal feed rates and space velocities, and equal-to-higher catalyst ages. Run 258 period samples were produced with the old distillation system not completely operating, and the feed coal ash content was about 1 wt % higher than in the other four comparison periods. Run 262 was unique in its use of the Molyvan L slurry catalyst precursor. In addition to the Molyvan L, 2 wt % iron oxide plus a sulfiding agent was used in every period being compared. During the Run 260 periods, there was no interstage gas-liquid separation, and the space velocities were quite low. The second-stage reactor temperature in 260C was intermediate to those of periods 262B and 262D. Period 260D was unique in temperature and configuration. Coal concentration in the feed was about 30 wt % for all periods compared.

Table 22 compares the yield and performance data reported by Wilsonville plant personnel for these periods. The Run 262 periods were relatively low in hydrogen consumption, C_1 - C_3 gas yield, and resid yield, intermediate in water yield, and TSL coal conversion, and relatively high in heterogas yield, overall C_4 + distillate yield, and ROSE-SR bottoms yield (organic rejection). Resid + UC conversion in the Run 262 periods was low to intermediate in the first stage and low to high in the second stage, relative to the other periods.

Table 23 gives the process oil properties, conversions and kinetic constants for the periods being compared. The solvent quality indexes of the Run 262 distillates are relatively low. The Run 262 distillates and resids are relatively low in hydrogen aromaticity. Indeed, the recycle distillates (V-131B and V-1067) from periods 262B and 262E were several percent lower in aromaticity than those from the next lowest period, 260D, which was made at a rather low space velocity. The inter-stage distillates and all the resids from periods 262B and 262E were similar in aromaticity to their period 260D counterparts. The paraffinicity of the Run 262 distillates was relatively high, in accord with Wilsonville's observations. The phenolic -OH concentrations of the distillates from periods 262B and 262E were typical of those from other periods (except 260D, which were lower in some cases). The resids from the Run 262 periods were intermediate to high in phenolic -OH concentration. The period 262B and 262E resid oil (hexane-solubles) concentrations spanned nearly the entire range of the other samples, but were mostly at the high end. Resid asphaltene concentrations of all the sample periods varied only by about 5 wt %. Resid preasphaltene concentrations in the Run 262 samples were relatively low for the recycle resids and the period 262B interstage resid. The period 262E interstage resid was high in preasphaltenes. The Run 262 conversions and kinetic constants were low, disregarding most of the 262B values. The total system 850°F⁺ conversions in 262B and 262E were significantly low, as were the conversions in each stage in 262E. The first-stage kinetic rate constant for 850°F⁺ conversion in 262E was similar to the Run 260 values, but the second-stage rate constant was much lower. However, the conversion activities in both stages for period 262E were similar to those from 260C. The second-stage conversion activity for period 262E was also similar to that for 260D.

Except for some of the resid -OH concentrations, many of the properties measured indicate that process oils from periods 262B and 262E were upgraded more than oils from the other periods. The Run 262 oils were similar in many ways to those from 260D, or in some cases to those from 260C. Although 850°F⁺ resid conversions were low in the Run 262 periods,

the first-stage kinetic rate constant and activity for conversion of 850°F⁺ resid in 262E were similar to those from 260C.

CONCENTRATION OF MOLYBDENUM IN TETRAHYDROFURAN-INSOLUBLE DISTILLATION RESID

Run 262 used as a dispersed-catalyst precursor Molyvan L, a commercial material in use in the petroleum industry as an antiwear agent, antioxidant, and friction reducer. Its catalytic activity in liquefaction is ascribed to the 8.1 wt % molybdenum (Mo) it contains. In order to study the activity and chemical nature of the Mo, a subcontract was initiated with Vander Sande Associates under the Participants Program. In this study, samples from the direct coal liquefaction process streams of Run 262 will be examined by Scanning Transmission Electron Microscopy (STEM) and Transmission Electron Microscopy (TEM). Knowledge of the concentration of Mo in the samples being examined will facilitate the microscopic analyses. Therefore, an interstage (R-1235) process stream sample from Run 262 period A was distilled and the 850°F⁺ resid was filtered to obtain tetrahydrofuran (THF)-insolubles. The 850°F⁺ distillation resid comprised 64.4 wt % of the whole oil and the THF-insoluble portion of the resid was 33.0 wt % of the resid (21.2 wt % of the whole oil). The ash content of the THF-insoluble material was 50.1 wt % (10.4 wt % of the whole oil). The whole process stream oil, the distillation resid, and the THF-insolubles were analyzed for major elements and molybdenum. Ash elemental analyses of the distillation resid, the THF-insoluble portion of the distillation resid, and the whole oil are given in Table 24. It was determined that 97% of the Mo present in the whole oil is in the distillation resid and 93% is resident in the ash of the THF-insoluble portion of the distillation resid. Within the precision of the Mo analysis (~2%), essentially all of the Mo remained in the resid upon distillation of the whole oil. It is possible that some (~5%) of the molybdenum was lost in the filtration of the THF-insoluble material through two possible mechanisms. Either this small amount of molybdenum is present in the whole oil in a THF-soluble form and thus was not retained in the insoluble material, or the molybdenum is in a non-soluble form with a particle size smaller than

2.5 μ m, which is the particle retention size of the filtering medium used in the preparation of the sample.

Based on these results, three samples of the THF-insoluble portion of the distillation resids from Run 262B were prepared and provided to Vander Sande Associates for examination. The Mo contents of the ash of the three samples are 5815 $\pm$ 31 ppm, 6023 $\pm$ 44 ppm, and 5046 $\pm$ 18 ppm for the R-1235, V-1067 and V-131B process streams, respectively. In period B of Run 262, the feed included coal with an ash content of 6.3% MF, 2.0 wt % Fe₂O₃ and 500 ppm of Mo. The Mo concentration in the ash of all three process streams should, therefore, be 6024 ppm. For the V-1067 and R-1235 samples, essentially 100% of the Mo is accounted for in the ash of the THF-insoluble samples, within the limits of accuracy of the measurement. Exactly why this is not the case with the V-131B samples, in which about 85% of the theoretical Mo content is present, is not clear. However, the ash content of the V-131B sample from period B (Table 2) is unexpectedly low; perhaps this sample is not representative. In periods A and B of Run 262, almost all of the Mo added reports to the THF-insoluble, non-distillable fraction of the process oils.

O-METHYLATION OF COAL LIQUIDS

SUMMARY

In this study, the phenolic -OH species in direct coal liquefaction derived materials were derivatized with methyl groups. The O-methylated materials were tested for solvent quality by a microautoclave conversion test. Results were compared to the starting material and a blank sample (material which had been subjected to the O-methylation procedure without O-methylation reagents). Starting materials and products of reaction were analyzed by proton NMR, elemental analysis, FTIR, and GC/MS. Samples derivatized include the tetrahydrofuran (THF)-soluble portion of a whole process stream, the THF-soluble portion of the 850°F⁺ resid of a process stream, and two 850°F⁻ distillates. In all cases, compared to the starting material, O-methylation of the samples produced a negative impact on coal conversion in the microautoclave test. It was shown that the formation of the desired methyl ethers did occur, to some extent.

Blocking the phenolic -OH group, however, did not result in improving solvent quality. The potential influences of residual reagent side reaction on the observed solvent quality changes were not evaluated.

INTRODUCTION

The phenolic -OH moieties in coal liquefaction process streams may be detrimental for the conversion of the coal liquids to higher quality products. They are prime consumers of hydrogen, and promote condensation (or retrograde) reactions. This behavior may directly affect the reactivity of the heavy resid portion of the process stream, in which the phenolic species are enriched. The non-distillable resid makes up roughly two-thirds of the material in the liquefaction system. It is important to understand the reactivity of the phenolic species in order to understand the mechanism and kinetics of the conversion of the resid. One approach to this task is to block the phenolic groups in the coal liquids by derivatization and to then measure and compare the donor solvent qualities of the derivatized and starting materials. In this study, the THF-soluble portion of a whole process oil, a THF-soluble distillation resid, and two distillates were derivatized, analyzed, and tested for donor solvent quality.

EXPERIMENTAL

O-methylation of four different direct coal liquefaction materials was undertaken using a modified version of the method of Liotta, et al.¹² The following procedure was used. The phenolic -OH content of the material chosen for O-methylation was first determined in tetrahydrofuran (THF) solution by Fourier-transform infrared (FTIR) spectroscopy.¹³ The O-methylation procedure was carried out on twenty-five grams of material which was weighed into a 500 mL round bottom flask. Two hundred milliliters of freshly distilled tetrahydrofuran (THF) was added. The flask and contents were placed in a nitrogen-flushed glove bag equipped with a stirring plate and top-loading balance. The entire assembly was located in a laboratory fume hood because of the hazardous nature of the iodomethane (CH_3I) used as the methylation reagent. The total milliequivalents of -OH present was calculated for the 25 g of material. An excess, usually on the order of 10 to 20% of the phenolic -OH protons,

of tetra-n-propylammonium hydroxide (TnPAH) was added, along with a three-fold molar excess of iodomethane. If a blank, or reference, sample was prepared, no CH_3I or TnPAH was added to the reaction flask. The material was stirred at room temperature for five days. The pH of the solution was tested with pH paper after five days and, in all cases, was found to be close to neutral. The flask was removed from the glove bag and the THF was removed by rotary vacuum distillation. The remaining material was washed with hot deionized water (100°C), in 100 mL aliquots, until the wash water gave a negative response for iodide ion, when tested with silver nitrate. Between seven and ten aliquots of water were necessary. The water washings were combined and, in a separatory funnel, washed with methylene chloride to remove any organic material which was extracted into the water. The methylene chloride layer was dried by rotary vacuum evaporation and the extracted organic material was returned to the reaction flask. Removal of water from the washed O-methylated material was accomplished by rotary vacuum evaporation. Addition of small amounts of acetone to the reaction flask to form an azeotrope (acetone:water, 88.5:11.5, B.P. 56°C) aided in the removal of the water. The sample was then left in a vacuum oven at 100°C overnight. The dried O-methylated sample was inspected for the presence of water by the FTIR method used for phenolic -OH quantitation (water present in sufficient quantity interferes with the phenolic -OH determination). If no water was detected, the phenolic -OH content was recorded. The O-methylated material (or blank) was weighed into a stainless steel shaker bomb and was reacted with Old Ben Mine No. 1 coal under modified equilibrium conditions.⁴ The THF- soluble material was washed from the bomb; conversion was based on the weight of the insoluble filter cake. Gas chromatography - mass spectrometry was used to examine a number of the samples prior to and after O-methylation and after microautoclave tests. Proton NMR spectrometry of a number of the materials was used to distinguish seven proton types.^{7,14} Elemental analyses were also obtained for the samples.

RESULTS AND DISCUSSION

Four different direct coal liquefaction derived materials were tested for solvent quality after reacting with methylation reagents designed to

selectively derivatize the acidic hydrogen in the samples. The phenolic -OH groups are converted in this reaction to relatively non-polar methyl ethers. The reaction procedure used is a modified version of the method of Liotta et al.¹² The four materials investigated were chosen for this study because of their relatively high phenolic -OH contents. They were all produced by the Close-Coupled Integrated Two-Stage Liquefaction process in the Advanced Coal Liquefaction Development Facility in Wilsonville, Alabama. Samples were obtained from three different runs. All of the samples were prepared by CONSOL R&D from whole process oils received from the plant. The first sample is the THF-soluble portion of a whole process stream, the recycle oil (V-131B) material balance composite, obtained from period B of Run 261. The second sample is the THF-soluble portion of the 850°F⁺ distillation resid, of the V-131B process stream, composited over an entire coal liquefaction run (Run 260). The third sample is the distillate (850°F⁻) portion of the interstage process stream (R-1235) obtained from a single run day in material balance period A of Run 260A. The fourth sample is the Run 258 composite distillate (850°F⁻) interstage process stream (R-1235) (composited over the entire run). See Table 25 for a complete description of the samples. Each sample was subjected to a set of experiments which consisted of a microautoclave conversion test with Old Ben Mine No. 1 coal, duplicate O-methylations followed by microautoclave conversion tests, and a blank O-methylation which entailed the same experimental procedures without the addition of TnPAH or CH₃I, also followed by a microautoclave conversion test.

Phenolic -OH content was measured by FTIR spectroscopy after each O-methylation and the blank experiment. In all cases the blank experiments produced some reduction in the phenolic -OH content (10-23%). O-methylation consistently reduced the phenolic -OH content by about 50%, regardless of whether the sample was a resid or distillate. A summary of the phenolic -OH contents and the coal conversions are given in Table 26. The phenol peak location provides some information on the nature of the remaining phenolic groups. In all but the Run 258 R-1235 distillate composite, the peak location shifted to higher frequency by 2-4 cm⁻¹ as a result of alkylation. This is a small shift, but peak

location by this method is highly reproducible (to within 1 cm^{-1}). This shift indicates that the phenols became less acidic as a result of becoming less condensed and/or more alkylated. (In the development of the method, it was found that the peak location could be relating to the acidity of the phenol and the electron-withdrawing or electron-donating nature of the ring substituents.) These data suggest that the more acidic, and hence more reactive, phenols were selectively derivatized in the O-methylation reaction. It cannot be determined from the infrared analysis if the disappearance of phenolic -OH groups is due to the formation of methyl ethers, or simply that the samples were washed of the water-soluble phenols. This question was addressed by use of gas chromatography and nuclear magnetic resonance (NMR) spectroscopy (see below).

Compared to the starting material, O-methylation of the THF-soluble process stream samples produced a negative impact on coal conversion. Coal conversions decreased 16-100% (relative), depending on the starting sample (Table 26). Separately prepared aliquots of O-methylated material gave consistent results, with one exception (O-methylation trial No. 2, Run 260A Distillate); this value is considered questionable based on a third experiment which used equal portions of O-methylated material from trial Nos. 1 and 2 (O-methylation No. 1 + No. 2, Run 260A, Distillate). By comparison, the blank O-methylation experiments produced a smaller decrease (1-13%) in solvent quality of the material, as measured by the conversion of the standard coal. This leads to the inference that sample handling during the O-methylation procedure is not responsible for the diminished solvent quality of the O-methylated material. Instead, the chemical reaction of the O-methylating agents with the samples to form methyl ethers must be detrimental to solvent quality. However, it is possible that residual unreacted reagent or side reactions somehow lowers solvent quality.

To test the stability of the samples being investigated, one distillate sample (Run 258, R-1235 composite) and the corresponding O-methylated material (trial No. 2) were subjected to microautoclave conditions in the absence of the standard Old Ben Mine coal. The distillate material,

initially completely THF-soluble, produced 0.03 wt % THF-insoluble material and the treated material produced 1.83 wt % THF-insoluble material, in the absence of the standard coal. It is apparent from this experiment that condensation (or retrogressive reactions) of the solvent with itself is not responsible for the significant decrease in coal conversion (which is measured as the total solubility of the reaction products, consisting of coal plus solvent).

Proton NMR data were obtained for each starting sample and selected O-methylated and blank materials (Table 27). NMR of the samples shows some systematic changes brought about by the O-methylation. There is a puzzling consistent increase in gamma protons and a decrease in the alkyl alpha protons for the O-methylated samples as compared to the starting material, regardless of whether the starting material is a resid or a distillate. There also is an increase in the condensed aromatic protons in all the blank samples which would be consistent with the removal of long chain alkanes and alkyl-substituted materials from the distillates and the heavier resids by the hot water washing. Indeed, on a mass basis the relative increase in the condensed aromatic protons is much greater for the distillates than the resid (Table 28), as would be expected due to the greater proportion of alkanes in the distillate. Alternately, this could reflect the loss of some less-aromatic, low boiling material from the sample due to handling. Some loss is evident in the gas chromatograms of the product (Figures 21 and 22).

The O-methylated products all exhibit a ^1H -NMR peak at ~ 3.7 ppm, not seen in the starting materials, that shows the formation of methoxy groups did occur in the reaction. The integration of these peaks roughly corresponds to the amount of phenolic -OH (as measured by FTIR) lost in each starting sample as a result of the O-methylation procedure.

The formation of methoxy-compounds also is confirmed by gas chromatography-mass spectrometry. The total ion chromatograms of the 260 A distillate, the blank, and the O-methylated product (No. 1) are shown in Figures 21a through 21c. A listing of the major peaks is given in Table 29. A similar set of chromatograms is given for the Run 258

distillate composite (Figures 22a through 22c). The corresponding peak assignments are given in Table 30. The appearance of methoxy groups in the treated samples shows that the O-methylation reaction was at least partially successful. There is some loss, though not complete, of phenolic material. This is confirmation of the FTIR data as described above.

CONCLUSION

It generally is concluded from this study that derivatization of the phenolic -OH groups in coal liquefaction derived materials can be partially effected by the use of modified version of the method of Liotta, et al. The reason for the incomplete reaction is not apparent. Similar studies with coal-derived materials are being carried out by researchers at the University of Chicago under the Participants Program of this contract. Their preliminary work indicates that derivatization of the phenolic -OH is also only partial.

The solvent quality of the starting material is significantly diminished by the O-methylation procedure. Background studies (using "blank" samples) seem to rule out the detrimental effect being caused by anything other than the derivatization of the material. However, the potential role of side reactions or residual reagent remains unresolved.

A number of avenues for further work are indicated by these findings. The University of Chicago group will be studying the reaction system to determine if the kinetics are such that a slowly-reacting group of phenolic compounds is being starved for reagent, i.e., the reaction is reagent-limited. Another avenue for research is the study of model compounds in the microautoclave reactor system. Questions about the reactivity of the methoxy groups and the production and destruction of reactive free radical compounds (in the absence and presence of coal) could be studied with the addition of free radical scavengers to the reactor.

PARTICIPANTS PROGRAM STATUS

SUMMARY

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

Phase I

- Final reports were received from Advanced Fuel Research (AFR) and National Institute for Petroleum and Energy Research (NIPER). CONSOL evaluations were written for each report. All Phase I subcontracts now are complete.
- The Virginia Polytechnic Institute and State University (VPI) and SRI International final reports were issued.
- SRI International will present work performed under the Participants Program at the 203rd National Meeting of the American Chemical Society. A copy of the preprint is appended to this report.

Phase II

- Purchase order contracts were issued to four potential participants.
- Contracts were signed and initiated with the University of Chicago, the University of Utah and Iowa State University. The proposed subcontract with the Massachusetts Institute of Technology was reassigned to Vander Sande Associates, a private consulting firm.
- Complete sample sets were shipped to each subcontractor. Complete analytical data and processing information was sent to each subcontractor, with the exception of Vander Sande Associates.
- Work is progressing on all Phase II subcontracts.

DISCUSSION

Phase I

The final version of the AFR and NIPER final reports were received and the CONSOL evaluations were written. The CONSOL evaluation and Executive summaries of the AFR and NIPER final reports are found elsewhere in this report.

The VPI and SRI final reports with CONSOL evaluations received DOE technical and patent approvals, and were issued. SRI presented their work at the 203rd National meeting of the American Chemical Society in April 1992. A copy of the preprint is appended to this report.

Phase II

Cost proposals and Representations and Certifications packages were received from the University of Utah. The statements of work and ancillary documentation were sent to DOE for technical review and approval. Technical approval was received for subcontracts with the University of Chicago and the University of Utah. Purchase order contracts were issued to each organization. In order to expedite initiation, the proposed subcontract with the Massachusetts Institute of Technology was reassigned to Vander Sande Associates, a private consulting firm. The statement of work, key personnel, and work location are unaltered by this change, although there are some cost savings. A contract with Vander Sande Associates was signed and initiated.

Signed contracts were received from University of Utah, Iowa State University, University of Chicago, and Vander Sande Associates. Samples were shipped to all subcontractors with the exception of three samples for Vander Sande Associates. These three samples will be derived from Wilsonville Run 263, from which samples have only recently been received. Analytical and processing information, pertinent to the samples which were sent, was issued to each of these participants, with the exception of the Wilsonville Run 262 and Run 263 processing information packages for the University of Pittsburgh and Vander Sande Associates.

Status reports for January, February, and March were received from Lehigh University. Their work is progressing on schedule. A status report was received from Iowa State University. They have initiated their work. Leon Stock (University of Chicago) visited CONSOL and reported on the progress of his work. Mohindar Seehra (WVU) reported that all TGA work is completed. John Vander Sande (Vander Sande Associates) reported that a preliminary examination of one sample was done. Battelle PNL will be submitting a final report by early next quarter.

CONSOL EVALUATION AND EXECUTIVE SUMMARIES OF FINAL REPORTS FROM ADVANCED FUEL RESEARCH AND THE NATIONAL INSTITUTE FOR PETROLEUM AND ENERGY RESEARCH

GENERAL DESCRIPTION

This section consists of two parts. Each part is comprised of the CONSOL summary of the Phase I subcontractor's program and the subcontractor's Executive Summary or Abstract. The two subcontracts described were conducted by Advanced Fuel Research (AFR) and the National Institute for Petroleum and Energy Research (NIPER).

ADVANCED FUEL RESEARCH

Summary

This study was designed to demonstrate the use of two FTIR techniques for the analysis of direct coal liquefaction process-derived materials. The two methods were quantitative FTIR analysis and thermogravimetric (TG) analysis with FTIR analysis of evolved products (TG-FTIR).

The quantitative FTIR analyses of both whole resids and THF-soluble resids provided quantitation of total hydrogen, aliphatic and aromatic hydrogen, total carbon, total oxygen, hydroxyl and etheric oxygen, and ash contents. The FTIR results were usually in agreement with values derived by other, more conventional methods. However, the accuracies of specific measurements, in comparisons with results from conventional methods, ranged from good to poor.

The TG-FTIR method provided proximate analyses of coals and resids. The data provided included the time dependent evolution profiles of the

volatile species and the elemental composition of the char. Reproducible data of gaseous species and pyrolysis tar yields for whole resid samples larger than 10 mg were obtainable. The yields and evolution profiles of certain volatiles (tar, CO, and methane) provided structural information on the samples.

There were some experimental and interpretational difficulties associated with both techniques. Optimization of the curve-resolving routine for coal-liquefaction samples would improve the quantitative FTIR accuracy. Aerosol formation limited the full application of the TG-FTIR technique with the THF-soluble resid samples. At this time, further development of these analytical methods as process development tools will be required before their use for that purpose can be recommended. The use of FTIR as an on-line analytical technique for coal liquefaction process streams requires demonstration before it can be recommended; however, such a demonstration may be warranted.

Program Description

This report describes the work performed by Advanced Fuel Research (AFR) under a subcontract to 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 development facilities

to the program participants. The participants are required to interpret their analytical data in the context of 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

AFR applied quantitative FTIR analysis using KBr pellets to nine whole coal liquefaction distillation resid (850°F+) and the corresponding tetrahydrofuran (THF)-soluble portions of those distillation resid. They also analyzed a whole process oil and four (solids-free) pressure-filter liquids. TG-FTIR analysis was performed on the same nine whole resid and THF-soluble resid that were analyzed by quantitative FTIR and also on three feed coals. A task summary is given in the work plan presented below.

The samples were produced at two different continuous liquefaction facilities: the Wilsonville pilot plant and the Hydrocarbon Research Inc. (HRI) bench unit. The major processing parameters which varied among the Wilsonville runs included feed coal and catalyst, though there were numerous other differences as well. Samples from Wilsonville were taken from three different locations in the plant. These samples are expected to represent different extents of coal liquefaction. The Wilsonville samples, with the exception of the single whole oil sample, were composites of samples taken over long periods of single runs. The whole oil sample was obtained from a single run day. The HRI samples were chosen to represent production of material as the catalyst was batch-aged during one liquefaction run.

Participant's Major Findings

The following principal observations for the application of quantitative FTIR and TG-FTIR to coal liquefaction materials were reported by AFR.

Generally, it was shown that numerous sample properties could be determined by the quantitative FTIR method. The properties determined included total hydrogen content, aromatic and aliphatic hydrogen

distribution, total carbon content, total oxygen content, hydroxyl group concentration, and ash content. Comparisons of the values obtained by quantitative FTIR to those obtained by conventional methods (such as NMR and elemental analysis) show that the FTIR method provides values which are consistent with the trends observed by other methods. However, the accuracy of the FTIR method, determined by comparison with results from other methods, is good in some cases and poor in others. For specific properties, the values obtained from FTIR averaged 77% to 130% of the values obtained by conventional methods. The inaccuracies are in some cases attributable to sample preparation; in other cases, the limitations are apparently inherent in the FTIR method. This is especially notable in the case of the mineral matter analyses. FTIR is unable to discern iron sulfides, a major component of the mineral matter.

Processing trends observable by the FTIR analysis included the increase in total hydrogen content and the decrease in hydroxyl and aromatic hydrogen contents across the second reactor of the Wilsonville plant, consistent with the upgrading of the coal liquid across that reactor. The expected decrease in product quality (higher aromaticity, oxygen functional group content, and carbon content) with catalyst age was observed with samples obtained during a catalyst aging study at the HRI bench unit.

The TG-FTIR method is divided into two steps; the pyrolysis of the sample under inert atmosphere and the combustion of the residual char in oxygen. In both steps, the evolved volatile species are monitored and analyzed by FTIR. Data obtained by TG-FTIR were compared to conventional analyses to ascertain the quality of the TG-FTIR method. Application of the method to coal proximate analyses yielded good agreement with conventional methods. The temperature range of the tar evolution peak is indicative of the boiling range of the material. This range for the resid samples was the same regardless of feed coal or sampling point in the liquefaction process; however, in all cases, the range was lower for resids than for the respective feed coals. The pyrolysis char yield correlated well with the fraction of condensed aromatic protons, as determined by other methods. The evolution of oxygen-containing gases

(CO, CO₂, and H₂O) is used to determine the relative amount of total oxygen in the sample. However, CO and CO₂ can be evolved from both organic oxygen groups and mineral carbonates. The evolution profile of the oxygen-containing gases can be used to partially resolve the contributions from organic functional groups and minerals. The total amounts of CO and methane evolved followed the same trend with sample type as char yield and hydroxyl concentration; i.e., coal >> interstage > second stage > recycle. The resids not only evolved less CO than the feed coals, they also evolved it at much higher temperatures. This reflects the removal of loosely-bound CO during liquefaction. The methane evolution temperature varied little with sample type. This suggests that liquefaction changes the total amount but not the distribution of methyl groups. Char and tar yields, and to a lesser extent gas evolution profiles, from the resids were found to depend upon the feed coal (or specific Wilsonville run) from which the sample was derived.

The use of FTIR as an on-line method is discussed in the AFR final report.¹⁵ Two recent technological developments are described: 1. new infrared-transmitting optical fibers and 2. rugged low-cost FTIR spectrometers. These two factors make on-line analysis by FTIR in direct coal liquefaction process streams feasible. There are, however, trade-offs in usable frequency range with fibers that are able to withstand high temperatures. Alternative near-line systems are currently commercially available and could be used for this application.

CONSOL Evaluation

The quantitative FTIR technique can provide a number of sample properties from a single analysis normally obtained by multiple analytical techniques. This could make the method very useful as a process development tool. However, data quality, when compared to the values obtained by the other methods, is not consistently good. For example, up to 4% ash was determined by FTIR in ash-free THF-soluble samples. It is expected that optimization of the curve-resolving data analysis method would improve the data quality. Some of the data obtained from the gas evolution profiles from the TG-FTIR analysis of the resids are not quantitative

because 1) the instrument has not yet been calibrated for NH_3 , COS , and CS_2 ; 2) CS_2 evolution mimics H_2O and can be confused with it; and 3) SO_2 evolution is found in two peaks, one the result of small traces of oxygen in the helium carrier gas. Apparently, only the CH_4 , CO_2 , CO , and H_2O evolution peaks were reported with quantitative reliability. However, it should be noted that the CO_2 measurement is sensitive to the state of oxidation of the sample. Interpretation of the CO_2 data is, therefore, more difficult. In addition to these experimental difficulties for the whole resid samples, reliable tar evolution peaks could not be obtained for the THF-soluble resid samples because of aerosol formation. The TG-FTIR technique, if fully optimized, could be able to provide structural information of the samples by first monitoring the evolution of the volatile species from pyrolysis and then the combustion gases from the char.

Commercially available FTIR equipment ranges in price from approximately \$20,000 to \$250,000. The TG-FTIR equipment, also commercially available, increases the cost of the FTIR instrument by about \$25,000. Consumables for the analyses, as performed under this subcontract, are on the order of \$10/sample. It requires less than one hour per sample to prepare and run a single sample by the quantitative FTIR method. The TG-FTIR analysis performed in these experiments requires approximately three hours per sample to complete.

The utility of the FTIR as an on-line analytical technique requires demonstration with process samples at approximate operating conditions before it can be recommended for process application.

Further Development

There are a number of avenues for further development of the techniques described here. Optimization of the curve fitting technique for direct coal liquefaction process samples would improve the accuracy and, therefore, the utility of the quantitative FTIR method for process development. More extensive statistical evaluations of the FTIR data would contribute to this utility. A study with the TG-FTIR technique of the CO and CO_2 evolution profiles of coal resid samples to establish the

origin of the gases (organic or inorganic) should be done. A demonstration of FTIR in an on-line application should be made to test the recent advances in the technology discussed in the attached report (pages 32-37).

Participant's Statement of Work

Fourier Transform Infrared (FTIR) spectroscopy can be used to provide organic structural information for coals, lignins, and products of thermal decomposition, and to yield quantitative information on the concentrations of hydroxyl, aliphatic and aromatic hydrogen and aromatic carbon present in a sample. Thermogravimetric FTIR (TG-FTIR) can be applied to the analysis of solid (but volatile) material. On-line FT-IR Monitoring (utilizing both an ATR cell and a fixed path-length transmission cell) has been used to couple the information as described above with real-time events. The application of these techniques to coal liquefaction process streams and solid or solid-containing heavy materials from coal liquefaction process streams has not been demonstrated and, as such, these techniques are novel and fit within the scope of the participants program.

CONSOL will supply AFR with twenty-six separate samples. The twenty-six samples (three coals, nine distillation resids, thirteen solids-free distillation resids, and one whole process oil) will be supplied to AFR with the following information, as appropriate: elemental analyses, ash content, ash elemental analysis, phenolic -OH concentration, calorific value, hydrogen classes by ^1H -NMR, and the full history of the sample (plant, process conditions, age, and storage conditions). Resid sample size will be at least 30 mg. Most resid samples will be brittle pitch-like materials that will be supplied as approximately minus 8 mesh (2.4 mm) pieces.

In order to fully evaluate the usefulness of the FTIR methods for coal liquefaction process development the following tests (totaling 45 in number) will be made using the twenty-six samples described above.

1. Quantitative IR analysis of nine whole resid materials produced by distillation of the process oils generated from three different feed coals and obtained from three different sampling points during coal liquefaction runs at the Wilsonville facility.
2. Quantitative IR analysis of the tetrahydrofuran (THF) soluble portion of the same nine resid materials.
3. Quantitative IR analysis of four solids-free resids obtained during a catalyst aging study at the HRI facility.
4. Quantitative IR analysis of a whole process oil sample obtained from the Wilsonville facility.
5. TG-FTIR analysis of three feed coals.
6. TG-FTIR analysis of the same nine whole resid materials as described above.
7. TG-FTIR analysis of the THF soluble portion of the same nine resid materials.
8. On-line test: Evaluation of the data obtained by analysis of a whole process oil will determine if an on-line test is feasible.

The functional groups (e.g., aliphatic, aromatic, and hydroxyl hydrogen, and O-C bonds) in each sample, which will be analyzed by quantitative FTIR, will be measured by curve-fitting techniques. The TG-FTIR technique will provide information on the time-dependent evolution of individual volatile species, weight of the non-volatile portion, and an analysis of C, H, and S in the non-volatile portion (by burning the residue and analyzing the combustion products).

Replicate analyses will be performed as appropriate to define precision.

AFR Executive Summary

Introduction

The objective of this work was to evaluate the use of two Fourier Transform Infrared (FT-IR) methods for characterization of products from coal liquefaction process streams. The first method is quantitative FT-IR analysis of samples pressed into KBr pellets. The functional group concentrations (e.g., aliphatic, aromatic and hydroxyl hydrogens) in each sample are determined using curve-resolving techniques. The second method was Thermogravimetric Analysis (TG) with FT-IR analysis of evolved products (TG-FTIR). In addition, an assessment was made of the application of on-line FT-IR analysis to coal liquefaction processes.

Work Accomplished

Quantitative FT-IR analysis was done of 23 samples.

- Nine whole resid samples produced by distillation of process oils generated from three different feed coals (Wyodak, Illinois, and Pittsburgh) and obtained from three different sampling points (interstage, recycle, second stage) during liquefaction runs at the Wilsonville facility.
- Nine THF-soluble portions of the above whole resids.
- Four additional solids-free resids obtained during a catalyst aging study at the HRI facility.
- A single whole process oil obtained from the Wilsonville facility.

In addition, quantitative TG-FTIR analysis was done of the following samples.

- The three feed coals.
- The nine THF-soluble portions of the nine resid samples described above.

The FT-IR analysis provides a measure of aliphatic hydrogen, hydroxyl hydrogen, aromatic hydrogen, the distribution of aromatic hydrogen (1-adjacent, 2-adjacent, 3 or more), aliphatic carbon, carbonyl, hydroxyl oxygen, and ether oxygen in the organic portion. It provides a measure of mixed clay, quartz, calcite, and kaolin for the mineral portion. The samples were made into KBr pellets (in duplicate) and then scanned. The results from the FT-IR analysis studies were used to determine the feasibility of an on-line test.

The TG-FTIR analysis provides information on the time-dependent evolution of individual volatile species (tar, CH₄, H₂O, CO₂, CO, SO₂, C₂H₄, CS₂, NH₃, COS, olefins), weight of the non-volatile residue, and analysis of the C, H and S in the non-volatile residue (by burning the residue and analyzing the combustion products such as CO, CO₂, SO₂ and H₂O). A standard temperature program is used for these samples.

Summary of FT-IR Results

- The FT-IR method provided reproducible, quantitative data for the organic functional groups. Some care was required in the baseline corrections used in the determination of oxygen functional groups which were present in relatively low concentrations.
- The FT-IR determinations of the aliphatic hydrogen contents for the THF-soluble portions of the Wilsonville Resids were in good agreement with the proton NMR data supplied by CONSOL. The FT-IR data for aromatic hydrogen content were consistent with the proton NMR data, although the latter numbers were higher by about 20% (relative basis).
- The FT-IR determinations of hydroxyl OH for the THF-soluble fractions were in good agreement with the data supplied by CONSOL.
- The FT-IR determinations of the oxygen content of the whole resid samples (based on measurements of the ether and hydroxyl oxygen) were in general agreement with the data on total oxygen content provided by CONSOL, although the data are widely scattered.

- The FT-IR determinations of the total hydrogen concentration for all of the samples (based on measurements of aliphatic, aromatic, and hydroxyl hydrogen) were generally in good agreement with the data on total hydrogen content supplied by CONSOL.
- The FT-IR determinations of the total carbon content for all of the samples (based on subtraction of hydrogen and oxygen contents from 100%) were generally in good agreement with the data on total carbon content supplied by CONSOL.
- The FT-IR values of the total ash content for the whole resid samples agreed well with the trends in the values supplied by CONSOL, although the latter numbers were lower by about 30%. This is an expected result, since the FT-IR measurement is closer to a low temperature ash measurement. However, problems with absolute mineral quantitation were identified in the FT-IR method which was developed and optimized for coal samples.
- The FT-IR data show clear trends in the Wilsonville whole resids through the various stages of the process. Between the interstage and 2nd stage, there is an increase in total hydrogen and a decrease in the -OH and aromatic hydrogen contents. The same general trend is observed when comparing the 2nd stage and recycle stream, although the differences are less dramatic.
- The FT-IR measurements of the fraction of aromatic hydrogen followed the same trends for the three sample points regardless of whether the whole resids or THF-soluble portions were examined. For other functional group concentrations, the measurements were not as well correlated.
- Some surprising trends were observed in the rank variation of the FT-IR results for the whole resids. Neither the phenolic -OH content or the aromatic hydrogen content followed the rank variation that would be expected based on analysis of the raw coals.

- The FT-IR data show clear trends in the catalyst aging study done at HRI. As the catalyst age increases, the product quality decreases steadily (higher aromaticity, oxygen functional group content, and carbon content).

Summary of TG-FTIR Results

- The TG-FTIR method provided good quantitative data on the coal liquefaction process samples with the following exceptions. Except for small sample sizes (<10 mg), the ash values from TG-FTIR were in good agreement with the values supplied by CONSOL. The problem occurs when the drift in the balance (<0.5 mg) is comparable to the amount of ash in the sample. It also was not possible to get quantitative measurements of the tar evolution from the THF-soluble portion of the resid samples. This is believed to be due to the formation of relatively large diameter aerosols which scatter the IR light in a manner that cannot be corrected for in the current version of the analysis software.
- For the sample sizes used (10-20 mg), the TG-FTIR method provides reproducible pyrolysis data on whole resids, THF-soluble fractions and coals for char yields and for gas species which are present in amounts larger than 0.5 wt %. The data for pyrolysis tar yields also are quantitative, except for the THF-soluble fractions.
- The analysis of the principal combustion products (CO_2 , CO , H_2O , SO_2) for the residue from the pyrolysis cycle indicated that the remaining material was >90 wt % (MAF) carbon in most cases. The results for the combustion cycle are not as reproducible as observed for the pyrolysis cycle, since this feature of the instrument has not yet been optimized.
- The pyrolysis char yields from TG-FTIR analysis for the whole resids and THF-soluble portions are correlated with the fraction of condensed aromatics from proton-NMR analysis (or the H_{ar} fraction from FT-IR analysis). The pyrolysis tar yield from TG-FTIR analysis is inversely correlated with these quantities.

- The proximate analysis results (fixed carbon, volatiles, moisture, ash) from TG-FTIR analysis of the raw coals are in excellent agreement with the data supplied by CONSOL, except for the moisture content, which is likely due to differences in handling the samples.
- The TG-FTIR method can determine the relative amount of oxygen in resid samples based on the analysis of CO, CO₂ and H₂O from pyrolysis. On this basis, it appears that samples 1, 2, and 3 from Run 251-III have either been significantly oxidized since the elemental analysis was completed or contain large amounts of minerals such as calcite which can decompose to produce CO and CO₂. One advantage of the method is that it can partially resolve the contributions of organic functional groups and minerals to the pyrolysis gas evolutions by examination of the shapes of the evolution profiles.
- The width of the tar peak of the whole resid samples is indicative of the boiling range of the materials. The boiling range for all three resid samples (interstage, second stage, recycle) does not vary much for the three coals. However, the temperature range for tar evolution is significantly lower than for the raw coal. This makes sense since the resids are derived from materials which have been pyrolyzed in the presence of a donor solvent which allows stabilization of reactive fragments.
- The amount of CO evolution from the whole resid samples is significantly lower than from the raw coals (except for the 251-III samples from the Wyodak coal) and generally decreases in the order coal >> interstage > second stage > recycle, thus following the same trends as the phenolic -OH content (from FT-IR) and the char yield (from TG-FTIR). The temperature for the maximum rate of CO evolution is significantly higher for the resids when compared to the raw coal, suggesting that the liquefaction process preferentially removes the loosely bound CO.

- The amount of CH₄ evolution from the whole resid samples is at least 50% lower than from the raw coal (except in the case of the Wyodak) and generally follows the order coal > interstage > second stage > recycle. The temperature of the maximum rate of CH₄ evolution is not much different for the resids when compared to the raw coal, suggesting that the liquefaction process changes the total amount but not the distribution of methyl groups.
- The ash analysis results from TG-FTIR indicate that the efficiency of the deash process varies significantly with coal type, which results in the ash content of the resids not following the same order as for the raw coals.

Conclusions and Recommendations

Both FT-IR and TG-FTIR have been clearly shown to provide a wide variety of useful information for process stream characterization. Both techniques can be applied to whole process oils, resids, or distillates, including ash components, and require relatively small samples (<50 mg). Significant differences are observed between process stages, coal types, and with catalyst aging. Both methods indicate that trends observed for the raw coals do not always hold when comparing the resid samples derived from these coals. A summary of the composition parameters that can be obtained by FT-IR and TG-FTIR is shown in Tables 1-1 and 1-2, respectively. In many respects, FT-IR is probably the single most useful technique for this purpose, since it can provide measurements on both organic and mineral components. The current FT-IR method can be made more quantitative for the mineral components and the organic functional groups by a re-optimization of the curve resolving program for coal liquefaction samples. FT-IR also is one of the few current techniques which is amenable to on-line analysis. FT-IR can provide information on total hydrogen content, hydroxyl content and aromatic hydrogen content, all of which are useful for monitoring product quality and catalyst activity. It is reasonable to assume that the chemical information provided by FT-IR could be correlated with other chemical and physical properties using chemometric techniques such as factor analysis. It is likely that on-line FT-IR measurements could be made in situ using a

sapphire fiber optic element in the Attenuated Total Reflectance (ATR) mode.

TABLE 1-1
SUMMARY OF FT-IR MEASUREMENTS

FT-IR Measurement	Alternative Technique
Hydroxyl Hydrogen	Chemical Titration
Aliphatic Hydrogen	¹ H-NMR
Aliphatic Carbon*	¹³ C-NMR
Aromatic Hydrogen	¹ H-NMR
Aromatic Hydrogen Distribution	---
Hydrogen Content	Elemental Analysis
Carbon Content*	Elemental Analysis
Hydroxyl Oxygen	Chemical Titration
Ether Oxygen	---
Carbonyl Oxygen**	---
Total Ash	TGA
Mineral Components	ICP

*Estimated

**Relative Values

TABLE 1-2
SUMMARY OF TG-FTIR MEASUREMENTS

TG-FTIR Measurement	Alternative Technique
<u>Direct</u>	
Volatiles Content	Proximate Analysis
Fixed Carbon	Proximate Analysis
Moisture	Proximate Analysis
Total Ash	Proximate Analysis
Mineral Components	ICP
C,H,N,S	Elemental Analysis
<u>Indirect</u>	
Char Yield → Condensed Aromatics	¹ H-NMR
CO Yield → Phenolic Content	FT-IR
CH ₄ Yield → Methyl Group Content	¹³ C-NMR
Tar Evolution Profile → Boiling Range	Distillation

The TG-FTIR method can provide proximate analysis information (volatiles, fixed carbon, moisture, and ash) for feed coals and residues. In principle, it can also provide elemental analysis information, if a post-

oxidizer accessory is used and two runs are made for each sample. Similar to the case of FT-IR, a very broad characterization of a sample can be achieved with a single instrument in a relatively short amount of time (30-60 min). The technique would be very useful in a quality control application for feed coals and heavy process streams like resids. It also has the potential to provide indirect measurement of the average structural components based on the pyrolysis measurements, as was demonstrated for methyl groups, phenolic groups and condensed aromatic rings. The utility of the TG-FTIR instrument for the second purpose will require additional study and correlation with other analytical measurements. However the potential appears to be significant.

NIPER

Summary

This study demonstrated the feasibility of using non-aqueous ion exchange liquid chromatography (NIELC) for the examination of the tetrahydrofuran (THF)-soluble distillation resids and THF-soluble whole oils derived from direct coal liquefaction. The technique can be used to separate the material into a number of acid, base, and neutral fractions. Each of the fractions obtained by NIELC was analyzed and then further fractionated by high-performance liquid chromatography (HPLC). The separation and analysis schemes are given in the accompanying report. With this approach, differences can be distinguished among samples obtained from different process streams in the liquefaction plant and among samples obtained at the same sampling location, but produced from different feed coals. HPLC was directly applied to one THF-soluble whole process oil without the NIELC preparation, with limited success. The direct HPLC technique used was directed toward the elution of the acid species into defined classes. The non-retained neutral and basic components of the oil were not analyzable by the direct HPLC method because of solubility limitations. Sample solubility is a major concern in the application of these techniques.

Program Description

This report describes the work performed at NIPER 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 process development 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 then is evaluated for its usefulness in analyzing direct coal liquefaction derived materials.

Participant's Methodology

NIPER used non-aqueous ion exchange liquid chromatography (NIELC) for preparative-scale separation of four THF-soluble distillation resid (850°F) and one THF-soluble whole oil. The resultant fractions were further analyzed by non-aqueous titration of acid fractions with the potassium salt of dimethyl sulfoxide (potassium dimsyl), non-aqueous titration of base fractions with HClO_4 , infrared spectroscopy, and analytical-scale separation (HPLC). An attempt was made to speciate oxygen functional groups in the strong acid fractions by ^{13}C -NMR analysis of them after O-methylation with ^{13}C -enriched methyl iodide. The product of the methylation reaction was not recoverable in the desired solvent (ethyl ether); this line of analysis was discontinued. The complete analytical scheme is given in Figure 1 (p. 19) of NIPER's final report.¹⁶ The HPLC method used with the NIELC-prepared acid fractions also was used alone, without NIELC pre-separation, to fractionate a THF-soluble process

oil. This direct HPLC approach met with some success. The HPLC methods used for the base and neutral NIELC fractions could not be applied without preseparation because of the low solubilities of the samples and overlapping elution of chemical compound classes.

The samples were produced at the Wilsonville two-stage direct coal liquefaction facility. A major processing parameter which varied among the Wilsonville runs was feed coal. Samples were taken from two locations in the plant: between the two reactors, and at the recycle oil tank. These samples are expected to represent different extents of coal liquefaction. The resid samples are composites of samples taken over long periods of single runs. The whole oil was obtained from the same run as one of the composite resids, but from a single run period. It was chosen from the same stream as the parent materials of one of the composite resids. The THF-soluble portions of the resids are solids at room temperature; the whole oil is a viscous liquid.

Participant's Major Findings

NIPER reported the following principal observations for the application of nonaqueous ion exchange liquid chromatography to coal liquefaction materials.

The NIELC scheme, originally developed for the analysis of high-boiling petroleum residues, was used in this work to analyze the direct coal liquefaction process-derived resid samples. This standard procedure, however, resulted in relatively low sample recovery (<90%) for four of five samples. Limited sample solubility proved to be a major problem in the preparative-scale NIELC separation scheme, and in subsequent HPLC and solution IR analyses. Some of the insolubility is attributed by NIPER to oxidation of the sample during and after the initial NIELC separation procedure. However, the solvents used in the original version of the method may not have been optimum for coal liquids; this appears to be a contributing factor in the limited success of the original NIELC scheme. Modifications were made to the NIELC separation scheme to tailor it for use with coal resids. The modified procedure was employed with the

sample that gave the poorest recovery (76%) with the standard procedure; with the modified procedure, recovery improved to near 100%.

Analysis of the base fractions shows that there is a significantly higher proportion of acetyltable bases, mostly primary and secondary amines, in the interstage samples than in the recycle material. It was shown that the acid fractions isolated by NIELC and HPLC are preponderantly multifunctional and that the isolated bases are mostly monofunctional. The weak acids isolated by NIELC contain a large concentration of carbonyl functionality. The presence of the carbonyls may be a result of sample oxidation during handling. As is typically true with petroleums, the weak acids are found to have a greater concentration of nitrogenous acids than of phenolic acids; the reverse of the strong acids. The compositions of the neutral fraction differed very little as a function of sampling point in the liquefaction process. The neutral fraction approximates the "oils" fraction obtained in the conventional analysis for oils, asphaltenes, and preasphaltenes.

Complete direct HPLC analysis of whole process oils was not feasible without pre-separation by NIELC. Solubility of base and neutral fractions and co-eluting compound types were problems in the direct separation of this material.

CONSOL Evaluation

Separation of coal-derived resids into acid/base/neutral classifications is somewhat ambiguous, as it is expected that a large portion of the high molecular weight coal-derived materials are multifunctional. The NIELC technique, however, was shown to have some potential for the analysis of direct coal liquefaction resid samples. It is projected that with full optimization for coal-derived materials, especially those with high molecular weight and polyfunctionality, such as distillation resids, the technique can be useful in characterizing process streams for process development. This optimization should include better quantitation, better definition of the composition of each fraction, and development of methods that are significantly more rapid. HPLC can be used for a rapid analysis of neutrals or bases; however, a pre-separation with NIELC

would be required first to produce the base or neutral fractions from the whole material. Direct application of HPLC (without a NIELC pre-separation) to whole process oils is not possible at this time. The use of solution IR to analyze resultant fractions is limited by sample solubility. Methods for solid sample analysis should be used for this application.

The NIELC technique is time-consuming and relatively costly on a per-sample basis. The following table, supplied by NIPER, provides costs and manpower requirements for the techniques employed in this work.

EQUIPMENT AND COST BREAKDOWN FOR COAL LIQUID ANALYSES

Analysis	Capital Equipment/\$	Expendables/\$	Time, hrs/Personnel ^a
Preparative separation into acids, bases, neutrals	Columns/500 Soxhlet extractors/200 Rotary evaporator/1000	Solvents/20 Ion exchange resins/50	40/Tech
Analytical-scale separations	HPLC + Data system/60K	Column/300 ^b Solvent/10	16 Setup/Res. Chem. ^c
A. Acids			2/Chem.
B. Bases			2/Chem.
C. Neutral-aromatics			1/Chem.
D. Saturates			1/Chem.
IR	IR spectrophotometer/ 20-60K	Cells/150 Solvent/2	2/Chem.
Nonaqueous titrations	Automatic titrator/20K Microbalance/7K Drybox/5K ^d	Electrodes/300	16 Setup/Chem. ^c
A. Acids		Reagents/5	3/Tech.
B. Bases		Reagents/5	3/Tech.
NMR	NMR spectrometer/300K	Reagents/50	18 Res. Chem.

(a) Technician, chemist (BS), research chemist (BS,MS).

(b) A separate column is required for each HPLC method.

(c) About 2 days is required to set up, calibrate, and optimize each HPLC and titration method.

(d) Required for titration of acids only.

Further Development

There are a number of avenues for further development of the separation techniques for the examination of coal liquefaction derived resids that were employed in this study. They include the following suggestions made by the researchers at NIPER: 1) NIELC methods development, such that

samples and resultant fractions are protected from oxidation. 2) HPLC detectors should be evaluated for uniformity of response. Recommended types for trial include FID or light-scattering detectors. 3) Improvement of sample solubility (possibly via derivatization techniques) should be explored on a range of resid samples and their fractions. This would allow infrared analyses, with liquid sampling systems, to be a more useful method for the examination of the chromatographically separated fractions. In addition to these suggested research directions, alternative analyses of sample fractions, inclusive of techniques designed to analyze solid materials, should be explored. Also, automation of the LC procedures (inclusive of multiple column, multiple solvent systems) should be looked into to make this a more user-friendly method for analyzing coal liquefaction process-derived samples. HPLC of whole process streams should be optimized to prevent co-elution of compound types.

Participant's Statement of Work

The complex mixtures which comprise coal liquids contain polar compounds and many hydroaromatic structures. It is important to gain a better understanding of the influence that the polar compounds and hydroaromatic compounds found in coal liquids have on coal liquefaction. Polar compounds may significantly affect the coal liquefaction process and the refining of crude products to finished products, as such they should be identified and quantified. Hydroaromatic structures, key in the liquefaction of coal as hydrogen donors and shuttlers, should be characterized by methods which can recognize differences between various ring structures. Analysis of coal liquefaction derived materials with a particular emphasis on these two compound classes is therefore important to obtaining a better understanding of the liquefaction process, and falls within the scope of the Participants Program.

NIPER will concentrate its effort on analysis of polar materials and hydroaromatic ring structures found in coal derived liquids. Quantitative preparative-scale separation of coal liquids into strong and weak acid, strong and weak base, and neutral (ABN) fractions will be done on five samples supplied by CONSOL to NIPER. The separations will be

performed by non-aqueous ion-exchange chromatography. The samples will be both tetrahydrofuran (THF) soluble portions of distillation resids and filtered whole process oils, as designated in the attached list. The samples will be separated into five fractions (strong acids, strong bases, weak acids, weak bases, and neutrals). The samples will be supplied with the following information (as available): elemental analyses, ash content, ash elemental analysis, phenolic -OH concentration, calorific value, hydrogen classes by ^1H -NMR, and the full history of the sample (plant, process conditions, age, and storage conditions). Sample size will be minimally 50 g. Aliquots of three of the neutral fractions (as designated in the attached list) will be further separated by analytical high performance liquid chromatography (HPLC) with gradient elution on derivatized silica columns into saturates and aromatic ring classes (mono-, di-, and polyaromatics). The corresponding acid and base fractions will similarly be further fractionated by HPLC. The acid fractions will be separated into phenols, carboxylic acids, pyrroles, and amides. The base fractions will be separated into primary and secondary amines, and aza-aromatics. The remaining portion of the ABN fractions of each sample will be made available to CONSOL for possible distribution to other participants in the Program. Confirmation of the analytical HPLC findings will be made with elemental analyses, non-aqueous titrations, and infrared spectroscopic analysis of the acid and base fractions. In addition to HPLC analysis of the separated ABN fractions, one sample will be analyzed directly by HPLC. NIPER will determine from this direct HPLC analyses if a fast analysis of the acidic and basic components of these materials can be accomplished without preseparation by non-aqueous ion-exchange chromatography.

Three of the strong acid fractions from above also will be speciated and quantified by 2D-NMR (^1H and ^{13}C) after replacement of the acid protons by $^{13}\text{CH}_3$ groups. The derivatization will be done with $^{13}\text{CH}_3\text{I}$ and KOH in N-methylpyrrolidone solvent. The NMR analysis will be accomplished using four types of measurement: proton NMR, quantitative ^{13}C -NMR with decoupling of protons, distortionless enhancement by polarization transfer (DEPTD) mode, and chemical shift (CHSHF) correlation procedures.

NIPER Abstract

Five coal liquefaction process streams were separated into acidic, basic and neutral classes using nonaqueous ion exchange liquid chromatography (NIELC). Three of the five sets of fractions were subjected to further analysis. The results indicated that primary aromatic amines and multifunctional acidic compounds produced in the initial stage of liquefaction were reduced in concentration after the second-stage reactor. Most other compositional parameters, e.g., the distribution of neutral-aromatics by ring number, were unaffected by the second-stage reactor.

Problems with sample solubility limited the applicability of some analytical techniques, particularly the NIELC method, and infrared or NMR-methylation techniques. However, the nonaqueous titration and most HPLC methods employed were directly applicable or required modifications which could be incorporated over the course of the work. Many of these techniques could be used routinely for monitoring coal liquefaction processes.

Section 3

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.^{4,5}

Section 4

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TABLE 1
OPERATING CONDITIONS AND YIELDS FOR MATERIAL BALANCE PERIODS
Wilsonville Run 262

Operating Period Date, 1991 Operation Days	261A, Transitional 7/17-20 6-9	262B 8/8,9,14,15 14,15,18,19	262C1 8/22-23 26,27	262C2 8/24-25 28,29
<u>Coal</u>				
Feed rate, MF lb/hr	242.0	247.7	301.4	295.9
Ash, wt % MF	6.4	6.3	6.5	6.5
Conc. in slurry, wt % MF	29.6	29.7	29.9	29.5
<u>Process Solvent, wt %</u>				
Resid	32.1	37.7	39.1	35.8
Cl	19.3	18.7	18.6	19.2
<u>First Stage</u>				
Reaction temp., °F (avg)	826	825	825	825
Inlet H ₂ partial pressure, psia	2740 ±12	2708 ±30	2722 ±70	2716 ±27
Total gas flow, scfh	5096	4814	4404	4490
Recycle gas, scfh	1024	920	542	568
Space vel., lb MF coal/hr/ft ³ (C=constant)	63.9C	65.4C	79.6C	78.1C
Iron Oxide, wt % MF coal	2	2	2	2
Moly Conc., ppm MF coal	1000	500	500	500
<u>Second Stage</u>				
Reactor temp., °F	760	761	790	790
Inlet H ₂ partial pressure, psia	2505 ±8	2500 ±5	2552 ±13	2560 ±5
Total gas flow, scfh	4570	4755	5125	5129
Recycle gas, scfh	3310	3367	2787	2964
Space vel., lb feed/hr/lb cat	4.7	4.8	5.8	5.8
Space vel., lb MF coal/hr/ft ³ cat	76.9	78.7	95.7	94.0
Catalyst type	Crit 324	Crit 324	Crit 324	Crit 324
Catalyst age, lb (res+Cl)/lb cat	1545 ±37	1424 ±60	1350 ±47	1337 ±48
lb MF coal/lb cat	706 ±17	692 ±22	692 ±24	685 ±24
Cat replacement rate, lb/ton MF coal	3	3	3	3
<u>ROSE-SRSM DAS type</u>	2114	2164	2224	2274
<u>Yield, wt % MAF coal</u>				
H ₂	-4.4 ±0.2	-5.4 ±0.1	-5.8 ±0.2	-5.4 ±0.1
Water	16.1 ±0.6	15.4 ±0.5	14.1 ±1.7	14.2 ±1.1
H ₂ S	0.5 ±0.1	0.1 ±0.3	0.6 ±0.0	0.2 ±0.3
CO, CO ₂	5.0 ±0.7	7.3 ±0.2	6.8 ±0.2	6.7 ±0.0
NH ₃	0.7 ±0.0	0.8 ±0.0	0.8 ±0.0	0.7 ±0.1
C ₁ -C ₃ gas	4.9 ±0.3	5.2 ±0.3	5.9 ±0.1	5.8 ±0.2
C ₄ + distillate	57.7 ±2.3	58.0 ±2.1	64.7 ±2.5	56.7 ±1.3
C ₄ -C ₆	1.3 ±0.1	2.5 ±0.2	2.8 ±0.0	2.7 ±1.3
IBP-350°F	14.8 ±2.7	9.9 ±1.4	13.0 ±3.5	13.0 ±1.3
350-450°F	8.2 ±1.1	7.2 ±1.2	8.3 ±0.8	7.8 ±0.3
450-EP	34.4 ±3.0	38.4 ±3.4	40.6 ±6.9	33.2 ±0.4
Resid	2.3 ±3.0	-0.1 ±2.3	-3.0 ±0.6	6.0 ±0.8
Int. Acc. UC	0.7 ±0.6	1.7 ±0.9	-1.1 ±0.5	0.1 ±0.7
Solid Product (ash-free)	16.4 ±1.8	17.0 ±0.7	16.9 ±1.3	15.0 ±0.3
H ₂ efficiency, %	13.0 ±0.6	10.8 ±0.4	11.3 ±0.8	10.5 ±0.3
C ₁ -C ₄ selectivity, %	8.5 ±0.6	9.0 ±0.3	9.1 ±0.5	10.2 ±0.1
<u>Coal conversion, wt % MAF</u>				
First stage	89.9 ±2.6	87.0 ±2.1	90.6 ±1.4	88.0 ±1.8
Second stage	93.0 ±1.1	92.2 ±0.5	92.9 ±0.4	92.7 ±0.4
Overall TSL	92.8 ±1.3	91.1 ±0.9	91.7 ±0.5	92.2 ±0.3
<u>Resid + UC conversion, wt % feed</u>				
1st stage	29.7 ±1.5	28.9 ±0.9	23.8 ±1.5	20.9 ±2.8
2nd stage	11.8 ±2.0	11.8 ±1.9	19.7 ±1.5	19.6 ±3.3
<u>Resid + UC conversion, wt % MAF coal</u>				
1st stage	61.9 ±1.5	62.8 ±1.3	53.8 ±4.1	45.4 ±5.9
2nd stage	18.7 ±1.6	18.7 ±2.6	33.4 ±2.9	33.5 ±6.1
Overall	80.6 ±2.6	81.4 ±2.0	87.1 ±1.2	78.9 ±0.2

1/6

TABLE 1 (Continued)

OPERATING CONDITIONS AND YIELDS FOR MATERIAL BALANCE PERIODS
Wilsonville Run 262

Operating Period Date, 1991 Operation Days	262D 9/8-12 34-38	262E 9/18-22 44-48	262F, Unstable 9/24,26,27,29 50,52,53,55
<u>Coal</u>			
Feed rate, MF lb/hr	299.7	346.2	342.8
Ash, wt % MF	6.4	6.3	6.5
Conc. in slurry, wt % MF	29.7	29.8	30.0
Process Solvent, wt %			
Resid	36.2	38.3	41.3
Cl	19.6	20.0	20.1
<u>First Stage</u>			
Reaction temp., °F (avg)	825	824	824
Inlet H ₂ partial pressure, psia	2795 ±26	2840 ±25	2862 ±15
Total gas flow, scfh	4461	4900	4967
Recycle gas, scfh	187	672	784
Space vel., lb MF coal/hr/ft ³ (C=constant)	79.2C	91.5C	90.6C
Iron Oxide, wt % MF coal	2	2	2
Moly Conc., ppm MF coal	200	100	200
<u>Second Stage</u>			
Reactor temp., °F	790	810	809
Inlet H ₂ partial pressure, psia	2530 ±9	2541 ±23	2530 ±24
Total gas flow, scfh	5125	5057	5165
Recycle gas, scfh	3054	2160	2663
Space vel., lb feed/hr/lb cat	5.8	6.6	-
Space vel., lb MF coal/hr/ft ³ cat	95.2	110.0	-
Catalyst type	Crit 324	Crit 324	-
Catalyst age, lb (res+Cl)/lb cat	1404 ±49	1315 ±51	-
lb MF coal/lb cat	727 ±25	674 ±26	-
Cat replacement rate, lb/ton MF coal	3	3	-
ROSE-SR SM DAS type	2234	2294	2404
<u>Yield, wt % MAF coal</u>			
H ₂	-5.5 ±0.2	-5.5 ±0.4	-4.2 ±0.3
H ₂ S	13.9 ±1.1	15.5 ±0.7	13.1 ±0.6
CO, CO ₂	0.5 ±0.1	0.5 ±0.1	0.4 ±0.1
NH ₃	5.5 ±0.3	6.3 ±0.4	6.9 ±0.6
C ₁ -C ₃ gas	0.7 ±0.0	0.6 ±0.1	0.3 ±0.0
C ₄ + distillate	5.3 ±0.3	6.0 ±0.4	5.5 ±0.3
C ₄ -C ₆	60.8 ±3.2	57.2 ±1.8	47.5 ±0.5
C ₇ -C ₈	2.1 ±0.1	2.3 ±0.3	2.2 ±0.2
BP-350°F	10.8 ±2.7	13.1 ±3.5	9.0 ±0.9
150-450°F	7.7 ±0.9	8.6 ±1.3	8.9 ±0.9
450-EP	40.1 ±6.2	33.2 ±3.2	27.4 ±1.1
Resid	-0.3 ±3.1	-0.4 ±2.5	11.0 ±2.0
Int. Acc. UC	0.6 ±0.6	-0.1 ±1.1	0.4 ±1.2
Solid Product (ash-free)	19.0 ±0.8	19.8 ±1.3	19.1 ±2.6
H ₂ efficiency, %	11.1 ±0.5	10.4 ±0.6	11.3 ±1.0
C ₁ -C ₃ selectivity, %	8.8 ±0.8	10.5 ±0.6	11.6 ±0.7
<u>Coal conversion, wt % MAF</u>			
First stage	89.1 ±2.6	86.7 ±2.5	86.3 ±3.0
Second stage	91.9 ±0.5	92.3 ±0.8	92.3 ±0.3
Overall TSL	90.1 ±0.5	91.6 ±0.8	91.3 ±0.9
<u>Resid + UC conversion, wt % feed</u>			
1st stage	24.7 ±1.3	21.4 ±1.6	22.9 ±2.7
2nd stage	16.5 ±2.0	18.8 ±1.1	9.8 ±4.8
<u>Resid + UC conversion, wt % MAF coal</u>			
1st stage	53.5 ±2.0	47.5 ±4.3	51.7 ±7.8
2nd stage	27.3 ±2.9	33.1 ±2.8	17.8 ±8.1
Overall	80.8 ±2.9	80.6 ±1.7	69.5 ±1.2

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TABLE 2
COMPONENT DISTRIBUTION OF V-131B SAMPLES
Wilsonville Run 262

Sample Number	Period	wt % of Sample			
		850°F Distillate	THF-Soluble Resid	IOM	Ash
24876	A*	34.9	42.4	10.4	10.7
24877	B	28.3	51.3	10.1	9.0
24791	C1	27.1	50.2	10.4	11.9
24792	C2	28.9	47.6	11.2	11.9
24795	D	29.1	50.3	10.0	10.3
24809	E	24.8	54.2	10.0	10.5
24834	F*	27.2	52.2	9.6	10.6

*Transitional or unstable period.

TABLE 3
COMPONENT DISTRIBUTION OF V-1067 SAMPLES
Wilsonville Run 262

Sample Number	Period	wt % of Sample			
		850°F Distillate	THF-Soluble Resid	IOM	Ash
23552	A*	34.3	43.3	9.8	11.6
22569	B	29.8	46.9	11.2	11.0
24793	C1	29.9	45.9	11.1	12.4
24794	C2	25.0	51.0	10.7	12.8
24797	D	28.0	47.9	12.0	11.3
24811	E	25.8	50.8	12.2	10.7
24833	F*	27.0	50.4	10.6	11.4

*Transitional or unstable period.

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TABLE 4
COMPONENT DISTRIBUTION OF R-1235 SAMPLES
Wilsonville Run 262

Sample Number	Period	wt % of Sample			
		850°F Distillate	THF-Soluble Resid	IOM	Ash
23551	A*	34.2	43.1	11.1	10.3
22595	B	26.8	49.1	11.9	10.8
24789	C1	22.8	52.5	12.1	11.5
24790	C2	22.1	53.4	12.1	11.7
24796	D	26.7	48.6	13.0	10.7
24810	E	19.9	55.2	13.7	10.7
24835	F*	21.3	54.3	13.1	10.8

*Transitional or unstable period.

TABLE 5
SOLUBILITY FRACTIONATION OF V-131B SAMPLES
Wilsonville Run 262

Period	wt % of THF-Soluble Resid		
	Oils	Asphaltenes	Preasphaltenes
A*	64.5	26.0	9.5
B	69.5	23.3	7.2
C1	63.4	27.0	9.6
C2	64.6	26.5	8.9
D	64.2	23.5	12.3
E	66.6	24.0	9.5
F*	59.6	27.3	13.1

*Transitional or unstable period.

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TABLE 6
SOLUBILITY FRACTIONATION OF V-1067 SAMPLES
Wilsonville Run 262

Period	wt % of THF-Soluble Resid		
	Oils	Asphaltenes	Preasphaltenes
A*	68.7	23.3	8.0
B	65.6	27.7	6.7
C1	63.5	23.5	13.0
C2	62.1	24.2	13.8
D	64.1	24.3	11.6
E	59.7	26.7	13.6
F*	59.4	29.0	11.6

*Transitional or unstable period.

TABLE 7
SOLUBILITY FRACTIONATION OF R-1235 SAMPLES
Wilsonville Run 262

Period	wt % of THF-Soluble Resid		
	Oils	Asphaltenes	Preasphaltenes
A*	63.5	23.8	12.8
B	67.0	22.4	10.6
C1	59.1	24.7	16.2
C2	60.6	23.9	15.5
D	58.2	25.6	16.2
E	58.1	23.7	18.2
F*	54.9	26.7	18.4

*Transitional or unstable period

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TABLE 8
PROTON DISTRIBUTION OF V-131B WHOLE SAMPLES
Wilsonville Run 262

Period	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
A*	13.9	4.2	16.1	9.2	17.3	25.7	13.6
B	11.9	3.0	22.5	8.2	18.0	25.6	10.8
C1	16.1	3.3	16.8	8.1	16.6	26.3	12.8
C2	15.0	2.6	17.4	8.3	17.1	25.8	13.7
D	16.7	3.2	15.7	7.7	16.4	27.6	12.7
E	19.1	3.3	16.0	7.9	14.0	27.3	12.3
F*	21.3	3.5	18.0	8.5	13.5	24.6	10.5

*Transitional or unstable period.

TABLE 9
PROTON DISTRIBUTION OF V-1067 WHOLE SAMPLES
Wilsonville Run 262

Period	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
A*	13.9	3.5	16.3	8.7	16.9	25.6	15.1
B	12.7	3.9	13.9	8.1	16.7	29.5	15.3
C1	15.0	3.5	17.1	9.0	17.7	25.6	12.1
C2	15.5	3.6	17.3	9.0	17.5	25.0	12.1
D	14.3	4.4	15.4	8.7	16.1	26.8	14.3
E	18.5	3.9	16.8	8.8	14.3	25.5	12.3
F*	22.2	4.0	19.1	9.1	14.2	21.6	9.8

*Transitional or unstable period.

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TABLE 10
PROTON DISTRIBUTION OF R-1235 WHOLE SAMPLES
Wilsonville Run 262

Period	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
A*	15.0	4.1	16.7	9.0	16.0	26.8	12.4
B	14.1	4.7	15.3	8.7	15.1	25.6	16.3
C1	16.9	4.0	18.3	9.1	15.9	24.4	11.3
C2	15.9	4.9	16.6	9.3	15.1	25.2	13.0
D	17.1	3.4	18.3	8.9	15.9	25.0	11.3
E	19.6	4.5	18.1	9.3	14.4	22.9	11.2
F*	21.8	2.5	21.0	9.4	14.8	22.1	8.4

*Transitional or unstable period.

TABLE 11
PROTON DISTRIBUTION OF V-131B DISTILLATE SAMPLES
Wilsonville Run 262

Period	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
A*	8.5	5.5	11.5	7.5	15.9	33.1	18.1
B	6.1	5.1	10.3	7.4	16.7	35.0	19.3
C1	8.0	3.7	11.6	7.4	16.4	36.0	16.9
C2	8.4	4.0	12.5	7.3	16.5	35.1	16.1
D	8.3	3.3	14.0	7.4	16.3	35.9	14.9
E	11.0	4.0	14.5	7.3	15.8	34.8	12.6
F*	12.7	4.2	15.1	8.0	15.1	33.3	11.5

*Transitional or unstable period.

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TABLE 12
PROTON DISTRIBUTION OF V-1067 DISTILLATE SAMPLES
Wilsonville Run 262

Period	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
A*	7.7	5.2	12.0	7.9	17.1	33.2	16.8
B	5.9	5.5	10.1	7.8	15.4	34.6	20.7
C1	7.8	4.6	13.6	8.3	17.9	33.1	14.6
C2	7.6	5.1	11.1	7.6	16.4	35.0	17.2
D	7.2	5.0	10.4	7.4	15.5	35.3	19.3
E	8.1	3.8	12.0	7.2	16.2	36.7	15.9
F*	12.8	6.4	13.5	8.5	12.8	32.5	13.4

*Transitional or unstable period.

TABLE 13
PROTON DISTRIBUTION OF R-1235 DISTILLATE SAMPLES
Wilsonville Run 262

Period	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
A*	10.2	5.4	14.8	8.9	16.9	31.1	12.6
B	7.8	6.1	12.2	8.7	15.3	33.2	16.8
C1	7.9	6.9	12.5	8.6	15.7	33.1	15.3
C2	8.6	5.9	12.7	9.1	14.9	33.2	15.6
D	8.4	5.2	12.0	8.1	14.8	35.8	15.7
E	9.2	6.6	12.2	8.9	13.2	35.2	14.7
F*	11.0	6.6	13.0	9.6	13.1	33.8	13.0

*Transitional or unstable period.

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TABLE 14
PROTON DISTRIBUTION OF V-131B RESID SAMPLES
Wilsonville Run 262

Period	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
A*	21.8	3.4	18.9	9.5	15.4	20.7	10.3
B	19.3	3.3	18.3	8.5	16.7	23.2	10.7
C1	20.3	3.4	19.6	8.8	17.0	21.0	10.0
C2	21.0	2.6	20.5	8.8	17.4	20.1	9.5
D	20.2	3.0	18.2	8.6	16.5	22.5	10.9
E	24.6	3.4	20.0	8.9	15.0	19.4	8.8
F*	26.4	3.9	20.5	9.5	13.5	17.9	8.3

*Transitional or unstable period.

TABLE 15
PROTON DISTRIBUTION OF V-1067 RESID SAMPLES
Wilsonville Run 262

Period	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
A*	19.8	3.3	18.5	8.7	16.4	22.5	10.8
B	18.8	2.9	19.4	8.5	16.8	23.4	10.1
C1	20.4	3.2	19.8	8.8	16.2	21.0	10.5
C2	19.4	3.6	18.0	8.3	16.2	23.2	11.3
D	20.6	2.8	19.2	8.3	15.8	23.3	9.9
E	24.4	2.6	21.3	9.0	15.2	18.6	8.9
F*	27.2	4.4	21.5	9.5	13.3	16.4	7.8

*Transitional or unstable period.

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TABLE 16
PROTON DISTRIBUTION OF R-1235 RESID SAMPLES
Wilsonville Run 262

Period	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
A*	21.9	2.7	21.6	8.6	16.3	20.5	8.4
B	17.5	4.5	17.9	9.0	14.6	21.7	14.8
C1	18.8	4.5	18.8	9.3	14.3	21.4	12.8
C2	18.5	4.9	18.1	9.2	14.1	21.7	13.4
D	20.1	2.8	19.8	8.8	16.3	20.9	11.2
E	23.1	4.4	19.1	9.1	13.5	21.1	9.8
F*	26.5	3.2	21.3	9.4	13.4	18.6	7.8

*Transitional or unstable period.

TABLE 17
PHENOLIC -OH CONCENTRATION BY FTIR
Wilsonville Run 262

Period	Phenolic -OH Concentrations, meq/g											
	V-131B				V-1067				R-1235			
	Dist.	ν , cm^{-1}	Resid	ν , cm^{-1}	Dist.	ν , cm^{-1}	Resid	ν , cm^{-1}	Dist.	ν , cm^{-1}	Resid	ν , cm^{-1}
A*	0.36	3312	0.87	3300	0.46	3314	0.89	3299	0.86	3314	1.14	3298
B	0.38	3316	0.78	3300	0.43	3315	0.80	3301	0.92	3313	1.07	3298
C1	0.34	3311	0.87	3299	0.39	3312	0.87	3300	0.96	3314	1.11	3298
C2	0.32	3311	0.89	3299	0.43	3311	0.90	3298	1.00	3314	1.02	3298
D	0.36	3309	0.90	3298	0.36	3313	0.90	3298	0.85	3313	1.14	3297
E	0.38	3307	0.85	3299	0.48	3309	1.07	3296	1.02	3313	1.11	3296
F*	0.67	3303	1.12	3297	0.92	3306	1.22	3298	1.24	3311	1.27	3296

*Transitional or unstable period.

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TABLE 18
MICROAUTOCLAVE TEST RESULTS
Wilsonville Run 262

Period	Coal Conversion, wt % MAF					
	V-131B		V-1067		R-1235	
	Dist.	Whole	Dist.	Whole	Dist	Whole
A*	68.9	75.2	74.6	59.9	70.3	76.1
B	66.2	37.0	68.7	80.8	62.7	46.6
C1	63.9	65.8	68.1	65.9	62.0	65.9
C2	62.7	69.4	68.3	71.9	65.2	53.1
D	57.8	60.7	63.5	78.7	59.0	39.7
E	59.2	27.7	65.7	66.0	58.7	58.8
F*	59.4	48.1	69.9	70.5	64.0	53.4

*Transitional or unstable period.

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TABLE 19
CONVERSION OF RESID COMPONENTS
Wilsonville Run 262

Period	Conversion, %						
	850°F* (a)	IOM	THF-Soluble Resid	Oil	Asphaltenes	Preasphaltenes	Phenolic -OH
First Stage							
A*	18.7	69.2	-40.5	-38.3	-28.6	-89.2	-84.0
B	30.1	72.3	-10.8	-6.8	-6.6	-63.2	-52.0
C1	13.2	67.5	-41.2	-29.6	-29.2	-138.3	-80.1
C2	11.6	68.2	-48.2	-39.0	-33.7	-158.1	-69.9
D	20.1	66.0	-25.1	-13.4	-36.2	-64.7	-58.4
E	13.2	63.9	-33.5	-16.4	-31.8	-155.7	-74.3
F*	12.7	65.2	-37.2	-26.4	-34.2	-92.7	-55.6
All Periods: Avg ±S.D.	17.1 ±6.6	67.5 ± 2.8	-33.8 ±12.4	-24.3 ±12.5	-28.6 ±10.1	-108.8 ±41.2	-67.8 ±12.6
Pds B-E: Avg ±S.D.	17.6 ±7.7	67.6 ± 3.1	-31.8 ±14.5	-21.1 ±13.0	-27.5 ±12.0	-116.0 ±48.1	-66.9 ±11.5
Pds A,C1,C2,E,F: Avg ±S.D.	13.9 ±2.8	66.8 ± 2.2	-40.1 ± 5.5	-29.9 ± 9.3	-31.5 ± 2.5	-126.8 ±33.6	-72.8 ±11.1
Second Stage							
A*	7.1	21.9	3.3	-4.6	5.3	39.6	24.5
B	-14.3	-12.9	-14.6	-12.2	-41.7	27.5	14.3
C1	14.7	11.3	15.5	9.2	19.6	32.2	33.8
C2	7.4	13.1	6.1	3.8	4.9	16.4	17.1
D	-1.0	4.1	-2.4	-12.8	2.8	26.7	19.2
E	6.8	9.3	6.2	3.6	-5.7	29.9	9.6
F*	7.8	17.6	5.4	-2.3	-2.7	40.4	9.2
All Periods: Avg ±S.D.	4.1 ± 9.3	9.2 ±11.3	2.8 ± 9.3	-2.2 ± 8.3	-2.5 ±19.1	30.4 ± 8.2	18.2 ± 8.7
Pds B-E: Avg ±S.D.	2.7 ±11.0	5.0 ±10.6	2.2 ±11.3	-1.7 ±10.1	-4.0 ±23.0	26.6 ± 6.1	18.8 ± 9.1
Pds A,C1,C2,E,F: Avg ±S.D.	8.8 ± 3.4	14.6 ± 5.1	7.3 ± 4.7	1.9 ± 5.5	4.3 ± 9.8	31.7 ± 9.7	18.8 ±10.5
Total							
A*	24.5	75.9	-35.8	-44.7	-21.7	-14.4	-39.0
B	20.1	68.7	-27.0	-19.9	-51.0	-18.2	-30.3
C1	26.0	71.2	-19.3	-17.6	-3.8	-61.5	-19.3
C2	18.2	72.4	-39.2	-33.8	-27.1	-115.8	-40.7
D	19.3	67.4	-28.0	-27.8	-32.4	-20.8	-28.0
E	19.1	67.3	-25.2	-12.2	-39.3	-79.2	-57.6
F*	19.5	71.3	-29.7	-29.3	-37.8	-14.9	-41.3
All Periods: Avg ±S.D.	21.0 ± 3.0	70.6 ± 3.1	-29.2 ± 6.6	-26.5 ±10.9	-30.4 ±15.0	-46.4 ±40.0	-36.6 ±12.2
Pds B-E: Avg ±S.D.	20.5 ± 3.1	69.4 ± 2.3	-27.7 ± 7.2	-22.3 ± 8.5	-30.7 ±17.5	-59.1 ±41.1	-35.2 ±14.7
Pds A,C1,C2,E,F: Avg ±S.D.	21.5 ± 3.5	71.6 ± 3.1	-29.8 ± 8.0	-27.5 ±12.9	-25.9 ±14.4	-57.2 ±43.5	-39.6 ±13.6

*Transitional or unstable period.

(a) Includes THF-soluble resid and IOM.

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TABLE 20
850°F⁺ CONVERSION AND KINETICS
Wilsonville Run 262

Period	First Stage					
	Temp., °F	Conversion (a)			K (e)	A, 10 ⁷ (e)
		CONSOL (b)	W'ville (c)	Ratio C/W (d)		
A*	826	18.7	29.7	0.630	1.08	1.68
B	825	30.1	28.9	1.042	2.07	3.25
C1	825	13.2	23.8	0.555	0.88	1.39
C2	825	11.6	20.9	0.555	0.76	1.20
D	825	20.1	24.7	0.814	1.46	2.30
E	824	13.2	21.4	0.617	1.00	1.60
F*	824	12.7	22.9	0.555	0.96	1.53
Avg for Stage 1:						
Avg All Periods		17.1	24.6	0.68	1.17	1.85
± Std. Dev.		6.6	3.5	0.18	0.45	0.71
Avg Periods B-E		17.6	23.9	0.72	1.23	1.95
± Std. Dev.		7.7	3.2	0.21	0.54	0.84
Avg Periods A,C1,C2,E,F		13.9	23.7	0.58	0.94	1.48
± Std. Dev.		2.8	3.5	0.04	0.12	0.19

Period	Second Stage								Total Conversion		
	Temp., °F	W'ville (e)	Cat Age (f)	Conversion (c)			K (e)	A,10 ⁷ (e)	CONSOL (b)	W'ville (c)	Ratio C/W (d)
				CONSOL (b)	W'ville (c)	Ratio C/W (d)					
A*	760	4.7	1545	7.1	11.8	0.602	0.36	1.37	24.5	38.0	0.644
B	761	4.8	1424	-14.3	11.8	-1.212	-0.60	-2.25	20.1	37.3	0.539
C1	790	5.8	1350	14.7	19.7	0.746	1.00	2.50	26.0	38.8	0.669
C2	790	5.8	1337	7.4	19.6	0.378	0.46	1.16	18.1	36.4	0.498
D	790	5.8	1404	-1.0	16.5	-0.061	-0.06	-0.14	19.3	37.1	0.520
E	810	6.6	1315	6.8	18.8	0.362	0.48	0.92	19.1	36.2	0.528
F*	809	6.6(g)	-	7.8	9.8	0.796	0.56	1.08	19.5	30.5	0.641
Avg for Stage 2 and Total:											
Avg All Periods				4.1	15.4	0.23	0.31	0.66	20.9	36.3	0.58
± Std. Dev.				9.3	4.2	0.70	0.51	1.50	3.0	2.7	0.07
Avg Periods B-E				2.7	17.3	0.04	0.26	0.44	20.5	37.2	0.55
± Std. Dev.				11.0	3.3	0.76	0.61	1.77	3.1	1.0	0.07
Avg Periods A,C1,C2,E,F				8.8	15.9	0.58	0.57	1.41	21.4	36.0	0.60
± Std. Dev.				3.3	4.8	0.20	0.25	0.63	3.5	3.3	0.08

*Transitional or unstable period.

- (a) First stage and total conversion: wt % resid + MAF coal + UC fed to first stage
Second stage conversion: wt % resid + UC fed to second stage
- (b) 850°F distillation end point, atm equivalent
- (c) 1050°F distillation end point, atm equivalent
- (d) Ratio of CONSOL conversion to Wilsonville conversion
- (e) Basis was lb total feed/hr/lb catalyst. K and A were calculated from CONSOL conversion data.
- (f) lb coal + resid + UC/lb catalyst
- (g) Assumed to be equal to period E value - see text

TABLE 21
COMPARISON OF WILSONVILLE RUNS 262, 260 AND 258
Operating Conditions

	258H	258M	260C	260D	262B	262E
Reference	11	11	10	10	This rpt	This rpt
<u>Conditions</u>						
% Volume Takeoff, Reactor 1	50	50	100	75	50	50
% Volume Takeoff, Reactor 2	50	50	75	100(a)	50	50
T ₁ , °F	841	852	825	790	825	824
T ₂ , °F	790	788	790	774(a)	761	810
Space Vel. Thermal Reactor (C = Constant)	65C	77C	31C	31C(a)	65C	92C
WHSV, lb Feed/lb Cat. hr	4.5	5.4	3.1	2.8	4.8	6.6
Resid/Cl in Recycle, wt %	40.7/20.2	40.5/20.4	40.4/20.7	38.6/20/0	37.7/18.7	38.3/20.0
Interstage Separator	Large	Large	Small*	Bypassed	Large	Large
Cat. Age, lb (resid + Cl)/lb Cat (Average)	~2572	~1314	~1368	~1415	~1424	~1315
Distillation System	Old**	Old**	New	New	New**	New
Cat. Repl. Rate, lb/T MF coal	1.5	3.0	3.0	3.0	3.0	3.0
Coal Feed Rate, MF lb coal/hr	247	291	251	253	248	346
Coal Ash, wt % MF	7.3	7.3	6.2	6.2	6.3	6.3
Mo Slurry Cat Addition Rate, ppm MF coal (b)	0	0	0	0	500	100

* Vapor-liquid separation was not occurring.

**T-102 was not working in all of periods 258H and 258M, and in part of 262B.

(a) The second stage was the thermal reactor.

(b) 2 wt % Fe₂O₃ + excess sulfiding agent was added in every period.

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TABLE 22
COMPARISON OF WILSONVILLE RUNS 262, 260 AND 258
Yield and Performance Data

Period	258H	258M	260C	260D	262B	262E
Reference	11	11	10	10	*	*
<u>Yields and Performance,</u> <u>wt % MAF Coal</u>						
H ₂	-5.4	-5.3	-6.3	-6.2	-5.4	-5.5
Water	13.7	12.9	18.8	18.6	15.4	15.5
H ₂ S, CO, CO ₂ , NH ₃	8.4	8.0	4.1	3.4	8.2	7.4
C ₁ -C ₃ Gas	9.2	8.8	11.2	5.6	5.2	6.0
C ₄ + Distillate	55.4	51.5	54.1	59.8	58.0	57.2
C ₄ + Naphtha	16.3	16.6	4.4	11.6	12.4	15.4
Middle Distillate	9.9	10.5	4.0	6.7	7.2	9.6
Distillate Solvent	29.2	24.4	45.7	41.5	38.4	33.2
Resid	4.9	3.8	7.5	0.3	-0.1	-0.4
ROSE-SR Bottoms	13.8	20.3	10.7	18.5	17.0	19.8
TSL Coal Conversion	93.1	89.1	94.2	88.5	91.1	91.6
Resid + UC Conv./1st, wt % feed	27.4	22.0	33.3	29.1	28.9	21.4
Resid + UC Conv./2nd, wt % feed	14.6	15.0	16.7	10.5	11.8	18.8

*This report

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TABLE 23

COMPARISON OF WILSONVILLE RUNS 262, 260 and 258
Process Oil Characteristics, Conversions and Kinetic Constants

	258H	258M	260C	260D	262B	262E
<u>SQI (a)</u>						
Recycle Distillate	76.0-79.6	80.8-81.3	74.8-77.1	71.6-76.7	69.2-71.1	72.7-75.8
Interstage	70.8	74.4	74.9	75.9	72.0	69.5
<u>Hydrogen Aromaticity, % of Protons (b)</u>						
Recycle Distillate	17.4-19.9	19.9-21.0	19.4-19.6	14.9-19.0	11.2-11.4	11.9-15.0
Interstage Distillate	23.0	26.1	20.9	13.5	13.9	15.8
Recycle Resid	37.1-40.8	40.1	35.9-36.1	27.5-27.9	21.7-22.6	27.0-28.0
Interstage Resid	40.3	44.9	38.4	26.2	22.0	27.5
<u>Paraffinic Hydrogen, % of Protons (c)</u>						
Recycle Distillate	38.2-42.6	36.2-37.2	40.5-43.2	46.0-47.2	54.3-55.3	47.4-52.6
Interstage Distillate	40.7	35.3	40.3	45.0	50.0	49.9
<u>Phenolic -OH Concentration, meq/g Sample</u>						
Recycle Distillate	0.57	0.35-0.39	0.42-0.45	0.31-0.42	0.38-0.43	0.38-0.48
Interstage Distillate	1.13	1.00	1.20	0.34	0.92	1.02
Recycle Resid	0.93-0.98	0.78-0.80	0.65-0.67	0.81-0.88	0.78-0.80	0.85-1.07
Interstage Resid	1.18	1.11	0.94	0.82	1.07	1.11
<u>Recycle Resid Components, wt %</u>						
Oils	59.5-60.2	56.3-58.0	68.3-69.0	57.8-60.4	65.6-69.5	59.7-66.6
Asphaltenes	22.6-23.9	26.1-26.7	21.5-22.8	24.5-24.8	23.3-27.7	24.0-26.7
Preasphaltenes	15.9-17.9	15.9-17.0	8.2-10.2	14.8-17.7	6.7-7.2	9.5-13.6
<u>Interstage Resid Components, wt %</u>						
Oils	55.6	55.8	61.3	59.2	67.0	58.1
Asphaltenes	22.8	26.9	25.3	23.8	22.4	23.7
Preasphaltenes	21.5	17.3	13.4	17.0	10.6	18.2
<u>850°F⁺ Conversion, %</u>						
First Stage	27.9	20.6	33.5	26.6	30.1*	13.2
Second Stage	15.3	13.5	11.3	14.4	-14.3*	6.8
Total	38.9	31.3	41.0	37.2	20.1	19.1
<u>Kinetic Rate Constants for 850°F⁺ Conv. (d)</u>						
First Stage	1.74	1.40	1.17	1.01	2.07*	1.00
Second Stage	0.81	0.84	0.99	1.10	-0.60*	0.48
<u>Activities for 850°F⁺ Conversion, 10⁷ (d)</u>						
First Stage	2.23	1.57	1.84	2.54	3.25*	1.60
Second Stage	2.03	2.16	0.99	1.10	-2.25*	0.92

- (a) SQI - Solvent Quality Index, predicted microautoclave donor solvent quality based on proton distribution of each distillate sample.
 (b) Sum of condensed and uncondensed aromatic protons.
 (c) Sum of alkyl beta and gamma (paraffinic) protons.
 (d) lb total feed/hr/lb catalyst.

*Results for separate stages are questionable.

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TABLE 24

ELEMENTAL ANALYSES OF WILSONVILLE RUN 262A R-1235 WHOLE PROCESS OIL,
RESID, AND THF-INSOLUBLE RESID ASH

	Whole Oil	Distillation Resid	THF-Insoluble Resid Ash
Mo	1071 ppm	1609 ppm	9560 PPM
Fe	1.63 wt %	2.46 wt %	14.80 WT %
SiO ₂	2.18 wt %	3.21 wt %	18.02 wt %
Al ₂ O ₃	1.25 wt %	1.95 wt %	11.02 wt %
Fe ₂ O ₃	2.29 wt %	3.52 wt %	21.16 wt %
CaO	1.67 wt %	2.55 wt %	14.69 wt %
P ₂ O ₅	0.27 wt %	0.41 wt %	2.63 wt %
Na ₂ O	0.05 wt %	0.08 wt %	0.40 wt %
TiO ₂	0.10 wt %	0.15 wt %	0.90 wt %
MgO	0.37 wt %	0.57 wt %	2.5 wt %
Cr		<0.01 wt %	<0.01 wt %
Cu		<0.01 wt %	<0.01 wt %
Ni		<0.01 wt %	<0.01 wt %
V		<0.01 wt %	<0.01 wt %
Zn		<0.01 wt %	<0.01 wt %

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TABLE 25
ANALYSIS OF O-METHYLATION SAMPLES

RUN NO. SAMPLE TYPE	SAMPLING LOCATION	FEED COAL	ULTIMATE ANALYSIS (MAF WT %)				
			C	H	N	S	O (By Diff.)
261 B THF-Sol Whole Oil	V-131B (RECYCLE)	Illinois Bituminous	89.65	8.16	0.67	0.13	1.39
261B THF-Sol Whole Oil, Treated #1			87.58	8.24	0.76	0.13	3.29
261B THF-sol Whole Oil, Treated #2			87.14	8.16	0.82	0.15	3.73
260 THF-Sol Resid	V-131B (RECYCLE)	Wyoming Subbituminous	89.27	6.75	0.97	0.07	2.94
260 THF-Sol Resid, Blank			90.49	6.80	1.09	0.03	1.59
260 THF-Sol Resid, Treated #1			87.65	6.82	1.15	0.04	4.25
260 THF-Sol Resid, Treated #2			86.81	6.79	1.22	0.04	4.95
260 A Distillate	R-1235 (INTERSTAGE)	Wyoming Subbituminous	87.75	9.61	0.56	0.07	2.01
260 A Dist, Blank			89.29	9.63	0.70	0.07	0.31
260 A Dist, Treated #2			88.99	9.96	0.63	0.06	0.35
258 Dist. Composite	R-1235 (INTERSTAGE)	Wyoming Subbituminous	87.62	8.82	0.69	0.06	2.81
258 Dist Comp, Blank			89.75	8.92	0.77	0.06	0.50
258 Dist Comp, Treated #1			88.26	9.01	0.56	0.04	2.13
258 Dist Comp, Treated #2			83.33	8.71	0.79	0.04	7.13

TABLE 26
PHENOLIC -OH CONCENTRATIONS AND SOLVENT QUALITIES
O-METHYLATION SAMPLES

SAMPLE	PHENOLIC -OH ¹		COAL CONVERSION ² (wt %)
	meq -OH/g Sample	Peak Location, cm ⁻¹	
Wilsonville Run 261B, V131B (Recycle)			
Whole Oil	0.40 ³	3302	80.8
THF-Sols, Whole Oil	0.41	3302	81.7
BLANK O-Meth	0.37	3299	77.8
O-Meth, THF-Sols, Whole Oil #1	0.10	3305	67.7
O-Meth, THF-Sols, Whole Oil #2	0.20	3304	68.9
Wilsonville Run 260, V131B (Recycle)			
THF-Sols, Composite Resid	0.82	3295	42.5
BLANK O-Meth	0.69	3297	42.1
O-Meth, THF-Sols, Composite Resid #1	0.45	3298	0.0
O-Meth, THF-Sols Composite Resid #2	0.42	3298	-6.9
Wilsonville Run 260A, R1235 (Interstage)			
Distillate	1.06	3309	68.2
BLANK O-Meth	0.81	3309	59.0
O-Meth, Distillate #1	0.47	3312	56.8
O-Meth, Distillate #2	0.45	3313	37.9
O-Meth, #1 + #2			53.3
Wilsonville Run 258, R1235 (Interstage)			
Distillate Composite	1.05	3307	72.0
BLANK O-Meth	0.87	3305	70.1
O-Meth, Comp. Distillate #1	0.65	3306	54.4
O-Meth, Comp. Distillate #2	0.62	3307	52.4

1. Phenolic -OH determined by FTIR
2. Modified Equilibrium Method; 9g Sample, 6g Old Ben Mine Coal, 30 min, 750°F
3. THF-soluble portion

TABLE 27
PROTON DISTRIBUTIONS OF O-METHYLATION SAMPLES

SAMPLE	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
Wilsonville Run 261B V131B (Recycle)							
THF-Sols, Whole Oil	17.0	3.9	16.2	8.4	17.8	23.1	13.6
BLANK O-Meth ^a							
O-Meth, THF-Sols Whole Oil #1 ^a							
O-Meth, THF-Sols Whole Oil #2 ^a							
Wilsonville Run 260 V131B (Recycle)							
THF-Sols, Composite Resid	26.9	4.4	18.3	8.7	13.8	18.6	9.4
BLANK O-Meth	27.1	4.2	18.4	8.8	14.5	18.2	8.8
O-Meth, THF-Sols, Comp. Resid #1	24.9	8.1	18.1	7.9	14.0	16.1	11.0
O-Meth, THF-Sols, Comp. Resid #2	24.7	6.4	18.6	8.1	14.9	16.6	10.8
Wilsonville Run 260A R1235 (Interstage)							
Distillate	13.0	6.1	13.1	9.9	12.9	30.9	14.1
BLANK O-Meth	15.2	4.3	13.9	8.7	14.6	30.5	12.8
O-Meth, Dist. #1	13.7	5.0	11.1	8.3	12.7	32.8	16.4
O-Meth, Dist. #2	13.0	3.8	13.2	8.6	14.4	32.5	14.6
Wilsonville Run 258 R1235 (Interstage)							
Distillate Composite	17.9	5.7	16.8	10.4	13.8	24.6	10.8
BLANK O-Meth	19.9	5.4	14.9	10.5	10.9	25.3	13.0
O-Meth, Comp. Distillate #1	18.5	5.9	14.3	9.6	13.1	24.7	13.8
O-Meth, Comp. Distillate #2	18.3	5.3	15.2	9.6	13.4	23.7	14.5

a. These data not available

TABLE 28
CONCENTRATIONS OF PROTON CLASSES,
O-METHYLATION SAMPLES

	wt % of Sample						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
260, V-131B							
Starting	1.79	0.29	1.22	0.58	0.92	1.24	0.63
Blank	1.84	0.29	1.25	0.59	0.99	1.24	0.60
No. 1	1.70	0.55	1.23	0.55	0.95	1.24	0.75
No. 2	1.67	0.43	1.26	0.55	1.01	1.13	0.73
260A, R-1235							
Starting	1.25	0.59	1.26	0.95	1.24	2.67	1.36
Blank	1.46	0.41	1.34	0.84	1.41	2.94	1.23
No. 2	1.29	0.38	1.31	0.86	1.43	3.24	1.45
258, R-1235							
Starting	1.58	0.50	1.48	0.92	1.22	2.17	0.95
Blank	1.78	0.48	1.33	0.94	0.97	2.26	1.16
No. 1	1.67	0.53	1.29	0.86	1.18	2.22	1.24
No. 2	1.59	0.46	1.32	0.84	1.17	2.06	1.26

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TABLE 29
PEAK IDENTIFICATION IN THE RUN 260A, DISTILLATE SAMPLES

Peak No.	Retention Time (min)	260 A Distillate	260 A Distillate, Blank O-Methylation	260 A Distillate O-Methylation No. 2
1	<7.50			
2	7.97			phenol
3	8.47			methoxy-methyl-benzene
4	8.84	methyl-phenol		methyl-phenol
5	8.90			methyl-phenol
6	9.16	methyl-phenol		methyl-phenol
7	9.47			
8	9.74			trimethyl-phenol
9	9.82			ethyl-methoxy-benzene
10	10.12	ethyl-phenol		ethyl-phenol
11	10.28			methyl-indan
12	10.33	dimethyl-phenol		dimethyl-phenol
13	10.39			dimethyl-phenol
14	10.43			methyl-indan
15	10.63	ethyl-phenol		
16	10.68	ethyl-phenol	ethyl-phenol	ethyl-phenol
17	11.17			naphthalene
18	11.70	propyl-phenol		propyl-phenol
19	11.75			methyl-tetralin
20	11.82	trimethyl-phenol		
21	12.05	ethyl-methyl-phenol	ethyl-methyl-phenol	
22	12.42			dimethyl-indan
23	12.51	propyl-phenol	propyl-phenol	propyl-phenol
24	12.69			dimethyl-indan
25	12.80	methyl-tetralin	methyl-tetralin	methyl-tetralin
26	13.37	methyl-tetralin		
27	13.47			trimethyl-benzaldehyde

Peak No.	Retention Time (min)	260 A Distillate	260 A Distillate, Blank O-Methylation	260 A Distillate O-Methylation No. 2
28	13.5	methyl-naphthalene	methyl-naphthalene	methyl-naphthalene
29	13.91	indanol		methyl-naphthalene
30	14.51	indanol	indanol	indanol
31	15.02			ethyl-tetralin
32	15.11	dimethyl-phenyl-ethanone		dimethyl-phenyl-ethanone
33	15.72	methyl-ethyl-benzene	methyl-ethyl-benzene	
34	15.97	ethyl-naphthalene	ethyl-naphthalene	ethyl-naphthalene
35	16.08	tetradecane	tetradecane	tetradecane
36	16.28	dimethyl-naphthalene	dimethyl-naphthalene	dimethyl-naphthalene
37	16.33	dimethyl-naphthalene	dimethyl-naphthalene	
38	16.63	dimethyl-naphthalene	dimethyl-naphthalene	dimethyl-naphthalene
39	16.75	dimethyl-naphthalene	dimethyl-naphthalene	dimethyl-naphthalene
40	17.19	dimethyl-naphthalene	dimethyl-naphthalene	dimethyl-naphthalene
41	17.51			methoxy-naphthalene
42	18.36	acenaphthene		acenaphthene
43	18.83	n-paraffin	n-paraffin	n-paraffin
44	18.98			trimethyl-naphthalene
45	19.23			C ₆ -indan
46	19.42			trimethyl-naphthalene
47	19.50			trimethyl-naphthalene
48	20.21		trimethyl-naphthalene	
49	20.36		butyl-tetralin	
50	21.21			trimethyl-naphthalene
51	21.46	methyl-biphenyl	methyl-biphenyl	methyl-biphenyl
52	21.66	n-paraffin	n-paraffin	n-paraffin
53	21.87	methyl-biphenyl	methyl-biphenyl	methyl-biphenyl
54	22.60	C ₂ -biphenyl	C ₂ -biphenyl	C ₂ -biphenyl
55	22.86	C ₂ -biphenyl	C ₂ -biphenyl	C ₂ -biphenyl
56	23.04		dimethyl-biphenyl	dimethyl-biphenyl
57	23.17	ethyl-biphenyl		ethyl-biphenyl
58	24.11			dihydro-phenanthrene
59	24.15	octahydrophenanthrene	octahydrophenanthrene	octahydrophenanthrene
60	24.29	methyl-fluorene	methyl-fluorene	methyl-fluorene

Peak No.	Retention Time (min)	260 A Distillate	260 A Distillate, Blank O-Methylation	260 A Distillate O-Methylation No. 2
61	24.47	dimethyl-biphenyl	dimethyl-biphenyl	dimethyl-biphenyl
62	24.56			hexamethyl-tetracosane
63	24.67	dimethyl-biphenyl	dimethyl-biphenyl	dimethyl-biphenyl
64	24.75	dimethyl-biphenyl	dimethyl-biphenyl	dimethyl-biphenyl
65	25.02	dimethyl-biphenyl	dimethyl-biphenyl	dimethyl-biphenyl
66	25.14	dimethyl-biphenyl	dimethyl-biphenyl	dimethyl-biphenyl
67	25.70	tetrahydroanthracene	tetrahydroanthracene	tetrahydroanthracene
68	25.82	tetrahydrophenanthrene	tetrahydrophenanthrene	tetrahydrophenanthrene
69	25.95			methylene-bis-methyl-benzene
70	26.23			methylene-bis-methyl-benzene
71	26.52	phenanthrene	phenanthrene	phenanthrene
72	26.72	dihydromethylanthracene		dihydromethylanthracene
73	27.01	Undetermined	Undetermined	Undetermined
74	27.18	n-paraffin	n-paraffin	n-paraffin
75	27.51			dimethyl-fluorene
76	27.61			dimethyl-fluorene
77	29.50	methyl-phenanthrene	methyl-phenanthrene	methyl-phenanthrene
78	29.64	methyl-phenanthrene	methyl-phenanthrene	methyl-phenanthrene
79	29.80	n-paraffin	n-paraffin	n-paraffin
80	29.92	methyl-phenanthrene	methyl-phenanthrene	
81	30.21			
82	30.68		Undetermined	
83	31.37	diethyl-biphenyl		methoxy-phenylethenyl-
84	31.84		Undetermined	Undetermined
85	32.33	n-paraffin	n-paraffin	n-paraffin
86	32.48	dimethyl-phenanthrene		dimethyl-phenanthrene
87	33.25	hexahydropyrene		hexahydropyrene
88	33.38	dihydropyrene	dihydropyrene	dihydropyrene
89	33.59	fluoranthene	fluoranthene	fluoranthene
90	34.74	n-paraffin	n-paraffin	n-paraffin

Peak No.	Retention Time (min)	260 A Distillate	260 A Distillate, Blank O-Methylation	260 A Distillate O-Methylation No. 2
91	34.90			pyrene
92	34.94	pyrene	pyrene	dihdropyrene
93	36.71		Undetermined	Undetermined
94	37.08	n-paraffin	n-paraffin	n-paraffin
95	37.44	butyl-phenanthrene	butyl-phenanthrene	
96	37.69			methyl-pyrene
97	37.76	methyl-pyrene	methyl-pyrene	
98	37.97	Undetermined	Undetermined	Undetermined
99	38.00		Undetermined	Undetermined
100	38.15			methyl-pyrene
101	38.20	methyl-pyrene	methyl-pyrene	
102	38.70	Undetermined		
103	39.06	Undetermined		
104	39.31	n-paraffin	n-paraffin	n-paraffin
105	40.24			dimethyl-pyrene
106	40.31	dimethyl-pyrene	dimethyl-pyrene	
107	40.43		dimethyl-pyrene	
108	40.59			
109	40.90			dimethyl-pyrene
110	41.45	n-paraffin	n-paraffin	n-paraffin
111	41.61		tetrahydro-benzanthracene	tetrahydro-benzanthracene
112	42.44	chrysene	chrysene	chrysene
113	43.01	Undetermined	Undetermined	Undetermined
114	43.52	n-paraffin	n-paraffin	n-paraffin
115	44.39		methyl-pyrene	methyl-pyrene
116	45.47	n-paraffin	n-paraffin	
117	46.09	dimethyl-benzophenanthrene	dimethyl-benzophenanthrene	dimethyl-benzophenanthrene
118	46.39		ethyl-chrysene	
119	46.64		dimethyl-pyrene	
120	47.37	n-paraffin	n-paraffin	n-paraffin
121	47.80	dimethyl-benzophenanthrene		
122	49.19	n-paraffin	n-paraffin	n-paraffin
123	50.26		n-paraffin	
124	50.94	n-paraffin	n-paraffin	n-paraffin

Peak No.	Retention Time (min)	260 A Distillate	260 A Distillate, Blank O-Methylation	260 A Distillate O-Methylation No. 2
125	52.64	n-paraffin	n-paraffin	n-paraffin
126	54.30	n-paraffin	n-paraffin	n-paraffin
127	55.89	n-paraffin	n-paraffin	n-paraffin

- Peak identifications based on searches of the Wiley/NBS Database and CONSOL's library of coal-derived compounds.
- Peak assignments based on a match of 70% (or greater) probability with the data bases.

- GC/MS Conditions:

Column - 30m x 0.25mm fused silica with DB5 coating

Temperature Program - 35-100°C @ 35°/min
100-320°C @ 4°/min

Mass Spec - 45-300 amu scan, 70eV

TABLE 30
GC PEAK IDENTIFICATION IN THE RUN 258 DISTILLATE SAMPLES

Peak No.	Retention Time (min)	258 Distillate	258 Distillate, Blank O-Methylation	258 Distillate O-Methylation No. 1
1	<7.50			
2	9.17	methyl-phenol	methyl-phenol	
3	10.63		ethyl-phenol	
4	10.66		ethyl-phenol	
5	11.15		naphthalene	
6	12.50	propyl-phenol	propyl-phenol	
7	13.55	methyl-naphthalene	methyl-naphthalene	methyl-naphthalene
8	13.91	methyl-naphthalene	methyl-naphthalene	methyl-naphthalene
9	14.51	indanol	indanol	indanol
10	15.97		ethyl-naphthalene	ethyl-naphthalene
11	16.28		dimethyl-naphthalene	
12	16.62		dimethyl-naphthalene	dimethyl-naphthalene
13	16.73		dimethyl-naphthalene	dimethyl-naphthalene
14	18.36	acenaphthene	acenaphthene	acenaphthene
15	18.83		n-paraffin	
16	18.98		trimethyl-naphthalene	trimethyl-naphthalene
17	20.36		butyl-tetralin	butyl-tetralin
18	21.10		fluorene	
19	21.46	methyl-biphenyl	methyl-biphenyl	methyl-biphenyl
20	21.87		methyl-biphenyl	methyl-biphenyl
21	22.57		dimethyl-biphenyl	dimethyl-biphenyl
22	22.83		dimethyl-biphenyl	dimethyl-biphenyl
23	23.17	dimethyl-biphenyl	dimethyl-biphenyl	dimethyl-biphenyl
24	24.09		dihydrophenanthrene	dihydroanthracene
25	24.27		methyl-fluorene	methyl-fluorene
26	24.47	dimethyl-biphenyl	dimethyl-biphenyl	dimethyl-biphenyl
27	24.73		dimethyl-biphenyl	
28	25.02		dimethyl-biphenyl	dimethyl-biphenyl
29	25.14		dimethyl-biphenyl	dimethyl-biphenyl
30	25.70	tetrahydroanthracene	tetrahydroanthracene	tetrahydroanthracene

Peak No.	Retention Time (min)	256 Distillate	258 Distillate, Blank O-Methylation	258 Distillate O-Methylation No. 1
31	25.82	tetrahydrophenanthrene	tetrahydrophenanthrene	tetrahydrophenanthrene
32	26.52	phenanthrene	phenanthrene	phenanthrene
33	28.73	phenylethenyl-phenol		
34	29.50	methyl-phenanthrene	methyl-phenanthrene	methyl-phenanthrene
35	29.64	methyl-phenanthrene	methyl-phenanthrene	methyl-phenanthrene
36	29.89		methyl-phenanthrene	methyl-phenanthrene
37	31.37			Unknown methoxy-aromatic
38	31.84			dimethylphenanthrene
39	32.33	n-paraffin	n-paraffin	n-paraffin
40	32.48		dimethyl-phenanthrene	dimethyl-phenanthrene
41	32.60		dimethyl-phenanthrene	dimethyl-phenanthrene
42	33.23		hexahdropyrene	hexahdropyrene
43	33.38	dihdropyrene	dihdropyrene	
44	33.59	fluoranthene	fluoranthene	fluoranthene
45	33.84			hexahdropyrene
46	34.74	n-paraffin	n-paraffin	n-paraffin
47	34.88	pyrene	pyrene	pyrene
48	34.95	indenoindene	indenoindene	
49	35.82	azapyrene	azapyrene	
50	37.08	n-paraffin	n-paraffin	n-paraffin
51	37.65	methyl-pyrene	methyl-pyrene	methyl-pyrene
52	37.84	methyl-pyrene	methyl-pyrene	methyl-pyrene
53	38.13	methyl-pyrene	methyl-pyrene	methyl-pyrene
54	38.63	undetermined		
55	39.00	undetermined	undetermined	undetermined
56	39.26	n-paraffin	n-paraffin	n-paraffin
57	39.71	dimethyl-pyrene	dimethyl-pyrene	dimethyl-pyrene
58	39.83	dimethyl-pyrene	dimethyl-pyrene	dimethyl-pyrene
59	40.21	dimethyl-pyrene	dimethyl-pyrene	dimethyl-pyrene
60	40.38		dimethyl-pyrene	
61	40.74		dimethyl-pyrene	
62	40.87		terphenyl	
63	41.32	tetrahydro-triphenylene	tetrahydro-triphenylene	tetrahydro-triphenylene
64	41.39	n-paraffin	n-paraffin	n-paraffin
65	42.23		chrysene	

Peak No.	Retention Time (min)	258 Distillate	258 Distillate, Blank O-Methylation	258 Distillate O-Methylation No. 1
66	42.42	chrysene	chrysene	chrysene
67	43.45	n-paraffin	n-paraffin	n-paraffin
68	44.31	methyl-pyrene	methyl-pyrene	methyl-pyrene
69	44.78		methyl-chrysene	
70	45.42	methyl-chrysene	methyl-chrysene	methyl-chrysene
71	47.31	n-paraffin	n-paraffin	n-paraffin
72	47.72		ethyl-chrysene	
73	49.14	n-paraffin	n-paraffin	n-paraffin
74	50.91	n-paraffin	n-paraffin	n-paraffin
75	52.61	n-paraffin	n-paraffin	

- Peak identifications based on searches of the Wiley/NBS Database and CONSOL's library of coal-derived compounds.
- Peak assignments based on a match of 70% (or greater) probability with the data bases.
- GC/MS Conditions:
Column - 30m x 0.25mm fused silica with DB5 coating
Temperature Program - 35-100°C @ 35°/min
100-320°C @ 4°/min
Mass Spec - 45-300 amu scan, 70eV

Figure 1. Simplified CC-ITSL Process Diagram for Wilsonville Run 262.
Resid injection system used in periods A and B is not shown.

Figure 2. Partial CC-ITSL Process Diagram for Wilsonville Run 262 Showing Major Distillate Streams.
Resid injection system used in periods A and B is not shown.

Figure 3. Component Distribution of Whole Feed (V-131B) Oils From Wilsonville Run 262.

Figure 4. Component Distribution of Whole Product (V-1067) Oils
From Wilsonville Run 262.

Figure 5. Component Distribution of Whole Interstage (R-1235) Oils From Wilsonville Run 262.

Figure 6. Solubility Fractionation of V-131B THF-Soluble 850°F* Resid Samples From Wilsonville Run 262.

Figure 7. Solubility Fractionation of V-1067 THF-Soluble 850°F⁺ Resid Samples From Wilsonville Run 262.

Figure 8. Solubility Fractionation of Interstage THF-Soluble 850°F⁺ Resid Samples From Wilsonville Run 262.

Figure 9. Proton Distribution of V-131B Distillate and THF-Soluble Resid Samples (850°F⁺ Cutpoint) From Wilsonville Run 262.

Figure 10. Proton Distribution of V-1067 Distillate and THF-Soluble Resid Samples (850°F* Cutpoint) From Wilsonville Run 262.

Figure 11. Proton Distribution of Interstage Distillate and THF-Soluble Resid Samples (850°F⁺ Cutpoint) From Wilsonville Run 262.

Figure 12. Phenolic -OH Concentrations of Distillate and THF-Soluble Resid Samples (850°F* Cutpoint) From Wilsonville Run 262.

Figure 13. Microautoclave Solvent Quality Assays of Samples From Wilsonville Run 262.

Figure 14. First-Stage and Total Conversions of THF-Soluble 850°F+ Resid and Coal + IOM for Wilsonville Run 262.

Figure 15. THF-Soluble 850°F⁺ Conversions for Wilsonville Run 262.

Figure 16. Conversion of oils (Hexane Solubles) in Wilsonville Run 262.

Figure 17. Conversion of Asphaltenes in Wilsonville Run 262.

Figure 18. Conversion of Preasphaltenes in Wilsonville Run 262.

Figure 19. Conversion of Phenolic -OH in Wilsonville Run 262.

Figure 20. Resid + UC Conversion Activity in Wilsonville Run 262.

Figure 21A. GC/MS Chromatogram of R-1235 850°F Distillates,
Wilsonville Run 260A.

Figure 21B. GC/MS Chromatogram of Product of Blank O-Methylation
R-1235 850°F Distillates, Wilsonville Run 260A.

Figure 21C. GC/MS Chromatogram of Product of Blank O-Methylation, Trial No. 2, R-1235 850°F Distillates, Wilsonville Run 260A.

Figure 22A. GC/MS Chromatogram of R-1235 850°F Distillate Composite, Wilsonville Run 258.

Figure 22B. GC/MS Chromatogram of Product of O-Methylation
R-1235 850°F Distillate Composite,
Wilsonville Run 258.

Figure 22C. GC/MS Chromatogram of Product of O-Methylation
Trial No. 1, R-1235 850°F Distillate Composite,
Wilsonville Run 258.

ABSTRACT

COAL LIQUEFACTION PROCESS STREAMS CHARACTERIZATION AND EVALUATION, QUARTERLY TECHNICAL PROGRESS REPORT, JANUARY 1 THROUGH MARCH 31, 1992

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

- Process oils from Wilsonville Run 262 were analyzed to provide information on process performance. Run 262 was operated from July 10 through September 30, 1991, in the thermal/catalytic Close-Coupled Integrated Two-Stage Liquefaction (CC-ITSL) configuration with ash recycle. The feed coal was Black Thunder Mine subbituminous coal. The high/low temperature sequence was used. Each reactor was operated at 50% of the available reactor volume. The interstage separator was in use throughout the run. The second-stage reactor was charged with aged Criterion 324 catalyst (Ni/Mo on 1/16" alumina extrudate support). Slurry catalysts and sulfiding agent were fed to the first-stage reactor. Molyvan L is an organometallic compound which contains 8.1% Mo, and is commercially available as an oil-soluble lubricant additive. It was used in Run 262 as a dispersed hydrogenation catalyst precursor, primarily to alleviate deposition problems which plagued past runs with Black Thunder coal. One test was made with little supported catalyst in the second stage.
- The role of phenolic groups in donor solvent properties was examined. In this study, four samples from direct liquefaction process oils were subjected to O-methylation of the phenolic groups, followed by chemical analysis and solvent quality testing.
- The status of the Participants Program is described.
- Summaries of the final reports under the Participants Program from Advanced Fuel Research and the National Institute for Petroleum and Energy Research are presented. Two technical presentations are appended.

END

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