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**COAL LIQUEFACTION PROCESS STREAMS
CHARACTERIZATION AND EVALUATION**

**Quarterly Technical Progress Report
April 1 through June 30, 1990**

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R. A. Winschel, F. P. Burke

July 1991

CONSOLIDATION COAL COMPANY
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4000 Brownsville Road
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ABSTRACT

COAL LIQUEFACTION PROCESS STREAMS CHARACTERIZATION AND EVALUATION, QUARTERLY TECHNICAL PROGRESS REPORT, APRIL 1 THROUGH JUNE 30, 1990

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

1. Feed coals and process oils from Wilsonville Run 259 were analyzed to provide information on process performance. Run 259 was operated in the catalytic/catalytic Close-Coupled Integrated Two-Stage Liquefaction (CC-ITSL) mode with ash recycle. Feed coals were conventionally cleaned and deep cleaned coal from the Ireland Mine (Pittsburgh seam). The catalyst used in both reactors was Shell 324 for most of the run; Amocat 1C was used for start-up and (unstable) period A.
2. A special set of samples from Wilsonville Runs 258 and 259 was analyzed to provide clues for the cause of interstage deposition problems during Run 258, which was operated with subbituminous coal.
3. Eight technical sites were visited to provide input to the Analytical Needs Assessment and to refine ideas for proposed research under the Participants Program. The site visits are summarized.

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Section 1

INTRODUCTION

This is the Technical Progress Report for the third quarter of activities under DOE Contract No. DE-AC22-89PC89883. It covers the period April 1 through June 30, 1990.

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 R&D Department of Consolidation Coal company (Consol R&D) 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 R&D will obtain samples from current process development activities in coal liquefaction and coal-oil coprocessing, and characterize them using established analytical techniques. In addition, selected samples will be 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 will be provided by a subcontracted project team.

In addition to samples from current process development programs, Consol R&D 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 HRI and UOP coprocessing development programs. These samples, which represent important stages in the recent development of coal liquefaction technology, also will be used in the analytical program.

CONTRACT OBJECTIVES

Consol R&D 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 will be chosen from ongoing DOE-funded liquefaction and coprocessing projects and from Consol's collection of coal liquids produced during the past ten years. Samples will be chosen based on their relevance to process development programs, and will be well-documented in terms of feedstocks, sampling location, time and operating conditions. The samples chosen will be sufficient to judge the applicability of the analytical methods being evaluated. These process oils will be analyzed by Consol R&D in a base characterization program using techniques established in previous Consol research. Selected samples also will be provided to project team participants (as subcontractors), other researchers active in the analysis of coal liquids, who will characterize them using a range of methods beyond those used in the base program. Subcontracts to approximately 10 to 15 organizations that have specialized analytical capabilities will be a major aspect of this work. Individual analytical specialists from the subcontractors will 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 will evaluate the utility of promising analytical techniques for providing useful information for coal liquefaction process development, and will apply those results 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 will include support in the form of providing results and interpretation of data obtained with the analytical techniques being assessed. However, more directly, appropriate process oils will be 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 will aid plant operations and planning. Also, these results will 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, when appropriate, in the corresponding section of the Discussion, no overall Summary section is provided in this report.

- Two feed coals and 31 process oils from Wilsonville Run 259 were analyzed to provide information on process performance. Run 259 was operated in the catalytic/catalytic Close-Coupled Integrated Two-Stage Liquefaction (CC-ITSL) mode with ash recycle. Feed coals were conventionally cleaned Ireland Mine coal (Pittsburgh seam) and a low-ash deep-cleaned Ireland Mine coal (cleaned at the EPRI Coal Quality Development Center in Homer City, Pennsylvania). Catalysts used were bimodal Amocat 1C and unimodal Shell 324 (both Ni/Mo/Al) in different segments of the run.
- Two deposit samples and two interstage separator overhead samples from Run 258 were analyzed to elucidate factors contributing to interstage deposition in Run 258. Two interstage separator overhead samples from Run 259 were analyzed for comparison.

- Eight technical sites were visited to provide input to the Analytical Needs Assessment and to refine ideas for proposed research under the Participants Program. The site visits are summarized here.

Section 2

RESULTS AND DISCUSSION

PROCESS OIL ANALYSIS - WILSONVILLE RUN 259

SUMMARY

Consol analyzed two feed coals and 31 process oils from Wilsonville Run 259, which was operated in the catalytic/catalytic close-coupled Integrated Two-Stage Liquefaction (CC-ITSL) mode with ash recycle. The Pittsburgh seam bituminous coals used were conventionally cleaned coal from the Ireland Mine preparation plant (high ash) and deep-cleaned Ireland Mine (low ash) coal produced at the EPRI CQDC facility. The catalyst used for start-up and material balance period A was bimodal Amocat 1C. The catalyst used for the remainder of the run was unimodal Shell 324. The major results from Consol's analyses are summarized below.

- In general, Wilsonville personnel found that the Ireland coal resid was difficult to convert to distillate. Relatively low space velocities, high temperatures and a high catalyst addition rate were used in an effort to improve resid conversion. Consol results showed some trends or features which may shed some light on the nature of the problem. The activity for 850°F⁺ conversion was typically quite low, perhaps as a result of the low space velocities. The resid from Ireland coal was found to be relatively high in hydrogen aromaticity and in asphaltene concentration. Perhaps the asphaltenes from this coal are particularly difficult to convert. The higher aromaticity may reflect a coal structural difference which contributes to this. An unusual increase in aromaticity with increasing (catalytic) reactor temperature suggested that operation may have been at hydrogenation equilibrium during part of the run. Alternatively, at those conditions, perhaps more cracking of alkyl side-chains occurred leaving the aromatic material unconverted. It would be difficult to determine if the Ireland coal resid was particularly detrimental to the catalyst. Calculated distillate solvent quality indices were

slightly low in Run 259, relative to comparison periods. Whole oil donor quality measured by microautoclave tests was typically poor to fair during Run 259, and a few samples showed exceptionally low donor quality. It is difficult to relate solvent quality to specific aspects of performance. However, the solvent quality of whole oils peaked in samples from periods A and H, when the high-ash Ireland coal was fed. Plant performance was better in some regards during period H, but was generally poor during period A.

- Conversions of 850°F⁺ material calculated from Consol analyses for Run 259 were similar to those obtained by Wilsonville for conversions of 1050°F⁺ material (resid + UC). On the basis of first-order kinetic calculations, catalyst activities (i.e. pre-exponential factors) for conversion of 850°F⁺ material in material balance period A (high-ash Ireland coal, 50% reactor volume, and aged Amocat 1C catalyst) were much higher than during the rest of the run. In periods B through J (low-ash Ireland coal except for period H in which high ash coal was used, 100% reactor volume, and fresh Shell 324 catalyst), the activities for 850°F⁺ conversion were extremely poor, especially in the first stage. The difference in 850°F⁺ conversion activities implies that changes in reactor dynamics (from the reactor volume change), the use of unimodal Shell 324 catalyst, and the use of low-ash Ireland coal were possible factors in the observed poor performance.
- Individual comparisons of oil properties and 850°F⁺ conversion performance were made between selected periods of Run 259 and Run 254 (Ohio 6 coal, the only coal previously run which is similar in rank to the Pittsburgh seam coal) and Run 257 (Illinois 6 coal). These comparisons involved 257J vs 259A (both with 50% reactor volumes), 257E vs 259H (both with 100% reactor volume), and 254I vs 259E. Period 259A was originally planned as a direct comparison with 257J. Relatively poor 850°F⁺ conversion kinetics were observed in these Run 259 periods than in the comparison periods, in spite of generally lower catalyst ages. The kinetic performance and oil property data suggest that relatively poor performance of the Shell 324 unimodal

catalyst, low reactivity of the resid produced from Ireland coal and inherent coal structural differences could be factors relating to the poor resid conversion kinetics in Run 259. Another factor could be the low resid purge rate that accompanied operations with the low-ash Ireland Mine coal. Generally, Run 259 samples were more aromatic than samples from the comparison periods, and the Run 259 resids contained relatively lower hexane solubles (oils) concentrations and higher asphaltenes concentrations. The calculated distillate solvent quality index was slightly lower for Run 259, relative to the comparison periods.

- An unexpected increase in process oil aromaticity accompanied the increase in first-stage reactor temperature from 810°F in period C to 825°F in period D. This behavior is contrary to previous Consol experience with Wilsonville samples from catalytic reactors, and suggests that the first stage may have been at or near hydrogenation equilibrium during periods C and D. This is the first apparent indication in the Wilsonville samples we have analyzed of a catalytic stage at or near hydrogenation equilibrium. In contrast to the decreased hydrogenation at higher temperature, there was a reduction in resid asphaltenes and preasphaltenes and in distillate and resid phenolic -OH concentrations. These indicate an expected increase in heteroatom removal at the higher temperature.
- The decrease in recycle solvent resid concentration from 50 wt % in period E to 40 wt % in period F was accompanied by changes in characteristics of the resid fractions of the V-131B and R-1235 streams. These included increased phenolic -OH concentrations, decreased oil concentrations, and increased asphaltene and preasphaltene concentrations in the THF-soluble portion of the resid. The decline in resid quality with 40 wt % resid recycle, relative to 50 wt % resid recycle, appears to result from a lower concentration of deashed resid (which is expected to be of better quality due to rejection of preasphaltene material in the deashing process) in the recycle stream. Alternatively, the lower resid recycle concentration results in a higher concentration of "virgin" resid in the products. The

virgin product would be less hydrotreated than recycled resid , resulting in the poorer resid quality observed.

- The data from period H (high-ash coal) were compared to data from period E, which gave the best overall performance with low-ash coal. Resid quality was higher in period H than in period E, contrary to expectations based on differences in operating conditions between the two periods. Slightly higher first-stage and total conversions of THF-soluble resid, and 850°F⁺ conversion activities (both stages) were noted for period H, relative to period E. Higher resid quality (oil properties) during period H seems to be explainable by a higher recycle of higher-quality deashed resid, relative to period E. Other confounding factors are present, however, and the relative effects of deashed and non-deashed resid on yields and resid conversion are not known. Additional explanations also are possible for better performance in period H with high-ash coal than in period E with low-ash coal. These include: some catalytic activity of the mineral matter in the high-ash coal, a lower purge rate of refractory, preasphaltene enriched resid when the low-ash coal is processed.
- Coal feed rate was decreased from 300 (MF coal) lb/hr in period D to 267 (MF coal) lb/hr in period E (at 50 wt % resid in the recycle solvent) and from 267 (MF coal) lb/hr in period F to 230 (MF coal) lb/hr in period G (at 40 wt % resid in the recycle solvent). These modifications produced expected changes in the characteristics of some of the residual process oils: These changes included increased oils content and decreased asphaltenes and preasphaltenes contents of the THF-soluble resids, and decreased resid phenolic -OH concentrations. The first-stage and total 850°F⁺ conversions increased by 8-10% (absolute) from period F to period G, but in contrast to Wilsonville data in Table 2, no change was noted between periods D and E.
- Small but expected changes in oil composition accompanied increases in catalyst age from period E (catalyst replacement rate of 4.0 lb/T MF coal per reactor) compared to periods I and J (batch catalyst

deactivation). These included increased resid aromaticity, increased asphaltene and preasphaltene concentrations, decreased oil concentration, and increased distillate and resid phenolic -OH concentrations. Changes in 850°F⁺ conversion activity were inconsistent and rather small.

- The distillate/resid/solids proportions of the whole oils were fairly consistent except when intentional operating changes were made in the recycle solvent composition (such as adjusting the resid and cresol-insolubles concentrations). Consol's 850°F⁺ resid concentrations in the V-131B recycle oil were consistently about 12 wt % higher than Wilsonville's target blends which are based on 1050°F⁺ resid. Consol's oil composition data indicate a gradual increase in distillate concentration through the liquefaction system.

WILSONVILLE RUN 259 OVERVIEW AND PLANT DESCRIPTION

Consol analyzed two feed coals and 31 process oils from Wilsonville Run 259, which was operated with Pittsburgh seam bituminous coal and two different catalysts. Run 259 was operated from January 18 through June 9, 1990, in the catalytic/catalytic Close-Coupled Integrated Two-Stage Liquefaction (CC-ITSL) mode of operation with ash recycle. Catalysts used were 1/12" Amocat 1C (bimodal Ni/Mo/Al) and 1/16" Shell 324 (unimodal Ni/Mo/Al). The Amocat 1C catalyst was used only through unstable period A. At any one time, the same catalyst was used in both reactors. The interstage separator and an improved product distillation system (described later in this section) were in use in Run 259. The feed coals used were Ireland Mine plant product (~15% ash, conventionally cleaned) and deep-cleaned Ireland coal (~4.5% ash, washed at the EPRI Coal Quality Development Center (CQDC) in Homer City, Pennsylvania).

The major objectives of Run 259 were: 1) to investigate the maximum distillate yield while processing deep-cleaned Pittsburgh seam coal in the catalytic/catalytic mode of operation with catalyst replacement in both stages, 2) to obtain a better defined boiling end-point for the distillate product, 3) to compare the performance of Ireland coal with

that of Illinois 6 coal, and 4) to test a "standard" ash level coal for comparison with the low-ash coal. The first two objectives were general objectives of the run. The third objective was addressed in material balance period A, which was a comparison with period 257J (Illinois 6 coal). This was a short test made with half-volume reactors and Amocat 1C catalyst. The fourth objective was addressed in period H. Operating variables for Run 259 were reactor volumes (50 vs 100%) coal feed rate (~230-356 MF lb/hr), coal ash content (standard coal (~15.0 wt %) vs deep-cleaned coal (~4.5 wt %)), coal concentration in the slurry (30-33 wt % MF), first-stage temperature (810-825°F), catalyst type (Amocat 1C vs Shell 324), catalyst replacement rate (0-4 lb/T MF coal, each stage), and catalyst age (0 to about 3200 lb (res + UC)/lb cat, depending on catalyst type and reactor).

Operating conditions (1) for those periods from which we were supplied samples appear in Table 1. Operating conditions and yields (1) for material balance periods appear in Table 2. A diagram of the Wilsonville plant, as configured for Run 259, appears in Figure 1. Run results were presented elsewhere (2).

The highest distillate yield obtained in Wilsonville Run 259 was 74 wt % MAF coal during period E (Table 2). With complete resid extinction, yield is projected to be 78 wt % MAF coal. Run 259G results were nearly identical to 259E results, although they were obtained at a somewhat lower space velocity. The deep-cleaned coal gave 4 wt % higher MAF coal conversion, 11 wt % higher MAF distillate yield, and 10 wt % lower MAF organic rejection than the higher ash Ireland plant product. Because resid extinction at higher space velocity was demonstrated with the high-ash coal, the distillate production (in pounds-per-hour) with the higher ash coal is projected to be about 20% (relative) higher than with the low-ash coal. However, it requires about a 45% higher MF coal feed rate, since the distillate yield is lower. The increased gas-oil recycle resulting from improvements to the distillation system made prior to the run was found to improve net distillate product quality (the boiling end-point was lowered to 750°F).

Beginning with Run 259, changes made to the distillation section of the plant became operational. A description of these changes is given below. The changes were made so that a better boiling cut point could be achieved for separation of plant product oil and recycle solvent. Additional changes were made to the process streams involved in solvent recycle.

The distillation system modifications consisted of changes in and around the T-102 distillation column, which separates the middle distillate product from the recycle solvent. In the early part of Run 258, the T-102 column stopped functioning properly and was taken off-stream for the duration of the run. During and after Run 258, changes were made to the column internals and the flow schemes around the column were revised. Prior to Run 259, column T-102 produced two overhead mid-range distillates streams, P-171 (the lightest) and V-138. Beginning in Run 259, the T-102 overhead liquids were combined into a single middle-distillate stream, V-182. The T-102 bottoms are sent to a solvent inventory tank (V-1074) and then recycled to the first stage, as has been done in the past. In the past, however, a portion of the V-1067 flashed bottoms product also was recycled directly. The V-1067 material is the feed to the vacuum flash. It contains ash, IOM, resid and distillate-range material. The V-1067 stream represents the recycled material prior to fractionation. In prior runs, the V-1074 stream and the deashed resid from the ROSE-SR unit constituted the remainder of the recycle solvent. Beginning in Run 259, the V-1074 stream will be the only source of distillate solvent for recycle. All of the V-1067 material will be sent to the vacuum flash unit, V-1082. The other two components of the recycle solvent are the V-1082 bottoms stream (i.e., the ROSE-SR unit feed stream, which contains the resid, IOM and ash portion of V-1067) and the deashed resid. The differences in former and present recycle flows can be summarized as follows: formerly a portion of the V-1067 stream was recycled directly, now it is all fractionated in T-102 and a portion of the T-102 bottoms is recycled instead. The other two recycle streams have not changed, except that the relative flow of V-1074 has increased.

ABBREVIATED HISTORY OF RUN 259

This section is paraphrased from Wilsonville technical review meeting handouts (1). On January 18, 1990, Run 259 started up feeding Ireland plant product coal in the catalytic/catalytic CC-ITSL configuration with ash recycle. The start-up solvent was from Run 258 in which Black Thunder subbituminous coal was fed. Each reactor used 50% of the available volume and was charged with 110 lb of 1/12" bimodal Amocat 1C catalyst previously used during Run 257 with Illinois 6 coal. The catalyst replacement rates in the first/second stages (reactors R-1235/R-1236) were 3.0/1.5 lb/T MF coal. The interstage separator was in use in order to improve interstage sampling and provide higher purity hydrogen to the second stage. The start-up conditions were 235 lb MF coal/hr coal feed rate, 50 wt % resid and 12 wt % cresol insolubles (CI) in the recycle solvent, 2.0 solvent-to-coal ratio, and first/second-stage temperatures of 790/760°F. A new feature in Run 259 was the implementation of distillation improvements to distillation column T-102, which distills the mid-range products (350°F+ overheads). This modification enables a clean cut point between plant distillate product and heavy solvent for recycle. In practice, solids recycle was sent from V-1082 vacuum flash bottoms (30-40 wt % CI, 60-70 wt % resid) instead of V-1067 (16-17 wt % CI, 35 wt % solvent, 48-50 wt % resid), thereby allowing all the distillate to be sent to the T-105/T-102 distillation system.

On January 21, the first-stage temperature was increased from the 790°F start-up value to the target value of 810°F. On January 22, the hydrogen purity in the first stage was increased from 85% to 92%. On January 26, more insulation was placed on the heads of both reactors. This reduced heat loss, resulting in higher delta Ts across the reactors. Prior to January 28, the coal conversion was low. Plant personnel attributed this to the subbituminous start-up oil which was eventually displaced by bituminous oil. On January 29, 12 wt % of the first-stage catalyst charge and 16 wt % of the second-stage catalyst charge was replaced by fresh catalyst. This adjusted the catalyst ages to the target equilibrium values (necessitated by an error in calculations). Some increase in the exotherm on the first-stage reactor was observed when new catalyst

was added for catalyst addition/withdrawal. From January 29 to shutdown on February 9, the R-1235 catalyst bed exotherm increased from -4.6 (relative) to 6.8 (relative), while the R-1236 catalyst bed exotherm remained fairly constant at 3.6 (relative). The T-102 column bottoms pump did not perform well prior to February 2, resulting in some column instability. On February 3 and 4, a relief valve on the first-stage reactor was leaking. This was expected to cause low gas yields, however, plant personnel believe that the total error in plant material balances amounted to only ~1 wt % MAF coal. February 5-9 was taken as material balance period A. However, it was considered unstable for several reasons: 1) there was ash carry-over in the ROSE-SR unit, 2) the interstage sample analyses were widely scattered, and 3) there was a large variation in distillate yield from about 40 to about 53 wt % MAF coal.

It was reported that sometime during the period from start-up to February 10 (no date specified), cavitation in the first-stage ebullation pump caused the gas rate to be below the target value. It also was generally reported that second-stage preheater temperature was very high, which plant personnel believe may affect resid conversion. On February 10, storm damage forced an early shutdown of the run. The Amocat 1C catalyst was withdrawn and both reactors were modified to operate with 100% of the available volume. The reactors each were charged with 440 lb (dry) fresh 1/16" Shell 324 unimodal catalyst on February 24-25 and presulfiding was performed. Two attempts to restart the run were made on February 28. However, plugging of the R-1235 plenum chamber required shutdown to remove the bottom head. On March 2, catalyst which had clumped together in the first-stage reactor was replaced with fresh sulfided Shell 324 catalyst. The fresh hydrogen compressor capacity was inadequate for the first-stage preheater and reactor. Therefore, on March 2 the first-stage preheater was supplied from a recycle hydrogen compressor.

The run was restarted on March 3. Each reactor contained 440 lb of fresh presulfided Shell 324 catalyst. The reactors were operated at 810/760°F after restart. The recycle solvent composition was 50 wt % resid and

12 wt % CI and a solvent-to-coal ratio of 2 was used. Batch aging of the catalyst was performed. Feed pump problems caused the flow to the first stage to be erratic in the early part of this portion of the run. The coal feed rate was increased to 400 MF lb/hr on March 5. On March 9-10, the unit was down for about 24 hours due to rupture of Dowtherm lines. When it came on-line, the catalyst in the reactors clumped together. A catalyst withdrawal, wash with V-182, and re-addition of catalyst to the reactor (March 12) were done to recover from the problem. During March 7-23 (during batch deactivation of the Shell 324 catalyst), the slurry viscosity was high enough that the circulating pumps would not operate properly. As a result, the coal concentration in the feed slurry was reduced from 33 to 30 wt % on March 13. A power outage occurred on March 16. Consequently, the coal feed rate was dropped to 350 MF lb/hr.

From March 14 to 18, both coal feed and gas rates were lowered several times to maintain hydrogen purity due to problems with the fresh hydrogen compressor. The slurry viscosity continued to climb at 30 wt % coal concentration, causing intermittent problems with recirculation and feed pumps. The plant was off coal feed several times on March 18. On March 19, the second-stage temperature was increased to 790°F to decrease the amount of resid that was being drummed out. The unit was taken off feed on March 19 due to problems in getting coal from the tote bin for slurry preparation. Soon after restart, the unit was shut down because of plugging in the plenum chamber of the R-1235 (first-stage) reactor. On March 20, catalyst was withdrawn and the first-stage reactor was cleaned out. Also on March 20, the compressor supplying hydrogen to the second stage failed. No material balance period was obtained from March 2 through March 20 because of the frequent operating problems.

On March 23, Shell 324 catalyst was added back to the first-stage reactor (R-1235) and the plant was restarted. Conditions were 810/790°F reactor temperatures, 300 MF lb/hr coal feed rate, 2.33 solvent-to-coal ratio, and 50 wt % resid and 6 wt % CI in the recycle solvent. Adjustments to the R-1235 catalyst charge were made on March 24 and 25, but otherwise the plant was operated without catalyst addition and withdrawal after the restart. These conditions resulted in a 60% reduction in slurry

viscosity. Smooth operation after March 23 was attributed mainly to the reduced coal feed rate. A short material balance period, 259B, was obtained during March 26-28 at 6 wt % CI concentration. On March 29, the target CI concentration in the recycle solvent was changed to 12 wt % due to improvement in operability of the plant. This did not adversely affect plant operation, even though it was accompanied by an increase in viscosity. However, the viscosity declined steadily between March 29 and April 26. On March 30, an interstage separator restriction caused all material to be sent to the second stage during repair (i.e., no separation took place). During April 1-4, period C was obtained at 810/790°F and 12 wt % CI concentration. Catalyst addition and withdrawal at 4 lb/T MF coal per reactor stage began on April 3 for the first stage and on April 4 for the second stage. The first-stage temperature was set to 825°F on April 7 in order to improve resid conversion. Material balance period 259D was obtained at these conditions.

In order to obtain an "all distillate" product, the coal feed rate was lowered to 265 MF lb/hr on April 14. Material balance period 259E was obtained at this coal feed rate. To determine the effect of reduced resid concentration on the product distillate boiling endpoint, the resid concentration in the recycle solvent was lowered from 50 wt % to 40 wt % on April 21. Period 259F was obtained at this resid concentration and 267 MF lb/hr coal feed rate. So that a greater effect of resid concentration on distillate boiling point could be seen, the coal feed rate was lowered from 270 to 230 MF lb/hr on April 27. Period 259G was obtained from April 30 to May 4 at these conditions.

On May 5, the plant began processing the high-ash Ireland coal at 320 MF lb/hr coal feed rate (increased from 230 MF lb/hr), 50 wt % resid in the recycle solvent (increased from 40 wt % in 259G), and 3.6 lb/T MF coal catalyst addition rate (each reactor). This catalyst replacement rate was equivalent to that used for the low ash coal, on a MAF coal basis. Excessive water carry-over to the T-105 tower feed tank from April 29 to May 7 may have affected the measurement of distillate streams. On May 7, the coal feed rate was temporarily reduced because of slurry recirculation problems. The coal conversion was lower than expected, and there

was insufficient resid recovered from the ROSE unit to blend the recycle solvent. Ash carry-over occurred when additional resid recovery was attempted. Therefore, on May 10 the coal feed rate was increased to 360 MF lb/hr to increase resid production. However, the 360 MF lb/hr coal feed rate was not high enough to maintain resid inventory resulting in depletion of the inventory to 13,000 lb (normally 18,000-20,000 lb). At low inventory levels, any process upset can cause the plant to shut down. Some tanks were operated below agitation levels during this time. The low inventory levels were attributed to differences between the lab analyses and the calculated recycle solvent resid content. Operation was considered marginally stable during this time.

A Dowtherm A leak into the V-1082 vacuum bottoms circulation line caused an outage on May 12 to repair the line. The run resumed on May 15. May 16-18 constituted balance period 259H. On May 18, a problem in the T-102 distillation column prevented obtaining a good vacuum in the column, and the column was down for repair for part of May 21. Since the fresh sulfided Shell 324 catalyst inventory was exhausted, catalyst from March 1 outage (clumped material) was used for catalyst replacements on May 20 and 21. On May 20-21, there were blending problems due to low recycle solvent inventory. The high-ash coal test was ended on May 21.

On May 22, the feed coal was again changed back to the deeply cleaned Ireland coal. Catalyst replacement in both reactors was stopped in order to batch age the catalyst to higher ages. The coal feed rate was set from 360 to 300 MF lb/hr. Cessation of catalyst addition and withdrawal significantly increased the coal slurry viscosity and reduced the first-stage reaction exotherm. This feed rate in combination with batch deactivation was helpful in increasing the recycle solvent inventory. Since the resid and recycle solvent inventories were increasing, the coal feed rate was reduced to 265 MF lb/hr on May 24 in order to continue batch deactivation at 259E conditions. Period 259I was obtained at these conditions. Due to a mislabeled tote bin, one batch of coal slurry prepared on June 2 or 3 (conflicting dates given) contained less than 30 wt % coal concentration; thus the coal feed rate was low. During batch deactivation, the slurry viscosity and resid preasphaltene

concentration continued to increase. Also during batch deactivation, the T-105/T-102 distillation columns were operated at conditions similar to those during catalyst replacement. This resulted in a continued decrease in heavy distillate (T-102 bottoms) production due to a decrease in resid conversion activity as the catalyst was aged. Near the end of the run, this caused difficulty in maintaining 38 wt % distillate content in the recycle solvent. Due to low recycle solvent inventories, the V-131B was operated below the agitation level in May and June. Lab analyses of V-131B after May 23 showed as much as 6 wt % more resid than the calculated stream blends. On June 4, the T-102 distillation column was down for several hours, due to outage of the preheater. Period 259J was obtained at the same conditions as 259I, except that catalyst ages were higher due to continued batch deactivation. The run ended on June 9, 1990.

SAMPLE DESCRIPTIONS

Consol received two feed coal samples and 31 process oil samples from Run 259. The coals received were Ireland Mine (normal plant product, pile sample, Wilsonville sample number 2715, sampled November 22, 1989, and received December 5, 1989) and deep-cleaned Ireland Mine coal (pile sample, Wilsonville sample number 2740, sampled December 4, 1989, and received December 20, 1989). Data also are reported for two laboratory coal samples evaluated by Wilsonville personnel prior to the run. Data for one of these, Wilsonville sample No. 95568, also was described in a prior report (3). The process oils consisted of a recycle oil (V-131B) sample, an interstage oil (R-1235) sample, and a product oil (V-1067) sample from each of the ten material balance periods A through J. An additional V-131B sample was supplied from period E. It was a composite taken during the period April 15-18, 1990. V-1067 is the second-stage flashed bottoms product. Although the interstage samples were labelled R-1235, R-1235 HP or R-1235 OTL, they will be referred to as R-1235 samples throughout this report. The HP suffix (and presumably the OTL suffix) designates that these samples were taken after the high-pressure flash (interstage separator in operation).

ANALYSES

Proton distributions were obtained by ^1H -NMR for each of the V-131B, interstage and V-1067 whole samples (Tables 11-13). All the whole samples were tested in the microautoclave at the modified equilibrium conditions (Table 21). Prior experience has shown that the microautoclave results may show high variability when the samples have high solids concentrations, as was the case in Run 259. The whole samples were distilled (Tables 5-7) to 320°C pot/270°C column/5 torr (850°F/atm). Each 850°F⁺ resid was analyzed by solubility fractionation (Tables 8-10), ^1H -NMR (Tables 17-19) and FTIR for phenolic -OH content (Table 20). Each 850°F⁻ distillate was analyzed by ^1H -NMR (Tables 14-16) and FTIR (Table 20). Microautoclave tests were made at the modified equilibrium conditions with each 850°F⁻ distillate (Table 21). Details of the sample work-up and analytical procedures have been presented elsewhere (10,11). All samples for proton distribution by NMR were dissolved in 99.96% deuterated pyridine (whole or resid samples) or in CDCl_3 (distillate samples) and integrated electronically. Selected samples were used to determine response factors for flame ionization detection of solubility fractions.

COAL AND PROCESS OIL PROPERTIES

Chemical and petrographic analyses of the plant product and deep-cleaned Ireland Mine coals are given in Tables 3 and 4. The deep-cleaned coal is lower in ash content and in total and pyritic sulfur contents, but slightly higher in oxygen content (by difference). Its ash is slightly lower in CaO and SiO_2 and slightly higher in Fe_2O_3 and Al_2O_3 . Petrography indicates that the deep-cleaned coal also has more reactive macerals and less inert macerals (mineral matter-free basis) than the conventionally cleaned plant product.

Properties of process oils from Run 259 are given in Tables 5 through 21 and presented graphically in Figures 2 through 12. The discussion is followed most easily by referring to the figures. Results presented for period E V-131B samples are averages from the two samples received.

Results from the two samples were in good agreement. Note that periods A and B are marked with asterisks because they represent unstable periods.

The compositions of the whole oils were fairly constant (Tables 5-7, Figures 2-4), except when intentional changes in certain operating conditions were made. These changes included lower recycled resid concentrations in periods F and G, higher coal ash content in periods A and H, and a lower recycled cresol insolubles (CI) concentration in period B. For most of the run (periods C, D, E, I, and J), IOM and ash levels were around 6 wt % each and 850°F⁺ THF-soluble resid and 850°F⁻ distillate stayed within a range of about 5 wt %. During these periods, V-131B oils contained about 20-25 wt % distillate and 62-66 wt % resid, the R-1235 oils contained about 22-27 wt % distillate and 57-64 wt % resid, and the V-1067 oils contained about 25-30 wt % distillate and 55-58 wt % resid. The concentration of THF-soluble 850°F⁺ resid found by Consol in the V-131B recycle oil was consistently about 12 wt % higher than Wilsonville's target resid concentration in the recycle blend. This difference results primarily from Wilsonville's use of a distillation endpoint of ~1050°F (4). Our resid concentrations include 850 x 1050°F material which is treated as distillate in Wilsonville's analytical scheme. Our oil composition data indicate a gradual increase in distillate concentration through the liquefaction system, from V-131B to R-1235, and then to V-1067. Lighter distillate liquids are not present in these samples. The sum of IOM and ash contents measured by Consol for each period agrees well with Wilsonville's target CI level in the V-131B recycle solvent. The relative levels of IOM and ash measured by Consol in the V-131B stream are sensitive to differences in coal conversion reported by Wilsonville (compare Table 2 with Table 5 and Figure 2).

Solubility fractions of the THF-soluble portion of the 850°F⁺ resids are shown in Figures 5 through 7 and given in Tables 8 through 10. Resid preasphaltenes in all samples generally increased from period A to period B or C, then decreased to period D or E, increased again to period F or G, and decreased to period H, and finally increased again to period J. The oil (hexane-soluble) contents of the resids generally mirror the

preasphaltene contents. Figure 5 shows a good example of this pattern in the V-131B resid data. Concentrations of preasphaltenes, asphaltenes and oils, were about 7 to 17 wt %, 18 to 26 wt %, and 57 to 75 wt %, respectively, in the V-131B and V-1067 resids. The interstage (R-1235) resids contained about 5 wt % more preasphaltenes and about 5 wt % less oils (hexane solubles) than the resids from the other two streams.

Resid and whole oil hydrogen aromaticities for all streams (Tables 11 to 13 and 17 to 19, Figures 8 to 10) increased from periods A through D, were approximately constant through period G, dropped for period H and then increased through period J. Distillate aromaticity (Tables 14 to 16, Figures 8 to 10) followed a similar trend, except that the aromaticity usually dropped slightly from period A to period B instead of increasing. The difference in aromaticity among the sample types was about 5% for the distillates, whereas it was about 10% for the resids. Distillate aromaticity ranged from 13 to 21%, and resid aromaticity ranged from 24 to 37%. The aromaticities of R-1235 distillates were about 1% higher than those of corresponding V-131B and V-1067 resids. The trend in distillate paraffinic hydrogen generally mirrored the hydrogen aromaticity trend (Figures 8 to 10). Hydroaromatic hydrogen (as indicated by cyclic β protons) stayed relatively constant through the run.

Phenolic -OH concentrations of V-131B distillates were virtually identical to those of their V-1067 counterparts (Tables 20 and Figure 11). For periods A, C, D, E and F, the V-131B and V-1067 resids also were equivalent; however, they differed somewhat in the other periods. Generally, each R-1235 distillate and resid was 0.1 to 0.2 meq OH/g higher in phenolic -OH concentration than its V-131B or V-1067 counterpart. Curiously, however, in period E, the phenolic concentration of V-131B, R-1235 and V-1067 resids were equivalent. The resid phenolic -OH concentrations of all streams increased from period A to C, decreased in period E, increased in period F, and decreased again in period H, and then increased again through period J. The distillate phenolic -OH concentrations followed a different pattern. They dropped from period A to B, then increased in period D, decreased in period H, and then

increased through period J. Responses to run conditions will be discussed in specific sections of the report. For V-131B and V-1067 samples, the distillate phenolic -OH concentration ranged from 0.11 to 0.27 meq/g sample, and the resid phenolic -OH concentration ranged from 0.57 to 0.81 meq/g sample. For the R-1235 samples, the distillate phenolic -OH concentration ranged from 0.23 to 0.47 meq/g sample, and the resid phenolic -OH concentration ranged from 0.62 to 1.01 meq/g sample.

The V-131B distillates were equivalent to their V-1067 counterparts in donor solvent quality (Table 21, Figure 12). Likewise, the whole oils are very similar in donor solvent quality. In almost all periods, the whole oils gave lower donor solvent quality in microautoclave tests than their distillate-only counterparts (Table 21, Figure 12). The exceptions were the V-131B and V-1067 samples from periods A and B. In period A, the V-131B and V-1067 whole samples gave about 7% MAF higher conversion than the corresponding distillates. In period B, the whole sample results were about equivalent to the distillate results for the V-131B and V-1067 samples. In all cases, the whole R-1235 samples gave worse results than their distillate counterparts. Also, in almost every case the donor solvent quality of R-1235 samples (whether distillates or whole oils) were lower than their V-131B and V-1067 counterparts. The exceptions occurred in periods A, D, and G. In unstable period A, the distillate samples were all equivalent in donor quality. In period G, the V-131B and R-1235 samples were equivalent in donor quality, and only slightly lower than the V-1067 oil. The V-131B and V-1067 whole oils from period D gave exceptionally low donor qualities in the microautoclave test. Those two results may be spurious. However, microautoclave results from the V-131B and V-1067 whole oils track each other quite well throughout the run, including period D. No repeats of these tests were performed, and no other data from these samples indicate why the period D results would be so low. An extremely low microautoclave conversion typically results from coking of the sample. In the absence of experimental problems, coking indicates a low availability of hydrogen, poor solvent quality, or other factors which result in retrogressive reactions. Note also that the R-1235 whole oils from periods I and J gave extremely low conversions in the microautoclave tests. As

in the case of the period D oils, it is difficult to determine if the values are spurious or really indicate extremely poor donor quality. Poor donor quality for the I and J samples is reasonable, since aromaticity and resid concentration was high for those periods; however, the results are lower than one might expect, a priori. The donor solvent quality of whole oils during Run 259 was typically poor to fair. These results suggest that there were a few periods of particularly poor whole oil solvent quality (for certain streams). Other than the general observations made in this section, little further discussion of whole-sample microautoclave results will be presented.

In general, distillate donor solvent quality of V-131B and V-1067 oils was fair for periods A through C and good for periods D through J. The best distillate donor solvent qualities occurred in periods F through H. Consistently, the higher distillate donor solvent quality occurred in period H. The reader is referred to the section on the effect of coal cleaning for discussion on resid quality and performance in period H. The R-1235 distillates had generally fair solvent qualities. V-131B and V-1067 whole samples had good donor solvent quality in periods A and H, but the donor quality in periods B, C, E, F and G was nearly as high (though only considered fair). The R-1235 whole samples had fair donor quality only in periods G and H, being poor in the other periods.

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 22). The 850°F⁺ conversions then were used to calculate conversion rate constants and conversion activities (Table 23). The conversion and kinetic calculations were made as described elsewhere (3). 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 (3).

Conversions of 850°F⁺ resid and its components calculated for each reactor stage and total system are given in Table 22. Figure 13 shows the first-stage and total 850°F⁺ and coal + IOM conversions for Run 259. It is clear that: 1) the 850°F⁺ first-stage and total conversions varied within a range of ~12% absolute (ignoring period A), and 2) the second stage provided very little additional conversion of coal + IOM, but provided a substantial part of the total 850°F⁺ conversion. Given in Figures 14-17 are the conversions of the 850°F⁺ resid components and their averages and standard deviations (periods A and B are excluded). With few exceptions, the first stage shows net yields (negative conversions) of the soluble resid and its various components (Figures 14-17). The resid component conversions vary over a larger range than the 850°F⁺ and coal + IOM conversions. On the average, the total conversion of all three soluble-resid components is slightly negative, indicating that there is a small net yield of each component. In each period, the second-stage conversion of soluble-resid components is positive, so there is net conversion of the resid components in the second stage. The trends for each of the oil (hexane-soluble) fractions generally follows the trend observed for the THF-soluble resid, since it is the largest component in the resid. Period H shows relatively high first-stage conversion of the oils (hexane-solubles) fraction, but low conversions of asphaltene and preasphaltene fractions in that stage. Period H stands out as being much lower than the other periods in total preasphaltene conversion and higher than the other periods in total oil (hexane-soluble) conversion. Period H was operated with the high ash coal and, therefore, it had a high purge rate of ash concentrate (in which the preasphaltenes also are concentrated). The low conversion (high net yield) of preasphaltenes observed during period H appears to reflect this.

In Table 23, the 850°F⁺ conversions obtained by Consol are compared with those obtained by Wilsonville. The associated kinetic rate constants and conversion activities obtained by Consol are given. The average ratios of Consol conversions to Wilsonville conversions (omitting unstable or transitional periods A and B) are 1.09 ± 0.06 for first stage, 0.86 ± 0.24 for second stage, and 0.99 ± 0.12 for the total system. The first-stage and total values are slightly higher than the corresponding global averages found for a comparison involving Wilsonville Runs 250 through 257 (3). Historically, the conversions obtained by Consol tend to be slightly low relative to those obtained by Wilsonville because of a difference in laboratory distillation conditions. Consol uses a 850°F atm equivalent distillation endpoint, whereas Wilsonville uses a 1050°F atm equivalent endpoint. Therefore, Consol is measuring conversion of 850°F⁺ material, but Wilsonville is measuring conversion of 1050°F⁺ material. The effect of this difference on measured conversions has been discussed elsewhere (3).

The kinetic rate constants and conversion activities for each reactor stage are given in Tables 23 and the activities are plotted in Figure 18. The first- and second-stage conversions and derived kinetics from period A are highly questionable. It appears that the interstage sample was not representative or that its analysis was incorrect. Since the total conversion for period A is reasonable and is close to the Wilsonville value, it is not in question. Reasonable estimates for the first- and second-stage 850°F⁺ during period A are 20.0 and 11.0%, respectively (based on a comparison of Consol results with Wilsonville results for other periods during the run). These estimates produce values for the rate constants and conversion activities which are much higher for period A than for the rest of the run (Table 23). In general, the activities for periods B through J of Run 259 are extremely low, especially in the first stage. In contrast, the estimated activities for period A are reasonably high. The extremely low activities after period A suggest that factors contributing to poor activity were the use of unimodal Shell 324 catalyst and/or the change in reactor dynamics associated with 100% reactor volume (relative to 50% volume operation in period A). The change back to the high-ash coal in period H seemed to increase conver-

sion activity by a small amount (Figure 17). Perhaps the return to high ash coal (along with other changes in conditions) was too brief to overcome the effects of prior processing at conditions B through G. The significance of the feed coal, per se, as a factor in the unusually low activity after period A is unknown. When low-ash coal is fed, less resid is rejected from the process. This may allow a build-up of refractory resid in the system which would cause poor overall activity. A return to high-ash coal would gradually purge the system of refractory resid, with a higher rate of rejection of refractory resid. This is consistent with the high yields of preasphaltenes during period H, if period H was taken before fully lined-out operations had been established. It also is possible that the mineral matter has some catalytic activity, which accounts for higher activity with the high-ash coal. It is not clear how long it would take for the system to equilibrate after switching to the high-ash coal, but with a resid inventory of 5 to 10 tons and a coal feed rate of 4 tons/day (as in period H), it must be many days. In general, the conversion activity after period A was quite low and showed little variation from period to period. Because the conversion activity depends directly on WHSV, it is possible that the kinetic expression used is inadequate to correct for temperature or other effects (such as higher-order effects). In this context, the observed trend in the reactivity over the course of the run may be dominated by WHSV and limited by the assumptions made in order to perform the calculations (e.g., that first-order kinetics apply and the assumed energy of activation).

EFFECT OF TEMPERATURE INCREASE IN FIRST STAGE

The first-stage average reactor temperature was increased from 810°F in period C to 825°F in period D. No other process condition was changed. This resulted in an increase of 3-5 wt % in the concentration of 850°F⁻ distillate in the R-1235 and V-1067 whole oils, with a corresponding decrease in the amount of 850°F⁺ resid. First-stage and total resid + UC conversions measured by Consol and Wilsonville were higher as a result of the temperature increase, although the second-stage conversion was lower. Thus, as is commonly observed, a change in the first-stage temperature changed the balance of resid + UC conversion performed by

each reactor. The largest change observed in Consol conversion data from period C to period D was an increase of about 15 wt % in the 850°F⁺ THF-soluble resid conversion in the first stage. A small increase and decrease, respectively, is indicated in the 850°F⁺ conversion activity for the first and second stages. Wilsonville's yield data indicated higher distillate yield and lower resid yield in period D relative to period C.

Several properties of the process oils also changed in apparent response to the first-stage temperature increase. The distillate and residual fractions of all the process oils became more aromatic by 2-3%. The distillate fractions became correspondingly less paraffinic by 2-4%. The residual fractions of the process oils contained 5 to 7 wt % more oils (hexane solubles), at the expense of preasphaltenes and asphaltenes. Phenolic -OH concentrations in the residual fractions decrease by 0.1-0.2 meq -OH/g sample, but showed no change in the distillates. The distillate donor solvent quality (measured by microautoclave test) increased by 5-7 wt % MAF coal conversion.

The increase in aromaticity of the process oils accompanying a temperature increase in the catalytic first stage is unexpected and contrary to previous Consol experience with Wilsonville samples. In the absence of confounding factors or other explanations, these results suggest that the first-stage may have been at or near hydrogenation equilibrium conditions around periods C and D. From an equilibrium standpoint, lower temperature favor hydrogenation. If kinetic limitations are present (as is apparently the usual case at Wilsonville) then operation at a higher temperature can result in increased hydrogenation. The results presented here represent the first apparent indication (without apparent confounding factors) of Wilsonville operation of a catalytic stage at or near hydrogenation equilibrium. This situation may exist as a result of somewhat extreme conditions (low space velocity, high temperature and high catalyst replacement rate) in use. It also may reflect structural differences in the coals and derived liquids. Another explanation is that the higher temperature cracks alkyl side-chains and leaves behind aromatic groups. We suggested⁴ that hydrogenation in the second-stage during periods K and L of Run 254 (Ohio 6 coal) may have been

equilibrium-controlled; however, a catalyst age increase at the same time prevented a clear indication of the cause.

The phenolic -OH concentration decreased with the temperature increase, an expected response, but one which runs counter to the aromaticity increase. The aromaticity and phenolic -OH concentration of process oils is typically correlated in Wilsonville ITSL runs. The resid solubility component data, which show an increase in oils content, and decreases in asphaltenes and preasphaltenes, are consistent with the reduction in phenolic -OH concentration. These data indicate more upgrading in period D as a result of the temperature increase, probably through increased removal of heteroatoms. It is curious that the data indicate decreased hydrogenation (increased aromaticity) yet increased defunctionalization (decreased phenolic -OH and resid preasphaltenes concentrations).

The distillate solvent quality was improved by operation with the higher first-stage temperature, probably because of reduced paraffin concentrations.

EFFECT OF SPACE VELOCITY DECREASES

In going from period D to period E and in going from period F to period G, the only run condition which was changed was the coal feed rate, which was decreased (thereby decreasing the space velocity, as well). The coal feed rate was decreased from 300.5 To 266.7 MF lb/hr from period D to E, a decrease of 11%. Space velocity decreases were from 2.3 to 2.1 lb feed/hr-lb cat (first stage) and from 2.3 to 2.2 lb feed/hr-lb cat (second stage). On a different basis, the space velocity decreased from 36.9 to 32.7 lb MF coal/hr-ft³ cat (each stage) from period D to period E. From period F to period G, the coal feed rate was decreased from 267.5 to 230.0 MF lb/hr, a decrease of 14%. Space velocity decreases were from 2.1 to 1.8 lb feed/hr-lb cat (first stage) and from 1.9 to 1.7 lb feed/hr-lb cat (second stage). On a coal feed and settled catalyst volume basis, the space velocity decreased from 32.8 to 28.2 lb MF coal/hr-ft³ cat (each stage) from period F to period G. The relative decreases were slightly greater in magnitude in the F-G compar-

ison than in the D-E comparison. However, the absolute decrease in coal feed rate was nearly the same in both cases. In the F-G comparison, the plant was operated with 40 wt % resid in the recycle solvent, whereas in the D-E comparison it was operated with 50 wt % resid in the recycle solvent. A few changes in process oil characteristics were noted which correspond to changes in space velocity. These changes occurred in resid and whole oil properties, but not in distillate properties. For the D-E comparison, the changes described below were observed in the R-1235 resid sample, whereas for the F-G comparison, corresponding changes were observed in the V-131B resid sample. These changes associated with lower space velocity consisted of 8 wt % increases in the oils (hexane-solubles) contents of the soluble resid, a similar decrease in the asphaltenes and preasphaltenes contents of the resids, and decreases in resid phenolic -OH concentrations of about 0.2 meq -OH/g sample. The R-1235 resid sample in period E appears to be unusually low in phenolic -OH concentration, relative to the other two streams. These changes all are in the directions expected for lower space velocity.

The resid property changes, which were previously noted, occurred in the R-1235 samples in the D-E comparison, but in the V-131B samples in the F-G comparison. The V-131B and V-1067 samples in the D-E comparison and the R-1235 samples in the F-G comparison show little or no corresponding changes. Perhaps this resulted from differences in the resid reaction chemistry with 50% vs 40% resid in the recycle solvent. Wilsonville's conversion data show a shift in the relative amount of resid conversion that took place in the two stages when the resid content in the recycle oil was decreased from 50 to 40 wt %.

Consol results showed no significant consistent change in first-stage or total 850°F⁺ conversion from D to E, but from F to G the first-stage and total 850°F⁺ conversions increased by 8-10% absolute.

EFFECT OF DECREASE IN RESID CONCENTRATION IN RECYCLE SOLVENT

The concentration of resid in the recycle solvent was lowered from 50 wt % in period E to 40 wt % in period F. No other change in process

conditions was made between these periods. This change in resid concentration resulted in changes in the characteristics of V-131B and R-1235 resid fraction. The oil (hexane-soluble) contents of the resid fractions of these two streams decreased by 8 wt %. Corresponding increases in preasphaltene and asphaltene contents were observed. Phenolic -OH concentrations in the resid fractions from both streams increased by about 0.2 meq/g sample. No other oil characteristics showed significant changes. The increase in phenolic -OH concentrations is related to the increase in preasphaltenes concentration, since preasphaltene fractions have been found to be high in phenolic -OH.

It appears somewhat contradictory that lowering the resid concentration results in lower resid quality (higher preasphaltenes, higher phenolic -OH concentration). It seems that the worst-quality component (the preasphaltenes) has been concentrated in a smaller quantity of resid. When compared on a whole oil basis, the concentrations of preasphaltenes and phenolic -OH in the V-131B and R-1235 oils in period F are still higher than in period E. The reason for the decrease in resid quality is not completely clear. Because the concentration of the preasphaltene components can be influenced by several factors, including the recycle of various components and the ROSE-SR unit performance, a simple rationale for the observed oil property changes may not be sufficient. However, one explanation will be offered that seems consistent with the results in this comparison and a later one between the high-ash and low-ash coals. At a fixed concentration of CIs in the recycle solvent, the 40 wt % resid recycle solvent will contain 10 wt % less deashed resid than is contained in the 50 wt % resid recycle solvent (as measured at Wilsonville). Since deashing in the ROSE-SR unit is known to reduce the preasphaltene content (and sometimes the asphaltene content), deashed resid is expected to be higher quality (which could be measured as lower aromaticity, lower phenolic -OH concentration, and higher oil concentration in the resid). The 40 wt % resid case should have lower resid quality because a larger fraction of the resid has not been deashed. An alternative explanation is that at lower resid recycle, more of the resid is "virgin" coal product. This material is less hydrotreated than

recycled resid, and could show properties consistent with lower resid quality, as noted above.

EFFECT OF CATALYST AGE INCREASE

Between periods I and J, batch catalyst aging was in effect. The catalyst age increased from 1634 to 1918 lb (resid + CI)/lb cat in the first stage and from 1292 to 1529 lb (resid + CI)/lb cat in the second stage. Period 259E was operated with catalyst addition/withdrawal and at lower catalyst age (1115 and 966 lb(resid + CI)/lb cat in the first and second stages, respectively), but at the same conditions otherwise. No other process conditions differed between these three periods. A number of oil characteristics changed by a small amount from period I to period J. However, when period E also is considered, some of the responses are inconsistent. Inconsistent responses included distillate concentration in the whole oils and distillate aromaticity. Those changes which took place consistently with increases in catalyst age are described below. There were small (~3 wt %) decreases in the oil (hexane-soluble) contents of the resid fractions from all streams when the catalyst age increased. These were accompanied by corresponding small increases in asphaltene and preasphaltene concentrations. Aromaticity of resids from all streams increased by about 2% with each increase in catalyst age. The phenolic -OH concentration of distillate and resid fractions from all streams also increased by about 0.1 meq/g sample when the catalyst age was increased. Though small in some cases, these changes are consistent with loss in the hydrogenation and defunctionalization ability of the catalyst. There was no effect of catalyst age on donor solvent quality of distillate oils. The resid + UC conversion activity showed inconsistent changes with catalyst age.

EFFECT OF COAL CLEANING

The effect of coal cleaning can be examined by comparing data from period E, which used deep-cleaned Ireland coal (4.4 wt % ash, dry), with data from period H which used the normal Ireland plant product (14.8 wt % ash, dry). There were, however, other run conditions which differed

between these two periods, confounding a simple interpretation of the results. Period H was operated with a much higher coal feed rate than period E (355.7 MF lb/hr in H, 266.7 MF lb/hr in E). In order to keep catalyst replacement comparable on an MAF coal basis, the catalyst replacement rate in period H was 3.6 lb/T MF coal, whereas in period E it was 4.0 lb/T MF coal. Due to resid inventory problems, the resid concentration in the recycle solvent was slightly lower in period H than in period E (47.3 wt % in H, 50.4 wt % in E), although nominally they were considered to be the same (50 wt %). Catalyst age was slightly higher during period H. The high coal feed rate, lower catalyst replacement rate and higher catalyst age are expected to result in less hydrogenation (higher aromaticity), higher phenolic -OH concentration and perhaps generally poorer resid quality, based on Consol's past experience. To the contrary, however, the aromaticities of the resid fractions of all streams were lower by 3 to 4 % in period H relative to period E. All whole oils were 1 to 2 wt % lower in IOM and 2 to 7 wt % higher in ash during period H. The V-1067 resid, and especially the V-131B resid, contained higher concentrations of oils (hexane solubles) in period H relative to period E. This occurred at the expense of asphaltene and preasphaltene concentrations. However, the R-1235 resid showed the opposite effect, since it increased significantly in preasphaltenes at the expense of hexane solubles in period H. The preasphaltene increase of 8 wt % in the R-1235 resid was mirrored in a corresponding increase of 0.2 meq/g sample in the R-1235 resid phenolic -OH concentration ongoing from period E to period H. The donor solvent qualities of the distillate oils from periods E and H were equivalent. Note, however, that the donor solvent qualities of the whole recycle oils peaked in periods A and H, when the high-ash coal was fed. First-stage and total 850°F⁺ THF-soluble resid (no IOM) conversions obtained by Consol data were about 10 % absolute higher in period H than in period E. There was no change observed in the corresponding second-stage conversions of THF-soluble resid. The 850°F⁺ (including coal and IOM) conversions showed no significant change, being dominated by UC (or IOM, in our terminology) conversions which changed little. The 850°F⁺ conversion activities in both stages were somewhat higher in period H and in period E.

The lower resid aromaticity in period H relative to period E goes against the expected results based on operating conditions. Wilsonville personnel reported a higher resid + UC conversion rate constant for period H relative to period E. They offered the catalytic activity of pyrite as a possible cause, since it is present in substantially greater concentration in the higher ash coal. There is another factor hidden in the operating conditions which may affect resid composition (as in our data) or resid + UC conversion rate constants (as observed by Wilsonville). With a low-ash coal, the relative proportions of ashy resid to deashed resid in the recycle solvent is higher than with a high-ash coal. Rough numbers were calculated by Consol from Wilsonville data. Recycle solvent composition was 41 wt % non-deashed resid, 10 wt % deashed resid, 12 wt % CI and 38 wt % distillate in 259E and 30 wt % non-deashed resid, 17 wt % deashed resid, 13 wt % CI and 40 wt % distillate in 259H. The resid portion of the recycle solvent in 259E is about 20% deashed material (deashing removes some asphaltenes and preasphaltenes). In 259H, the resid portion of the recycle solvent is about 40% deashed material. It is possible that deashed and non-deashed resid behave differently, in donor properties and in "reactivity" (convertability to distillate). It is possible that some portion of observed differences in performance and oil characteristics between the two coals can be attributed to secondary effects such as this (which results from plant operating constraints). For example, we found the oil (hexane-soluble) fraction of a Wilsonville resid from a different run to have better donor solvent properties than the corresponding whole resid. (This work will appear in a quarterly report covering the period January 1 - March 31, 1991.) We note that there appeared to be no difference in Wilsonville's reported catalyst activity (naphthalene test) or catalyst carbon content, which would implicate catalyst performance differences between the two periods. Because of the confounding effects of some of these plant operating constraints, it is desirable to clearly understand them and, when possible, eliminate them by modifying procedures or even modifying the plant. The difference in the proportion of deashed and non-deashed resid in these two periods may explain the observed difference in resid quality, but the impact on overall performance is unknown. Note that an association of higher resid quality with higher deashed resid content is

reasonable and appears consistent between this comparison and a prior one relating to the resid concentration in the recycle solvent (periods E and F). From a performance standpoint, other explanations can be offered for better performance in period H with high-ash coal than in period E with low-ash coal. These include the catalytic activity of the mineral matter in the high-ash coal, and the lower purge rate of refractory resid when the low-ash coal is processed, as discussed previously in the section on kinetics.

COMPARISON OF RUN 259 WITH OTHER RUNS

Balance period A of Run 259 (declared an unstable period) was made as a comparison with period J of Run 257. Although operating conditions such as reactor temperature, catalyst age, and space velocity in period 259A were similar to period 257J with Illinois 6 coal, there were major operational differences. Distillation and recycle changes began to be used in Run 259. The interstage separator was used in Run 259, but not in Run 257. Because there is a region between the interstage separator and interstage preheater where no external hydrogen is supplied, the conditions for processing Ireland coal were less favorable than for the Illinois coal. The reduced hydrogen availability and high preheater outlet temperature between the reactor stages may have affected the reactivity of the Ireland coal resid toward conversion. Wilsonville measured lower first-stage resid conversion in period 259A, relative to period 257J. It was speculated that the resid reactivity was lower, as described above and that first-stage catalyst activity was low, since there was evidence for some loss of nickel in the first-stage catalyst. No other run periods are available for direct comparison. Nevertheless, it may be instructive to obtain a qualitative comparison of Run 259 results with those of prior runs. In the discussion to follow, three periods from Run 259 are compared with selected periods from Runs 254 (Ohio 6 coal) and 257 (Illinois 6 coal).

Table 24 shows the major operating variables for run periods being compared. Note that 257J is being compared with 259A, 257E with 259H, and 254I with 259E in three separate comparisons. The first comparison

is between Illinois 6 coal and the high-ash Pittsburgh seam coal (Run 257J and Run 259A) at 50% reactor volume. Other than the factors mentioned above, run conditions were the same in the two periods. The second comparison (257E and 249H) is between the same two coals, but at 100% reactor volume. There were differences in coal feed rate, catalyst type and age, first-stage, and second-stage temperature, coal concentration and space velocity in addition to the separator, distillation and recycle differences. The third comparison is between the low-ash Ohio 6 coal in period 254I and low-ash Pittsburgh seam coal in period 259E. There are differences in coal feed rate, catalyst type and age, first-stage temperature, space velocity, interstage separation, and distillation and recycle differences. The Ohio 6 coal comparison is of interest because it is the only other coal run at Wilsonville which is similar in rank to the Pittsburgh coal.

Some relevant process performance data are given below for these six periods.

Period	257J	259A	257E	259H	254i	259E
Distillate Yield, wt % MAF Coal	65.8	50.8	66.5	72.9	76.0	73.9
Resid Yield, wt % MAF Coal	1.2	19.5	2.1	-3.5	2.0	4.3
Ash Conc., wt % MAF Coal	18.5	19.2	18.8	20.2	6.7	8.9
TSL Coal Conversion, wt % MAF	91.7	91.2	92.6	91.4	96.6	95.2
Resid + UC Conversion, wt %	26.5	15.6	26.4	21.5	27.2	22.6
Feed	12.2	13.2	12.1	16.5	14.9	17.4
1st Stage	35.5	26.7	35.3	34.5	38.0	36.1
2nd Stage						
Total						

Differences in distillate yields between 257J and 259A and between 257E and 259H were substantial. In the first case, Run 259 results were worse

than the 257 results, whereas in the second case they were better. Results from 254I were slightly better than 259E.

Characteristics of oils and conversions and kinetic data from the six periods are compared in Table 25. In that table, "recycle distillate" refers to V-131B and V-1067. Run 259 solvent quality indices were lower than in their respective comparison periods 257E and 254I. The recycle distillate from period 259E was less aromatic than that from period 254I, but the interstage distillate and recycle and interstage resids were more aromatic than in period 254I. Period 259A samples were slightly more aromatic than in 257J, whereas period 259H samples were considerably more aromatic than in period 257E. Higher aromaticity indicates less hydrogenation if differences in coal structure can be excluded. Distillate paraffinic hydrogen was slightly lower in oils from period 259A than 257J, and higher in 259E oils than in 254I oils. Phenolic -OH concentration was slightly lower in the interstage distillate and resid from 259A relative to 257J. Phenolic -OH concentration was lower in the 259H distillates, but higher in the 259H resids, relative to period 257E. The oils from period 259E were all lower in phenolic -OH concentration than their 254I counterparts, except for the recycle resid. The Run 259 resid samples were lower in oils (hexane solubles) and higher in asphaltenes than their respective counterparts. The preasphaltenes were lower in 259A than in 257J resids. The recycle resid from 259E was higher in preasphaltenes than that from 254I, but the interstage resids were approximately equivalent. It is not known if the consistent differences can be attributed to differences in coal structure.

The data show that total 850°F⁺ conversion was higher in 259H than in 257E, but lower in 259A than in 257J and lower in 259E than in 254I. The conversions obtained by Consol were similar to those obtained by Wilsonville, although Wilsonville's are based on 1050°F⁺ conversion. It is evident that kinetic rates and activities were relatively low in Run 259. Note that an apparent bad interstage sample in 259A necessitates the use of estimated first- and second-stage conversions to obtain other kinetic information for period 259A. The kinetic rates and conversion activities were lower in the Run 259 periods relative to the comparison periods

(although in period 259A, they were similar to or only slightly lower than those in period 257J). The combination of Ireland low-ash coal and Shell 324 catalyst gave especially poor kinetic performance. The 259 resids were consistently more aromatic and contained less oils (hexane solubles) and more asphaltenes. All three Run 259 periods had higher second-stage 850°F⁺ conversions than their counterparts from the other runs - perhaps the use of interstage separation in Run 259 was a factor.

In summary, there is evidence which may indicate that there was less hydrogenation (especially in resids) in Run 259 relative to comparison periods. There are consistent differences in the resid compositions: the Run 259 resids contain less hexane solubles (oils) and more asphaltenes than those from the comparison periods. To the extent that these differences are not attributable to differences in coal structure, they appear due to differences in run performance. The relatively high resid aromaticities and resid asphaltene concentrations during Run 259, however, may indicate that the Ireland coal resid is somehow fundamentally different. Perhaps the asphaltenes produced are particularly difficult to convert to distillate. Poor kinetic performance of the first stage, especially for 850°F⁺ resid conversion occurred in Run 259, in spite of lower catalyst age than in the comparison period. Although the calculated distillate solvent quality index was slightly low during Run 259, it is difficult to assess its impact on performance. Furthermore, it tells us nothing about the residual material.

SPECIAL SAMPLES FROM WILSONVILLE RUN 258

INTRODUCTION

Because there was extensive interstage deposition in Run 258 with subbituminous coal, Wilsonville personnel were interested in any information which might relate to the cause of the problem. For this reason, they requested that Consol analyze deposit samples and interstage distillates from two periods of operation in which deposition took place. It was thought that analyses of the interstage distillates (the liquid portion of interstage separator overheads) and the R-1235 interstage samples (the separator bottoms previously analyzed by Consol) would provide clues to the nature of the material producing the deposits.

SAMPLE DESCRIPTIONS AND ANALYSES

Two samples of Run 258 V-1258 interstage separator deposit samples dated 7/17/89 (after period D, Wilsonville Sample No. 97678) and 11/17/89 (after period M, Wilsonville Sample No. 2700) were supplied by Dr. C. Cantrell at Wilsonville. Also supplied were two V-164 thermal distillate samples dated 7/14/89 (from period D, Wilsonville sample No. 97588) and 11/3/89 (from period M, Wilsonville sample No. 2406). The V-164 samples were from periods of operation preceding shutdowns because of deposit formation. For comparative purposes, two V-164 samples also were supplied from Run 259 (dated 4/14/90, period E, Wilsonville sample No. 5963 and dated 5/18/90, period H, Wilsonville sample No. 8637). The samples were from operation with Spring Creek coal (258D), Black Thunder coal (258M), low-ash Ireland coal (259E), and high-ash Ireland coal (259H).

Samples were analyzed by methods in routine use at Consol. V-164 and V-1258 samples were analyzed by ¹H-NMR for proton distribution. V-164 samples and the THF-soluble portion of V-1258 were analyzed by FTIR for phenolic -OH concentration. The THF-solubility and ash content of the V-1258 samples were determined. The THF-soluble portion of each V-1258 sample was analyzed by solubility fractionation.

RESULTS

Analytical results are presented in Table 26. Note that the V-1258 deposit from Black Thunder operation is virtually all coke-like, as indicated by the extremely high IOM content. The soluble-portion of this sample is higher in aromaticity and resid preasphaltenes, and lower in resid oils content than the other deposit sample. Wilsonville personnel noted a worse interstage plugging problem with Black Thunder coal than with Spring Creek coal. Consol's work with routine samples from Run 258 showed that process samples from Black Thunder operation were more aromatic than those from Spring Creek operation. This was largely due to differences in operating conditions during those portions of the run. High aromaticity may, however, relate to a higher coking propensity of process oils produced during Black Thunder operation. The interstage distillate samples from Run 258 (in which deposition occurred) were more aromatic, less hydroaromatic and less paraffinic than the interstage distillates from Run 259 (in which plugging did not occur). The Run 258 samples also were more phenolic than the Run 259 samples. These results are to be expected from a thermal first stage in Run 258, relative to a catalytic first stage in Run 259. Although they are more aromatic and phenolic than the Run 259 samples, the V-164 samples from Run 258 do not appear to be particularly unusual, based on experience with a variety of process oils from liquefaction.

Stream flow rates were provided by Wilsonville for periods D and M of Run 258 (6). The main deposition occurred in the line between the R-1235 first-stage reactor and the V-1258 interstage separator and in the separator itself. The flow of V-164, the separator overheads, was 96.3 lb/hr in period 258D and 123.0 lb/hr in period 258M. Corresponding flows of the separator bottoms (i.e., the interstage samples, which we are calling R-1235 samples) were 723.2 lb/hr in period 258D and 867.2 lb/hr in period 258M. The V-164 liquids comprised 11.8 and 12.4%, respectively, of the liquid flow from the first-stage reactor in periods 258D and 258M. The other 88% of the stream causing deposition was the usual interstage (bottoms) sample which we have referred to as the R-1235

sample. These samples were analyzed and reported previously by Consol (7).

The analyses of the R-1235 samples from periods 258D, 258M, 259E and 259H are compared in Table 27. The Run 258 samples were consistently more aromatic and less hydroaromatic than the Run 259 samples. The Run 258 whole samples contained more 850°F⁺ THF-soluble resid and more IOM than the Run 259 samples. The THF-soluble resid also contained more preasphaltenes and less oils than those from Run 259. The Run 258 distillates and resids were considerably more phenolic than those from Run 259. Although donor solvent quality (microautoclave test) was about the same for Run 258 and Run 259 distillate samples, it was worse for Run 258 whole samples than for Run 259 whole samples. Furthermore, the results for the 258M whole sample (produced during Black Thunder operation) were extremely poor, probably as a result of coking. It may be that the microautoclave test with whole samples provides a reasonable indicator of the real performance, from a standpoint of coke deposition. The combined factors of high aromaticity, high phenolic -OH concentration and high solids concentration (especially IOM) seem to point toward coke deposition as the cause of the Run 258 problem. Operation with a thermal first stage is certainly a factor in this, since thermal conditions keep the first two factors high. Phenolic species have been implicated as contributors to retrogressive reactions and highly aromatic liquids are expected to coke. It would appear that operational changes which lower any or all of these factors should help eliminate the deposition problem. These results appear to be consistent with the findings of an examination of the problem by Alan Davis and co-workers at Penn State (8). They concluded that coke formation was a major factor in the deposition when Black Thunder coal was processed. With Spring Creek coal, however, other factors such as calcium carbonate and pyhrotite were found to dominate.

SITE VISITS FOR PARTICIPANTS PROGRAM AND ANALYTICAL NEEDS ASSESSMENT

SUMMARY

Site visits were made to ten facilities (inclusive of U.S. DOE/PETC and MITRE Corp.) to discuss analytical needs as they pertain to direct coal liquefaction

TEAMING ARRANGEMENTS

Site visits were made to the facilities of eight of the nine technical proposers (see Reference 9). In chronological order, they were:

<u>Date of Visit</u>	<u>Organization</u>	<u>Host</u>
5/4/90	University of Kentucky (CAER)	F. J. Derbyshire
5/7/90	Advanced Fuel Research (AFR)	P. R. Solomon
5/15/90	Battelle PNL	J. A. Campbell
5/16/90	Western Research Institute (WRI)	F. P. Miknis
5/17/90	SRI International	R. Malhotra
5/18/90	NIPER	R. P. Anderson
6/5/90	Alberta Research Council (ARC)	R. J. Parker
6/27/90	The Pennsylvania State University	A. Davis

The purpose of these meetings was to discuss analytical needs related to direct liquefaction and to refine the proposed work for the collaborative effort to better fit those needs, within the guidelines of the contract. No binding arrangements were made during these meetings, and each proposer was to be contacted with a detailed work plan, based on the discussions of these meetings, during the fourth quarter of this contract. A set of recommendations for analytical work was drafted from each visit. These recommendations are listed below.

University of Kentucky

1. Microscopic Examination of Resids. The techniques here are well developed, but the application is novel. Therefore, this would appear to be an excellent fit with our project objectives. Consol will select five to ten archival samples to serve as a basis for a

"feasibility" test, to be followed by more recent samples from HRI or Wilsonville if the initial results warrant. We will request a more detailed description of the proposed analytical work from CAER to define the program plan and costs.

2. Group Separation/Radioisotope Incorporation. Because CAER has applied this technique only to pentane-soluble oils, its use at present is somewhat limited. However, the prospect of combining isotope labeling by incorporation of a reactant species with a simple LC separation and detection procedure makes this a potentially useful empirical test for resid characterization. We will evaluate the technique for the separation of heavy distillates (~1100°F) using both the quantitative FID detector and the incorporation of a radioactive label in phenol. Consol will select samples for a feasibility study and decide on reaction conditions based on CAER recommendations. We will encourage CAER to continue development of a technique applicable to residual pentane insolubles, and consider it for inclusion in the program at a later date if sufficiently developed.
3. Round Robin Analyses. CAER will be considered for participation in any round robin programs that are formulated, probably in the areas of quantitative NMR and solubility fractionation analyses.

Advanced Fuel Research

1. Quantitative IR (pellet) analysis of whole resids (including solids) and THF-soluble resids.
2. Quantitative IR of whole samples, including distillate.
3. The use of six to eight archival samples as a feasibility test.
4. TG⁺ analysis of whole and THF-soluble resids.
5. TG⁺ analysis of feed coals.

6. Analyses of samples from an HRI process demonstration run to assess catalyst age effects.
7. Analyses of samples from a current Wilsonville run to simulate on-line monitoring.

The application of on-line monitoring is somewhat problematic, because the current methodology is only applicable to distillates. It could be used to analyze product streams. However, our opinion is that these product streams are readily amenable to conventional methods of analysis, and therefore are of less interest in this project. The idea behind Item 7 above is to obtain conventional IR data on resid-containing process oil samples, to determine the potential benefits of on-line monitoring, and thus to provide an incentive for further development of the necessary methodology for an actual application.

It also appears that the availability of preheater exit samples from Wilsonville could be very beneficial in this program. We will explore the possibility of obtaining these samples with the Wilsonville personnel.

Battelle PNL

1. ^{13}C -NMR spectroscopy
2. Field Desorption Mass Spectrometry
3. UV-visible spectroscopy for on-line monitoring
4. Supercritical fluid techniques.

It would appear that much of the work could be centered on archival samples, similar to those used by Schindler to relate resid composition by ^1H -NMR to conversion kinetics. In the case of Item 3, an initial feasibility study could be followed by simulated off-line monitoring tests, perhaps using more current samples from various Wilsonville or HRI process streams.

Western Research Institute

It would be useful to assess the applicability of hydrogen accounting methods to process streams such as those at Wilsonville. The method requires total hydrogen consumption and heteroatom and hydrocarbon gas yield data, and the NMR analyses of the relevant coal and process oils.

We also should explore the use of spectral deconvolution to measure pseudocomponent contents of coals, resids, and converted products as a basis for an extended kinetic model. As a feasibility test, we could examine various coals and their products to determine the general qualitative applicability of the spectral data treatment to a broad range of materials.

Finally, we could examine the utility of using the aromatic H/C ratio as a process performance indicator. This would require the analysis of a number of samples, for example from material balance periods from Wilsonville or HRI runs, to relate the parameter to some other measure of process performance.

SRI International

The use of FIMS and the determination of alkyl carbon-oxygen bonds in resid-containing liquefaction oils are under consideration.

The trimethyliodosilane derivatization method appears to be a novel approach to determining at least some of the oxygen functionality. SRI believes that the method can be applied to residual oils with little additional development. Although more sophisticated methods, such as cyclic voltametry, could be used as an analytical finish, simple iodine quantitation could be used in initial work to evaluate analytical feasibility.

The application of FIMS profiling to a reasonably large sample set (10 to 20 samples) would allow a demonstration of the value of this technique. Samples would be selected to evaluate the utility of the FIMS

for addressing the resid reactivity issue, and factor analysis could be evaluated for data analysis.

The use of probe or tracer molecules could be of interest, if it can be linked to an analytical need. This is a topic for further discussion.

NIPER

Because of the poorly defined nature of coal-derived resids, we recommend that we pursue application of NIPER's methods to resids or resid-containing samples. The following items are recommended.

1. Quantitative preparative ABN separation of THF-soluble resids or whole samples and elemental analysis of the fractions. The separated fractions will be further analyzed as below, and possibly by other program participants.
2. HPLC to quantitatively speciate the acid and base components of THF-soluble resids or whole samples. The current procedure is to apply HPLC only to previously separated acid, base or neutral fractions. John Green noted that direct HPLC of the unseparated sample should be feasible with little development work. If so, a fast analysis of the acidic and basic components of oils would be possible. We may want to analyze separated acid and base fractions from several samples by HPLC for comparison.
3. Quantitative 2D-NMR of derivatized acid fractions from Item 1 and possibly non-aqueous titrations for comparison. We need to define the applicability of the 2D-NMR procedure for resid-containing samples with NIPER. The 2D-NMR and non-aqueous titrations would be performed only on a subset of the samples from Item 1 because of costs.
4. High-temperature GC analyses of THF-soluble resids or whole oils and comparison of results with SFC analysis. This item will be of

interest only if NIPER has successfully expanded the applicability of these methods to samples other than waxes.

Alberta Research Council

Resid characterization as related to conversion activity should be explored. Relevant areas in which ARC has particular expertise include:

- Separations
- Structure analysis
- ESR

Time limitations prevented us from fully defining a proposed program. However, Item 2 above, as applied to some of the samples sent for analysis to other subcontractors, could complement this program well. We also recommend further exploratory discussions on the potential use and benefits of ESR analysis.

The Pennsylvania State University

1. Qualitative microscopic examination of the gold tube carbonization product materials to compare and contrast different processing conditions and feed coals. The projected number of samples to be examined for the first phase of the work is twenty.
2. In order to provide some insight into process kinetics, petrographic identification of solid materials in the process streams and deasher would be made. If made available, samples from the preheater would fit into the program in this portion of the work. Approximately thirty samples initially would be examined.

The analytical needs, as were envisioned by these proposers, will be incorporated in the Analytical Needs Assessment document which will be submitted under separate cover.

OTHER VISITS AND CONTACTS

In addition to site visits with the eight proposers, visits were made to PETC and MITRE Corporation to discuss the analytical needs for direct liquefaction with personnel from these two organizations.

The following topics were discussed at PETC.

- There is a need to determine if standard petroleum tests, such as ASTM methods, are applicable to coal-derived products. Standard petroleum analyses are not considered completely appropriate for the material which is 650°F coal liquid. It may be necessary to develop a set of tests which are specific to coal liquids.
- Suggested was the use of calorimetry to analyze differences in aromatic ring condensation. It was noted that Delbert Etaugh (Univ. of Utah) is active in this field. His work has involved pure compounds. How this was applicable to mixtures was not discussed.
- Electrochemical techniques may be useful. Suggested was the utilization of chemical-specific electrodes (e.g., one just for thiophenic materials) to study resid materials. It was noted that Steve Weber (Univ. of Pittsburgh) is working in this area.
- The need for a better understanding of resid reactivity and the kinetics of resid conversion was discussed. It was noted that there is little information available on the kinetics of resid conversion, (even for petroleum resids) when the resid is recycled to extinction.
- Methods for looking at heteroatom removal need to be improved. Nitrogen is considered a special problem because levels greater than 1 to 10 ppm can deactivate some refining catalysts. Functional group analysis methods, such as derivatization/spectroscopic methods, would be useful here.

- Of considerable interest are methods to look at ether functionality. It was pointed out that no one single analytical method was useful for a direct determination of oxygen in coal liquids. A single direct determination method was considered very important.
- Methods to follow cracking reactions, such as occur during resid conversion, also are in need of development. Nuclear magnetic resonance (NMR) methods, including 2D-NMR, may be useful in this area.
- Analytical methods to determine ring size and condensation may be important to determine the reactivity of the resids. The questions to be answered include: Will a given type of aromatic ring structure in the coal or coal liquids crack or condense? How many rings in the system are naphthenic or hydroaromatic? Are the values obtainable from NMR analyses accurate? Can independent methods confirm NMR results? Can aliphatic groups on the rings be characterized in terms of number, position, size, etc? (NMR gives only averages). In what kind of structures are the rings located? How are they distributed? It was noted that combined rotation and magic angle spinning (e.g., CRAMPS) techniques show promise in addressing these questions.
- A determination of the solubility of hydrogen in the liquid phase is desired. A question of how it is dependent on the coal feed was raised. A method to measure the partial pressure of hydrogen in the outlet of the reactor system also is desired. It is generally unknown even for microautoclave and tubing bomb experiments. The work at the Univ. of Pittsburgh on an on-line hydrogen partial pressure meter was cited.
- The topics of coal cleaning and petrography were touched upon briefly. When coals are cleaned, macerals may be selectively rejected. How does this influence the convertability of the coal? Can the coal cleaning be tailored to reject only the "inert"

macerals which are largely responsible for these insoluble materials?

- There was a short discussion of the possibilities of using near infrared spectroscopic techniques for on-line analysis of liquefaction streams, though no specific application was identified.
- There was a general consensus that sampling the process stream between the preheater and the first reactor in the Wilsonville facility would be advantageous for study of the initial reactivity of the coal in the direct coal liquefaction process.

MITRE personnel provided recommendations for three general areas in which analytical work needs to be done.

1. The fate of resid in the integrated system. This will include a better model of resid upgrading, both thermally and catalytically, so that we have a better basis for reactor space velocities.
2. The extent of reactions in slurry tanks and preheaters.
3. The refining requirements of the raw liquid products so as to be more accurate in our estimations of upgrading costs to specification fuels.

Two samples were sent directly to Conoco from the Wilsonville facility. These samples will be analyzed by methods used for standard petroleum refinery feeds.

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 (10,11).

Section 4

REFERENCES

1. Southern Clean Fuels, Wilsonville Advanced Coal Liquefaction R&D Facility, Handouts from Technical Meetings No. 103 (March 14, 1990), No. 104 (May 16, 1990), and No. 105 (July 11, 1990).
2. Gollakota, S. V.; Davies, O. L.; Vimalchand, P.; Lee, J. M.; Cantrell, C. E. "Recent Progress at Wilsonville in the Direct Liquefaction of Two Low-Ash Powder River Basin Coals and a Deep Cleaned Pittsburgh Seam Coal", Proceedings of the Direct Liquefaction Contractors' Review Meeting, U.S. Department of Energy, Pittsburgh, PA, September 1990.
3. Burke, F. P.; Winschel, R. A.; Robbins, G. A. "Coal Liquefaction Process Solvent Characterization and Evaluation - Final Report", DOE Contract DE-AC22-84PC70018, August 1989.
4. Winschel, R. A.; Robbins, G. A.; Burke, F. P. "Coal Liquefaction Process Solvent Characterization and Evaluation, Technical Progress Report, January 1 through March 31, 1988", DOE Contract DE-AC22-84PC70018, March 1989.
5. Winschel, R. A.; Robbins, G. A.; Burke, F. P. "Coal Liquefaction Process Solvent Characterization and Evaluation, Technical Progress Report, July 1 through September 30, 1988", DOE Contract DE-AC22-84PC70018, March 1989.
6. C. E. Cantrell, Southern Clean Fuels, letter to G. A. Robbins, Consol R&D, dated April 4, 1990.
7. Robbins, G. A.; Winschel, R. A.; Burke, F. P. "Coal Liquefaction Process Streams Characterization and Evaluation, Quarterly Technical Progress Report, October 1 through December 31, 1989", DOE Contract DE-AC22-89PC89883, October 1990.
8. Davis, A.; Schobert, H. H.; Mitchell, G. D.; Artok, L. "Catalyst Dispersion and Activity Under Conditions of Temperature-Staged Liquefaction, Technical Progress Report for the Period April to June 1990", DOE Contract DE-AC22-89PC89877, August 1990.
9. Robbins, G. A.; Brandes, S. D.; Winschel, R. A.; Burke, F. P. "Coal Liquefaction Process Streams Characterization and Evaluation, Quarterly Technical Progress Report, January 1 through March 31, 1990", DOE Contract DE-AC22-89PC89883, February 1991.
10. Burke, F. P.; Winschel, R. A.; Robbins, G. A. "Recycle Slurry Oil Characterization Final Report - October 1983 through March 1984", DOE Contract DE-AC22-80PC30027, March 1985.
11. Winschel, R. A.; Robbins, G. A.; Burke, F. P. "Coal Liquefaction Process Solvent Characterization and Evaluation, Technical Progress Report, July 1 through September 30, 1985, DOE Contract DE-AC22-84PC70018, December 1985.

TABLE 1
DAILY OPERATING CONDITIONS FOR SAMPLES RECEIVED
Wilsonville Run 259

Date 1990	Operation Day	Balance Period	Coal Ash. wt % MF	First Stage					Second Stage		
				Avg. Temp., °F	Space Velocity		Catalyst Age		Avg. Temp., °F	Catalyst Age	
					lb feed/ cat hr	lb MF coal/ hr-ft ² cat	(Resid + Cl)/ lb cat	lb MF coal/ lb cat			
2-7	20	A*	15.0	809	6.8	74.5	1343	626	760	2717	1305
3-28	43	B*	4.81	810	2.4	37.0	934	407	790	748	401
4-5	51	C	4.82	810	2.5	38.9	1107	470	791	961	501
4-13	59	D	4.74	826	2.3	36.6	1125	473	790	968	501
4-17	63	E	4.68	825	2.1	32.9	1131	474	790	968	500
4-23	69	F	4.79	825	2.1	32.8	1132	475	791	961	499
5-2	77	G	4.58	825	1.8	28.2	1153	492	790	914	485
5-18	92	H	17.34	825	2.8	43.3	1270	536	790	1001	526
5-30	104	I	4.73	825	2.10	33.1	1651	691	791	1306	680
6-8	113	J	4.66	824	2.09	32.8	1971	821	791	1573	810

*Unstable or transitional operating period

For other conditions, see Table 2.

TABLE 2
CONDITIONS AND YIELDS - MATERIAL BALANCE PERIODS - Wilsonville Run 259

Representative Operating Period Date, 1990	259A (Unstable) 2/5-9	259B (Transit'l) 3/26-28	259C 4/1-2,4-6	259D 4/9-13	249E 4/16-20	259F 4/22-24,26	259G 4/30,5/1-4
Operation Days	18-22	41-43	47-48,50-52	55-59	62-66	68-70,72	76-80
Coal							
Feed rate, MF lb/hr	234.0	301.6	305.4	300.5	266.7	267.5	230.0
Ash, wt % MF	15.0	4.5	4.6	4.6	4.4	4.5	4.4
Conc. in slurry, MF wt %	33.0	30.0	30.0	30.0	30.0	30.0	30.0
Process Solvent, wt %							
Resid	48.0	50.9	49.3	49.9	50.4	39.5	40.3
Cl	12.5	5.9	12.0	12.0	12.0	11.6	12.0
First Stage							
Reaction temp., °F (avg)	810	810	810	825	825	824	825
Inlet H ₂ part. press., psia	2680	2640	2650	2610	2650	2,690	2710
Space velocity, lb feed/hr-lb cat	6.8	2.3	2.4	2.3	2.1	2.1	1.8
lb MF coal/hr-ft ³ cat	74.4	37.0	37.5	36.9	32.7	32.8	28.2
Catalyst type	Amocat 1C	Shell 324	Shell 324	Shell 324	Shell 324	Shell 324	Shell 324
Cat. age, lb (resid+Cl)/lb cat	1387+62	895+39	1122+23	1135+21	1115+55	1157+16	1141+16
lb MF coal/lb cat	647+25	385+13	475+8	479+8	485+6	484+7	487+6
Cat. replace. rate, lb/ton MF coal	3.0	0.0	4.0**	4.0	4.0	4.0	4.0
Second Stage							
Reaction temp., °F (avg)	760	790	790	790	790	790	790
Inlet H ₂ part. press., psia	2390	2510	2490	2500	2490	2490	2500
Space vel, lb feed/hr-lb cat	6.5	2.3	2.3	2.2	1.9	1.9	1.7
Space vel, lb MF coal/hr-ft ³ cat	74.4	37.0	37.5	36.9	32.7	32.8	28.2
Catalyst type	Amocat 1C	Shell 324	Shell 324	Shell 324	Shell 324	Shell 324	Shell 324
Cat. age, lb (resid+Cl)/lb cat	2710+60	718+33	925+27	959+18	966+24	940+15	924+13
lb MF coal/lb cat	1364+26	385+13	487+12	494+8	488+6	490+7	490+6
Cat. replace. rate, lb/ton MF coal	1.5	0.0	4.0**	4.0	4.0	4.0	4.0
ROSE-SR - DAS type	2474	2704	2704	2704	2664	2674	2644
Yield, wt % MAF Coal							
H ₂	-4.7+0.1	-5.9+0.3	-6.1+0.2	-6.6+0.2	-6.8+0.1	-6.3+0.4	-6.8+0.1
Water	5.6+0.9	6.4+0.3	6.4+0.5	6.7+0.5	6.7+0.8	7.1+0.4	6.5+0.6
H ₂ S, CO, CO ₂ , NH ₃	5.0+0.2	4.4+0.1	4.3+0.1	4.3+0.1	4.7+0.2	4.5+0.1	4.7+0.1
C ₁ -C ₃ gas	4.4+0.5	5.5+0.2	6.4+0.5	8.8+0.7	8.3+0.1	8.6+0.3	8.9+0.2
C ₄ +distillate	50.8+3.1	75.1+3.8	65.3+3.2	69.8+1.6	73.9+2.5	63.0+3.4	73.7+2.9
C ₄ naphtha	12.6+0.5	20.1+2.0	20.7+2.8	24.0+1.7	23.9+2.7	23.8+2.1	22.7+0.7
Middle disillate	5.8+0.3	9.5+0.7	9.3+0.5	10.5+0.3	12.1+1.3	9.4+0.2	10.3+0.4
Distillate solvent	32.4+2.7	45.5+3.7	35.2+4.9	35.2+2.8	38.0+3.4	29.9+1.5	40.7+3.0
Resid*	19.5+1.2	1.1+4.1	12.9+2.3	7.6+1.5	4.3+2.1	13.4+2.6	4.0+2.1
Ash concentrate (ash-free)	19.2+1.0	13.2+0.5	10.8+1.0	9.4+0.3	8.9+0.6	9.7+1.6	8.9+0.5
H ₂ Efficiency lb C ₄ +dist/lb H ₂ cons	10.7+0.8	12.7+1.1	10.7+0.5	10.6+0.2	10.9+0.5	10.0+0.5	10.9+0.5
C ₁ -C ₃ Selectivity to C ₄ +dist. (x100)	8.8+1.3	7.3+0.6	9.8+0.7	12.6+1.0	11.2+0.4	13.6+1.0	12.0+0.7
Coal Conversion, wt % MAF							
1st stage	89.8+0.6	93.4+2.9	93.3+0.6	91.8+0.4	92.8+1.0	93.8+0.7	93.1+0.6
1st and 2nd stage	92.3+0.3	94.9+0.2	95.3+0.1	95.5+0.1	95.7+0.1	95.7+0.2	95.7+0.1
Overall TSL	91.2+0.5	93.7+0.1	94.3+0.2	94.8+0.3	95.2+0.3	95.3+0.2	95.1+0.1
Resid + UC Conversion, wt % feed							
1st stage	15.6+2.0	18.5+1.2	16.3+1.4	21.9+0.7	22.6+1.7	20.7+1.2	25.5+1.1
2nd stage	13.2+3.3	22.1+1.1	19.2+1.4	16.9+1.5	17.4+1.8	20.0+2.5	20.6+1.9

*UC accumulation included
**Catalyst addition/withdrawal started April 3 and 4 in 1st and second stages, respectively.

TABLE 2 (Continued)
CONDITIONS AND YIELDS - MATERIAL BALANCE PERIODS - Wilsonville Run 259

Representative Operating Period	259M	259I	259J
Date, 1990	5/16-19	5/28-31	6/5-8
Operation Days	90-93	102-105	110-113
Coal			
Feed rate, MF lb/hr	355.7	268.0	265.5
Ash, wt % MF	14.8	4.5	4.5
Conc. in slurry, MF wt %	29.6	30.2	30.0
Process Solvent, wt %			
Resid	47.3	48.9	49.2
Cl	12.6	12.0	11.9
First Stage			
Reaction temp., °F (avg)	825	825	824
Inlet H ₂ part. press., psia	2713	2676	2684
Space velocity,			
lb feed/hr-lb cat	2.8	2.1	2.1
lb MF coal/hr-ft ³ cat	43.6	32.9	32.6
Catalyst type	Shell 324	Shell 324	Shell 324
Cat. age, lb (resid+Cl)/lb cat	1247+24	1634+46	1918+46
lb MF coal/lb cat	526+9	684+16	800+16
Cat. replace. rate, lb/ton MF coal	3.6	0**	0.0
Second Stage			
Reaction temp., °F (avg)	791	791	791
Inlet H ₂ part. press., psia	2503	2513	2510
Space vel, lb feed/hr-lb cat	2.7	1.9	1.9
Space vel, lb MF coal/hr-ft ³ cat	43.6	32.9	32.6
Catalyst type	Shell 324	Shell 324	Shell 324
Cat. age, lb (resid+Cl)/lb cat	1017+23	1292+38	1529+38
lb MF coal/lb cat	535+10	673+16	788+16
Cat. replace. rate, lb/ton MF coal	3.6	0.0	0.0
ROSE-SR SM - DAS type	2434	2644	2684
Yield, wt % MAF Coal			
H ₂	-6.2+0.2	-6.5+0.2	-6.0+0.1
Water	4.6+0.3	5.1+0.6	6.1+0.3
H ₂ S, CO, CO ₂ , NH ₃	5.4+0.2	4.2+0.1	3.9+0.1
C ₁ -C ₃ gas	6.0+0.4	8.4+0.3	8.2+0.3
C ₄ +distillate	72.9+2.9	64.5+1.3	57.0+2.3
C ₄ naphtha	18.6+0.3	19.3+1.6	19.6+0.9
Middle distillate	8.1+0.5	8.9+0.4	8.4+0.2
Distillate solvent	46.1+3.6	36.2+1.4	28.9+1.9
Resid*	-3.5+2.4	15.3+1.6	20.4+1.4
Ash concentrate (ash-free)	20.2+0.6	9.1+0.4	10.3+0.6
H ₂ Efficiency lb C ₄ +dist/lb H ₂ cons	11.7+0.3	9.9+0.2	9.6+0.4
C ₁ -C ₃ Selectivity to C ₄ +dist. (x100)	9.4+0.8	13.1+0.3	14.5+1.1
Coal Conversion, wt % MAF			
1st stage	91.4+0.5	93.8+0.9	92.2+1.0
1st and 2nd stage	93.0+0.2	96.0+0.1	95.4+0.1
Overall TSL	91.4+0.4	95.4+0.2	94.6+0.3
Resid + UC Conversion, wt % feed			
1st stage	21.5+0.9	19.3+1.7	17.7+0.7
2nd stage	16.5+1.6	16.8+1.9	14.5+1.3

*UC accumulation included

**Batch deactivation started on May 23.

TABLE 3
CHEMICAL ANALYSES OF IRELAND MINE (PITTSBURGH SEAM) COAL
Wilsonville Run 259

Sample	Plant Prod. (a)	1.3 S.G. Float (b)	Plant Prod.	Deep- Cleaned
Sample No.	95568	99630	2715	2740
Sample Type	Lab	Lab	Pile (Feed)	Pile (Feed)
Moisture, wt % as det.	1.92	1.39	1.86	0.85
Proximate, wt % dry basis				
Volatile Matter	40.35	43.81*	39.19	43.82
Fixed Carbon	50.50	52.12*	46.15	51.50
Ash	9.15	3.75	14.66	4.68
Ultimate, wt % MAF basis				
Carbon	-----	82.14	81.84	81.24
Hydrogen	-----	5.79	5.62	5.97
Nitrogen	-----	1.34	1.29	1.37
Oxygen (diff)	-----	7.00	5.91	8.07
Sulfur, Total	4.71	3.67	5.30	3.28
Pyritic	-----	0.46	2.64	0.71
Sulfatic	-----	<0.01	0.02	<0.01
Organic (diff)	-----	3.21	2.64	2.57
Chlorine	-----	0.059	0.048	0.065
HHV, Btu/lb MAF basis	-----	14994	14830	14807
Elemental, wt % of ash				
Na ₂ O	-----	0.95	0.44	0.35
K ₂ O	-----	1.59	1.96	1.48
CaO	-----	3.88	3.54	2.69
MgO	-----	1.02	0.83	0.79
Fe ₂ O ₃	-----	25.19	23.88	26.08
TiO ₂	-----	1.04	0.84	0.95
P ₂ O ₅	-----	0.12	0.35	0.12
SiO ₂	-----	38.88	46.00	40.24
Al ₂ O ₃	-----	24.23	19.93	22.70
SO ₃	-----	3.75	2.46	3.10
Unaccounted	-----	-0.65	-0.23	1.50

(a) From a one-gallon sample of candidate feed coal.

(b) 1.3 S.G. float sample from EPRI CQDC tests with 55-gallon sample of Ireland Plant Product.

*These values are from a separate analysis of the same sample that also gave: Moisture = 1.57%, Ash = 4.07% (dry), Total Sulfur = 3.68% (dry).

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TABLE 4
PETROGRAPHIC ANALYSES OF IRELAND MINE (PITTSBURGH SEAM) COAL
Wilsonville Run 259

Sample	Plant Prod. (a)	1.3 S.G. Float (b)	Deep- Cleaned
Sample No.	95568	99630	2740
Sample Type	Lab	Lab	Pile (Feed)
Mean Maximum Reflectance (R ₀), %	0.73	0.71	0.72
Maceral Analysis, vol. % (c)			
Reactives	82.0 (87.5)	89.0 (91.9)	88.0 (91.1)
Vitrinite	76.6 (81.8)	85.2 (88.0)	83.4 (86.3)
Type 6	22.0 (23.5)	37.0 (38.2)	25.3 (26.2)
Type 7	50.8 (54.2)	48.2 (49.8)	56.0 (58.0)
Type 8	3.8 (4.1)	-- (--)	2.1 (2.2)
Exinite	4.3 (4.6)	3.3 (3.4)	3.3 (3.4)
Resinite	-- (--)	-- (--)	-- (--)
1/3 Semifusinite	1.1 (1.2)	0.5 (0.5)	1.3 (1.3)
Inerts	18.0 (12.5)	11.0 (8.1)	12.0 (8.9)
2/3 Semifusinite	2.2 (2.3)	1.0 (1.0)	2.6 (2.7)
Micrinite	6.5 (6.9)	5.1 (5.3)	4.3 (4.5)
Fusinite	3.0 (3.2)	1.7 (1.8)	1.7 (1.8)
Mineral Matter, vol. %, as determined	6.3 (--)	3.2 (--)	3.4 (--)

(a) From a one-gallon sample of candidate feed coal.

(b) 1.3 S.G. float sample from EPRI CQDC tests with 55-gallon sample of Ireland Plant Product.

(c) Value in parentheses are on a mineral matter-free basis.

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TABLE 5
COMPONENT DISTRIBUTIONS OF V-131B SAMPLES
Wilsonville Run 259

Sample				wt % of Sample			
Date	Time	Number	Period	850°F Dist	THF-Sol. Resid	10M	Ash
2-07-90	1500	3831	A*	26.4	60.0	3.8	8.5
3-28-90	0650	5085	B*	28.9	64.5	2.9	2.7
4-05-90	1155	5486	C	25.5	61.7	6.1	6.1
4-13-90	1830	5918	D	24.3	62.9	5.9	6.4
4-17-90 (a)	1710	7024	E	25.0	62.6	5.6	6.1
4-23-90	2225	7337	F	35.6	51.4	6.0	6.5
5-02-90	1300	7875	G	33.8	53.2	5.8	6.4
5-18-90	2210	8645	H	24.0	63.5	3.6	8.1
5-30-90	0605	9214	I	20.5	65.7	5.8	6.5
6-08-90	0805	9688	J	24.4	62.6	6.2	6.2

*Unstable or transitional period.

(a) Average of 4/17/90 sample and composite period E samples

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TABLE 6
COMPONENT DISTRIBUTIONS OF V-1067 SAMPLES
Wilsonville Run 259

Sample				wt % of Sample			
Date	Time	Number	Period	850°F ⁻ Dist.	Resid	IOM	Ash
2-07-90	1500	3812	A*	29.5	52.0	5.3	12.1
3-28-90	1500	5102	B*	31.1	58.6	4.3	3.9
4-05-90	1500	5492	C	26.5	58.6	6.7	6.8
4-13-90	DC	5899	D	30.1	55.8	6.5	7.1
4-17-90	1500	7006	E	31.5	54.7	6.5	6.8
4-23-90	1500	7322	F	37.4	49.1	6.3	6.8
5-02-90	1500	7881	G	38.1	46.9	6.7	7.6
5-18-90	1500	8630	H	27.5	53.7	5.4	12.7
5-30-90	1500	9236	I	30.4	55.0	6.4	7.7
6-08-90	DC	9700	J	28.2	57.8	6.5	6.9

*Unstable or transitional period.

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TABLE 7
COMPONENT DISTRIBUTIONS OF R-1235 SAMPLES
Wilsonville Run 259

Sample (a)				wt % of Sample			
Date	Time	Number	Period	850°F ⁻ Dist	THF-Sol. Resid	IOM	Ash
2-07-90	0600	3796	A*	26.3	58.6	4.6	9.6
3-28-90	0600	5084	B*	26.9	63.5	4.5	3.6
4-05-90	0600	5476	C	22.0	64.1	6.4	6.3
4-13-90	1700	5912	D	27.7	58.6	6.4	6.6
4-17-90	1700	7000	E	26.2	60.4	6.1	6.3
4-23-90	1700	7335	F	33.0	53.3	6.6	6.5
5-02-90	0600	7858	G	34.4	51.4	6.7	6.8
5-18-90	0500	8602	H	25.7	57.0	4.9	11.3
5-30-90	0500	9213	I	21.9	64.3	5.8	6.8
6-08-90	1700	9699	J	24.2	62.3	6.3	6.3

(a) Samples from 2-7, 4-17, 4-23 and 5-2 were labelled R-1235 HP. Samples from 3-28, 4-5, and 4-13 were labelled R-1235 OTL. Samples from 5-18, 5-30 and 6-8 were labelled R-1235.

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TABLE 8
SOLUBILITY FRACTIONATION OF V-131B SAMPLES
Wilsonville Run 259

Date	wt % of THF-Soluble Resid		
	Oils	Asphaltenes	Preasphaltenes
2-07-90	72.5	20.6	6.8
3-28-90	61.9	23.2	14.9
4-05-90	59.4	26.1	14.4
4-13-90	66.4	23.5	10.1
4-17-90 (a)	67.4	22.5	10.1
4-23-90	59.9	25.3	14.8
5-02-90	67.2	23.1	9.7
5-18-90	75.2	17.5	7.4
5-30-90	63.3	24.5	12.2
6-08-90	60.6	25.0	14.4

(a) Average of 4/17/90 sample and composite period E sample.

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TABLE 9
SOLUBILITY FRACTIONATION OF V-1067 SAMPLES
Wilsonville Run 259

Date	wt % of THF-Soluble Resid		
	Oils	Asphaltenes	Preasphaltenes
2-07-90	71.6	21.5	6.9
3-28-90	56.9	25.8	17.2
4-05-90	59.1	25.3	15.6
4-13-90	65.5	25.0	9.4
4-17-90	65.4	24.2	10.4
4-23-90	63.7	24.1	12.2
5-02-90	66.7	22.2	11.1
5-18-90	68.5	20.4	11.0
5-30-90	64.4	23.3	12.2
6-08-90	60.4	26.1	13.5

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TABLE 10
SOLUBILITY FRACTIONATION OF R-1235 SAMPLES
Wilsonville Run 259

Date	wt % of THF-Soluble Resid		
	Oils	Asphaltenes	Preasphaltenes
2-07-90	64.7	21.8	13.4
3-28-90	53.3	25.6	21.0
4-05-90	54.6	27.3	18.1
4-13-90	59.1	25.6	15.2
4-17-90	65.8	24.2	9.9
4-23-90	58.6	23.8	17.6
5-02-90	55.7	25.5	18.8
5-18-90	59.8	23.6	16.6
5-30-90	55.5	26.5	18.0
6-08-90	54.8	26.6	18.6

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TABLE 11
PROTON DISTRIBUTIONS OF V-131B WHOLE SAMPLES
Wilsonville Run 259

Date	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
2-07-90	16.2	4.7	16.5	9.6	16.9	23.2	12.8
3-28-90	17.7	3.8	16.8	8.5	13.3	26.9	13.0
4-05-90	19.6	4.5	16.9	8.6	16.5	21.3	12.6
4-13-90	23.0	3.0	19.5	8.8	16.8	19.3	9.7
4-17-90 (a)	22.1	4.3	17.5	9.3	16.2	19.2	11.5
4-23-90	21.8	2.3	18.3	8.3	17.2	22.0	10.0
5-02-90	21.7	4.1	17.8	8.4	16.6	20.3	11.1
5-30-90	21.5	5.4	17.1	8.7	15.2	19.7	12.4
6-08-90	22.8	5.4	17.4	9.0	14.7	19.0	11.7

(a) Average of 4/17/90 sample and composite period E sample.
/ls

TABLE 12
PROTON DISTRIBUTIONS OF V-1067 WHOLE SAMPLES
Wilsonville Run 259

Date	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
2-07-90	16.2	4.3	16.9	9.8	18.0	22.3	12.5
3-28-90	16.3	5.1	15.4	9.2	16.7	22.2	15.2
4-05-90	18.9	4.1	17.9	9.0	17.6	20.6	12.0
4-13-90	20.8	3.8	18.6	9.2	17.3	19.3	11.0
4-17-90	20.6	4.2	17.5	8.9	16.6	21.0	11.1
4-23-90	20.3	2.9	19.1	9.3	17.7	19.8	11.0
5-02-90	18.9	4.8	16.8	8.7	17.4	20.4	12.8
5-18-90	18.5	4.0	17.8	8.9	18.5	20.7	11.6
5-30-90	20.8	4.2	17.9	9.0	17.0	19.7	11.5
6-08-90	21.6	5.4	17.9	9.5	17.0	18.3	10.3

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TABLE 13
PROTON DISTRIBUTIONS OF R-1235 WHOLE SAMPLES
Wilsonville Run 259

Date	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
2-07-90	16.8	5.3	17.0	9.8	17.4	21.2	12.5
3-28-90	18.5	4.8	16.6	9.1	16.8	21.8	12.5
4-05-90	20.6	4.9	17.5	9.0	15.6	19.9	12.4
4-13-90	24.5	3.1	19.2	9.1	15.7	18.2	10.2
4-17-90	23.7	3.8	18.5	9.4	16.0	18.2	10.4
4-23-90	23.3	3.2	19.3	9.2	16.2	18.6	10.2
5-02-90	22.3	4.9	15.8	9.2	16.5	19.9	11.3
5-18-90	18.4	5.9	15.9	9.6	15.8	20.8	13.6
5-30-90	21.0	6.8	16.1	9.5	14.7	19.1	12.8
6-08-90	23.4	6.7	16.6	9.5	14.0	17.8	12.0

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TABLE 14
PROTON DISTRIBUTIONS OF V-131B DISTILLATE SAMPLES
Wilsonville Run 259

Date	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
2-07-90	10.5	4.3	15.2	8.5	17.5	30.5	13.4
3-28-90	9.5	3.9	12.6	7.3	18.9	30.7	17.2
4-05-90	10.5	4.2	13.3	7.5	18.9	29.9	15.6
4-13-90	12.7	4.3	14.9	7.9	18.4	27.8	14.0
4-17-90 (a)	12.6	4.7	14.2	8.0	17.7	28.0	15.0
4-23-90	13.9	4.2	15.7	8.1	18.4	27.1	12.7
5-02-90	16.0	4.5	14.7	7.7	17.6	26.2	13.4
5-18-90	11.0	4.9	13.4	7.9	18.5	28.4	16.0
5-30-90	12.6	4.3	15.4	8.1	18.1	27.6	14.0
6-08-90	14.4	4.2	15.9	8.0	17.1	27.4	13.1

(a) Average of 4/17/90 sample and composite period E sample.

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TABLE 15
PROTON DISTRIBUTIONS OF V-1067 DISTILLATE SAMPLES
Wilsonville Run 259

Date	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
2-07-90	9.0	5.2	15.6	9.5	19.3	27.4	13.9
3-28-90	9.4	3.6	14.6	8.2	22.3	28.0	13.9
4-05-90	9.4	4.6	14.0	8.4	20.6	27.3	15.7
4-13-90	10.4	5.6	14.6	8.7	19.9	26.5	14.4
4-17-90	10.5	4.9	15.2	8.9	20.1	25.2	15.2
4-23-90	11.3	5.3	15.2	8.5	19.5	25.7	14.5
5-02-90	10.7	5.2	14.9	8.6	20.7	25.8	14.2
5-18-90	10.3	5.5	14.6	8.6	19.8	25.7	15.6
5-30-90	11.1	5.2	15.2	8.6	19.9	26.2	13.9
6-08-90	12.1	5.5	14.6	8.8	19.1	25.9	14.1

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TABLE 16
PROTON DISTRIBUTIONS OF R-1235 DISTILLATE SAMPLES
Wilsonville Run 259

Date	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
2-07-90	10.2	5.3	15.0	9.4	18.0	27.9	14.3
3-28-90	10.4	3.7	14.0	8.2	20.4	28.1	15.2
4-05-90	10.3	5.1	13.2	8.2	19.0	27.9	16.2
4-13-90	13.0	5.8	15.1	9.2	17.8	24.9	14.2
4-17-90	12.1	6.1	13.7	8.8	18.4	26.1	14.8
4-23-90	13.8	5.4	15.2	8.8	17.4	25.3	14.0
5-02-90	13.0	5.9	13.2	8.6	17.9	25.8	15.5
5-18-90	11.4	5.9	11.9	9.0	19.3	27.6	15.0
5-30-90	12.0	5.9	14.2	9.1	17.6	26.4	14.7
6-08-90	14.2	5.0	16.5	9.5	18.0	24.6	12.1

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TABLE 17
PROTON DISTRIBUTIONS OF V-131B RESID SAMPLES
Wilsonville Run 259

Date	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
2-07-90	20.5	4.6	19.6	9.5	16.9	18.4	10.6
3-28-90	24.6	1.6	21.7	8.9	17.3	16.9	9.1
4-05-90	25.5	4.4	20.6	9.5	15.4	15.6	9.0
4-13-90	28.1	4.0	21.3	9.4	15.3	14.1	7.9
4-17-90 (a)	27.1	4.6	21.0	9.4	15.1	14.5	8.5
4-23-90	28.9	4.1	21.2	9.2	15.1	14.2	7.4
5-02-90	29.4	3.4	21.4	9.2	15.3	13.9	7.3
5-18-90	24.2	4.3	19.4	9.0	15.6	17.2	10.4
5-30-90	27.5	4.2	20.7	9.2	14.9	15.2	8.2
6-08-90	28.6	5.6	19.9	9.2	14.0	14.0	8.6

(a) Average of 4/17/90 sample and composite period E sample.

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TABLE 18
PROTON DISTRIBUTIONS OF V-1067 RESID SAMPLES
Wilsonville Run 259

Date	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
2-07-90	20.2	3.8	21.4	9.5	18.0	17.7	9.4
3-28-90	25.7	2.6	21.7	9.0	16.7	16.2	8.2
4-05-90	26.2	4.4	21.0	9.5	15.6	15.1	8.2
4-13-90	29.2	3.6	21.6	9.0	15.1	13.9	7.7
4-17-90	28.8	4.2	21.7	9.2	14.7	13.6	7.8
4-23-90	28.6	4.7	21.4	9.2	14.4	13.7	8.0
5-02-90	28.7	4.0	21.5	9.4	15.3	13.6	7.5
5-18-90	24.8	3.6	20.4	9.2	16.2	16.8	9.1
5-30-90	27.7	5.9	19.8	9.4	14.3	14.2	8.7
6-08-90	30.1	5.2	21.3	9.6	13.6	12.6	7.7

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TABLE 19
PROTON DISTRIBUTIONS OF R-1235 RESID SAMPLES
Wilsonville Run 259

Date	Proton Distribution, %						
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
2-07-90	21.7	4.8	21.0	10.0	15.8	16.8	9.8
3-28-90	27.0	2.9	22.3	9.5	15.2	15.4	7.7
4-05-90	27.5	4.4	21.8	9.7	14.7	14.0	8.0
4-13-90	33.1	2.3	23.6	9.5	13.7	12.1	5.7
4-17-90	30.6	3.8	22.2	9.8	14.1	12.3	7.1
4-23-90	30.3	5.3	21.0	9.5	13.7	12.5	7.6
5-02-90	30.9	4.3	21.3	9.3	14.3	12.6	7.3
5-18-90	25.6	4.5	20.3	9.2	15.2	16.2	8.9
5-30-90	30.1	4.5	21.4	9.2	13.5	13.7	7.5
6-08-90	31.9	4.7	21.6	9.6	13.2	12.1	6.9

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TABLE 20
PHENOLIC -OH CONCENTRATION BY FTIR
Wilsonville Run 259

Date	Phenolic -OH Concentrations, meq/g											
	V-1318				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}
2-07-90	0.27	3311	0.70	3301	0.26	3314	0.70	3300	0.37	3312	0.87	3298
3-28-90	0.11	3311	0.69	3298	0.11	3315	0.75	3297	0.23	3311	0.93	3296
4-05-90	0.12	3310	0.77	3296	0.15	3313	0.78	3296	0.29	3310	0.98	3295
4-13-90	0.16	3308	0.62	3297	0.16	3311	0.65	3297	0.33	3309	0.80	3295
4-17-90 (a)	0.16	3307	0.64	3297	0.14	3311	0.62	3296	0.31	3309	0.62	3295
4-23-90	0.16	3308	0.78	3294	0.15	3310	0.68	3296	0.29	3308	0.87	3294
5-02-90	0.15	3308	0.60	3297	0.13	3311	0.63	3296	0.27	3308	0.84	3295
5-18-90	0.16	3308	0.57	3297	0.14	3311	0.67	3294	0.27	3310	0.81	3294
5-30-90	0.17	3307	0.69	3296	0.19	3309	0.75	3295	0.36	3309	0.91	3292
6-08-90	0.23	3305	0.76	3296	0.26	3309	0.81	3294	0.47	3307	1.01	3292

(a) average of 4/17/90 sample and composite period E sample.

TABLE 21
MICROAUTOCLAVE TEST RESULTS
Wilsonville Run 259

Date	Coal Conversion, wt % MAF					
	V-131B		V-1067		R-1235	
	Dist	Whole	Dist	Whole	Dist	Whole
2-07-90	77.9	83.3	78.4	84.0	77.3	56.0
3-28-90	76.6	79.9	76.4	75.3	70.5	65.5
4-05-90	74.7	70.9	75.7	72.9	70.0	51.5
4-13-90	82.0	49.2	82.1	54.4	74.9	64.3
4-17-90	81.8 (a)	73.8 (a)	81.4	78.8	75.9	64.3
4-23-90	84.4	75.6	83.8	80.1	78.6	64.7
5-02-90	85.3	73.7	84.4	77.8	80.2	74.5
5-18-90	85.5	81.1	83.4	83.2	78.2	73.1
5-30-90	83.2	69.4	83.6	61.6	75.3	42.0
6-08-90	81.6	66.5	83.8	69.8	75.6	46.3

(a) Average of 4/17/90 sample and composite period E sample.

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TABLE 22
CONVERSION OF RESID COMPONENTS
Wilsonville Run 259

Period	Conversion, %					
	850°F ⁺ (a)	Oils	Asphal- tenes	Preasphal- tenes	Coal + IOM	THF-Soluble Resid
<u>First Stage</u>						
A*	1.0	-44.2	-71.1	-218.5	83.3	-61.6
B*	19.3	-9.0	-39.7	-78.4	86.8	-26.6
C	16.9	-22.3	-39.2	-67.3	82.5	-33.1
D	24.8	-5.2	-28.7	-77.8	82.6	-18.2
E	22.8	-19.4	-31.6	-20.5	83.4	-22.3
F	21.0	-31.5	-26.5	-59.9	81.8	-34.5
G	29.2	2.4	-30.0	-128.2	82.5	-17.7
H	23.8	9.5	-53.4	-155.2	84.2	-13.8
I	22.8	-6.6	-31.5	-79.4	84.7	-21.6
J	19.3	-16.1	-36.6	-65.9	82.8	-28.4
All Periods:						
Avg ±S.D.	20.1 ±7.5	-14.2 ±16.0	-38.8 ±13.7	-95.1 ±57.0	83.5 ±1.5	-27.8 ±13.7
A,B Omitted:						
Avg ± S.D.	22.6 ±3.7	-11.1 ±13.6	-34.7 ±8.6	-81.8 ±41.9	83.1 ±1.0	-23.7 ± 7.5
<u>Second Stage</u>						
A*	28.1	22.1	30.6	63.7	8.6	29.6
B*	14.6	9.1	14.1	30.2	11.8	14.8
C	14.2	8.3	21.5	27.0	3.0	15.3
D	10.9	1.9	13.6	45.3	5.6	11.5
E	14.7	16.6	16.1	11.9	1.3	16.1
F	11.6	4.3	10.8	39.0	8.8	11.9
G	17.5	2.2	28.9	51.8	10.5	18.4
H	15.0	4.0	27.5	38.4	1.9	16.2
I	22.6	12.3	33.6	43.3	2.6	24.5
J	14.4	6.6	16.9	38.5	5.8	15.3
All Periods:						
Avg ±S.D.	16.4 ±5.2	8.7 ±6.6	21.4 ±8.2	38.9 ±14.1	6.0 ±3.8	17.4 ±5.6
A,B Omitted:						
Avg ± S.D.	15.1 ±3.7	7.0±5.2	21.1 ±8.1	36.9 ±12.3	4.9 ±3.4	16.1 ±4.1
<u>Total</u>						
A*	28.8	-12.4	-18.8	-15.5	84.8	-13.8
B*	31.1	0.9	-19.9	-24.5	88.4	-7.8
C	28.7	-12.2	-9.3	-22.1	83.1	-12.7
D	33.0	-3.2	-11.3	2.7	83.6	-4.6
E	34.2	0.5	-10.4	-6.2	83.6	-2.7
F	30.2	-25.9	-12.8	2.4	83.4	-18.4
G	41.5	4.6	7.6	-10.0	84.4	3.9
H	35.2	13.1	-11.2	-57.2	84.6	4.6
I	40.3	6.6	12.7	-1.6	85.1	8.2
J	31.0	-8.4	-13.6	-2.0	83.8	-8.8
All Periods:						
Avg ±S.D.	33.4 ±4.5	-3.6 ±11.3	-8.7 ±10.6	-13.4 ±18.1	84.5 ±1.5	-5.2 ±8.8
A,B Omitted:						
Avg ± S.D.	34.3 ±4.6	-3.1 ±12.3	-6.0 ±10.2	11.8 ±20.1	83.9 ±0.7	-3.8 ±9.2

*Unstable or transitional
(a) Includes THF-soluble resid and IOM.

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TABLE 23

850°F* CONVERSION AND KINETICS
Wilsonville Run 259

Period	First-Stage				Second-Stage				Total Conversion	
	Conversion (c)		K (a)	A ₁₀₇ (a)	Conversion (c)		K (a)	A ₁₀₇ (a)	Consol (d)	Consol (e)
	Consol (d)	W'ville (e)			Consol (d)	W'ville (e)				
A* (f)	1.0	15.60	0.07	0.13	28.1	13.20	2.54	9.66	28.8	26.7
B*	19.3	18.50	0.55	1.05	14.6	22.10	0.39	0.98	31.1	36.5
C	16.9	16.30	0.49	0.93	14.2	19.20	0.38	0.95	28.7	32.4
D	24.8	21.90	0.76	1.19	10.9	16.90	0.27	0.67	33.0	35.1
E(AV)	22.8	22.60	0.62	0.98	14.7	17.40	0.33	0.82	34.1	36.1
F	21.0	20.70	0.56	0.89	11.6	20.00	0.25	0.62	30.2	36.6
G*	29.2	25.50	0.74	1.17	17.5	20.60	0.36	0.90	41.6	40.8
H	23.8	21.50	0.87	1.38	15.0	16.50	0.48	1.18	35.2	34.5
I	22.8	19.30	0.62	0.98	22.6	16.80	0.55	1.37	40.2	32.9
J	19.3	17.70	0.50	0.80	14.4	14.50	0.32	0.79	30.9	29.6
A(EST) (g)	20.0	15.60	1.70	3.25	11.0	13.20	0.80	3.06	28.8	26.7
Avg (All)	20.1	20.0	0.58	0.95	16.4	17.72	0.59	1.80	33.4	34.1
± Std Dev	7.5	3.1	0.22	0.33	5.2	2.76	0.69	2.77	4.5	4.0
Avg (-A,B)	22.6	20.7	0.65	1.04	15.1	17.74	0.37	0.91	34.2	34.7
± Std Dev	3.7	2.9	0.15	0.19	3.7	2.04	0.10	0.25	4.6	3.3

Period	Ratio Consol/Wilsonville		
	Stage 1	Stage 2	Total
A* (f)	0.064	2.129	1.078
B*	1.043	0.661	0.851
C	1.037	0.740	0.887
D	1.132	0.645	0.940
E (AV)	1.009	0.845	0.947
F	1.014	0.580	0.825
G	1.145	0.850	1.018
H	1.107	0.909	1.023
I	1.181	1.345	1.225
J	1.090	0.993	1.043
Avg (All)	0.982	0.970	0.984
± Std Dev	0.328	0.462	0.120
Avg (-A,B)	1.090	0.863	0.988
± Std Dev	0.064	0.238	0.121

*Unstable or transitional

- (a) lb total feed/hr/lb catalyst
 (b) lb coal + resid + UC/lb catalyst
 (c) first stage and total conversion: wt % resid + MAF coal + UC fed to first stage.
 second stage conversion: wt % resid + UC fed to second stage
 (d) 850°F distillation end point, atm equivalent
 (e) 1050°F distillation end point, atm equivalent
 (f) Results for individual stages in period A are highly questionable.
 (g) Estimate based on assumed conversions of 20.0/11.0 wt % MAF in 1st/2nd stages, respectively.

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TABLE 24
COMPARISON OF WILSONVILLE RUNS 254, 257 AND 259
Operating Conditions

	257J	259A	257E	259H	254I	259E
Reference	5	This report	5	This report	4	This report
Coal	(a)	(b)	(a)	(b)	(c)	(d)
Coal Ash Content, wt % MF	11.2	15.0	11.4	14.8	5.94	4.4
% of Available Volume in Both Reactors	50	50	100	100	100	100
Coal Feed Rate	234.8	234.0	402.3	355.7	297	266.7
Coal Conc. in Slurry, wt % MF	33.3	33.0	33.2	29.6	29.4	30.0
Resid in Recycle Solvent, wt %	50	48	49.9	47.3	50.5	50.4
Cl in Recycle Solvent, wt %	12	12	12.1	12.6	12.2	12.0
Interstage Separator	No?	Yes	No	Yes	No	Yes
T ₁ , °F	809	810	791	825	811	825
T ₂ , °F	760	760	760	791	790	790
Catalyst	Am 1C	Am 1C	Am 1C	Shell 324	Shell 317	Shell 324
Cat. Age, lb (Resid + Cl)/lb Cat.	1367/2248	1387/2710	1434/2313	1247/1017	~1400/2400	1115/966
WHSV, lb Feed/lb Cat. -hr	6.7/7.0	6.8/6.5	4.3/4.3	2.8/2.7	3.5/3.4	2.1/1.9

(a) Burning Star 2
(b) Ireland High Ash
(c) Crooksville Low Ash
(d) Ireland Low Ash

Note: All runs catalytic/catalytic. Distillation and recycle changes were in effect in Run 259.

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TABLE 25

COMPARISON OF WILSONVILLE RUNS 254-257 AND 259
Process Oil Characteristics, Conversions and Kinetic Constants

	257J	259A (Unstable)	257E	259H	254I	259E
<u>SOI (a)</u>						
Recycle Distillate	78.4-80.6	78.9-81.6	81.8-83.0	78.0-81.2	84.0-85.6	76.8-82.4
Interstage	78.3	79.3	83.7	77.3	81.2	78.8
<u>Hydrogen Aromaticity, % of Protons (b)</u>						
Recycle Distillate	12.2-12.3	11.2-14.8	11.7-12.2	15.8-15.9	17.9-18.0	15.4-17.2
Interstage Distillate	14.0	15.5	12.5	17.3	17.2	18.2
Recycle Resid	22.1-23.3	24.0-25.1	18.9-19.8	28.4-28.5	29.6-30.7	30.4-33.0
Interstage Resid	25.4	26.5	20.5	30.1	30.4	34.4
<u>Paraffinic Hydrogen, % of Protons (c)</u>						
Recycle Distillate	44.1-46.4	41.3-43.9	42.2-43.4	41.3-44.4	35.5-36.5	40.4-44.2
Interstage Distillate	44.3	42.2	41.0	42.6	38.7	40.9
<u>Phenolic -OH Concentration, meq/g Sample</u>						
Recycle Distillate	0.24-0.28	0.26-0.27	0.20	0.14-0.16	0.23	0.14-0.16
Interstage Distillate	0.45	0.37	0.32	0.27	0.35	0.31
Recycle Resid	0.66-0.74	0.70	0.49-0.52	0.57-0.67	0.59	0.62-0.67
Interstage Resid	0.95	0.87	0.67	0.81	0.78	0.62
<u>Recycle Resid Components, wt %</u>						
Oils	71.5-75.2	71.6-72.5	75.6-78.6	68.5-75.2	76.7-79.0	65.4-67.5
Asphaltenes	15.3-15.4	20.6-21.5	13.2-13.3	17.5-20.4	14.6-15.0	22.5-24.2
Preasphaltenes	9.5-13.1	6.8-6.9	8.2-11.0	7.4-11.0	6.5-8.3	10.1-10.4
<u>Interstage Resid Components, wt %</u>						
Oils	68.6	64.7	71.7	59.8	75.0	65.8
Asphaltenes	16.6	21.8	14.3	23.6	14.5	24.2
Preasphaltenes	14.8	13.4	14.0	16.6	10.6	9.9
<u>850°F Conversion, %</u>						
First Stage	26.2	20.0 (e)	23.6	23.8	34.1	22.8
Second Stage	9.6	11.0 (e)	8.9	15.0	7.9	14.7
Total	33.3	28.8	30.5	35.2	39.3	34.1
<u>Kinetic Rate Constants for 850°F Conv. (d)</u>						
First Stage	2.38	1.70 (e)	1.33	0.87	1.82	0.62
Second Stage	0.74	0.80 (e)	0.42	0.48	0.43	0.33
<u>Activities for 850°F Conversion, 10⁷ (d)</u>						
First Stage	4.63	3.25 (e)	3.29	1.38	3.44	0.98
Second Stage	2.84	3.06 (e)	1.60	1.18	1.03	0.82

(a) SOI - 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.

(e) Bad interstage sample suspected, values shown are estimated (see text).

TABLE 26

ANALYSES OF V-164 AND V-1258 SAMPLES FROM WILSONVILLE RUNS 258 AND 259

Sample Analyses								
Sample Type	Date	Period	Coal (a)	Proton Types, % of Protons (b)			Conc. of phenolic -OH, meq-g Sample	
				Aromatic	Hydroaromatic	Paraffinic		
V-164	7/15/89	258D	SC	15.1	16.8	46.7	-	
V-164	11/5/89	258M	BT	16.9	15.3	45.8	1.29	
V-164	4/14/90	259E	LI	9.6	23.6	52.1	-	
V-164	5/18/90	259H	HI	9.7	22.5	53.8	-	
V-1258	7/17/89 (THF-sols)	≈258D	SC	20.2	15.6	33.8	0.68 (d)	
V-1258	11/17/89 (THF-sols)	≈258M	BT	28.9 (c)	13.9 (c)	39.7 (c)	0.47 (d)	

Component Distribution of V-1258 Samples						
Coal	Remarks	Components of Whole Sample, wt %			Components of THF-Solubles, wt % Solubles	
		IOM	Ash	THF-Solubles (Diff)	Oils	Asphaltenes
SC	Tarry	8.5	32.9	58.6	69.9	26.9
BT	Solid	68.9	29.2	1.9	61.6	27.3
						3.2
						11.1

(a) Coals are: SC = Spring Creek, BT = Black Thunder, LI = Low-Ash Ireland, HI = High-Ash Ireland

(b) Proton types are: aromatic = sum of condensed and uncondensed aromatic protons, hydroaromatic = cyclic beta protons, paraffinic = sum of alkyl beta and gamma protons.

(c) Poor ¹H-NMR spectrum obtained because of low concentration of THF-solubles in the whole sample.

(d) Measured and reported basis of THF-soluble portion.

TABLE 27

ANALYSES OF R-1235 SAMPLES FROM WILSONVILLE RUNS 258 AND 259

Proton Distributions													
		Proton Type, % of Protons											
Date	Period	Coal	Whole Samples				Distillates				THF-Soluble Resids		
			Arom.	Hydro-arom.	Paraff.	Arom.	Hydro-arom.	Paraff.	Arom.	Hydro-arom.	Paraff.		
7/15/89 11/15/89	258D 258M	SC BT	30.7 37.3	13.2 10.9	26.3 24.4	22.0 26.1	14.3 12.7	36.6 35.3	38.8 44.9	12.1 9.6	18.8 15.3		
4/13/89 5/18/89	259E 259H	LI HI	27.6 24.3	15.7 15.8	28.4 34.4	18.6 17.3	17.8 19.3	36.5 42.6	35.4 30.1	13.7 15.2	17.8 25.1		

Other Analyses											
Period	wt % of Whole Sample			wt % of THF-Soluble Resid			Conc. of Phenolic -OH meq/g Sample		% MAF Conversion in Microautoclave		
	850°F Dist.	THF-Sol-850°F Resid	ION	Ash	Oils	Asphaltenes	Dist.	Resid	Dist.	Whole	
258D	26.8	49.0	11.0	11.9	49.4	30.0	1.09	1.18	78.6	57.3	
258M	24.4	48.2	15.0	11.2	55.8	26.9	1.00	1.11	74.9	40.5	
259E	27.7	58.6	6.4	6.6	59.1	25.6	0.33	0.80	74.9	64.3	
249H	25.7	57.0	4.9	11.3	59.8	23.6	0.27	0.81	78.2	73.1	

NOTE: Refer to footnotes in Table 26 for explanation of coal codes and proton types.

Figure 1. Plant Configuration for Wilsonville CC-ITSL Run 259.

Figure 2. Component Distribution of Whole V-131B Oils From Wilsonville Run 259.

Figure 3. Component Distribution of Whole V-1067 Oils From Wilsonville Run 259.

Figure 4. Component Distribution of Whole R-1235 Oils From Wilsonville Run 259.

Figure 5. Solubility Fractionation of V-131B THF-Soluble 850°F⁺ Resid Samples From Wilsonville Run 259.

Figure 6. Solubility Fractionation of V-1067 THF-Soluble 850°F⁺ Resid Samples From Wilsonville Run 259.

Figure 7. Resid Distribution of R-1235 THF-Soluble 850°F+
Resid Samples From Wilsonville Run 259.

Figure 8. Proton Distribution of V-131B Distillate and THF-Soluble Resid Samples (850°F⁺ Cutpoint) From Wilsonville Run 259.

Figure 9. Proton Distribution of V-1067 Distillate and THF-Soluble Resid Samples (850°F* Cutpoint) From Wilsonville Run 259.

Figure 10. Proton Distribution of R-1235 Distillate and THF-Soluble Resid Samples (850°F⁺ Cutpoint) From Wilsonville Run 259.

Figure 11. Phenolic -OH Concentrations of Distillate and THF-Soluble Resid Samples (850°F+ Cutpoint) From Wilsonville Run 259.

Figure 12. Microautoclave Solvent Quality Assays of 850°F Distillate Samples From Wilsonville Run 259.

Figure 13. First-Stage and Total 850°F+ and Coal + IOM for Wilsonville Run 259.

Figure 14. THF-Soluble 850°F⁺ Resid Conversions for Wilsonville Run 259.

Figure 15. Conversions of 850°F⁺ Resid Hexane Solubles (Oils) in Wilsonville Run 259.

Figure 16. Conversions of 850°F+ Resid Asphaltenes in Wilsonville Run 259.

Figure 17. Conversions of 850°F⁺ Resid Preasphaltenes in Wilsonville Run 259.

Figure 18. 850°F⁺ Conversion Activities for First and Second Stages in Wilsonville Run 259.

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